European Chemicals Bureau

Institute for Health and Consumer Protection

European Chemicals Bureau

Existing Substances

European Union Risk Assessment Report

CAS No:	1333-82-0 7775-11-3 10588-01-9 7789-09-5 7778-50-9

EINECS No:	215-607-8 231-889-5 234-190-3 232-143-1 231-906-6

chromium trioxide
sodium chromate
sodium dichromate
ammonium dichromate
potassium dichromate

CAS: 1333-82-0, 7775-11-3, 10588-01-9, 7789-09-5, 7778-50-9
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European Union Risk Assessment Report

CHROMIUM TRIOXIDE, SODIUM CHROMATE, SODIUM DICHROMATE, AMMONIUM DICHROMATE AND POTASSIUM DICHROMATE

CAS-No.: 1333-82-0, 7775-11-3, 10588-01-9, 7789-09-5 and 7778-50-9

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RISK ASSESSMENT

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RISK ASSESSMENT

Final Report, 2005

United Kingdom

This document has been prepared by the UK rapporteur on behalf of the European Union. The scientific work on the environmental setions was carried out by the Building Research Establishment (BRE), under contract to the rapporteur.

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This final report refers extensively to 3 reviews.These reviews are provided as accompanying documents to this report and are available as a weblink in the references section.

Foreword

We are pleased to present this Risk Assessment Report which is the result of in-depth work carried out by experts in one Member State, working in co-operation with their counterparts in the other Member States, the Commission Services, Industry and public interest groups.

The Risk Assessment was carried out in accordance with Council Regulation (EEC) 793/93[1] on the evaluation and control of the risks of "existing" substances. "Existing" substances are chemical substances in use within the European Community before September 1981 and listed in the European Inventory of Existing Commercial Chemical Substances. Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of these substances if they are produced or imported into the Community in volumes above 10 tonnes per year.

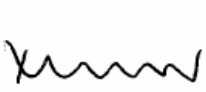
There are four overall stages in the Regulation for reducing the risks: data collection, priority setting, risk assessment and risk reduction. Data provided by Industry are used by Member States and the Commission services to determine the priority of the substances which need to be assessed. For each substance on a priority list, a Member State volunteers to act as "Rapporteur", undertaking the in-depth Risk Assessment and recommending a strategy to limit the risks of exposure to the substance, if necessary.

The methods for carrying out an in-depth Risk Assessment at Community level are laid down in Commission Regulation (EC) 1488/94[2], which is supported by a technical guidance document[3]. Normally, the "Rapporteur" and individual companies producing, importing and/or using the chemicals work closely together to develop a draft Risk Assessment Report, which is then presented at a Meeting of Member State technical experts for endorsement. The Risk Assessment Report is then peer-reviewed by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) which gives its opinion to the European Commission on the quality of the risk assessment.

If a Risk Assessment Report concludes that measures to reduce the risks of exposure to the substances are needed, beyond any measures which may already be in place, the next step in the process is for the "Rapporteur" to develop a proposal for a strategy to limit those risks.

The Risk Assessment Report is also presented to the Organisation for Economic Co-operation and Development as a contribution to the Chapter 19, Agenda 21 goals for evaluating chemicals, agreed at the United Nations Conference on Environment and Development, held in Rio de Janeiro in 1992.

This Risk Assessment improves our knowledge about the risks to human health and the environment from exposure to chemicals. We hope you will agree that the results of this in-depth study and intensive co-operation will make a worthwhile contribution to the Community objective of reducing the overall risks from exposure to chemicals.



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[1] O.J. No L 084, 05/04/1993 p.0001 – 0075

[2] O.J. No L 161, 29/06/1994 p. 0003 – 0011

[3] Technical Guidance Document, Part I – V, ISBN 92-827-801 [1234]

0 OVERALL RESULTS OF THE RISK ASSESSMENT

CAS Numbers: 1333-82-0
7775-11-3
10588-01-9
7789-09-5
7778-50-9

EINECS Numbers: 215-607-8
231-889-5
234-190-3
232-143-1
231-906-6

IUPAC names: Chromium trioxide
Sodium chromate
Sodium dichromate
Ammonium dichromate
Potassium dichromate

Environment

This risk assessment covers the following areas of the life cycle of the five chromium (VI) substances:

Production
Pigment production
Chromium oxide production
Tanning salts
Wood preservative formulation
Wood preservative application
Treated wood in use
Metal treatment formulation
Metal treatment - electroplating, passivating, anodising, brightening
Mordant dyeing

In addition the following processes are not considered to have significant releases to the environment and so do not present a risk: chromium metal production; chromium dioxide production; and Montan wax production. Use of chromium (VI) compounds in the oxidation of sulphur dyes is discussed, but not assessed as this no longer occurs in Europe.

Conclusion (i) There is need for further information and/or testing.

This conclusion applies to sediment for all areas except for mordant dyeing. The effect concentration used in the risk characterisation is derived from data for aquatic organisms, and could be refined with data for sediment dwelling organisms. Although there may be value in trying to establish the relative sensitivity of sediment and aquatic organisms, measures to reduce water concentrations as a result of the assessment will also lead to reduced sediment levels.

This conclusion also applies to indirect exposure of predators through the mussel-based food chain for all areas except production, wood preservative application and mordant dyeing. Further work could be done to test whether the mussel-based food chain is of concern, for example through further investigation of the uptake of chromium into organisms other than fish, characterisation of the nature of the chromium in organisms and consideration of the toxicity of

chromium in other forms to organisms consuming prey containing chromium. However it should be noted that reductions in the emissions of chromium (VI) to water will reduce the estimated levels in biota as well.

At present it is not proposed to carry out any further work – this will be reviewed once the risk reduction strategy has been developed.

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

For the aquatic compartment this conclusion applies to use in mordant dyeing, and production (two sites only).

For sediment this conclusion applies to use in mordant dyeing.

For wastewater treatment plants, this conclusion applies to production, wood preservative application, anodising and use in mordant dyeing.

For the terrestrial compartment, this conclusion applies to production and to use in mordant dyeing.

This conclusion also applies to all areas for the air compartment and for indirect exposure of predators though the fish-based food chain.

Conclusion (iii) There is a need for limiting the risks: risk reduction measures which are already being applied shall be taken into account.

This conclusion applies to all areas for the aquatic and terrestrial compartments, with the exception of mordant dyeing (both compartments) and production (terrestrial only, although the conclusion only applies to one production site for the aquatic). It also applies to wastewater treatment plants for all areas, with the exception of production, wood preservative application, anodising and mordant dyeing.

Human health effects

It should be noted that this assessment and therefore the conclusions presented below do not address possible risks to human health as a result of exposure to Cr (VI) in cement, nor does it address the possibility of exposure to Cr (VI) in leather goods and wood imported into the EU. In relation to cement, although this is a potential source of exposure to Cr (VI), the source of the Cr (VI) in cement is unclear and there is no direct evidence that it derives from any of the five substances covered in this risk assessment. In relation to wood and leather goods, chromium is utilised in treatment of wood and leather. The treatment processes applied within the EU are such that any exposure is to chromium in the trivalent state, not the hexavalent state. However, the treatment processes used in wood and leather goods imported from outside the EU are not known and therefore an assessment of human health risks from the possible presence of Cr (VI) in such imported goods has not been made.

Workers

Conclusion (i) There is need for further information and/or testing.

Conclusion (i) is reached for repeated dose toxicity to the respiratory tract and to the kidney. Further information is required to clarify the NOAELs and dose-response characteristics for effects on the respiratory tract and kidney.

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

Conclusion (ii) is reached for acute toxicity for full shift exposures since MOS values indicate there is no cause for concern.

Conclusion (iii) There is a need for limiting the risks: risk reduction measures which are already being applied shall be taken into account.

In view of the genotoxic and carcinogenic properties of these Cr (VI) compounds, there are concerns for all exposure scenarios. In addition, there are concerns for acute toxicity as a result of short-term peak exposures, for skin and eye irritation, respiratory tract sensory irritation, skin sensitisation, occupational asthma and reproductive toxicity (fertility and developmental toxicity). Conclusion (iii) is therefore reached for these endpoints.

Consumers

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

Conclusion (ii) is reached for all endpoints other than mutagenicity and carcinogenicity for the handling of dry CCA-treated wood, both for adults and for children exposed via wooden playing structures.

Conclusion (iii) There is a need for limiting the risks: risk reduction measures which are already being applied shall be taken into account.

Conclusion (iii) is reached for mutagenicity and carcinogenicity because no threshold below which there would be no risk to human health can be identified for these endpoints. However, it should be noted that exposure levels for consumers are very low.

It is noted that consideration has been given in this assessment to the possibility of consumer exposure to Cr (VI) as a result of handling wood which has been recently treated with CCA and is not fully dried. Although handling of such wood should normally be prohibited under appropriate legislation, it should be recognised that if it occurred, there would be concerns for health effects.

Humans exposed indirectly via the environment

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

Conclusion (ii) is reached for all endpoints other than mutagenicity and carcinogenicity.

Conclusion (iii) There is a need for limiting the risks: risk reduction measures which are already being applied shall be taken into account.

Conclusion (iii) is reached for mutagenicity and carcinogenicity because no threshold below which there would be no risk to human health can be identified for these endpoints. However, it should be noted that exposure levels are very low.

<u>Human health (risks from physico-chemical properties)</u>

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

Conclusion (ii) is reached because there are no risks from the physico-chemical properties of these five hexavalent chromium compounds.

CONTENTS

TABLES

1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION

This information is presented in tabular form (**Table 1.1**).

Table 1.1 Identification of substances covered in the risk assessment

Substance	CAS no	EINECS no	Molecular weight (without hydration)	Formula	Synonyms
Chromium trioxide	1333-82-0	215-607-8	99.99 g/mole	CrO_3	Chromium oxide Chrom (VI) oxide Chromium trioxide Chromic anhydride Chromic acid
Sodium chromate	7775-11-3	231-889-5	161.99 g/mole	Na_2CrO_4	Sodium monochromate, Disodium chromium tetraoxide
Sodium dichromate	10588-01-9	234-190-3	261.96 g/mole	$Na_2Cr_2O_7$	Disodium dichromate, Disodium dichromium heptaoxide
Ammonium dichromate	7789-09-5	232-143-1	252.06 g/mole	$(NH_4)_2Cr_2O_7$	Ammonium bichromate, Di-ammonium dichromate
Potassium dichromate	7778-50-9	231-906-6	294.22 g/mole	$K_2Cr_2O_7$	Dipotassium dichromate, Potassium bichromate

1.2 PURITY / IMPURITIES, ADDITIVES

1.2.1 Purity

The information is presented in tabular form (**Table 1.2**).

Table 1.2 Purity of the substances

Substance	Purity (weight %)	Typical impurities	Impurity content (weight %)
Chromium trioxide	>99.5%	sodium hydrogen sulphate	~0.08%
Sodium chromate	99%	none stated	-
Sodium dichromate	>99.3%	water; sodium sulphate; sodium chloride.	~0.4% ~0.15% ~0.09%
Ammonium dichromate	98.5%	water; sodium sulphate.	~1.5% ~0.02-0.04%
Potassium dichromate	99.7%	water; sodium dichromate.	~0.03% ~0.28%

1.2.2 Additives

There were no stated additives used with these substances.

1.3 PHYSICO-CHEMICAL PROPERTIES

The physical state of the substances is summarised in **Table 1.3**.

Table 1.3 Physical state at ntp

Substance	Appearance
Chromium trioxide	Dark red deliquescent crystals, flakes or powder
Sodium chromate	Slightly deliquescent yellow crystals in hydrated form (usually tetra or deca hydrated)
Sodium dichromate	Reddish to bright orange deliquescent crystals in hydrated form usually dihydrated
Ammonium dichromate	Bright orange/red crystals – non hygroscopic
Potassium dichromate	Bright orange-red crystals - not hygroscopic or deliquescent

The other physico-chemical properties are summarised in **Table 1.4**. Information is taken from IUCLID, CRC (1995), Newth (1896) and Merck (1989).

Physico-chemical parameters such as boiling point, octanol-water partition coefficient and vapour pressure have little meaning for solid ionic inorganic compounds such as these five chromates. The melting and decomposition characteristics of these compounds are well known and can be accessed in literature dating back to the 19th century. The most pertinent parameters are the high water solubility and the strong oxidising properties in acidic solutions to organic materials, particularly in the case of chromium trioxide. Ammonium dichromate will support combustion and decomposes exothermically above its melting point and can be explosive under some conditions. All of these substances, with the exception of sodium chromate, form acidic solutions in water.

Table 1.4 Physico-chemical properties

Property	Chromium trioxide	Sodium chromate	Sodium dichromate	Potassium dichromate	Ammonium dichromate
Melting point	196°C	decahydrate loses H_2O and melts at ~20°C; anhydrous salt melts at ~762°C	becomes anhydrous at 100°C and salt melts ~357°C	~398°C	starts to decompose at ~180°C - this can become self sustaining at ~225°C
Boiling point	n/a decomposes at ~250°C to Cr_2O_3 and O_2	n/a	n/a decomposes above 400°C	n/a decomposes above 500°C	n/a decomposes above 180°C
Relative density	~2.7	~2.4 - 2.7	~2.5	~2.7	~2.15
Vapour pressure	n/a: inorganic ionic compound	n/a: inorganic ionic compound	n/a: inorganic ionic compound	n/a: inorganic ionic compound	n/a: inorganic ionic compound
Solubility (H_2O) at 20 °C	~1,667 g/l (a 1% solution has a pH<1)	~530 g/l (the aqueous solution is alkaline (pH 9))	~2,355 g/l (a 1% solution has a pH ~4)	~115 g/l (a 10% solution has a pH ~3.5)	~360 g/l (a 1% solution has a pH ~4)
Partition coefficient (Log K_{ow})	n/a: inorganic ionic compound	n/a: inorganic ionic compound	n/a: inorganic ionic compound	n/a: inorganic ionic compound	n/a: inorganic ionic compound
Flash point	n/a: inorganic ionic compound	n/a: inorganic ionic compound	n/a: inorganic ionic compound	n/a: inorganic ionic compound	n/a: inorganic ionic compound; see auto - ignition
Autoignition and flammability	n/a: decomposes at 250°C to Cr_2O_3 and O_2	n/a	n/a: decomposes above 400°C	n/a: decomposes above 500°C	flammable - can self ignite at ~180°C and above. Reaction self sustaining and very exothermic
Explosivity	n/a	n/a	n/a	n/a	explosive if heated in a closed container. Used in pyrotechnics. Explosivity does not meet criteria for class I explosive.
Oxidising properties	violent oxidising agent	mildly oxidising - strong oxidiser in acidic conditions	strong oxidising agent	Strong oxidising agent	oxidising agent

1.4 CLASSIFICATION

The classification and labelling of the chromates has been agreed at technical levels to be listed in Annex I to Directive 67/548/EEC following the adoption of the 29th Adaptation to Technical Progress, as follows:

Sodium chromate

Classification

Carc. Cat. 2;R45 Muta. Cat. 2;R46 Repr Cat. 2;R60-61 T+;R26 T;R25-48/23 C;R34 Xn;R21 R42 /43 N;R50-53

- R21 harmful in contact with skin
- R25 toxic if swallowed
- R26 very toxic by inhalation
- R34 causes burns
- R42 may cause sensitisation by inhalation
- R43 may cause sensitisation by skin contact
- R46 may cause heritable genetic damage (Muta. Cat. 2)
- R48 danger of serious damage to health by prolonged exposure
- R49 may cause cancer (Carc. Cat. 2)
- R50/53 very toxic to aquatic organisms; may cause long-term adverse effects in the aquatic environment
- R60 may impair fertility (Repr. Cat. 2)
- R61 may cause harm to the unborn child (Repr. Cat. 2)

Labelling

T+;N
R: 45-46-60-61-21-25-26-34-42/43-48/23-50/53
S: 53-45-60-61

Sodium dichromate

Classification

O;R8 Carc. Cat. 2;R45 Muta. Cat. 2;R46 Repr Cat. 2;R60-R61 T+;R26 T;R25-48/23 C;R34 Xn;R21 R42/43 N;R50-53

- R8 contact with combustible materials may cause fire
- R21 harmful in contact with skin
- R25 toxic if swallowed
- R26 very toxic by inhalation
- R34 causes burns
- R42 may cause sensitisation by inhalation
- R43 may cause sensitisation by skin contact
- R46 may cause heritable genetic damage (Muta. Cat. 2)
- R48 danger of serious damage to health by prolonged exposure
- R49 may cause cancer (Carc. Cat. 2)
- R50/53 very toxic to aquatic organisms; may cause long-term adverse effects in the

aquatic environment
- R60 may impair fertility (Repr. Cat. 2)
- R61 may cause harm to the unborn child (Repr. Cat. 2)

Labelling

T+;N;O
R: 45-46-60-61-8-21-25-26-34-42/43-48/23-50/53
S: 53-45-60-61

Potassium dichromate

Classification

O;R8 Carc. Cat. 2;R45 Muta. Cat. 2;R46 Repr Cat. 2;R60-R61 T+;R26 T;R25-48/23 C;R34 Xn;R21 R42/43 N;R50-53

- R21 harmful in contact with skin
- R25 toxic if swallowed
- R26 very toxic by inhalation
- R34 causes burns
- R42 may cause sensitisation by inhalation
- R43 may cause sensitisation by skin contact
- R46 may cause heritable genetic damage (Muta. Cat. 2)
- R48 danger of serious damage to health by prolonged exposure
- R49 may cause cancer (Carc. Cat. 2)
- R50/53 very toxic to aquatic organisms; may cause long-term adverse effects in the aquatic environment
- R60 may impair fertility (Repr. Cat. 2)
- R61 may cause harm to the unborn child (Repr. Cat. 2)

Labelling

T+;N;O
R: 45-46-60-61-8-21-25-26-34-42/43-48/23-50/53
S: 53-45-60-61

Ammonium dichromate

Classification

E;R2 O;R8 Carc. Cat. 2;R45 Muta. Cat. 2;R46 Repr Cat. 2;R60-61 T+;R26 T;R25-48/23 C;R34 Xn;R21 R42/43 N;R50-53

- R2 risk of explosion by shock, friction, fire or other sources
- R8 contact with combustible materials may cause fire
- R21 harmful in contact with skin
- R25 toxic if swallowed
- R26 very toxic by inhalation
- R34 causes burns
- R42 may cause sensitisation by inhalation
- R43 may cause sensitisation by skin contact

- R46 may cause heritable genetic damage (Muta. Cat. 2)
- R48 danger of serious damage to health by prolonged exposure
- R49 may cause cancer (Carc. Cat. 2)
- R50/53 very toxic to aquatic organisms; may cause long-term adverse effects in the aquatic environment
- R60 may impair fertility (Repr. Cat. 2)
- R61 may cause harm to the unborn child (Repr. Cat. 2)

Labelling

E; T+;N
R: 45-46-60-61-2-8-21-25-26-34-42/43-48/23-50/53
S: 53-45-60-61

Chromium (VI) trioxide

Classification

O;R9 Carc. Cat. 1;R45 Muta. Cat. 2;R46 Repr Cat. 3;R62 T+;R26 T;R24/25-48/23 C;R35 R42/43 N;R50-53

- R9 explosive when mixed with combustibile material
- R24toxic in contact with skin
- R25 toxic if swallowed
- R26 very toxic by inhalation
- R35 causes severe burns
- R42 may cause sensitisation by inhalation
- R43 may cause sensitisation by skin contact
- R46 may cause heritable genetic damage (Muta. Cat. 2)
- R48 danger of serious damage to health by prolonged exposure
- R49 may cause cancer (Carc. Cat. 1)
- R50/53 very toxic to aquatic organisms; may cause long-term adverse effects in the aquatic environment
- R62 possible risk of impaired fertility (Repr. Cat. 3)

Labelling

O;T+;N
R:45-46-9-24/25-26-35-42/43-48/23-62-50/53
S:53-45-60-61

2 GENERAL INFORMATION ON EXPOSURE

This assessment is concerned with the production and use of five hexavalent chromium compounds: sodium chromate, sodium dichromate, potassium dichromate, chromium trioxide and ammonium dichromate. It does not assess risks arising from other sources of chromium in the environment, although these are mentioned where relevant.

2.1 MANUFACTURE

The production of the five hexavalent chromium compounds begins with the chromium ore, chromite, $MgFe^{II}(Fe^{III}CrAl)_2O_4$. Chromite ore is mined in Russia, the Philippines, southern Africa and Finland. The first step in the manufacture of the compounds is the extraction of the chromium as sodium chromate through the high temperature alkaline oxidation of ground ore using kilns. The vast majority of sodium chromate produced is converted into sodium dichromate, and the other compounds are produced either directly or indirectly from this.

Chromite ore is also used for other purposes, the main one being the production of stainless steel. As the ore is added directly to the charge for the steel furnace this process does not involve any of the substances covered by this risk assessment and so the process and its products are not considered further.

The International Uniform Chemical Information Database (IUCLID) contains information on three manufacturers of the five hexavalent chromium compounds. One of these manufacturers was due to cease production at the end of 1998, although data from this site when it was in operation are included later in this assessment. All three manufacturers produce (or produced) a range of hexavalent chromium compounds and also some chromium (III) compounds.

2.1.1.1 Sodium chromate (Na_2CrO_4)

Sodium chromate is the first chemical produced from chromite ore in the manufacture of chromate chemicals. The ore, containing approximately 30% chromium, is first dried, crushed and ground in ball mills. Sodium chromate is made by alkaline (sodium carbonate) oxidation in kilns at temperatures in the range of 1,000-1,200°C. After about 4 hours the reacted material leaving the kilns is either crushed and cooled before extraction of the water soluble components or quenched directly to form slurry containing sodium chromate, aluminate and vanadate in the aqueous phase. The slurry is conditioned to precipitate soluble alumina before separating the unreacted mineral residue, some of which is recycled to the kiln process after drying to aid extraction efficiency. The chromate solution is passed through other conditioning stages to remove soluble impurities. For example, sodium hydroxide and calcium hydroxide are used to precipitate soluble vanadium impurities as calcium vanadate. The latter is removed by pressure filtration and excess calcium is precipitated as the carbonate by treatment with sodium carbonate. At this stage, the partially purified solution contains around 35% sodium chromate.

2.1.1.2 Sodium dichromate ($Na_2Cr_2O_7$)

Except for limited sales of sodium chromate, all sodium chromate produced by the kiln processes is converted in situ to sodium dichromate by acidification, either with high pressure carbon dioxide or sulphuric acid.

The conversion of the chromate to dichromate with carbon dioxide takes place in a series of stirred autoclaves. The sodium hydrogen carbonate by-product is removed by centrifugation and calcined, yielding sodium carbonate, which is recycled for alkaline roasting. The degree of conversion after acidification with carbon dioxide is about 80 to 90%. A further acidification step with sulphuric acid is necessary to achieve the desired conversion rate.

Sulphuric acid is used to acidify the sodium chromate to convert chromate to dichromate. Passage through a train of evaporators produces a solution containing around 70% sodium dichromate. Then there are subsequent multiple stage evaporations of the sodium dichromate solution to achieve a final concentration of approximately 73%, by weight, sodium dichromate.

The sodium dichromate solution is then pure enough for use either as an on-site raw material in the manufacture of a range of both hexavalent and trivalent chromium compounds, or for sale as a solution or as a solid crystalline anhydrous or dihydrate product.

2.1.1.3 Chromium trioxide (CrO_3)

Chromium trioxide (chromic acid) is made by the reaction between sodium dichromate and sulphuric acid in one of two ways:

- sulphuric acid and 73% sodium dichromate solution are reacted isothermally and the precipitated product goes through a series of steps (compaction, breaking down and screening out of fines) to give a product with the required particle size.
- anhydrous sodium dichromate and sulphuric acid are reacted, with additional heat input if necessary, to produce a molten mixture of chromium trioxide and sodium bisulphate which is then separated by density. The molten chromium trioxide is allowed to cool before being flaked for packaging.

2.1.1.4 Potassium dichromate (K_2Cr_2O7)

Potassium dichromate can be made from sodium dichromate solution by double decomposition with potassium chloride followed by selective cooling and evaporative crystallisation. Another method of production relies upon the reaction between solutions of chromium trioxide and potassium hydroxide and results in a product of much greater purity, which is suitable for chrome metal production.

2.1.1.5 Ammonium dichromate ($(NH_4)_2Cr_2O_7$)

There are two methods of producing ammonium dichromate, both are performed in aqueous solution and rely on selective crystallisation of the ammonium dichromate product. One of the methods is the reaction between sodium dichromate and ammonium sulphate. The other is the reaction between chromium trioxide solution and liquid ammonia.

2.1.2 Production Volumes

Global production capacities for the major chromium (VI) compounds have been estimated by the industry as follows: sodium chromate 910 kT/year; sodium dichromate (as dihydrate) 838 kT/year; chromium trioxide 184 kT/year. Current (2002) demand is estimated at ~82% of

capacity. World production of the other two chromium (VI) compounds is much lower, at ~5 kT/year each.

The companies that produce the chromium (VI) products in the EU trade with each other to make other hexavalent products. This makes the figures for the quantities produced potentially larger than the actual quantities used and available, due to some double counting. They also base the production figures on sodium dichromate dihydrate equivalent ($Na_2Cr_2O_7.2H_2O$).

A number of factors tend to indicate that the EU produces more chromium (VI) products than it actually does. This is due to chemical changes to the product. If a company buys in, for example, sodium dichromate and changes it to lead dichromate for resale the company seems to have "produced" extra dichromate on site, but in fact has just changed the cation. Production figures for sodium chromate have been supplied, but this all goes on to be converted into other chromium compounds. Thus some of the chromium may be accounted for twice.

The scope of this assessment is restricted to five chromium (VI) compounds so once the chromium (VI) has been converted to a chromium (III) substance then this is not considered further in the assessment.

Table 2.1 gives the EU production figures for the five chromates for 1997 (from information from the manufacturers).

Table 2.1 1997 EU annual production figures for the five chromium (VI) compounds

Chromium (VI) compound	Annual production (tonnes)
sodium chromate	103,000
sodium dichromate	110,000
chromium trioxide	32,000
potassium dichromate	1500
ammonium dichromate	850

Europe is a net exporter of chromium (III) and chromium (VI) products, but localised importing may occur from outside the EU. After taking into account these exports and imports, the amounts of the substances used in the EU are estimated to be 17,000 tonnes of chromium trioxide and 25,000 tonnes of dichromate (as sodium dichromate dihydrate).

2.2 USE

This section deals with the use of the five chromium (VI) compounds that are the subject of this assessment as source materials for other chromium (VI) and chromium (III) compounds, in wood preservatives, in metal treatments and in a number of minor uses.

The main uses of the five chromium (VI) compounds are listed in **Table 2.2**.

Table 2.2 Main uses of the five chromium (VI) compounds

Chromium (VI) compound	Use
sodium chromate	manufacture of other chromium compounds
sodium dichromate	manufacture of other chromium compounds, manufacture of wood preservation products, vitamin K manufacture, mordant in dyeing, wax manufacture and metal finishing
chromium trioxide	metal finishing, manufacture of wood preservation products, catalyst manufacture, chromium dioxide manufacture and pigment manufacture
potassium dichromate	pigment manufacture, manufacture of wood preservation products, dye manufacture, catalyst manufacture, chromium metal manufacture and colouring agent in ceramics
ammonium dichromate	magnetic tape manufacture, catalyst manufacture, mordant in dyeing and pigment manufacture

2.2.1.1 Manufacture of other chromium containing chemicals

As already noted in Section 2.1, some of the chromium (VI) substances that are the subject of this assessment are made from other members of the group (which is dealt with above). This section only deals with the manufacture of other substances from the five hexavalent chromium compounds.

2.2.1.2 Manufacture of pigments and dyes

Chromium-containing pigments fall into two categories: those that remain as chromium (VI) and those made by reduction to chromium (III).

Of the chromium (VI) pigments, the main cations attached to the chromate anion for use in pigments and dyes are lead, strontium, barium and zinc. Lead chromate pigments are used mainly in paints and as colorants in plastics, due to their high colour fastness. Zinc chromate is used as a component of anticorrosive paints in the aircraft industry. Strontium and barium chromates are used mainly for fireworks. These pigments are made using precipitation techniques from the soluble dichromate followed by washing, filtration and drying.

Chromium (III) oxide pigments are made by mixing sodium dichromate with boric acid and water and reacted in a furnace at 700°C to produce green chrome (III) oxide. After removal from the furnace, the substance is washed to remove any residual chromium (VI) before filtration and drying. Chrome (III) oxide pigments are used in cosmetics, soap, washing powder and paints.

Sodium dichromate is also used as a mordant in wool dyeing. This use is dealt with below.

2.2.1.3 Manufacture of chromium (III) sulphate ($Cr_2(SO_4)_3$)

Chromium (III) sulphate and basic chrome sulphate Cr $(OH)SO_4$ is manufactured under many trade names for use in leather tanning. These salts have the general name of chrome tan. They are made by the reduction of sodium dichromate in the presence of sulphuric acid. By varying the sulphuric acid: chromium (VI) ratio, chromium (III) sulphates of differing basicity are produced. Variations exist on this method, the main one being bubbling sulphur dioxide through sodium dichromate solution. The basicity required is dictated by the nature of the customer's tanning operation. After reduction is complete, steam can be bubbled through to remove any excess sulphur dioxide and decompose any thionate produced. At this stage any desired additives are added, the solution is aged and then spray dried. The product is supplied to the customer as a powder, which contains no residual chromium (VI).

Another variation on the method is to use a reducing sugar for the reduction of sodium dichromate and sodium chromate to make chrome tan salts.

Chrome tanning salts are made at many sites in the EU. They are also obtained as a by-product from other processes, for example wax production and vitamin K production. This is the biggest use of sodium dichromate in the EU.

Ninety percent of the world's leather is tanned with basic chromium sulphate. Tanning of leather is a chemical process in which chemicals like chromium are fixed into the fibres in order to stabilise the hide. The process of tanning is essentially a stabilisation of the collagen in the leather by blocking reactive functions. In the tanning process the chromium (III) is bonded to the leather, usually by bathing the leather in a bath containing brine and chromium (III) salts for 16 hours.

2.2.1.4 Wood preservation products

Wood having a medium to high risk of insect or fungal attack can be treated with aqueous copper chrome arsenate (CCA). Chromium, as a wood preservative, acts as a mordant or fixative whereby it permanently fixes toxic elements such as copper and arsenic, which prevent the growth of wood-destroying organisms, onto the wood lignins. During this process in the EU, chromium (VI) is turned into chromium (III). The process utilised in non-EU countries is not known and therefore the potential for the presence of chromium (VI) in CCA treated wood imported into the EU is not known. For this reason, this risk assessment covers only wood that is treated with CCA within the EU.

2.2.1.4.1 CCA manufacture

CCA wood preservatives are made by mixing together copper oxide, chromium trioxide, arsenic acid and nickel sulphate solution. These reagents interact to produce a complex solution of copper chromates and arsenates. The reaction can be described simply as an acid/metal oxide reaction:

XO	+	2HA ---------->	XA_2	+	H_2O
Metal Oxide		Mineral Acid	Metal Salt		Water

The formulation of the preservative chemicals is generally undertaken in a mixing tank to form a concentrate, in the form of a paste or liquid.

In the UK, CCA products are defined by BS 4072 as Type I and II, in terms of the relative amounts of hydrated salts. Other definitions have been used in the past. The current definitions for Types I and II are:

Type I	33% $CuSO_4.5H_2O$	
	41% $Na_2Cr_2O_7.2H_2O$	(14.3% chromium (VI))
	26% $As_2O_5.2\ H_2O$	
Type II	35% $CuSO_4.5H_2O$	
	45% $Na_2Cr_2O_7.2H_2O$	(15.7% chromium (VI))
	20%. $As_2O_5.2H_2O$	

2.2.1.4.2 CCA use

Over 100,000 tonnes of CCA are traded world wide annually. The amount of formulation delivered to the wood is between 4 – 24 kg/m^3. The amount delivered is dependent upon the type of wood and its intended use.

CCA products are supplied as concentrates in the form of powders, liquids and pastes. The concentrates are diluted with water prior to use. The concentration of these solutions is 2 to 5% w/v.

The most commonly used method of applying CCA to wood is by a process known as high pressure treatment. This involves placing the wood in a treatment vessel, applying a vacuum and transferring CCA solution from an operational storage vessel to the treatment vessel. The treatment vessel is then pressurised for a minimum period of one hour. After releasing the pressure, the CCA solution is returned to the storage vessel and a vacuum is applied to remove residual CCA solution. During this process, chromium (VI) is reduced to chromium (III) and chromium arsenate is formed.

2.2.1.5 Manufacture of chromium metal

Chromium metal is made from chromium (III) oxide by the aluminothermic process. In this process, chromium (III) oxide is mixed with aluminium powder, alloying additions, oxidising and conditioning reagents in a refractory vessel. The reaction is exothermic and self-sustaining. Potassium dichromate is used as an oxidising agent in this process.

It requires the highest grade of chromium (III) oxide, the production of which was discussed earlier. The chromium metal produced is 97-99% pure; the main impurities are aluminium, iron and silicon.

Chromium metal has very limited uses on its own, but is primarily used in high performance alloys with nickel and cobalt. The alloying process is not considered further.

2.2.2 Metal treatment

The main process which involves chromium is electroplating (chrome plating), but other uses are in conversion coatings (passivating and anodising) and in brightening. The electroplating sector constitutes approximately 43% of the total number of companies with metal finishing activities. A description of each process is given below.

2.2.2.1 Formulation of metal treatment products

There are many different companies throughout the EU who make formulations for use in metal treatment. The formulations are usually confidential. However, the same two basic mixing processes are used to manufacture them: dry mixes or liquid mixes. The process is essentially one of mixing components together into a product and then packaging. Chromium trioxide is the most common chromium (VI) compound used.

2.2.2.2 Chromium plating

Electroplating is the deposition of metallic coatings on a base material by an electrochemical process. The article to be electroplated is made the cathode by connecting to a negative lead and is immersed in a solution containing dissolved salts of the metal to be deposited.

Many substances can be plated: iron; nickel; steel; stainless steel; zinc castings; aluminium; some alloys and plastic. Metal parts are plated for a number of reasons: to impart hardness; to improve wear and corrosion resistance; to improve the appearance of the part and to restore worn parts. The purpose of chrome plating is to give a more decorative and/or corrosion and wear resistant surface. Chromium trioxide is the usual source of chromium (VI).

2.2.2.2.1 Chromium plating methods

There are four methods of chromium plating: barrel; manual; semi-automatic and automatic.

Barrel plating is used for plating small parts at low cost. Either the parts and solution are rotated together in an open-ended barrel or parts are enclosed in a cage and transferred manually or automatically from one plating solution to another. The advantages of using barrel plating are low cost and a more enclosed process, so reducing exposure to the plating solutions.

Manual plating is a series of tanks that contain the appropriate plating and cleaning solutions. Parts are placed on racks or hangers and manually transferred from tank to tank. This type of plating process is labour intensive and, as platers spend a larger proportion of their working time at the tanks, there is a relatively higher risk of exposure. However, the use of this method is declining because of the high costs associated with labour intensive processes.

In semi-automatic plating, parts are manually loaded on to jigs and then the operator moves the jigs between the baths using an overhead hoist in a predetermined sequence. The operator usually stands on a platform by the side of the plating line. This method usually results in lower exposure than manual plating as the operators can distance themselves from the plating solutions for large amounts of time.

The main difference between automatic and semi-automatic plating is that the movement of the jigs is controlled electronically in automatic plating and therefore the operator spends very little time near the plating solutions, except when there is a problem with the process.

2.2.2.2.2 Chromium plating processes

There are two main distinct types of chromium plating processes; decorative and hard chrome plating. It is possible to use chromium (III) salts for decorative chrome plating and there has been an increase in chromium (III) decorative plating in recent years at the expense of chromium

(VI) decorative plating. It is not, as yet, technically possible to substitute chromium (III) for chromium (VI) in hard chrome plating.

Decorative chrome plating

Decorative bright chrome plating gives the brilliant bluish-white finish which is seen on many common domestic products, e.g. plumbing fixtures and car body parts. Decorative chrome plating uses 350 - 450 g/l chromium trioxide, has typical plating times of less than five minutes and typically uses currents of 600 to 1,000 amps. Typical coating thickness is 0.3 - 0.8 μm.

Hard chrome plating

Hard chrome plating is a way of protecting a variety of industrial devices from wear and friction, e.g. cylinders liners and piston rings for internal combustion engines. Hard chrome plating uses 200-250 g/l of chromium trioxide and has typical plating times of between one and four hours; typical currents used are 1,000 to 4,000 amps. It gives a much thicker coating than decorative plating, typically 2.5 - 500 μm.

Usually, hard chrome plating processes are run for much longer, at higher currents and chromium concentrations than decorative plating.

Electrolytic chromium/chromium oxide coated steel

Steels used in packaging, e.g. cans, are non-alloyed steel flat products and are used for drinks or food products. Depending on the application, the steel can be covered with a metal coating (tin or chromium) or with an additional organic coating. The two main steels used for packaging products are tinplate and electrolytic chromium coated steel (ECCS). Their technical specifications are described in EN10202. They are both certified for food contact materials.

After tinning, tinplate is subject to a passivation treatment in which chromium and chromium oxides are deposited on to the surface, to improve resistance to oxidation and improve suitability for lacquering and printing. The most widely used passivation process for tinplate is a cathodic treatment in a solution of sodium dichromate (3.5 to 9 mg/m^2). ECCS is always used lacquered. On the surface of the strip a coating mass between 50 and 140 mg/m^2 (total chromium) is applied.

Chromium (VI) is used in both processes, but is reduced to chromium metal and chromium (III) on the final product. Consumer exposure to chromium (VI) is therefore likely to be negligible from this source.

2.2.2.3 Conversion coatings

Conversion coatings are produced by the chemical treatment of metallic surfaces to give a barrier layer of complex chromium compounds on the metal surface, to protect the base metal from corrosion. It can also provide a good base for subsequent painting, give a chemical polish and/or colour the metal. There is a range of processes which fit under this heading; the two involving chromium compounds are passivating and anodising. The compositions of the treatment baths are proprietary and can vary greatly and may contain either chrome (VI) or chrome (III). The coatings can be applied either by immersion or electrolytically.

2.2.2.3.1 Anodising

Anodising is an electrolytic process designed to produce an oxide film integral with the surface of the metal. Its only commercial application at present is as a corrosion resistance treatment for aluminium. When the process is used as a decorative treatment for products such as domestic hardware, door furniture, partitioning, shop fronts and display stands, a coating of approximately 7-15 μm thick is applied. For architectural applications, such as to coat window frames and decorative panelling, the deposit is usually approximately 25 μm thick.

Chromium trioxide anodising is one of several categories of aluminium anodising, and accounts for a relatively minor proportion of anodising activity. Total chromium (as CrO_3) concentrations in this process are 30-100 g/l.

2.2.2.3.2 Passivating

Passivating is a chemical treatment applied to a metal product to enhance corrosion resistance. Items for passivating are generally immersed in the passivating solution, which consists of an aqueous solution of inorganic chemicals, traditionally based on chromium trioxide or sodium dichromate. No electric current is used. Passivation is usually only one in a series of treatments to protect the base metal. The concentration of chromium chemicals in the solution can vary depending on the metal being protected. Typical concentrations are: for cadmium and zinc 135-180 g/l sodium dichromate; for copper 220-280 g/l chromium trioxide; and for copper alloys 100-120 g/l chromium trioxide.

2.2.2.4 Brightening

This process may be part of the surface preparation before a major process such as electroplating. Chromates are used only for copper, zinc and their alloys. Brightening basically involves dipping the substrate into a solution of chromium salts to remove scale, oxide films and tarnish. Chromate baths are not normally made up specifically for this purpose, but where a bath is already made up for plating or other use it may also be used for this purpose.

2.2.3 Magnetic tapes

Chromium dioxide (CrO_2) is used to make magnetic tapes. It is superior to iron oxide as it has a higher resolution and a higher frequency response.

Only one manufacturer in the EU makes magnetic chromium dioxide. This is made by reacting chromium trioxide with chromium (III) oxide in an autoclave. This is done at 350°C and 300 bar. Chromium dioxide is black/brown in colour and has a composition between CrO_3 and Cr_2O_3. The chromium (III) oxide used in the production of magnetic chromium dioxide must be of a high quality.

2.2.4 Montan wax manufacture

One wax producer in Europe uses sodium dichromate to produce montan waxes in the Gersthofen process. In the reaction the chromium (VI) is reduced to chromium (III). The process is totally enclosed and the chrome (VI) used is continuously electrochemically regenerated.

These waxes are polyhydric alcohol esters, which are made by an oxidative reaction with chromates. The waxes produced are primarily for different types of plastics e.g. in food packaging. The chrome (III) produced is used on-site by the company to make leather tanning salts, dyes and pigments.

2.2.5 Vitamin K manufacture

Vitamin K is a group of chemicals containing the 2-methyl-1,4-naphthaquinone group. They are made by the oxidation of 2-methylnaphthalene with sodium dichromate. This produces vitamin K3 which is 2-methyl-1,4-naphthaquinone. This is the precursor for the other K vitamins. For the other K vitamins, alkyl groups are added at the 3 position on the 2-methyl-1,4-napthaquinone group. K1 and K3 are mainly used in animal feeds and as a drug to help blood coagulate. In the process of production the sodium dichromate reacts to give chromium (III) sulphate, which is a saleable by-product.

2.2.6 Mordant in wool dyeing

Sodium dichromate is used as a mordant in wool dying. It is added to fix the dyes to the wool. The chromium (VI) in the reaction is reduced to chromium (III). The process can be operated in three ways. The chromium can be added to the bath first, to penetrate the fibres before addition of the dye - this is pre-chroming. The second method is to add the dye and the chromium together. The third method allows the dye to disperse through the fibres first before fixing it with the chromium. This latter method, known as after chroming, is the only process in significant use. In some cases other reducing agents are added to reduce the chromium (VI) in the bath. Varying quantities of sodium dichromate are added dependent upon the dye used.

2.2.7 Catalysts

Chromium/iron catalysts are mainly used in “high temperature shift” reactions. These catalysts are usually chromium (III) oxide and iron oxide formulations, with iron being the major component. Catalyst production is a highly automated process, which requires minimal labour input.

Catalysts based on different formulations are currently being developed to replace chromium/iron catalysts.

2.2.8 Minor uses

2.2.8.1 Oxidant in dyeing of cotton

Sodium dichromate was used to fix sulphur dyes into cotton. Sulphur dyes were added to cotton (and other cellulosic materials) by initially reducing them by alkaline reduction into a soluble form. This was then followed by oxidation (using sodium dichromate) to the insoluble form once the dye has been allowed to penetrate the cotton. It was usually done in continuous processes at a temperature of 60-80°C. The use of dichromate for these processes is in general decline as other, more environmentally acceptable, oxidising agents are available.

2.2.8.2 Photography

In photography, potassium dichromate is used as a bleach in black and white film. It was used in the production of black and white movie film, but little monochromatic film is developed now.

2.2.8.3 Drilling muds

Sodium dichromate has also been used in drilling muds in the oil industry. This use of sodium dichromate has been phased out.

2.2.8.4 Corrosion inhibitor in cooling water

Sodium dichromate has been used as a corrosion inhibitor in cooling water, but its use in this area has declined almost completely. Comments from the water treatment industry in the UK suggest that widespread use ceased around 20 years ago.

2.2.8.5 Manufacture of activated carbon

Chromium trioxide is impregnated into activated carbon powder in some respirators. This is a relatively minor use. The chromium trioxide powder is mixed with other chemicals before the activated carbon is enclosed in gauze and used in the manufacture of respirators. This application is being phased out and a substitute is actively being sought for the chromium trioxide.

2.2.8.6 Other uses

In addition to those listed, there may be use of chromium (VI) compounds in certain reprographic processes, involving photochemical reduction to chromium (VI). No specific information has been obtained in relation to this area. A further area suggested for the use of the substances is in battery production. The little information found in this area suggests that batteries containing specialised chromium (VI) compounds may be being developed, but there are few details. This use could be considered as similar to production of other chemicals. The producers of the five chromium (VI) substances are not aware of any direct sales to any companies involved in these areas.

None of the minor uses are considered further in this assessment.

2.2.9 Distribution of chromium (VI) use

The distribution of the use of chromium (VI) compounds between the areas described above is as follows (dichromates are all considered under sodium dichromate). This distribution is used in estimating the environmental releases in Section 3.

Chromium trioxide is primarily used in four applications:

- 53% in metal treatments (9,010 tonnes chromium trioxide)
- 31% in wood treatments (5,270 tonnes chromium trioxide)
- 6% in the production of magnetic media (1,020 tonnes chromium trioxide)

- 10% for other uses including the production of potassium and ammonium dichromate (1,700 tonnes chromium trioxide)

Sodium dichromate is used in the following applications:

- 54% in the production of chrome sulphate (13,500 tonnes sodium dichromate)
- 31% to produce chromium trioxide (7,750 tonnes sodium dichromate)
- 15% for other uses such as chromium (VI) pigment production, use as an oxidising agent etc. (3,750 tonnes sodium dichromate)

Note that the percentage for chrome sulphate production includes areas such as vitamin K production where the chrome sulphate could be considered as a by-product of the actual process.

This breakdown of the areas of use has been simplified so that it is based on only two substances. A number of the use areas of chromium (VI) can involve the use of either dichromate or chromium trioxide - for example, formulations for wood treatment can be described in terms of either form - so that reference to the use of one form for a particular use does not mean that the other form cannot be used. This approach has been chosen to provide a consistent set of tonnages for use in the later environmental exposure assessment. As the emissions are based on chromium rather than on any of the substances, it is felt that this approach will not lead to any significant discrepancies.

2.2.10 Other sources of exposure

Cement is a potential source of exposure to Cr(VI). The source of the Cr (VI) in cement is unclear. There is however, is no direct evidence that it derives from any of the five substances covered in this risk assessment. Hexavalent chromium is usually present as an endogenous component of cement and there may be some contribution to the total Cr VI concentration as a result of leaching from kiln linings during cement processing. Therefore this potential source of exposure will not be addressed further.

2.3 CONTROLS

Council Directive 76/464/EEC of May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community requires that all discharges into inland surface water, territorial waters and internal coastal waters which are liable to contain any of the substance are subject to specified prior authorisation by the competent authority in the Member State concerned.

Under Council Directive 80/68/EEC of December 1979 on the protection of groundwater against pollution caused by certain dangerous substances, Member States are required to investigate all direct discharges into ground water and any disposal or tipping for the purpose of disposal which might lead to indirect discharge into groundwater, and to take appropriate measures they deem necessary to limit all indirect discharges into groundwater due to activities on or in the ground.

The total concentration of antimony, arsenic, lead, chromium, cobalt, copper, manganese, nickel, vanadium, tin and their compounds in exhaust gases from incineration plants, measured as the average value over a sample period of a minimum of 30 minutes and a maximum of eight hours must not exceed the emission limit value of 0.5 mg/m^3 (new plants) or 1 mg/m^3 (old plants). (Council Directive 94/67/EEC on the incineration of hazardous waste).

In the UK, surface water which is to be abstracted for drinking water must contain less than 0.05 mg/l of total chromium (95% of samples). The National Environmental Quality Standards for the protection of sensitive aquatic life (e.g. salmonid fish) are dependent on the total water hardness, and range from 5 µg Cr/l for waters with less than 50 mg/l hardness (as $CaCO_3$) to 50 µg Cr/l in waters above 250 mg/l hardness. More stringent values may be appropriate locally for particularly sensitive organisms. Levels for the protection of other aquatic life range also vary with hardness and range from 150 to 250 µg Cr/l. The quality standard for the protection of saltwater life is 15 µg Cr/l. All EQS values relate to annual average concentrations of the dissolved form.

In France, emissions of chromium (VI) to water are limited to 0.1 mg Cr/l if the emissions are > 1g/day, and emissions of total chromium are limited to 0.5 mg Cr/l if the emissions are > 5g/day.

The German soil protection directive (Bundesbodenschutzgesetz BBodSchG, 1999) includes precautionary limits ('Vorsorgewerte') which are levels which should guarantee a long-term protection of the soil (including all possible uses in future). In case of chromium the values are 100 mg/kg for clay soil, 60 mg/kg for loam/silt and 30 mg/kg for sandy soil.

The limit threshold of chromium in sewage sludge is 900 mg/kg dw according to the German national directive (Klärschlammverordnung AbfKlärV, 1992). The maximal tolerable input via sludge on agricultural soils is 1,500 g/ha/annum.

The German water quality criterion for aquatic communities ('Zielvorgabe') uses the fourfold of the background concentration, which is 10 µg/l Cr-total (LAWA, 1997).

For suspended matter a quality criterion of 320 mg Cr/kg is given for Germany (LAWA, 1997).

The German national directive (Abwasserverordnung AbwV, 2000) sets limits for chromium in wastewater. For chromium (VI) a limit of 0.1 mg/l is set for a range of industries (production/formulation of chromium in the chemical industry; other use in the chemical industry; production of concrete, fibrated concrete, lime and dolomite; textile production and refinement; metalworking and refinement; deposition of waste above ground; photographic processes; production of semi-conductor elements; production of printing forms, printed products and graphic products), with a limit of 0.05 mg/l for leather production and fur refinement. There are also limits for total chromium for these and other industries, either as a concentration limit or as a quantity released per unit of production.

A series of HELCOM recommendations relate to emissions of chromium to water from a range of processes and uses (**Table 2.3**).

Table 2.3 Helcom recommendations on chromium

Helcom Recommendation 14/2 on limitation of discharges into water and emissions to the atmosphere from production and formulation of pesticides	The limit values of 0.5 mg Cr (total)/l and 0.1 mg Cr (VI)/l as 2h or 24 h samples should not be exceeded in wastewater from production and formulation of pesticides. These measures concern only plants producing or formulating more than 5 tonnes/annum of active substance(s).
Helcom Recommendation 16/5 on requirements for discharging of wastewater from the chemical industry	The limit values of 0.5 mg Cr (total)/l and 0.1 mg Cr (VI)/l should not be exceeded in the effluent into water bodies or municipal treatment plants from chemical industry. This concerns new plants by 1 January 1996 and existing plants by 1 January 2000.
Helcom Recommendation 16/6 on restriction of discharges and emissions from the metal surface treatment	Limit values of 0.7 mg Cr (total)/l and 0.2 mg Cr (VI)/l should not be exceeded in discharges into sewers or surface waters without any dilution before discharge from metal surface treatment. However, plants discharging small loads of metals (as sum of total Cr, Cu, Pb, Ni and Zn) less than 200 g/day should not exceed limit value of 2.8 mg Cr (total)/l. This recommendation should apply primarily to plants in which surfaces are plated with metals electrolytically or chemically.
Helcom Recommendation 16/7 on basic principles in wastewater management in the leather industry	Wastewater discharges from leather industry into water bodies or municipal sewerage systems should not exceed the limit values of 0.075 kg Cr (total)/tonne leather as annual mean and 1.5 mg Cr (total)/l as 24 h-value or shorter sampling period.
Helcom Recommendation 16/8 on limitation of emissions into atmosphere and discharges into water from incineration of household waste	Aqueous discharges after wet condensation systems or flue gas scrubbers should, for new plants incinerating household waste not exceed 150 mg Cr/tonne incinerated waste.
Helcom Recommendation 16/10 on reduction of discharges and emissions from production of textiles	Cr (VI) should not be used as oxidation agent for sulphur dyes in textile industry. The limit values of 0.2 mg/l for Cr (VI) and 0.7 mg/l for Cr (total) should not be exceeded for discharges from production of textiles into water bodies and municipal treatment plants.

Parcom Recommendation 97/1 concerns reference values for effluent discharges from wet processes in the textile processing industry. For plants that perform colouring and/or finishing of textile materials, fibre conditioning or pre-treatment of textiles, reference values for discharges of total chromium are set as for 50 mg/kg of textile treated, or as a concentration of 0.5 mg/l. For chromium (VI), the values are 10 mg/kg of textile treated or 0.1 mg/l as a concentration. Either basis (load or concentration) can be used to set discharge limit values.

Migration limits have been established within Council Directive 88/378/EEC, for the presence of chromium in children's toys. Bioavailability resulting from the use of toys must not, as an objective, exceed 0.3 mg chromium per day.

3 ENVIRONMENT

3.1 ENVIRONMENTAL EXPOSURE

3.1.1 General discussion

The five prioritised chromium (VI) substances were selected for assessment primarily because of concerns for human health. However, there are some practical problems in assessing their environmental impacts. This is because there are a large number of sources of chromium release to the environment. As well as the use of these substances, releases also arise from the use of other chromium substances, cement production, processing of other ores containing chromium as an impurity, wear of metal alloys containing chromium, and natural releases from weathering of rocks and soils. There are will therefore be a wide variety of ambient background concentrations across Europe. Geochemical factors play an important role in speciation and fate of the five compounds, and these also vary across Europe. A major research programme would be necessary to fully investigate the importance of all these influences. The Rapporteur has therefore chosen a pragmatic way of assessing these substances, and this is briefly summarised below.

Releases of chromium (VI) from any sources are expected to be reduced to chromium (III) in *most* situations in the environment (see Section 3.1.1.2.1). The impact of chromium (VI) as such is therefore likely to be limited to the area around the source. Therefore this risk assessment focuses on the local impact of emissions from the production and use of the five prioritised chromium (VI) compounds (including toxicity arising from their conversion to chromium (III) ions). The behaviour of chromium in the environment is discussed, but the wider background emissions of chromium from other sources are not considered. Hence the concentrations calculated in the assessment are local ones (as Clocal), and the assessment is based on the added risk that they may present. This is an application of the 'added risk' approach, which assumes that only the anthropogenic amount of a substance, i.e. the amount added to the natural background concentration, is considered to be relevant for the effect assessment of that substance. Thus, a possible contribution of the natural background concentration to toxic effects is ignored. It is also assumed that any requirements for essentiality are already met by the background levels of chromium, so that this is not relevant to the assessment. It is recognised that the wider background contributions may need to be considered when considering the effects of risk management measures. The information on releases in the risk assessment report can also be used in any future assessment of chromium (III) compounds.

The behaviour of chromium species in the environment can be influenced by environmental factors, such as pH and water hardness. These factors are discussed in the relevant sections of this report, but detailed relationships between properties and environmental factors are not developed. In order to take some account of the potential variation in properties across the EU, two environmental conditions are considered in the calculation of the PECs. One is intended to represent acidic environments (pH below 6) and the other to represent neutral-alkaline environments (pH greater than 6). These should not be seen as detailed alternative environments, but may be used to illustrate differences in behaviour in different areas.

3.1.1.1 Releases into the environment

The five hexavalent chromium substances are of low volatility and so emissions to air are unlikely from most processes. Specific information provided by manufacturers and users indicates that there are some releases to air from production and from some use steps; these are expected to be in particulate form.

There are potential releases to water as some of the processes take place in water. Local water concentrations are not adjusted for transformation or degradation processes according to the Technical Guidance Document; only dilution and adsorption are taken into account. This has been handled in this assessment by expressing the water concentrations either as chromium (VI) or as chromium (III), with the assumption that all of the chromium in the dissolved phase is available. These calculations reflect the plausible extremes and allow the consideration of the ends of the risk spectrum. In most real situations the ion composition will be between these extremes, with chromium (VI) in discharges being converted into chromium (III) over time and at a rate depending on the local environmental conditions. Hence the real picture is potentially very complex, and the information available is not sufficient to allow this to be described accurately. The calculations have therefore been simplified out of necessity. It is recognised that this approach may result in the over-estimation of risk under some circumstances. However, this can be considered when risk management measures are developed.

There are no direct emissions to land, although the particulate emissions to air are likely to be deposited to land. Sludge application is another potential route to land; however, from comments from producers and users it is more usual for solid waste and sludges to be disposed of to landfill.

The potential environmental effects of chromium in general and chromium (VI) in particular have been noted for some time. Hence there are control measures in place in many areas to reduce or prevent the release of chromium (VI). For water these usually take the form of reduction of the chromium (VI) to chromium (III), through the addition of organic matter or the use of reducing agents such as iron (II) salts. This is then followed by precipitation of chromium (III) from solution through the formation of insoluble hydrated oxides. The solid waste produced is disposed of to landfill.

3.1.1.1.1 Releases during production

The five substances are largely used to make other substances and so can be categorised as intermediates. Some of the substances also have direct uses in metal treatment and wood preservation and as reactants in the production of other chemicals and processes such as dyeing. The Technical Guidance default emission table for each of these areas would be Table A1.1, and the default emission factors would be 0 to air and 0.003 to water.

All of the production steps leading to the five substances can be considered to occur on the same site and to be effectively part of one larger process. From Section 2, the production of chromium trioxide was 32,000 tonnes. Combining the dichromates as sodium dichromate gives a production of 112,000 tonnes. The allocation of the substances to an industry category has an effect on the fraction of main source selected from the B-tables. For example, if chromium trioxide is considered as an intermediate then the fraction is 0.75, but if the table for metal extraction, refining and processing is used then the fraction is 0.5. Using the larger fraction on the total EU tonnage (as there are only a small number of producers) gives a tonnage of

24,000 tonnes per year at a site. For dichromate, the majority of the production is used in synthesis, giving a fraction of 0.6 and a tonnage of 67,200 tonnes.

Actual emission data have been provided for all three production sites in the EU, and these will be used in the assessment in preference to the default values. The emissions data are presented in **Table 3.1**.

Table 3.1 Chromium (VI) emissions from production sites

Site	Emission to air (kg/year)	Emission to water (kg/year)	Comments for water emissions
1	3,677 (1996) 5,611 (1997)	474 (1996) 400 (1997)	
2	565 (1996)	none	excess of reducing agent in washing water
3	65	<216	estimated from detection limit and flow rate for site

These releases cover all the processing of chromite ore and the production of the five hexavalent chromium substances in the EU. They also include some of the subsequent processing of these substances into other products which takes place at these sites.

Information on possible releases to land has also been provided. At site 1 there is a licensed waste landfill site at the production site. The landfill waste is estimated to contain approximately 15 mg/kg hexavalent chromium, equivalent to an annual load of 1.7 tonnes chromium. At site 2, residual solid sodium hydrogen sulphate, which contains approximately 1% chromium (VI) oxide, from the production of chromium trioxide is disposed of at the company's local landfill site. The content of chromium (VI) oxide in the waste is regulated. Site 3 has a solid waste treatment plant that receives solid waste from the kiln and the sludge from the wastewater treatment plant. Chromium (VI) impurities in the solid waste from this facility are present at a concentration of 8 mg/kg. The solid waste is eventually transported to a waste-disposal site.

3.1.1.1.2 Releases from use as an intermediate

As noted above, the figures for releases from production sites also include releases from further processing of the chromium chemicals. Some information has also been obtained from companies that use the five chromium chemicals but are not producers, and this information has been used to improve the estimates of releases where possible. For the remainder of the chromium compounds used in this area, the default values from the Technical Guidance have been used. References to Tables in this section are to Appendix 1 of Chapter 3 of the TGD.

Pigment production

Various types of pigment are produced from sodium dichromate by precipitation techniques, the main product being lead chromate. The amount of sodium dichromate used in pigment production is taken as 2,000 tonnes. The default emission factors from Table A3.3 are 0.007 to wastewater and 0 to air. From industry information a representative site would use 670 tonnes of sodium dichromate per year; using Table B3.2 indicates this would be used over 168 days. These figures give emissions of 1.9 tonnes/year, 11 kg/day expressed as chromium.

Information on releases has been provided by a company that produces pigments. There are no emissions to air from the sodium dichromate solution. The whole of the production water is

collected and all the soluble chromium (VI) is reduced with excess of an iron (II) salt to insoluble chromium (III) compounds in water treatment facilities and then eliminated by precipitation. Chromium (VI) is not detected in the treated wastewater.

Chromium (III) oxide

This oxide of chromium is made on the production sites and releases from this process on these sites are included in the estimates above. It is also made on site by manufacturers of magnetic media via the decomposition of ammonium dichromate. Releases from this process are considered below (see Section 3.1.1.1.6). This section deals with other production of the substance.

The amount of sodium dichromate used in the production of chromium oxide is taken as 7,750 tonnes from Section 2. The default emission factors from Table A3.3 are 0.007 to wastewater and 0 to air. Based on industry information a representative site would use -around 340 tonnes of sodium dichromate per year. From Table B3.2 the local emissions are assumed to occur over 78 days a year. These values give emissions of 0.94 tonnes/year and 12 kg/day, as chromium.

Chrome tanning salts

Chromium sulphate, basic chrome sulphate and other related chromium (III) compounds are made at the production sites and at other locations. This is the major use of sodium dichromate away from the production sites. These substances are used in the tanning of leather. The majority of tanneries buy the salts ready made, i.e. in the form of chromium (III) compounds. A small number of tanneries purchase sodium dichromate and convert it on site into the tanning salts. Information from one such site is presented below. Such sites are considered to be covered under emission estimates in this section. Chromium sulphate can also be produced as a by-product from the use of sodium dichromate as an oxidant, for example in the production of vitamin K. The majority of this use is also included in this section. An exception is wax production, where a range of by-products is made at one location (and specific information is available). This is dealt with separately.

The amount of sodium dichromate used in the production of chrome sulphate is taken as 13,500 tonnes from Section 2. The default emission factors from Table A3.3 are 0.007 to wastewater and 0 to air. A representative producer of chrome sulphate would use 1,490 tonnes of sodium dichromate per year, over 300 days. The resulting emission rates are 4.2 tonnes/year, 14 kg/day, as chromium.

Information has been provided by a tannery that purchases chromium (VI) (in the form of sodium dichromate). The company purchases over 60 tonnes of sodium dichromate (anhydrous) a year. The discharge to water from the site is 840 g of chromium a day into a river. This is as total chromium, and it is assumed that this is in the form of chromium (III). The estimated loss of total chromium is around 1%.

3.1.1.1.3 Releases from use in wood treatment

Formulation

Formulation of wood preservative treatments is typically undertaken by mixing the raw materials in a vessel to form a concentrate. The product is transferred to bulk storage or to a drumming plant prior to timber treatment on or off the site. The formulations are typically transported as liquids or pastes. Pastes are diluted on site prior to use. The formulation area will commonly have bunding to prevent accidental releases reaching the environment.

It should be noted that wood preservative treatments other than CCA contain chromium (VI) in the form of the five substances that are the subject of this assessment. The whole amount of chromium use in this area has been treated here as CCA for simplicity.

No specific information on releases from formulation is available. From Section 2, 31% of chromium trioxide is used in wood treatment, which corresponds to 2,740 tonnes of chromium. The average chromium content of the standard formulations given in Section 2 is 15%, hence the amount of CCA formulation is 18,270 tonnes. There is no specific industry category for wood treatment and so IC = 0 (others) has been used. Table A2.1 gives a release fraction of 0.003. A representative formulator of wood preservatives would produce -around 4,600 tonnes of CCA formulation per year, over 300 days. These figures lead to estimated emissions of 2.1 tonnes/year, 6.9 kg/day, as chromium.

Processing

The main sources of loss of preservative solution from wood treatment processes include leaks and drips from treatment vessels and solution drippings from treated timber. These types of releases can be effectively contained by using bunded areas. In the UK the British Wood Preservation and Damp Proofing Association has a code of practice for the design and operation of wood treatment plants. Solid wastes may also be generated, such as sludges from the base of storage tanks and contaminated sawdust, produced for example by mopping spills and leaks (HMIP, 1995; DoE, 1995). During the actual impregnation process approximately 50% of the chromium (VI) is immediately absorbed by the wood. Complete fixation (reduction of chromium (VI) to chromium (III)) within the wood is dependant upon the temperature and humidity. For moderate relative humidity at 20°C fixation occurs between 48-100 hours. Elevated temperatures increase the rate.

The formation of solid sludges was formerly a major problem during the industrial treatment of wood using CCA. These are caused by reaction of the wood preservative with wood. As treating solutions are frequently reused, such sludges can build up in the preservative solution. However, changes to the formulation of the preservatives have reduced this problem.

Wood treatment does not fit easily into any of the available industry categories in the TGD. Lilja and Kovanen (1995) estimated the maximum emissions to soil and water from timber treatment in Finland to be 0.18-0.45% of chromium, or 3.1-7.7 kg per 1,000 m^3 of treated wood. Emissions to air were thought to be negligible. They also estimated the amounts of contaminated solid wastes as 0.1-0.3 m^3 for impregnated wood waste and 0.08-0.2 for CCA-contaminated sludges. These wastes were estimated to contain 0.02-0.09% of the copper, chromium and arsenic in the preservatives used.

From the formulation section above, the amount of CCA preservative used is 18,270 tonnes. From Table B3.14 in the TGD the fraction of main source is 0.5; applying this to the regional

tonnage would give the amount used on a site as 914 tonnes. However, more detailed information is available.

A survey of timber treatment operators in the UK found that the average number of treatment cycles per day was 4, with 92% of the sites surveyed operating 6 cycles or less. The normal timber load per cycle was 10 m^3 on average, which would correspond for 6 cycles to a daily processing of 60 m^3. Assuming operation for 300 days gives an annual processing figure of 18,000 m^3 of timber. From Section 2 the application rate for CCA is 4-25 kg/m^3 wood, depending on the use - a realistic general use figure would be 9 kg/m^3 (industry information). Thus this amount of wood would require 162 tonnes of preservative for treatment. A major supplier of timber treatment formulations in the UK commented that there are around 350 treatment plants in the UK. Most sites would use typically 10-50 tonnes of CCA per year, with only a few sites using more than this. The value of 162 tonnes per year estimated above is therefore taken as representing a reasonable worst case. Applying the emission estimates from Lilja and Kovanen (1995) above gives releases (in terms of chromium) of 0.15-0.36 kg/day.

These releases are derived from the emission factors for chromium as a percentage of that used; the factors relating losses to volume of timber give emissions which are of a similar order to those above. The factors are for emissions to soil and water; for this assessment the releases are split equally between these two compartments.

The draft emission scenario document for wood preservatives produced by the OECD (OECD, 2001) has information from The Netherlands, the USA and Canada on emissions from CCA treatment of wood. Based on the information presented in this draft on chromium releases, and using the assumptions above in relation to the amount of wood treated and the application rate, estimates can be made of chromium release to water of between 0.4 g/year and 53 kg/year. The estimates above in this assessment give releases to water of 24 - 54 kg/year, which agree with the high end of those based on the OECD information. The current estimates will be used in the assessment.

3.1.1.1.4 Releases from use in metal treatment

Formulation

Users of chromium compounds in metal treatment may buy individual substances or may obtain pre-formulated packages. As there is no information on which to base a breakdown between these possibilities, for the purpose of this assessment it has been assumed that all of the chromium used goes through a formulation step. In Section 2, it was estimated that 9010 tonnes of chromium trioxide are used for metal treatment. From Table A2.1 in the Technical Guidance, the emission factors for the formulation step are 0.003 to water and 0.0025 to air. From Table B2.3 in the Technical Guidance the fraction of main source is 0.8 (this is based on the tonnage of chromium trioxide rather than that of the formulations, in the absence of information on the proportion of chromium trioxide in the formulations). Applying these figures gives the following local releases:

air - 6 kg/day; water - 7.2 kg/day

Information has been provided by a formulator of metal treatment products. They use -around 350 tonnes per year of chromium (VI) compounds. The site has an effluent treatment system, which reduces chromium (VI) to chromium (III) and precipitates the chromium as sludge with

other metals. Estimated emissions to water are <1 kg/year, as chromium (III). A similar release to air is also estimated. The vast majority of chromium waste is disposed of in the sludge sent to landfill.

Processing

The following information on releases from the use of chromium compounds in metal finishing is taken from a study of the UK industry (Brown et al., 1997), which is referred to hereafter as the UCD. A typical metal finishing process involves a number of stages as described in Section 2. These processes are carried out in separate stages, although they may be on a continuous production line. After each stage the articles being processed are usually rinsed in water to avoid cross-contamination. On removal of the articles from the treatment bath a certain amount of the process solution is taken with them and lost from the bath. This is known as drag-out; the amount of drag-out is dependent on the type of article being processed and the nature of the process. On immersion in the rinse bath this 'drag-out' solution is diluted in the rinse water, and eventually removed in the wastewater effluent. This is where releases to water may arise. Rinsing systems usually operate on a counter-current system.

In order to calculate releases from metal finishing processes it is necessary to know certain characteristics about the technologies employed. Information from the UCD has been used below to estimate possible releases from the following processes that may involve the use of chromium compounds: electroplating (the major use); passivating; anodising; and brightening. It is possible that several of these processes could take place at the same location, but they are treated independently in this assessment.

The emission estimates in the following sections do not take into account any removal of chromium from the effluents before discharge to the sewer. Effluents may be treated to reduce the chromium (VI) to chromium (III) which can then be removed by precipitation.

Electroplating

The UCD describes a typical electroplating operation as using a 5,000 litre treatment bath, with two rinse baths of 1,000 litres each and a counter-current rinse flow of 100 litres/hour. For chromium, the after-treatment line is likely to be longer, typically with two rinse baths, a neutralising bath and two further rinse baths. Electroplating can be carried out in automatic, semi-automatic or manual plants. A realistic large-scale chromium plating operation could process 40 m^2/hour of metal and operate for 12 hours per day, for 240 days per year (industry information).

The drag-out rate for rack deposition, the most widely used process for chromium, is typically 5 litres per 100 m^2 of surface treated. Thus the drag out volume is

$$5 \text{ l}/100 \text{ m}^2 \cdot 40 \text{ m}^2/\text{hour} = 2 \text{ l/hour}$$

For decorative hexavalent chromium electroplating solutions the concentration of chromium trioxide is 350-450 g/l. Thus the maximum rate of removal of chromium trioxide in the drag out is

$$450 \text{ g/l} \cdot 2 \text{ l/hour} = 0.9 \text{ kg/hour}$$

Electroplating plants which operate at temperatures above ambient are able to recycle some of the drag-out release to the treatment bath as the volume of the bath reduces by evaporation.

Chromium plating baths operate at 40°C, and an estimated 25% of the drag-out can be returned to the bath. Thus the reduced emission of chromium trioxide is 0.68 kg/hour. This is in a flow rate of 100 l/hour, so the concentration is 6.8 g/l chromium trioxide, or 3.5 g/l chromium.

The total discharge for a 12 hour day will be 8.2 kg/day chromium trioxide. For 240 days of operation this equates to 2 tonnes per year.

Electroplating baths receive top-up additions of chemicals to replace the losses through drag-out. The contents are not usually disposed of with any regularity, but may be transferred to other tanks in order to clean out solid wastes accumulating in the tank and any articles that have dropped into the tank. The solutions are then returned.

Hard chromium coatings generally involve lower drag-out rates (in terms of volume per hour) as the thicker coatings take a longer time to produce and so the items spend longer in the baths. Very large pieces may be plated with chromium; in these cases it is unlikely that a counter-current rinse system will be used, but rather the items will be rinsed above the bath after treatment and the rinsing returned directly to the treatment bath. The scenario above is therefore taken as a reasonable worst case for electroplating in general.

Passivating

This process may be used to add further corrosion resistance to other types of coating or prior to subsequent painting. It would not be used on a chromium electroplated article.

Similar assumptions to those above will be used for the processing rate, so that the drag-out rate is 2 l/hour. The typical size of the treatment bath is however smaller at 1,000 litres. The highest concentration of chromium trioxide used is 280 g/l for copper and copper alloys. This gives a release rate in the drag out of 0.56 kg/hour. With a counter-current rinse flow of 100 l/hour, this gives a concentration of 5.6 g/l. For 12 hours operation the release amount is 6.7 kg/day, and the annual release is 1.6 tonnes.

The passivating solutions are disposed of, with a typical replacement frequency being every two weeks. The solutions are assumed to contain the active components at their effective concentrations, so that the amount of chromium trioxide disposed of is 1,000 litres · 280 g/l or 280 kg.

Anodising

Anodising is an electrolytic process which produces an oxide film integral with the surface of the metal. It is used almost exclusively with aluminium. Most anodising is carried out with sulphuric acid solutions, but a small amount uses chromium trioxide.

The typical size for the treatment bath in an anodising process is 5,000 litres. Using the same assumptions about the processing rate as for electroplating, the drag out rate is 2 litres per hour. The typical concentration of chromium trioxide in the treatment bath is 80 g/l, so that the release rate in the drag out is 0.16 kg/hour. This process takes place at temperatures above ambient and so there is the possibility of returning rinse water to the treatment bath. At a rate of 25% return this reduces the release to 0.12 kg/hour. In a rinse flow of 100 l/hour this is a concentration of 1.2 g/l. For 12 hours operation the release is 1.4 kg/day, and the annual release is 0.35 tonnes.

Brightening

As part of the pre-treatment of metals for other processes, they may undergo a brightening step to remove scale, oxide films and tarnish. For copper and copper alloys, and zinc and zinc alloys this can involve chromium compounds. This is again a small volume use. The same assumptions about the rate of processing as for electroplating are used, together with a treatment bath size of 1,000 litres. The maximum concentration of chromium trioxide used in the baths is 350 g/l for zinc and alloys. The release for a drag out rate of 2 litres per hour is 0.7 kg/hour, a concentration of 7 g/l in the rinse flow of 100 litres per hour. For 12 hours operation the release is 8.4 kg/day, and the annual release is 2.0 tonnes.

3.1.1.1.5 Releases from use in chromium metal production

Chrome metal is made from high purity chromium (III) oxide, with potassium dichromate used as an accelerator. In the EU only two sites produce chrome metal, one in the UK and the other in France. The process is a dry one involving the mixing and firing of chromium (III) oxide and aluminium powder with other reagents, including potassium dichromate. One company uses 700 tonnes a year of potassium dichromate in this process. Discharges are less than 1 kilogram a year total chromium to air and less than 7 kilograms of total chromium to wastewater. As the process is a reduction process and chromium (VI) makes up only a small part of the initial chromium charge the vast majority of the small quantities discharged are considered to be in the form of chromium (III). These releases are considered to be insignificant and not considered further in the assessment. The process does not produce any liquid waste requiring specific treatment relating to chromium. The dust collected on site is disposed of at landfill; an estimated 15 tonnes of chromium (VI) are disposed of this way over a twelve month period.

3.1.1.1.6 Releases from use in chromium dioxide production

Chromium dioxide is made by the reaction of chromium trioxide with chromium (III) oxide at high temperature and pressure. The chromium (III) oxide is made by the decomposition of ammonium dichromate. There is believed to be only one manufacturer of chromium dioxide in the EU. They have supplied information on release monitoring. The flow gas of the reactor is washed intensively in a cleaning treatment. Chromium trioxide is an easily water soluble substance and is completely washed out. This is confirmed by regular air sampling of the emitted gas by washing in water bottles and measurement of chromium trioxide by photometry. No detectable chromium trioxide is found. Therefore there are no emissions to air. Aqueous effluents are treated with iron (II) salts. The effectiveness of the treatment is monitored through daily measurement of 24 average samples of the effluent by photometry. The concentration is always under the detection limit of 0.05 mg chromium (VI)/litre.

3.1.1.1.7 Releases from use in Montan wax production

One company uses sodium dichromate in the production of waxes, in the process converting chromium (VI) into chromium (III). They have supplied information on environmental releases. The emissions into the air of the plant are monitored regularly. No chromium emissions are detectable. Chromium-containing wastewater, mainly from cleaning and washing processes, is normally reused in the manufacturing process. The amount of wastewater that cannot be recycled is treated within the production plant by precipitating removed chromium as chromium (III)

hydroxide. This chromium hydroxide is also reused in the plant. As the treated wastewater still contains organic substances, it is discharged into the site owned wastewater treatment plant. Excess sewage sludge from the wastewater treatment plant is incinerated in a modern waste incineration plant. Chromium containing organic waste material is incinerated in an external incineration plant for hazardous wastes, from which waste materials are assumed to be disposed of in accordance with regulations. As there are no significant releases from the production plant, this use is not considered further in the assessment.

3.1.1.1.8 Releases from use of sodium dichromate in dyeing

Mordant dyeing

In mordant dyeing sodium dichromate is used to fix the dye to the wool fibres. Information on the general dyeing process is taken from the Emission Scenario Document on dyes in the Technical Guidance document.

The average dye operation processes 1,500 kg fabric/day. The weight of dye used per day is dependent upon the shade of dye. Mordant dyes are used to produce deep shades, so 37-52 kg a day of dye would be used in an average dye operation.

The reaction between the dichromate and the wool is complex, but in simple terms the chromium (VI) is reduced to chromium (III) and then binds the dye to the wool. Thus most of the chromium is retained on the wool. Excess amounts of dichromate can have detrimental effects on the wool. Therefore operators try to minimise the excess of chromium whilst still producing the required degree of dyeing. An early approach to calculating the amount of dichromate needed was to use between one quarter and a half of the mass of the dye (as sodium dichromate). Hence the 52 kg of dye per day calculated above would require 13-26 kg of sodium dichromate.

More recently, lower chrome methods have been developed to reduce emissions of chromium further. Chrome factors were developed for individual dyes to enable a reduced addition of dichromate to be calculated. A simple formula for calculating such factors is

$$C = 0.2 + 0.15D$$

where C= mass % of chromate added and D= mass % of dye.

For a maximum dye concentration of 3.5% (from the TGD Emission Scenario Document) the formula gives the required concentration of sodium dichromate as 0.725%. For a set of modern mordant dyes, the chrome factors ranged from 0.25 to 0.45% (Duffield and Hopper, 1987). The highest of these values will be taken as representative of the worst case. (Note that lower factors can be used if the dyeing process includes the addition of sodium sulphate at the appropriate stage during the after-chroming step, and that residual chromium levels can be reduced further by the use of oxidising agents such as thiosulphate, again during the after- chroming process step). From above, the maximum amount of wool dyed was 1,500 kg/day; the amount of sodium dichromate used at 0.45% of this is 6.75 kg/day.

The fixation rate of mordant dyes is around 94%, but this is not appropriate for the chromium used. Duffield and Hopper (1987) carried out a series of experiments with the aim of optimising the mordant dyeing of wool, by minimising the fibre damage and the chromium in wastewater, without affecting the properties of the chrome dyestuffs. They took as their baseline, i.e. poorest performing, conditions the use of the 50% rule as mentioned above. For the six dyes in their

study, the highest concentration of chromium (VI) measured in water after the dyeing process was 2.8 mg/l. This was present in 13 litres of water, so that the amount of chromium remaining was 36.4 mg. The original addition was of 15 g of potassium dichromate per 1 kg of wool, or 5.3 g of chromium. Thus the worst-case emission was 0.69%. Using an addition of dichromate based on chrome factors the maximum concentration of chromium (VI) was 2.18 mg/l, corresponding to an emission factor of 0.54%. The use of other agents such as sodium sulphate and thiosulphate as indicated above reduced the level of chromium (VI) in water for most of the dyes to below the detection limit of 0.1 mg/l, which corresponds to a release factor of 0.024%.

For the purpose of this assessment the release factor of 0.54% will be taken as representing a possible worst case for modern dyeing practice. It is recognised that many if not most of current operations will achieve lower emissions than this. From above, the amount of sodium dichromate used per day is 6.75 kg. Hence the release to the treatment plant is 6.75 · 0.54%, or 36 g per day as sodium dichromate.

Sulphur dyes

Sodium dichromate was used to oxidise sulphur dyes to their insoluble form after they have been introduced into the fibre as the reduced form. Information from European dye producers states that dichromates are no longer used in this area. Alternative oxidising agents such as bromate with metavanadate or hydrogen peroxide have replaced it. The calculations below are therefore presented for information only, and are not used further in the risk assessment. Information on the dyeing process is taken from the Emission Scenario on dyeing in the Technical Guidance.

Sulphur dyes were predominantly used on cotton and in continuous processes. The Emission Scenario gives a processing rate of 4,000 kg cotton per day for continuous dyeing, with water consumption of 6 l/kg and a liquor ratio of 1:1. The Society of Dyers and Colourists in the UK suggested the concentration of sodium dichromate used in this process was up to 2 g/l. For this assessment it is assumed that the volume of the oxidation bath is similar to that of the dye bath. At a liquor ratio of 1:1, 4,000 kg fabric requires an effective dye bath of 4,000 litres. Hence the amount of dichromate used would be 8 kg/day. It is assumed that all of the added dichromate is required to react with the dye and that all the chromium is converted to chromium (III). This corresponds to 3.2 kg of chromium per day.

Unlike the use of dichromate as a mordant, this use does not result in the incorporation of chromium into the fibres. Therefore there is the potential for all of the chromium used to be released. It has been assumed throughout these estimates that there is no removal of chromium from the effluent before release to the WWTP, except where specific information has been provided. So it will be assumed here that all the chromium used is released to water. Thus the daily local release is 3.2 kg.

3.1.1.1.9 Releases from use of products

For most of the products made using the five chromium compounds there are not thought to be significant releases of chromium (VI). The other chemicals produced contain little or no chromium (VI), metal treatment results in a film of chromium metal and dye use results in strongly bound chromium (III). The exception is wood treated with preservatives where there is the potential for releases over the lifetime of the wood. Information on levels in areas around treated wood is presented later in this assessment. The majority of the chromium impregnated into the wood is converted into chromium (III), and any chromium (VI) released to soil will also

be rapidly converted. Elevated levels of chromium have been found in soil close to treated wood. The levels decrease with depth and distance from the wood. A similar pattern has also been found in sediments, so that the contamination from this source is limited.

It is not possible to calculate an emission rate from these measurements. Braunschweiler et al. (1996) reviewed the removal of chromium and the other constituents of CCA from treated wood samples in the laboratory. In one study they found up to 1% removal of chromium in leaching experiments. In another study looking at the effects of acid rain on leaching from treated timber, a higher rate of loss for chromium (6%) was seen when using water with a pH of 3. However, at a pH of 5.6 the leaching was considerably reduced and no loss of chromium was seen. It is not clear how these results can be related to losses in the environment. However these releases are largely to soil and the available information shows that the chromium does not migrate to any significant extent from the area around the treated wood. Therefore they will be treated as local concentrations using the measured levels close to treated materials.

CCA-treated timber may also be used in circumstances where it is in contact with surface water, where there is more possibility for any chromium released to move away from the source. Two studies on levels of the elements from CCA in sediments related to treated wood are reported in Section 3.1.2.2, but there is no information on levels in water or on the rate of removal of the elements from the wood. One of the studies showed chromium levels in sediment to be similar to those in background sediments. Both studies related to wood used in estuarine situations.

Braunschweiler et al. (1996), as part of a risk assessment for CCA, calculated levels of chromium in surface water. These calculations have been included in Section 3.1.2.1.2 as possible concentrations on a local scale. There is no information on what fraction of treated timber is used in contact with water. Unless a significant proportion of the treated timber is used in water then it appears unlikely that there will be a major release of chromium to the environment through this route.

3.1.1.1.10 Releases from disposal

The only products containing chromium which may be released on disposal are considered to be treated wood and possibly dyed textiles. By the time of their disposal it is likely that all the chromium will be in the form of chromium (III). For products disposed of to landfill, the reducing conditions which should be found in well-operated sites means there is no possibility of conversion to chromium (VI) (and any chromium (VI) will be reduced) and that the chromium (III) will be immobilised. Studies on landfill leachates in the UK have shown no problems with chromium.

For disposal by incineration, the few related studies have been reviewed by Braunschweiler et al. (1996). There is no full study on the fate of chromium from burning timber, but the available information indicates that it is associated mainly with the ash. In some countries, treated timber is considered as hazardous waste and will only be incinerated in plants dealing with such waste; it is therefore assumed that there will be no significant emissions. Where treated timber is not identified separately, there may be a possibility for release depending on the fate of the ash after incineration. However, if this is then land filled then the same comments as above will apply. It is not possible to assess emissions from this route, but it is considered based on the evidence that they will be minor.

3.1.1.1.11 Summary of releases

The releases estimated in the above sections, expressed as chromium, are summarised in **Table 3.2**. In addition, estimates for the total releases in the EU from these processes have also been made using the same assumptions as for the local emissions (with the exception of those from metal treatment use, where the TGD default emission of 0.5 has been used as a worst case). These estimates could be used to compare with chromium emissions from other sources.

Table 3.2 Summary of emissions

Process	compartment	tonnes/year	kg/day	Continental (tonnes/year)
Production	Air water	5.6 0.4	19 1.3	6.2 0.6
Pigment production	water	1.9	6.3	5.6
Chromium (III) oxide production	water	0.94	3.1	22
Chrome tanning salt production	water	4.2	14	38
Wood preservative formulation	water	2.1	6.9	8.2
Wood preservative application	Water soil	0.054 0.054	0.18 0.18	6.2 6.2
Metal treatment formulation	Air water	1.1 0.93	3.1 3.7	14 12
Metal treatment use	water	0.11-1.3	0.73-4.4	2,342
Mordant dyeing	water	0.004	0.014	1.1

3.1.1.2 Behaviour on release to the environment

Once released into the environment, all of the five chromium (VI) compounds considered in this assessment will behave similarly. The following sections discuss the main degradation and transformation processes that may occur for chromium (VI) in the environment. It should be noted that many of these processes are not taken into account in the derivation of the local concentrations later in the assessment.

3.1.1.2.1 Degradation and transformation

The most important degradation/transformation reactions for chromium compounds in the environment involve their oxidation/reduction behaviour. Such redox reactions can occur by both abiotic and biotic processes. These processes are summarised below under the appropriate headings. However, since the end-products of the biotic and abiotic processes are essentially the same, it is difficult to unambiguously separate the two processes, especially in experiments using natural systems.

Abiotic processes

Photochemical reactions

It has been shown that chromium (VI) can be photochemically reduced by UV-light to chromium (III) in neutral to alkaline solution in the presence of zinc oxide. The reduction was thought to

occur by electrons formed by the action of light on the semiconductor material (Domènech and Muñoz, 1990). However, as zinc oxide is not a common constituent of surface waters, the environmental significance of this reaction is thought to be low (Palmer and Wittbrodt, 1991).

Hug et al. (1997) studied the effects of light on the iron catalysed reduction of chromium (VI) in aqueous solution containing various organic ligands (e.g. oxalate and citrate). The conditions used were designed to simulate those found in contaminated wetlands and soil or slightly acidic atmospheric water. The light source used in the study was a high-pressure xenon lamp, with a Pyrex glass filter to remove wavelengths <300 nm and all experiments were carried out at 25°C. The range of concentrations used in the experiments was: chromium (VI) 5-20 µmole/l ≡ 0.26-1.04 mg Cr/l; pH 5-7; oxalate 25-100 µmole/l or citrate 100 µmole/l. In addition, experiments were carried out at lower pH (3-4) and higher chromium (VI) and oxalate concentrations to simulate more polluted waters found in acid mine drainage, in acidic organic horizons of forest soils and in acid sulphate soils. No chromium reduction was observed on photolysis of chromium (VI) in the absence of added iron (III). On the addition of iron (III) (at concentrations of 0.13-6.7 µmol/l ≡ 7.3-374 µg Fe/l), a rapid reduction (e.g. >95% reduction in 20-40 minutes) of chromium (VI) was seen in the experiments. A tentative reaction scheme was put forward, involving formation of an iron (III)-oxalate complex which absorbs light forming iron (II) species, which reduces the chromium (VI), and radical species which could also react with chromium (VI). The overall rate of reaction was found to decrease linearly with increasing pH above pH 5.5. The authors considered that, since there are many organic ligands which could form similar complexes with iron (III) in the environment, the process could be a significant removal process for chromium (VI) in the environment. Soluble organic complexes with chromium (III) were thought to be formed in the reaction.

The atmospheric reduction of chromium (VI) to chromium (III) is facilitated by UV light and reducing agents such as V^{2+}, V^{3+}, VO^{2+}, Fe^{2+}, HSO_3^- and As^{3+}. The estimated atmospheric half life for this reduction is in the range of 16 hours to 4.8 days (Kimborough et al, 1999). As the atmosphere is not expected to be a major compartment for chromium (VI) substances, such processes are unlikely to be significant in their fate.

Oxidation/reduction

In the environment, chromium (VI) is a strong oxidising agent and can react with a wide range of reducing agents to form chromium (III). Oxidation reactions of chromium (III) are known, although manganese oxides are thought to be the only significant inorganic oxidants found in the environment (Rai et al., 1989). Some of the known reactions are summarised in **Table 3.3**, together with values for the equilibrium constants where measured.

The kinetics of the reduction of chromium (VI) to chromium (III) by ferrous ions derived from minerals such as haematite (3% Fe(II) by weight) and biotite (11.7% Fe(II) by weight) has been studied by Ealy and Rai (1989). The experiments were conducted at 25°C using continuously aerated water. Chromium (VI) (as potassium dichromate) (initial concentration either around 5 mg Cr/l or 50 mg/l) was added to the water, along with ground samples of the mineral and the rate of reduction was determined under varying conditions of pH and ionic strength. Rapid reduction to chromium (III) was seen in the experiments within a few hours and the reduction was shown to be due to the presence of ferrous ions derived from the minerals. The extent of the reaction (i.e. amount of chromium(IV) reduced) was shown to be proportional to the ratio of the mineral surface area to the solution volume, and was also shown to be strongly pH dependent (both the rate and extent of reduction was shown to decrease with increasing pH over the range experimental pH range of 3.5-6 and 9-12; in the pH range 6-9 the rates of reduction were

relatively independent of pH), and were also dependent on the anions present in solution. The results were explained in terms of a two stage process where, firstly, the ferrous ion enters into solution as a result of surface dissolution or redox reaction of the mineral, followed by reaction of the chromate/dichromate ion with the ferrous ion in the aqueous phase. Thus any parameter that increased the concentration of ferrous ions in solution increased the rate of reaction. It was shown that at pH >10, the ferrous ions are oxidised by dissolved oxygen at a rate that competes with the reaction with chromium (VI). This effect occurred at lower pHs in the presence of phosphates. This led to the conclusion that high pH and/or high phosphate concentrations are likely to reduce the efficiency of chromium reduction by ferrous ions. At low pH, the dissolution rate of the minerals was increased, leading to an increasing rate of reduction of the chromium (VI). Certain anions, such as sulphate, also increased the reaction rate by increasing the rate of dissolution of ferrous ions from the minerals.

Table 3.3 Oxidation/reduction reactions of chromium in the environment

Reaction	Comment	Reference
$2Cr(OH)_2^+ + 1.5O_2 + H_2O \Leftrightarrow 2CrO_4^{2-} + 6H^+$ $[CrO_4^{2-}]/[Cr(OH)_2^+] = 7 \cdot 10^{15}$	Thermodynamic equilibrium at pH 6.5-8.5	Schroeder and Lee (1975)
Reaction of chromium (VI) with reducing agents		
$Cr_2O_7^{2-} + 8H^+ + 3C_6H_4(OH)_2 \Leftrightarrow 2Cr^{3+} + 3C_6H_4O_2 + 7H_2O$ $\log K_{eq} = 64$	Reaction with dihydroxy phenols	Saleh et al. (1989)
$2Cr_2O_7^{2-} + 3C^0 + 16H^+ \Leftrightarrow 4Cr^{3+} + 3CO_2 + 8H_2O$	General reaction with carbon sources	Palmer and Wittbrodt (1991)
$2HCrO_4^- + 3HSO_3^- + 6H^+ \Leftrightarrow 2Cr^{3+} + 2SO_4^{2-} + S_2O_6^{2-} + 6H_2O$	Reaction with sulphites (excess sulphite)	Palmer and Wittbrodt (1991)
$2HCrO_4^- + 3HSO_3^- + 5H^+ \Leftrightarrow 2Cr^{3+} + 3SO_4^{2-} + 5H_2O$	Reaction with sulphites (excess chromate)	Palmer and Wittbrodt (1991)
$Cr_2O_7^{2-} + 3S^{2-} + 14H^+ \Leftrightarrow 3S + 2Cr^{3+} + 7H_2O$ $\log K_{eq} = 187$	Reaction with sulphides	Saleh et al. (1989)
$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \Leftrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ $\log K_{eq} = 57$	Reaction with ferrous iron	Saleh et al. (1989)
$CrO_4^{2-} + 3Fe^{2+} + 7H_2O \Leftrightarrow 3Fe(OH)_3 + Cr(OH)_2^+ + 3H^+$		Scroeder and Lee (1975)
Reaction of chromium (III) with oxidising agents		
$2Cr^{3+} + 3MnO_2 + H_2O \Leftrightarrow 3Mn^{3+} + Cr_2O_7^{2-} + 2H^+$ $\log K_{eq} = -10.16$	Reaction with manganese oxide	Saleh et al. (1989)

Fendorf and Li (1996) studied the kinetics of the reduction of chromium (VI) by ferrous ions over the pH range 6.0-8.0. The object of the study was to derive the rate equation for the reaction and to see if the rate of reaction was sufficient over this pH range to compete with the oxidation of iron (II) by oxygen. A range of chromium (VI) (as sodium chromate; 0.01-0.5 mmol/l ≡ 0.52-26 mg Cr/l) and iron (II) (as ferrous chloride; 0.01-1.0 mmole/l ≡ 0.56-56 mg Fe/l) concentrations were used. Over the pH range used, no significant difference in the rate of reactions was seen during the experiment. The reaction was found to be first order with respect to the concentration of chromium (VI) but had a fractional (0.6) order dependence on the iron (II) concentration, possibly indicating that the ferrous iron was involved in several steps of the overall reaction. Overall, the reaction was found to be described by the following rate equation:

$$-\frac{d[Cr(VI)]}{dt} = k_{Cr}[Fe(II)]^{0.6}[Cr(VI)]$$

where k_{Cr} = 56.3±3.7 $mol^{-0.6}$ min^{-1} $l^{0.6}$ (temperature of reaction not stated)

Based on these data and the known kinetics of the reaction of iron (II) with oxygen, Fendorf and Li (1996) concluded that even at low chromium (VI) concentrations (e.g. 10 µmol/l ≡ 0.52 mg/l) the chromium reduction reaction can compete effectively with the reaction of iron (II) with oxygen. Reduction of chromium (VI) was predicted to be limited by the presence of oxygen only at high pH (>8) or at very low chromium (VI) concentrations (<<10 µmole/l ≡ << 0.5 mg Cr/l). Under the conditions used in these experiments, the reduction of chromium (VI) to chromium (III) was very rapid (complete in <0.5 minutes).

The influence of pH on the reduction of chromium (VI) by soil fulvic acids has been investigated (Wittbrodt and Palmer, 1995). In the experiments, chromium (VI) (concentration 0.01-0.2 mmole/l ≡0.52-10.4 mg Cr/l) was added to solutions of fulvic acid (concentration 25-250 mg/l) at 25°C and the time-dependent reduction of the chromium (VI) was monitored at various pHs. Reduction of chromium (VI) was seen at all pHs tested (pH 1-7), the rate increasing with decreasing pH, increasing fulvic acid concentration and decreasing initial chromium (VI) concentration. The shape of the reaction curves obtained indicated an initial rapid reduction, followed by a slower rate of reduction that could not be simply modelled by simple first or second order kinetic equations (an empirical equation was derived that adequately fitted the results) and so it is not possible to derive precise half-lives for the reaction from the data. From the plots given in the paper, around half of the added chromium (VI) was reduced in time periods ranging from <1-~100 days.

Grove and Ellis (1980) studied the solution/extraction behaviour of chromium (III) (as chromic chloride) and chromium (VI) (as chromium trioxide/chromium trioxide) in various soils. The soluble chromium (III) added to the soil was found to be rapidly converted to insoluble chromium (III) compounds. In the chromium (VI)-treated soils, the concentration of water soluble chromium present in the soil was found to decrease less rapidly than found for chromium (III) and was also found to decrease less rapidly on alkaline soils than on acid soils. The authors proposed the following mechanism, where the reduction of the chromium (VI) to chromium (III) (with subsequent formation of insoluble chromium (III) species) occurs more rapidly on acid soils than alkaline soils:

$$CrO_3 + H_2O \Leftrightarrow H_2CrO_4 \Leftrightarrow 2H^+ + CrO_4^{2-}$$

$$CrO_4^{2-} + 6H^+ + 3e^- \Rightarrow Cr^{3+} + 4H_2O$$

Losi et al. (1994) reported that organic-amended soil was able to effectively reduce chromium (VI) to chromium (III) at neutral pH, but the same soil was less effective at reducing chromium (VI) when non-amended. The authors concluded that reduction of chromium (VI) in soil occurred by both chemical and biological processes, with each accounting for roughly half of the reduction seen. Low oxygen concentrations in the soil where also found to increase the rate of reduction.

The reduction of chromium (VI) was studied in buffered solutions containing 100 µg/l chromium (VI) and various reducing agents (Schroeder and Lee, 1975). Reduction to chromium (III) was found to occur when Fe^{2+} was added to the water but the extent of reaction was found to vary

with both the iron concentration and pH, as Fe^{2+} is also oxidised by oxygen in the pH range of the study (pH = 7.1-9.1). At an initial Fe^{2+} concentration of 0.4 mg/l, around 73% of the chromium (VI) present was reduced at pH=7.5, but at an initial pH of 9.1 only 20% of the chromium (VI) was reduced as oxidation of the Fe^{2+} by oxygen is more favoured at increasing pH. Rapid reduction of chromium (VI) was found to occur when Na_2S ($1 \cdot 10^{-3}$ mole/l) was added to the solution at pH 9.0. The effect of pH on this reaction was not studied. Similarly, some organic compounds containing sulfhydryl groups such as cysteine and mercaptosuccinic acid (at a concentration of $1 \cdot 10^{-3}$ mole/l and pH 9.1) also rapidly reduced chromium (VI) under the conditions used. Finally, the reduction of chromium (VI) was studied in natural (lake) water samples. Here, chromium (VI) (concentration 100 µg/l) was added to the water sample, with or without prior filtering, and monitored for 14 days. No significant reduction of chromium (VI) was seen in any sample over the 14 day period.

Deng and Stone (1996) showed that chromium (VI) could be reduced to chromium (III) by mandelic acid or methyl mandelate in acid solution in the presence of titanium dioxide. Without the titanium dioxide catalyst, the reaction was very slow and only occurred at low pH (pH<3). However, in the presence of titanium dioxide (1 g/l) the rate of reduction of to chromium (III) was found to be relatively rapid and increased with decreasing pH over the range pH 6-3. The reaction mechanism was thought to involve adsorption of the chromium (VI) to the titanium dioxide (the adsorption was shown to increase with decreasing pH), followed by reduction by the mandelic acid or methyl mandelate.

The kinetics of oxidation and reduction of chromium under environmental conditions has been investigated by Saleh et al. (1989). Experiments were carried out with three types of sediment and soil, clay, and five different types of water phase. The model compounds used in the experiments were sodium dichromate as a source of chromium (VI) and chromium chloride as a source of chromium (III). Liquid-phase batch experiments were carried out using the various water samples spiked with 10 mg/l of either chromium (VI) or chromium (III). The soil, sediment and clay experiments were carried out at the same water concentrations, with varying amounts of solid materials added. In addition to this, microcosm experiments were carried out by introducing several dishes of sediment into aquaria through which the water phase was continuously re-circulated. In all experiments the concentration of total chromium, filterable chromium and chromium (VI) was determined. In some samples, the concentration of chromium (III) was also determined directly. The properties of the various water and solid phases used in the experiment are summarised in **Table 3.4**.

Table 3.4 Properties of water and solid phases used in the kinetic investigations of chromium oxidation/reduction (Saleh *et al*, 1989)

Water sample	pH	Organic carbon	Total alkalinity as $CaCO_3$	Hardness (as $CaCO_3$)
Pure water	5.50	<0.50 mg/l	<0.10 mg/l	<0.10 mg/l
Synthetic rainwater	3.75	0.60 mg/l	<0.10 mg/l	<0.10 mg/l
Synthetic hard water	7.90	1.46 mg/l	93 mg/l	100 mg/l
Lake water	7.20	10.39 mg/l	33.3 mg/l	
Pure water (with fulvic acid)	4.50			<0.10 mg/l

Soil and sediment samples	CEC (meq/100 g)	pH	Total iron (mg/g)	Total manganese (mg/g)	% organic carbon	% solids
Clay	100.8	7.92	48.82	12.8	0.02	100
Lake Sediment	10.3	5.36	19.25	20.9	1	36
River Sediment 1	9.0	6.10	54.07	20.3	0.78	52
River Sediment 2	12.1	6.55	27.79	~15	0.24	70
Natural soil	11.9	6.75	39.62	12.1	0.72	81
Reference soil	20	7.25	71.36	19.1	0.35	100
Potting soil	90.4	7.12			13.0	46
Garden soil	26.9	7.40			2.85	72.45

Note: CEC = cation exchange capacity

In total, 22 experiments were carried out. In the experiments investigating the reduction of chromium (VI) in water, the results indicated that chromium (VI) was relatively stable to reduction under aerobic conditions over 41 days, and little reduction was observed even in water containing secondary effluent from a wastewater treatment plant under aerobic and anaerobic conditions. In experiments where reducing agents such as S^{2-} or Fe^{2+} were added to the water, reduction half-lives of instantaneous to a few days, depending on the conditions used, were found, with re-oxidation back to chromium (VI) occurring only very slowly. In experiments using chromium (III), oxidation half-lives of around 9 years were determined. Oxidation was slightly faster (half-lives of around 2-3.5 years) when an oxidant (50 mg/l of MnO_2) was added. Soluble inorganic and organic chromium (III) complexes were detected in some experiments (Saleh et al., 1989).

In experiments using a water and solid phase, no measurable reduction or adsorption of chromium (VI) was seen in solutions containing 10% clay or natural soil over 14 days under aerobic or anaerobic conditions. In lake water containing 10% lake sediment, rapid reduction of chromium (VI) was seen under aerobic ($t_{½}$ = 15 minutes) and anaerobic ($t_{½}$ = instantaneous) conditions. In experiments with water containing 1% sediment or soil, reduction of chromium (VI) was also observed with the reaction occurring much faster under anaerobic conditions ($t_{½}$ = instantaneous to 21.5 days) than aerobic conditions ($t_{½}$ = 11-230 days). Each sediment or soil system was shown to have a characteristic reducing capacity that was related to the amounts of reducing agents present in the sample. In most cases, the reducing capacity was related to the organic carbon content of the solid phase. In experiments using chromium (III), slow formation

of chromium (VI) was generally observed (0.2-2.5% conversion over 44 days), with a slightly higher formation (2.7% over 25 days) occurring in lake water containing 1% lake sediment (Saleh et al., 1989).

In the microcosm experiments, sediments were found to play an important role in reducing chromium (VI) to chromium (III), with the reducing capacity of the sediment being related to the percentage organic carbon, and the amount of Fe^{2+}, S^{2-} or other reducing agents present (Saleh et al., 1989).

Schroeder and Lee (1975) studied the transformations of chromium (VI) and chromium (III) in simulated natural waters. The oxidation of chromium (III) by dissolved oxygen was studied using buffered solutions (pH 5.9-9.9) containing 100-125 µg/l of chromium (III). At a temperature of around 22-26^{o}C, the rate of oxidation to chromium (VI) was slow, with about 3% of the added chromium (III) reacting in 30 days. At higher temperatures the rate of oxidation increased markedly, indicating that the reaction had high activation energy. It was concluded that in the environment, the chromium (III) is likely to be removed from solution by other processes (such as adsorption) before any significant oxidation to chromium (VI) by dissolved oxygen can occur.

The effect of manganese dioxide (MnO_2) on the rate of oxidation of chromium (III) in buffered solution was determined by adding various concentrations (25, 100 and 250 mg/l) to the solutions, with stirring to maintain a uniform suspension. The rate of oxidation of chromium (III) was found to depend on the concentration of MnO_2 present (half-life of 42 minutes at a MnO_2 concentration of 25 mg/l; half-life of 3 minutes at a MnO_2 concentration of 250 mg/l). When the experiments were repeated using natural water, the rate of oxidation of chromium (III) was strongly inhibited. This effect was thought to be due to cations such as Ca^{2+} or Mg^{2+} present in the natural water occupying sorption sites on the MnO_2. The authors again indicated that under conditions present in the environment, other processes (adsorption) are likely to occur before significant oxidation of chromium (III) by MnO_2 can take place in the water phase (Schroeder and Lee, 1975).

Eary and Rai (1987) studied the effects of dissolved oxygen, chromium concentration, mineral surface area and pH on the oxidation of chromium (III) to chromium (VI) by manganese dioxide in aqueous solution at 27^{o}C. No significant oxidation of chromium (III) was observed over 24 days in solutions without manganese dioxide, and the dissolved oxygen concentration was shown to have very little effect on the oxidation of chromium (III) by manganese dioxide, indicating that the oxidation was occurring directly by reaction with the manganese dioxide. In most experiments, the rate of oxidation was found to be initially rapid, and then slowed significantly after 20-100 hours, with the concentration of chromium (VI) increasing slowly over time even after 500 hours. The rates of chromium (III) oxidation were found to increase with increasing surface area of the manganese dioxide, although other factors such as MnO_2 dissolution and the possible formation of intermediate manganese dioxide reaction products made exact interpretation of the data difficult. The extent of chromium (III) oxidation was thought to be limited, in the experimental systems used, by the adsorption of the anionic chromium (VI) to the reactive sites in acidic solutions, and by the formation of insoluble $Cr(OH)_3$ in neutral or alkaline solution, where the overall rate of oxidation of chromium (III) to chromium (VI) is very slow.

Bartlett and James (1979) found that 135 out of 150 soils tested by a quick laboratory screening method had the ability to oxidise chromium (III) (as chromic chloride) to chromium (VI). Of the soils tested, oxidation of chromium (III) did not occur in soils with very low manganese dioxide

concentrations. The oxidation was found to be rapid, with peak concentrations of chromium (VI) being found in the soils over 1 day, with a subsequent slower decrease over several months (presumably by reduction back to chromium (III)). The mean oxidising capacity of a subset of 50 of the soils was determined as 0.2 μmol Cr/g of soil.

As part of a study monitoring levels in an estuary downstream from the discharge of a leather tannery, Walsh and O'Halloran (1996b) collected sediment samples from the area. Analysis of sediment samples indicated that the highest total chromium concentrations were associated with the particles of lowest grain size and that some sediments were able to oxidise a small amount of chromium (III), when added to the sediment, to chromium (VI) (maximum seen was 3.5% in 24 hours), followed by a slower reduction of the chromium (VI) back to chromium (III). These findings were thought to represent a relatively rapid oxidation of chromium (III) by manganese oxides followed by diffusion of the chromium (VI) produced to the anaerobic layers of the sediment, where reduction back to chromium (III) occurred. Similar processes have been reported to occur in flooded soils (Bartlett, 1991).

Abu-Saba and Flegal (1995) carried out a study on the levels of dissolved chromium (VI) and chromium (III) present in San Francisco Bay. They found that the bay-wide average concentration of dissolved chromium (VI) was 2.1 nM (0.11 μg/l), but that the concentration was significantly lower (0.6 nM (0.03 μg/l)) in a low salinity (1-9‰) shallow region of the bay, where there was a relatively high level of contact between sediments and overlying water. The authors attributed the low-levels of chromium (VI) found in the shallow region to reduction to chromium (III) (the chromium (III) levels found in this area were above the bay average). In another shallow area of the bay, this time of higher salinity (23-26‰), no evidence for reduction of chromium (VI) was seen.

Biotic processes

The factors affecting the microbial reduction of chromium (VI) by a mixed anaerobic culture have been studied by Chen and Hao (1996). Anaerobic sludge from a domestic wastewater treatment plant was enriched in the chromium-reducing bacteria by incubation with sodium acetate as the sole carbon source and chromium (VI). Batch experiments were carried out using mixed liquors from the enrichment cultures and initial chromium (VI) concentration of ~20-60 mg/l. No reduction of chromium (VI) was seen in experiments without sodium acetate, and the amount of chromium (VI) reduced was found to be proportional to the amount of acetate added (proportion of 0.2 mg Cr (VI) reduced/mg sodium acetate degraded). Reduction of chromium (VI) was also shown to occur at similar rates with other carbon sources, such as propionate, at a slower rate with lactate and ethanol, but no reduction of chromium (VI) was seen with either glucose or citrate as carbon source. The rate of reduction of chromium (VI) was found to depend on the initial biomass concentration. Certain electron acceptors such as sulphate (at 120 mg SO_4^{2-}/l) and nitrate (at 150 mg N/l) caused a slight inhibition of the reduction reaction, and reduction was almost completely inhibited under aerobic conditions (this effect was reversible once anaerobic conditions were recreated). The reaction rate was also shown to be pH dependent, reaching a maximum rate of reduction of 0.15 mg Cr/mg volatile suspended solids/hour at pH 7.3. The optimum temperature for the reaction was 32°C. Other metals were found to be inhibitory to the reduction of chromium (VI) in the order copper>nickel>cadmium>zinc, whereas lead (at concentrations >2 mg/l) was found to increase the reduction rate.

In a later experiment, Chen and Hao (1997) investigated the reduction of chromium (VI) in an anaerobic chemostat fed with acetate-containing synthetic medium in a continuous process. The

acclimated anaerobic culture used was derived from the anaerobic digester from a domestic wastewater treatment plant. The system was operated at 20°C and 35°C using an initial influent chromium (VI) concentration of 26 mg Cr/l and various dilution rates within the reactor. The removal of chromium (VI) was found to be dependent on the dilution rate of the system. At dilution rates of 0.15 day^{-1} (i.e. chromium loading inside the reactor of 4 mg Cr/l/day), almost 100% removal of chromium was seen in the system at both 20°C and 35°C. At higher loadings (decreased dilution or increased influent concentration), the removal of chromium (VI) from the system was reduced (i.e. 18% removal was seen at a dilution of 0.35 day^{-1} at 20°C (chromium loading inside the reactor 9 mg Cr/l/day). Overall, the system at 35°C exhibited a higher chromium (VI)-reducing capacity than the system at 20°C, possibly related to the higher microbial growth rate at 35°C. The optimum chromium (VI) mass loading in the system was estimated to be around 5 mg Cr/l inside the reactor.

The reduction of chromium (VI) by a highly chromium-resistant consortium of sulphate-reducing bacteria isolated from an electroplating sludge has been studied by Fude et al. (1994). They found that 80-95% of the chromium (VI) (as potassium dichromate) added to the bacterial culture at concentrations between 50 and 2,000 mg Cr/l could be removed from solution. It was thought that reduction of the chromium (VI) to insoluble chromium (III) was occurring via H_2S which was formed as a result of sulphate reduction by the bacteria. Smillie et al. (1981) also found that bacterially-produced hydrogen sulphide reduced chromium (VI) to chromium (III) in a marine environment receiving effluent from a tannery.

Shen et al. (1996) studied the reduction of chromium (VI) (~10 mg Cr/l as potassium chromate) in anaerobic microcosms (containing 50 g of aquifer material in 200 ml of mineral medium; temperature 22°C) using benzoate (15 mg/l) as the sole electron donor in the system. Reduction of chromium (VI) with concurrent degradation of benzoate was seen to occur rapidly when nitrate (KNO_3 concentration 1 mmole/l) was added to the system. No reduction of chromium (VI) or degradation of benzoate was seen in the system during the first seven days of the experiment before the nitrate was added. Once all the chromium (VI) had been reduced (12 days after addition of the nitrate), the microcosm was re-spiked with chromium (VI) and a much more rapid reduction of the chromium was seen (complete removal within 4-5 days). The authors concluded that the indigenous species present in the system were capable of reducing chromium (VI) in a process linked to the anaerobic oxidation of benzoate after stimulation of the micro-organisms with nitrate.

As well as experiments using mixed bacterial cultures, several bacterial species have been identified that can reduce chromium (VI) to chromium (III), for example *Pseudomonas ambigua, Pseudomonas fluorescens, Pseudomonas putida, Pseudomonas aeruginosa, Enterobacter cloacae, Escherichia coli, Desulfovibrio vulgaris, Chlamydomonas* sp., *Agrobacterium radioabacter* and *Aeromonas dechromatic* (DeLeo and Ehrlich, 1994; Horitsu et al., 1987; Ishibashi et al., 1990; Llovera et al., 1993; Losi et al., 1994; Lovley and Phillips, 1994; Ohtake et al., 1990; Ohtake and Hardoyo, 1992; Shen and Wang, 1994a and 1994b; Suzuki et al., 1992; Wang et al., 1989; Wang et al., 1990). Most of these experiments have been carried out using anaerobic conditions, but reduction of chromium (VI) has also been demonstrated under aerobic conditions (usually at a slower rate) with some bacterial strains (e.g. *Escherichia coli*), when suitable electron donors (e.g. glucose, acetate, propionate, glycerol, glycine) are present (Shen and Wang, 1994b).

Gopalan and Veeramani (1994) isolated a chromium tolerant *Pseudomonas* sp. from chromium-contaminated wastewaters from a tannery. Using bench scale continuous-stirred aerobic reactors inoculated with this microorganism at 28-30°C and pH 6.8, a steady-state reduction of 81-100%

of chromium (VI) was seen for influent concentrations of 5-124 mg Cr/l using a hydraulic retention time of 72 hours.

Sulzbacher et al. (1997) investigated the use of anaerobic biological methods to reduce the concentration of chromium (VI) present in filter sludge from an electrochemical process. The batch experiments used the aqueous fraction of the sludge, which had a dry matter content of 0.3%, a pH of 2.76 and a total chromium content of 7.8 mg/l. The amount of chromium (VI) present in this solution was below the limit of detection and so in order to carry out the experiments, the filter sludge aqueous phase was amended with 10 mg Cr(VI)/l (as potassium dichromate). The solutions were incubated under anaerobic conditions at 30^{o}C for 7 days in order to investigate a number of variables (pH, sulphate concentration, addition of yeast as a carbon source, amount of filter sludge liquid used). A strain of *E. cloacae* was used as inoculum. Gas development was monitored during the experiments as an indication of biological activity, and was generally found to be highest on the first day of the experiments. The results of the experiments indicated that chromium (VI) concentrations of 2.5 mg Cr/l could be reduced to below detectable levels, particularly where low waste (filter sludge aqueous phase) concentrations and high yeast concentrations favoured high biological activity. No effect of pH (between pH 6-8) or addition of sulphate (up to 20 mmole/l) was seen on the process. At higher waste concentrations, an inhibition of biological activity may occur resulting in a lower rate of reduction of chromium (VI) to chromium (III). Although the reduction of the chromium (VI) concentration could be explained in terms of active biological processes, other potential mechanisms such as sorption/reduction by organic material generated in the system could also be occurring.

Fujie et al. (1994) demonstrated the feasibility of reducing chromium (VI) to chromium (III) in metal plating wastewater using an anaerobic bioreactor inoculated with a strain of *E. cloacae*.

Summary of degradation/transformation processes

There is a large body of evidence indicating that chromium (VI) can be reduced to chromium (III) under anaerobic conditions found in the environment by both biotic and abiotic processes, including reaction with iron (II), sulphides, organic matter and anaerobic micro-organisms. The reduction is generally favoured by increasing concentration of the reductant and lower pH. Thus, the reduction of chromium (VI) would be expected to occur most rapidly in acidic soils with high iron, sulphide or organic carbon contents. Under such conditions, reduction of chromium (VI) to chromium (III) may be complete within a few hours.

Under aerobic conditions and at higher pHs (around 7-8 and above), chromium (VI) appears to be more stable to reduction than is seen at lower pHs under anaerobic conditions. This is particularly the case where low concentrations of reductants such as iron (II) are present. Chromium (VI) in surface water appears to be relatively stable under these conditions (this will particularly be the case in seawater where the pH is generally relatively high). The same is also likely to be the case in aerobic sediments and soils, but here chromium (VI) is considered to be relatively mobile (see Section 3.1.1.2.2) and so would be expected to migrate to the anaerobic layers where reduction to chromium (III) could occur. Therefore, under aerobic conditions, the rate of reduction of chromium (VI) to chromium (III) may be limited by the rate of transport of the chromium ion to suitable environments for the reduction to occur.

Oxidation of chromium (III) to chromium (VI) can occur, but the process is only likely to be significant in aerobic soils and sediments where high concentrations of manganese dioxide (the only known environmental oxidant for chromium (III)) exist. Under these conditions, a few %

(e.g. 2-3%) of the chromium (III) present may oxidise to chromium (VI). Again, any chromium (VI) formed in the soil or sediment may be subsequently transported to anaerobic layers where rapid reduction back to chromium (III) could occur. The oxidation reaction is thought to be limited by the low solubility of chromium (III) under neutral to alkaline conditions, and the adsorption of anions to the active sites on the manganese dioxide under more acidic conditions.

For the risk assessment, it will be assumed that for acidic (or neutral, where high concentrations of reductants for chromium (VI) exist) soils, sediments and waters, chromium (VI) will be rapidly reduced to chromium (III) and that 3% of the chromium (III) formed will be oxidised back to chromium (VI). The net result of this is that of the estimated chromium (VI) release to the environment, 3% will remain as chromium (VI) and 97% will be converted to chromium (III).

Under less favourable conditions, e.g. alkaline conditions (~pH>8) and/or neutral conditions, where low concentrations of reductants for chromium (VI) exist, it will be assumed that the rate of reduction of chromium (VI) to chromium (III) is slow, with a long half-life of around 1 year. Such conditions are found in seawater, where a pH of around 8 is typical.

3.1.1.2.2 Adsorption

The estimation methods given in the main Technical Guidance Document for determining adsorption coefficients for soil, sediment and suspended sediment are not applicable to chromium compounds, as indicated in the Annex on assessment of metals. Measured values are available for a variety of soil and sediment types. These are discussed in the following Sections and will be used to derive suitable adsorption coefficients for use in modelling the behaviour of chromium (VI) in the environment.

Wherever possible, the distinction is made between the adsorptive behaviour of chromium (VI) and chromium (III). However, as seen in Section 3.1.1.2.1, chromium (VI) can, under some conditions, rapidly react with constituents of soils and sediments to form chromium (III), which could possibly affect and complicate the interpretation of the results. In experiments where the adsorption of total chromium is determined, it can be assumed that adsorption seen was mainly due to relatively insoluble chromium (III) complexes since these are the dominant form of chromium in the environment. The available data are summarised in **Table 3.7** at the end of this Section.

Adsorption to soil

Janssen et al. (1997a) determined the adsorption coefficient for total chromium in 20 Dutch soils using a field-based approach. The soils chosen for the study were known to contain elevated levels of certain heavy metals, including chromium. The top 20 cm of each soil was sampled and the pore water from the soil was collected by centrifugation. The concentration of total chromium in the pore water and the solid phase were then analysed. Soil-water partition coefficients (Kp_{soil}) of 524-24,217 l/kg were determined for total chromium. A wide range of soil types was used in these experiments. Analysis of the various soil parameters (such as pH, organic matter content, clay content, iron and aluminium oxyhydroxide contents, dissolved organic carbon content of pore water and ionic strength of pore water) lead to the following relationship between the soil properties and the partition coefficient:

$$\log Kp_{soil} = 0.13 \cdot pH + 0.43 \cdot \log Al_{ox} - 0.42 \cdot \log DOC + 2.75 \quad R^2 = 0.75$$

where Al_{ox} = concentration of aluminium oxyhydroxides in solid phase (mmole/kg)
DOC = dissolved organic carbon content of pore water (mmole/l)

Soil pH was found to be most important in determining the Kp_{soil} value for total chromium (with the Kp_{soil} increasing with increasing pH), but other factors such as dissolved organic carbon (DOC) in the pore water, and the concentration of aluminium oxyhydroxides present in the soil where also found to correlate with the Kp_{soil}. The pH dependence was explained by the competition of H^+ for binding sites in the soil. The negative dependence of Kp_{soil} on the dissolved organic carbon content was thought to be due to binding of the chromium by the dissolved organic carbon in competition with binding to the solid phases of the soil. These properties are typical of the behaviour of the acidic chromium (III) species rather than the chromium (VI) oxyanions found in the environment (see discussion later) and so the Kp values obtained probably refer to chromium (III).

As the dissolved organic carbon content of most soil pore water is unknown, the above regression equation was recalculated using only bulk soil parameters (Janssen et al., 1997a). In this case the following relationship was found:

$$\log Kp_{soil} = 0.15 \cdot pH + 0.50 \cdot \log Al_{ox} + 2.22 \qquad R^2 = 0.69$$

Although the correlation in this case is less good than when the DOC is included, in practice this is a more useful equation to use as it depends only on the soil pH and aluminium oxyhydroxide contents.

The adsorption of both chromium (VI) and chromium (III) to soil has been studied by Hassan and Garrison (1996). Three soils were used in the experiment and each soil was spiked with either chromium (VI) (as potassium chromate) or chromium (III) (as chromic chloride) and analysed for the interconversion and distribution of the chromium species over various time periods. The partition studies were carried out by adding 30 ml of an aqueous solution of the chromium ions (concentration 1 mg/l for chromium (VI) and 10 mg/l for chromium (III)) to a tube containing the soil (1.5 g for chromium (VI) and 0.15 g for chromium (III)), and allowing the system to equilibrate for 48 hours (chromium (VI)) or 6 hours (chromium (III)). The measured values for Kp_{soil} at various pHs are shown in **Table 3.5**.

Table 3.5 Variation of Kp_{soil} with pH (Hassan and Garrison, 1996)

Soil	Organic carbon	Kp_{soil} (l/kg)	
	content	Cr(III)	Cr(VI)
Loam	1.92%	298 at pH 4.70	39.9 at pH 4.26
		720 at pH 5.36	24.9 at pH 5.28
		557 at pH 5.62	13.3 at pH 5.98
		788 at pH 5.82	6.1 at pH 6.57
		2,823 at pH 6.00	0.2 at pH 8.06
		5,075 at pH 6.52	0.5 at pH 11.10
		15,382 at pH 6.54	0.8 at pH 11.69
		14,346 at pH 6.69	1.0 at pH 11.94
Loess	0.11%	19.716 at pH 6.03	45.6 at pH 2.19
		20,833 at pH 6.20	46.5 at pH 2.52
		23,961 at pH 6.37	52.3 at pH 3.47
		24,066 at pH 6.55	45.4 at pH 5.75
		31,296 at pH 6.73	12.1 at pH 8.29
		35,525 at pH 7.15	1.5 at pH 11.13
		47,583 at pH 7.37	1.5 at pH 11.68
		55,918 at pH 7.41	2.0 at pH 11.98
Clay	3.75%	330 at pH 3.63	17.0 at pH 1.83
		382 at pH 3.81	21.2 at pH 1.99
		536 at pH 4.03	26.9 at pH 2.29
		768 at pH 4.48	44.6 at pH 2.86
		2,405 at pH 5.15	24.9 at pH 6.81
		13,370 at pH 5.61	2.0 at pH 10.35
		27,151 at pH 5.82	1.4 at pH 11.40
		23,658 at pH 6.16	1.4 at pH 11.77

These relate the total concentration of chromium in soil to the concentration of either chromium (III) or chromium (VI) measured in solution. In the experiments with chromium (III), chromium (VI) was detected in the pore water and was thought to be as a result of oxidation by manganese oxides (maximum yield of chromium (VI) seen was up to 2% after 6 hours). The chromium (III) was found to be removed from solution very quickly, indicating that adsorption was a rapid process (equilibrium reached after 6-24 hours). On the other hand, chromium (VI) was found to be removed from the water phase at a much lower rate, indicating that some of this removal may have been due to reduction by soil minerals (e.g. ferrous iron or sulphide) or by complexation with organic matter, rather than purely by adsorption onto the solid phase. As can be seen in **Table 3.5**, the adsorption (as measured by Kp_{soil}) of chromium (III) to soils are much larger than that found for chromium (VI). The pH effects on Kp_{soil} were explained by the cationic nature of chromium (III) and the anionic nature of chromium (VI) species in the system, and the charge on the soil organic carbon (which is a function of pH). Thus in acidic solution, the adsorption sites are positively charged (negatively charged sites are neutralised) and so the adsorption of the

positively charge chromium (III) cations is reduced and that of the negatively charged chromium (VI) anions is increased slightly. At higher pH, the insoluble Cr $(OH)_3$ species precipitates (above pH of around 4) and so increases the apparent Kp_{soil} for chromium (III), whereas, for chromium (VI) species, the increasing negative charges on the soil reduce the adsorption of the chromium (VI) anions. For similar reasons, the adsorption of chromium (III) was found to decrease when other cations which could compete for the binding sites were added to the pore water.

Payá Pérez et al. (1988) studied the adsorption of chromium (III) (as ^{51}Cr-chromic chloride) and chromium (VI) (as ^{51}Cr-chromate) onto sand, sandy soil and a sandy loam. Both column and batch experiments were carried out. The results of the experiment are shown in **Table 3.6**.

Table 3.6 Kp_{soil} values for sandy soils (Pérez et al., 1988)

Soil type	Soil properties					Kp_{soil} (l/kg)	
	% sand	% silt	% clay	% organic matter	Soil pH	Cr(VI)	Cr(III)
Sand	100%					0.35-17.4	27 (pH 4) 12 (pH 6) 23 (pH 8)
Sandy soil	92%	8%		0.77%	5.28-6.56	*	197 (pH 4) 105 (pH 6) 21 (pH 8)
Sandy loam	78%	6%	16%	1.62%	5.19-6.48	6.6-18.4	608 (pH 4) 185 (pH 6) 116 (pH 8)

Note: *reduction to chromium (III) occurred.

Column experiments were carried out using chromium (VI) with sand and sandy soil. With the sand, the chromium (VI) was found to move through the column rapidly (the relative velocity to that of water was 0.74) and the equilibrium sand-water partition coefficient was determined as 17.4 l/kg. Batch experiments with chromium (VI) and sand gave a lower sand-water partition coefficient of 0.35 l/kg. These results indicate that chromium (VI) is very mobile in sand. In the column experiments using chromium (VI) with the sandy soil, no chromium could be eluted from the column. Analyses of the column indicated that all the chromium (VI) had been reduced to chromium (III) on the column and so a partition coefficient could not be determined. Batch experiments were carried out for chromium (VI) using the sandy loam and a wide range of chromium concentrations. Here, chromium (VI) was found to be reduced to chromium (III) over time (experiments lasted up to 90 hours), resulting in changes in the apparent adsorption with time. The soil-water adsorption coefficients obtained for chromium (VI) in the experiments by fitting the data to either Langmuir or Freundlich isotherms were in the range 6.6-18.4 l/kg. In batch experiments with chromium (III), the soil-water adsorption coefficient was found to increase with increasing organic carbon content. The effect of pH on the adsorption of chromium (III) was investigated. It was found that at pH>5.5 the chromium (III) in the aqueous phase precipitates out, but at higher pH (>7) soluble organic matter forms complexes with the chromium (III) so increasing the concentration in the aqueous phase, and reducing the adsorption of chromium (III) to the soil.

The adsorption of chromium (VI) (as a chromate) was investigated in alluvial material collected at a depth of 1 m below the soil surface (Stollenwerk and Grove, 1985). The <2mm size fraction of the material was used in the experiments and this was identified as consisting of quartz,

plagioclase feldspar, muscovite, hematite and magnetite. Iron oxide coatings on the particulates were also apparent. The organic matter content of the material was 1 g/kg (0.1%) and the material had a pH of 6.45. Column and batch experiments were used to investigate the adsorption and desorption of chromium (VI) from solution. In the column experiments with an initial chromium (VI) concentration in the water phase of 50 mg/l, an adsorption partition coefficient of 2.3-2.4 l/kg was determined. Desorption experiments, carried out over 232 days indicated that around 50% of the chromium present on the column was removed rapidly, but as time passed, it became increasing difficult to remove the remaining chromium present on the column. Further extraction experiments carried out under various conditions indicated that some of the chromium (VI) initially adsorbed had been incorporated into the structure of iron oxides present in the alluvial material, probably as chromium (III). In the batch experiments, the adsorption coefficient was found to reduce from 52 l/kg at a chromium (VI) concentration of 0.02 mg/l, to a value of 1.7 l/kg at a chromium (VI) concentration of 72.8 mg/l. Anions, such as sulphate and phosphate, were found to reduce the adsorption of chromium (VI) by competing for the positively charged sites present on the alluvial material.

The leaching rates of total chromium from spruce forest soils have been investigated by Tyler (1978). Two soils were used in the study, one from close to a brass foundry, which contained high concentrations of heavy metals (total chromium concentration 3.6 mg/kg) and one from a control site (total chromium concentration 0.98 mg/kg). The soils were sampled from the purely organic needle mor layer and were packed into leaching beds to a depth of 40 mm (the normal thickness of the mor horizon from the area). Artificial rainwaters of differing pH were used to leach the metals from the soil. The leaching water was added at a rate of 2 l every second day until 125 l had been applied to the beds (125 l of solution was equivalent to 2,700 l/m^2 of surface area). The 10%-residence time for chromium (time taken for a 10% decrease of the total concentration of chromium in the mor horizon) was estimated to be around 15-20 years in the control soil and 50-150 years in the polluted soil over a pH range of 2.8-4.2, using the known precipitation rate of the area. The leaching rate was found to increase slightly with decreasing pH over the range studied.

Adsorption to sediment and suspended sediment

Ciceri et al. (1992) studied the behaviour of chromium in natural sediments using benthic chambers placed in the Tyrrhenian Sea. The sediment in the area was a silty-clay with a total organic carbon content of 1.6% and a total carbon content of 3.6%. The salinity at the site was 3.8-3.85‰ and the pH was 8.2-8.3. The water depth at the site was 27 metres. The concentration of total chromium in seawater (dissolved; <0.4 µm) at the site was around 0.12-0.13 µg/l with little variation with depth. The total concentration of total chromium in suspended matter (>0.4 µm) was found to decrease with depth (24 µg/g at 5 metres, falling to 3.5 µg/g at a depth of 22 metres). From these data, suspended matter-water partition coefficients (Kp_{susp}) of 29,200-200,000 l/kg can be estimated. A negative flux from sediment to water was found in the systems, meaning that there was a net transfer of chromium from the overlying water to sediment in the system.

The distribution of total chromium between the water phase and suspended sediments has been studied in sediment samples from the Rhine-Meuse delta (Golimowski et al., 1990). The values of Kp_{susp} estimated from the data ranged from 1.4-5.5$\cdot 10^5$ l/kg in the Rhine, 1.4-5.7$\cdot 10^5$ l/kg in the Waal and 3.4-5.6$\cdot 10^5$ l/kg in the Maas.

Van Der Kooij et al (1991) derived values of Kp_{susp} based on monitoring data of levels of total chromium in surface waters (before and after filtering) from The Netherlands. Both freshwaters

and saline waters were included and values were derived for 13 waters. The overall range of Kp_{susp} measured was 126,000-786,000 l/kg in fresh waters, with a median value of 290,000 l/kg. Similar values were obtained in saline waters (i.e. Kp_{susp} = 324,000 l/kg (1 sample; 0.1-0.5% salinity), Kp_{susp} = 306,000-320,000 (2 samples; 1-5% salinity) and Kp_{susp} = 228,000 l/kg (1 sample; >10% salinity).

A more recent survey of waters in The Netherlands (Van Den Berg and Zwolsmann, 2000) reported a median value of 218,000 l/kg.

Young et al (1987) studied the adsorption of chromium (III) to river sediments. The experiments were carried out at pH 8.3, where the dominant chromium species were $Cr(OH)_3$ and $Cr(OH)_2^+$. The sediment used had a mean organic carbon content of 2.65% on a dry weight basis. Adsorption partition coefficients (Kp_{sed}) were determined over various time periods and the values obtained for chromium were 25,600 l/kg after 4 hours, 30,800 l/kg after 24 hours and 32,300 l/kg after 48 hours. It was considered that the value of Kp_{sed} had reached equilibrium after 24 hours. Desorption of the chromium from the sediment was found to be slow, with little or no desorption occurring over 24 days in clean water. The desorption rate could have been limited by the kinetics of dissolution of the insoluble forms of chromium (III) likely to be present in the system. The experimental values for Kp_{sed} agreed with values obtained from analysis of 20 bottom sediments and pore water concentrations from the area (Kp_{sed} = 60-44,800 l/kg; mean 7,100 l/kg). Higher values were obtained from analysis of measurements of suspended matter and filtered water concentrations in the area (in this case the suspended matter-water partition coefficients (Kp_{susp}) were in the range 30,100-1,059,600 l/kg; mean 322,400 l/kg).

The effect of pH on the sediment-water partitioning of chromium has been studied using three contaminated sediments containing chromium. In the experiments, a solid:solution ratio of 1:1000 was used, and chromium (III) was added to the aqueous phase (at a concentration of 50 ppb). At pHs>6, chromium was strongly adsorbed onto the solid phase (Kp_{sed} ~ 120,000 l/kg), but the adsorption was found to reduce with decreasing pH below 6, giving a Kp_{sed} value of around 11,000 l/kg at pH 4.5. The sediments were also subjected to sequential extraction to investigate the fractionation of the metals within the sediment. These results showed that around 41.4-59.0% of the chromium in the sediment was essentially non-labile, and only a very small amount (<0.04%) was in the exchangeable fraction. Of the other fractions investigated, 1.1-5.9% of the total chromium was in the carbonate fraction, 17.7-45.1% was associated with iron and manganese oxides and 8.6-22.5% was associated with the organic fraction (Young et al., 1992).

The adsorption of chromium (III) and chromium (VI) to marine sediment has been studied by Wang et al. (1997). In the study, two sediments (one with 2% dry weight loss on ignition and one with 10% dry weight loss on ignition (dry weight loss on ignition is a measure of the organic matter content)) were incubated with a solution of either ^{51}Cr(III) or ^{51}Cr(VI) in seawater (28%) for 5 days. The pH of the system was around 7.8-8.0. Analysis of the sediments exposed to ^{51}Cr (VI) indicated that the chromium had been reduced to chromium (III). The values obtained for Kp_{sed} were 34,000 l/kg for chromium (III) in the low organic matter content sediment and those for the chromium (VI) exposed sediment were 940 l/kg in the low organic matter content sediment and 2,300 l/kg in the high organic matter content sediment.

Braunschweiler et al. (1996) reported the results of an unpublished study on the adsorption coefficients for chromium (III) and chromium (VI) to suspended sediments in the Netherlands. The values reported were Kp_{susp} = 25,000-800,000 l/kg for chromium (III) and 250-50,000 l/kg for chromium (VI).

Discussion of adsorption coefficients for chromium

Table 3.7 summarises the published values for $Kp_{water\text{-}solids}$ for both freshwater and marine environments. The values are reported according to a variety of methods and may not be directly comparable; however, they do give a general indication of the partitioning of chromium (VI) in the environment relative to that of total chromium and/or chromium (III) for several environmental compartments. In general, chromium (III) is more likely to partition to solids in the sediment and soil. For the water column, chromium (VI) and chromium (III) have similar adsorption partition coefficients for suspended solids, which are greater than those found for sediment and soil.

Chromium (VI) exists mainly as highly soluble oxoanions in the environment (see Section 3.1.1.3) and is expected to be mobile in soils and sediments. The adsorption of chromium (VI) is pH dependent. Under alkaline conditions, chromium (VI) is not readily sorbed and remains highly mobile. In acidic oxidised sediments with a high content of iron and manganese oxides or clay minerals, chromium (VI) should be adsorbed more strongly onto the sediment as the higher net positive charge present in acidic sediment should provide more or stronger sites for adsorption of the chromium (VI) anions. The adsorption is thought to occur with the mineral fraction, especially those with exposed hydroxyl groups on their surface such as iron and aluminium oxides and montmorillonite. Decreasing pH results in increasing protonation of the mineral surface and hence increasing adsorption of the chromium (VI)-containing anions (Rai et al., 1989). However, other anions present in natural systems such as SO_4^{2-} can also compete with the adsorption of chromium (VI), resulting in lower adsorption of chromium (VI) than might be expected (Palmer and Wittbrodt, 1991). In the environment, iron oxides are the primary site of adsorption for chromium (VI) in acidic to neutral soils, with some contribution also from minerals with aluminium-OH groups (Rai et al., 1989).

Table 3.7 Summary of measured partition coefficients (Kp) for chromium

Phase	Kp (l/kg)			Comments	Reference
	Total Cr	Cr(VI)	Cr(III)		
Suspended sediment partition coefficients					
Kp_{susp}		250-50,000	25,000-800,000	Freshwater and saltwater Netherlands estimate	Braunschweiler et al. (1996)
	126,000-786,000 median 290,000			Freshwater, based on routine water quality data from The Netherlands	Van Der Kooij et al. (1991)
	30,100-1,059,600; mean 322,400			Freshwater River suspended sediments, United States - based on monitoring data	Young et al. (1987)
	324,000			Saltwater (0.1-0.5‰), based on routine water quality data from The Netherlands	Van Der Kooij et al. (1991)
	306,000-320,000			Saltwater (1-5‰), based on routine water quality data from The Netherlands	
	228,000			Saltwater (>10‰), based on routine water quality data from The Netherlands	
	140,000-570,000			Freshwater (Rhine-Meuse delta)	Golimowski et al. (1990)
	29,200-200,000			Saltwater (Tyrrhenian Sea), silty-clay sediment, organic carbon content 1.6%, salinity 3.8‰, pH 8.2-8.3.	Ciceri et al. (1992)
Sediment-water partition coefficients					
Kp_{sed}		940[a]	34,000	Saltwater, organic matter content ~2%, pH 7.8-8.0	Wang et al. (1997)

Table 3.7 continued overleaf

Table 3.7 continued Summary of measured partition coefficients (Kp) for chromium

		2,300[a]		Saltwater, organic matter content ~10%, pH 7.8-8.0	
			25,600-32,800	Freshwater, pH 8.3, organic carbon content 2.65%	Young et al. (1987)
	60-44,800; mean 7,100			Freshwater River sediments, United States - based on monitoring data	
			11,000	Freshwater, pH=4.5	Young et al. (1992)
			120,000	Freshwater, pH >6	
Soil-water partition coefficients					
Kp_{soil}	524-24,217			Dutch field soils, pH~3.8-7.9; 2-21.8% organic matter	Janssen et al. (1997)
		13-40	298-788	Loam; pH <6; 1.92% organic carbon	Hassan and Garrison (1996)
		<1-6.1	2,823-15,382	Loam; pH >6; 1.92% organic carbon	
		45.4-52.3		Loess; pH<6; 0.11% organic carbon	
		1.5-12.1	19,716-55,918	Loess; pH>6; 0.11% organic carbon	
		17-44.6	330-27,151	Clay; pH<7; 3.75% organic carbon	
		1.4-2.0		Clay; pH>7; 3.75% organic carbon	
		0.35-17.4[b]	12-27	Sand, pH 4-8	Pérez et al. (1988)
			21-197	Sandy soil, pH 4-8, 0.77% organic matter	
		6.6-18.4[b]	116-608	Sandy loam, pH 4-8, 1.62% organic matter	

Note: a) reduction to chromium
III) occurred in these sediments
b) variation with pH not determined

Overall, chromium (VI) anions can be considered to be mobile in sediments in the environment, except possibly under highly acidic conditions.

Chromium (III) appears to be much more strongly adsorbed to soils and sediments than chromium (VI). The adsorption of chromium (III) onto soil follows the pattern typical of cationic metals and increases with increasing pH (lowering pH results in increased protonation of the adsorbent leading to fewer adsorption sites for the cationic metal) and the organic matter content of the soil and decreases when other competing (metal) cations are present. Certain dissolved organic ligands may also reduce the adsorption of chromium (III) to the solid phase by forming complexes which enhance the solubility of chromium (III) in the aqueous phase (Richard and Bourg 1991).

Based on the available measured values for the adsorption coefficients the values indicated below will be used in the risk assessment. These values are not taken directly from specific tests, but have been chosen by the Rapporteur to be representative for acidic-neutral and neutral-alkaline environments. The values do not correspond to any specific individual test results, nor are they derived statistically from the available data (since these are insufficient to allow meaningful values to be derived). Instead they were selected by inspection of the data to reflect the available information under the two sets of conditions and to reflect the differences between these. Acid-neutral environments are considered to be those at pH 5 and below; neutral-alkaline environments are taken to be those at pH 6 and above. For chromium (VI), the choice of a reliable value, particularly for suspended sediment and sediment, is difficult as reduction to chromium (III) (resulting in enhanced adsorption) cannot be ruled out in most of the available

data. The values chosen for Kp_{susp} and Kp_{sed} are therefore the best estimate that can be made assuming that the adsorption of chromium (VI) is substantially less than that seen for chromium (III) and that the adsorption is higher under acidic conditions than alkaline conditions. There are much better data available for the values of Kp_{soil} for chromium (VI), allowing more reliable values to be chosen.

Chromium (VI)	Acid conditions	Alkaline conditions
	Kp_{susp} = 2,000 l/kg	Kp_{susp} = 200 l/kg
	Kp_{sed} = 1,000 l/kg	Kp_{sed} = 100 l/kg
	Kp_{soil} = 50 l/kg	Kp_{soil} = 2 l/kg
Chromium (III)	Acid conditions	Alkaline conditions
	Kp_{susp} = 30,000 l/kg	Kp_{susp} = 300,000 l/kg
	Kp_{sed} = 11,000 l/kg	Kp_{sed} = 120,000 l/kg
	Kp_{soil} = 800 l/kg	Kp_{soil} = 15,000 l/kg

The equivalent values for the dimensionless form of the partition coefficient using the methods given in the Technical Guidance document are:

Chromium (VI)	Acid conditions	Alkaline conditions
	$K_{susp\text{-}water}$ = 500 m^3/m^3	$K_{susp\text{-}water}$ = 50 m^3/m^3
	$K_{sed\text{-}water}$ = 500 m^3/m^3	$K_{sed\text{-}water}$ = 50 m^3/m^3
	$K_{soil\text{-}water}$ = 75 m^3/m^3	$K_{soil\text{-}water}$ = 3.2 m^3/m^3
Chromium (III)	Acid conditions	Alkaline conditions
	$K_{susp\text{-}water}$ = 7,500 m^3/m^3	$K_{susp\text{-}water}$ = 75,000 m^3/m^3
	$K_{sed\text{-}water}$ = 5,500 m^3/m^3	$K_{sed\text{-}water}$ = 60,000 m^3/m^3
	$K_{soil\text{-}water}$ = 1,200 m^3/m^3	$K_{soil\text{-}water}$ = 22,500 m^3/m^3

3.1.1.2.3 Behaviour during wastewater treatment processes

Chemical and physical treatment

Wastes containing large amounts of chromium (VI) are usually treated before discharge to sewer and/or a biological wastewater treatment plant. The most common methods for lowering the concentration in wastewater involve reduction of chromium (VI) to chromium (III) using ferrous sulphate, sodium bisulphite, sodium metabisulphite or sulphur dioxide at low pH, followed by raising the pH to around 9.5, to precipitate the insoluble chromic hydroxide formed. The precipitate is collected and disposed of; in the UK this would be by a registered contractor and disposal would usually be to landfill site. This method is common to a range of metal-containing effluents. Other methods that can be used, or have been suggested for use, are based on ion-exchange (Towhill, 1978), or carbon adsorption (Singh and Tiwari, 1997).

Chuan and Liu (1996) studied the leaching behaviour of chromium from leather tannery sludge. The sludge sample used was taken from the coagulation-precipitation primary treatment unit and was air-dried and ground (<20 mesh) before use in the experiment. The pH of the sludge was 7.26 and had a total organic carbon content of 0.91% and a cation exchange capacity of 2.98 meq/100 g. The total chromium content of the sludge was 17,200 mg/kg dry weight. Batch experiments were used to study the leaching of chromium from the sludge with typically 10 g of sludge being shaken with 70 cm^3 of water for 48 hours. The leaching of total chromium from the sludge was found to be pH dependent, reaching a minimum value at around pH 5.5-7.5, a pattern

that would be expected if the main chromium species present was chromium (III) hydroxide (the solubility of which follows a similar pH dependence). No dissolved chromium (VI) species were detected in the leachate. The total dissolved chromium concentrations were also found to decrease as the redox potential of the system became more oxidising (aeration) and no notable oxidation of chromium (III) to chromium (VI) was noted to be occurring in the system. Overall, low mobility of chromium (III) was found from the sludge, and little or no chromium (VI) was found in the sludge.

Biological wastewater treatment plants

Several surveys of removal of total chromium during wastewater treatment plants have been undertaken. The results are summarised in **Table 3.8**.

Brown et al. (1973) studied the behaviour of chromium in 6 municipal wastewater treatment plants in the United States. The plants used a variety of treatment methods and the results are shown in **Table 3.8**. Overall, the average removal of total chromium from water was around 58% in plants with secondary treatment and around 27% in plants using primary treatment only. Within the plants, it was found that the removal efficiency from the influent increased with efficiency of suspended solids removal in the plant.

Higher removals (84-97%) were found in secondary and tertiary treatment plants in a more recent study (Shafer et al., 1998). Most of the removal occurred in the primary clarifier by adsorption onto particulate matter.

Table 3.8 Removal of total chromium during wastewater treatment

Type of treatment plant	% chromium removal	Reference
Primary treatment with no digestion procedure - direct vacuum filtration and sludge incineration (inflow 54 million gallons/day)	36%	Brown et al. (1973)
Primary treatment – primary sludge digested, centrifuged and incinerated (inflow 24 million gallons/day; 70-85% industrial)	26%	Brown et al. (1973)
Primary treatment – series sludge digestion with lagoon disposal of sludge (inflow 15 million gallons/day)	17%	Brown et al. (1973)
Primary treatment – sludge digested, centrifuged and incinerated (inflow 4 million gallons/day)	29%	Brown et al. (1973)
Activated sludge secondary treatment - sludge digested, vacuum filtered and landfilled (inflow 5 million gallons/day)	78%	Brown et al. (1973)
Trickling filter secondary treatment - sludge digested, vacuum filtered with lagoon disposal (inflow 8 million gallons/day)	38%	Brown et al. (1973)
23 Activated sludge municipal treatment plants - value based on mean influent and effluent concentrations	75%	Sung et al. (1986)
Pilot-scale activate sludge treatment plant - chromium (VI) added continuously to influent	44%	Barth et al. (1965)
Activated sludge secondary treatment - sludge digested and disposed of to lagoon (inflow 495 million litres/day)	81-97%	Nielsen and Hrudey (1983)
Tertiary treatment – rotating biological contactors - final sand filtration (inflow 0.5 million gallons/day)	97%	Shafer et al. (1998)
Secondary treatment - activated sludge (inflow 40-60 million gallons/day)	84%	Shafer et al. (-1998)

Sung et al. (1986) carried out a survey of the removal efficiency for chromium in 23 full-scale municipal sewage treatment plants (mainly using activated sludge) in the United States. Samples

of raw sewage, primary effluent, secondary effluent and the final discharge was collected from the plants and analysed for concentrations of total chromium. Based on the mean concentration in the raw sewage (0.51 mg/l) and the discharge (0.12 mg/l), it can be estimated that around 75% of the total chromium was removed in the process on average. The removal efficiency for chromium at individual plants was found to vary markedly. Of the 23 plants surveyed, 9 showed >90% removal, 5 showed 75-89% removal, 5 showed 50-74% removal, 2 showed 25-50% removal and 2 showed <25% removal.

Another study of removal of total chromium during wastewater treatment has been reported by Chen et al. (1974). The plant used a combination of primary treatment (settling tanks), secondary treatment (aeration tanks and settling tanks) and tertiary treatment (sludge digestion). The plant discharged around 1,286,900 m^3/day of effluents consisting of around 880,500 m^3/day of primary effluents, 378,500 m^3/day of secondary effluents and 18,900 m^3/day of digested sludge. Most of the chromium present in primary effluent was associated with the particulate phase but, because the suspended particle concentration in secondary effluent was low in this particular plant, the secondary effluent was found to contain a higher fraction of the dissolved metal. In the sludge, more than 90% of the chromium was associated with the particulate phase. The results are shown in **Table 3.9**.

Table 3.9 Behaviour of chromium during wastewater treatment (Chen et al., 1974)

Phase	Total chromium concentration	Chromium concentration in dissolved phase
Primary effluent	300-315 µg/l	100-147 µg/l
Secondary effluent	50-60 µg/l	30-47µg/l
% removal	80-84%	53-80%
Sludge	1,700-2,500 mg/kg dry wt.	

Nielsen and Hrudey (1983) determined the ratio of soluble/total chromium in wastewater during treatment at an activated sludge plant. Dissolved chromium in the study was defined as that which could pass through a 45µm filter. The overall removal of chromium seen at the plant was 81-97%. The ratio of soluble/total chromium in the effluent streams was found to increase during treatment (median ratio was 0.09 in raw sewage; 0.18 in primary effluent; 0.55 in final effluent) indicating that removal of chromium was preferentially by the particulate phase.

From the available data on chromium behaviour in wastewater treatment plants, it is clear that a high percentage (typically >80% in plants with secondary treatment) is removed from the water phase by adsorption onto the particulates and sludge. In Section 3.1.1.2.2 it was seen that under most conditions chromium (III) adsorbs more strongly onto particulate matter than chromium (VI), and so a removal figure of 80% by adsorption onto sewage sludge could be considered as a reasonable worst-case figure for removal of chromium (III) during wastewater treatment. Most of the chromium (III) in the effluent from wastewater treatment plants appears to be associated with the particulate phase.

For chromium (VI), some reduction to chromium (III) would be expected to occur during biological wastewater treatment, however this may be limited in plants using aerobic activated sludge secondary treatment. Therefore removal of chromium (VI) from the water phase during wastewater treatment would be due to both adsorption and reduction. Since chromium (VI) is more soluble and generally shows lower adsorption to particulate matter than chromium (III), then it is appropriate to choose a lower removal rate for chromium (VI) during wastewater

treatment. A worst-case figure of 50% removal by adsorption onto sewage sludge could be considered.

During anaerobic wastewater treatment, reduction of chromium (VI) to chromium (III) would be facilitated and the overall removal of chromium (VI) would be expected to be much higher than the figure given above (removal rates approaching 100% have been seen in laboratory-scale experiments (see Section 3.1.1.2.1). Anaerobic digestion of sewage sludge would also be expected to reduce chromium (VI) to chromium (III).

The following worst-case values will be used for removal during wastewater treatment in the risk assessment:

Chromium (VI)	Chromium (III)
50% adsorbed onto sewage sludge	80% adsorbed onto sewage sludge
50% in effluent	20% in effluent (associated mainly with the particulate phase)

3.1.1.2.4 Bioaccumulation

The estimation methods given in the Technical Guidance Document for determining bioconcentration or bioaccumulation factors for fish, earthworms and uptake in the food chain are not applicable to chromium compounds. Measured values are available for a variety of systems. These are discussed in the following Sections and will be used to derive suitable bioconcentration/bioaccumulation factors for use in modelling the environmental behaviour of chromium (VI).

Uptake from water and sediments

Fish

The uptake and accumulation of chromium by fish appears to be lower than for other aquatic organisms. Bioconcentration factors (BCFs) of around 1 l/kg have been determined for chromium (VI) using rainbow trout over 22-30 days exposure, with a value of 2.8 l/kg being reported in trout muscle for a longer exposure of 180 days (USEPA, 1980; Fromm and Stokes, 1962; Calamari et al., 1982).

Camusso et al. (1995) carried out a study on the accumulation of chromium in fish. Caged rainbow trout (each 110-170 g weight) were exposed for 30 days at two sites on the river Po, one upstream and one downstream of a polluted tributary. Fish were removed periodically (at days 7, 15 and 30) and analysed for the concentration of total chromium in gills, spleen, kidney, muscle and vertebral bone. Chromium was found to accumulate mainly in the spleen, muscles and gills, with the maximum increase in concentration being around 4 times that found in the pre-exposed fish in muscle. On an estimated whole body (wet weight) burden basis the total amount of chromium in the control fish was 18.7 mg, compared to the total amount of 21 and 32.9 mg in fish placed upstream and downstream of the tributary respectively.

Janus and Krajnc (1990) reported BCF values between 18 and 90 for rainbow trout that were exposed for 2 years in a lake polluted with chromates from cooling towers (as quoted in Braunschweiler et al., 1996).

The effect of pH on the uptake and distribution of chromium (VI) in rainbow trout has been investigated by Van der Putte et al. (1981) as part of a series of three experiments to determine

the mode of toxic action of chromium (VI). Fingerling fish were exposed to $Na_2{}^{51}CrO_4$ for 2-4 days at chromium concentrations between 2 and 50 mg Cr/l. All tissues reached equilibrium within the exposure period. Concentrations of 6.5 and 50.0 mg Cr/l were found to be lethal to the fish. Significantly more ^{51}Cr was found in the fish exposed at a pH of 6.5 than at a pH of 7.8, but whole body BCFs were generally in the range 0.5-1 l/kg. The highest ^{51}Cr concentrations were generally found in the gills at pH 6.5, but at pH 7.8, similar high concentrations as found in the gills were also found in the digestive tract, liver and kidney. When returned to clean water, ^{51}Cr was rapidly lost from blood and digestive tract at pH 6.5, but less rapidly at pH 7.8. At pH 6.5, 85% of the chromium from whole body and 93% of the chromium from gills was eliminated in 3 days. In contrast, at pH 7.8, only 25% of the ^{51}Cr was eliminated from whole body and 12% was eliminated from gills. The results indicated that pH was important in the uptake, tissue distribution and retention of chromium (VI) in rainbow trout (Van der Putte et al, 1981).

Buhler et al. (1977) examined the uptake and distribution of chromium in rainbow trout reared for two years in river water containing 0.25 µg Cr (VI)/l or between 1-10 µg Cr (VI)/l. Whole body residues of chromium of around 29 µg/kg wet weight and 18 µg/kg wet weight were determined in fish from the two exposures respectively, giving approximate whole body BCFs of the order of 18-116 l/kg. The highest concentrations of chromium were found in the opercular bone, spleen, liver, gastrointestinal tract and kidney. When the fish from the 1-10 µg Cr/l exposure group were exposed to a much higher concentration of chromium (VI) (2.5 mg Cr/l) for a short time period, a rapid increase in the whole body concentration was observed, with the concentrations in most tissues reaching equilibrium within 1 day. The whole body weight concentration reached 0.87 mg/kg wet weight after 22 days exposure, giving an estimated whole body BCF of around 0.4 l/kg. This additional chromium was not distributed as seen in the long-term exposures, but was concentrated in the cell cytosol, especially in the liver and kidney. The authors postulated that two different chromium "pools" might be present in fish, one giving concentrations of chromium in fish similar to levels found in water (giving BCFs ~1 l/kg), and one with a slower rate of exchange, leading to concentrations of total chromium in fish above the level in water. It was thought that these two "pools" could be related to rapid uptake of chromium (VI) with BCF~1 l/kg, followed by a slower reduction to chromium (III) in the fish. Similar two part uptake and elimination has been seen with marine polychaete worms (*Hermione sp.*) and freshwater clam (*Lampallis radiata*) (Towhill et al., 1978).

The effect of fish bodyweight on the uptake and distribution of chromium (VI) (as potassium dichromate) has been studied in Goldfish (*Carassius auratus*) with bodyweights between 2 and 12 g. The tests were carried out at pH 7, at a temperature of 22°C and a chromium (VI) concentration of 20 mg Cr/l. The chromium solutions were renewed once per week over the 32-42 day exposure period. Some of the larger fish died at the exposure concentration used. The mean levels of total chromium found in the exposed fish are shown in **Table 3.10**. Of the organs analysed, only the levels found in liver appeared to vary with exposure period, reaching a level of 773 mg/kg dry weight in large fish after 8 days and 1,315 mg/kg dry weight in small fish after 11 days. After this time period, the liver levels decreased slightly, but were still significantly elevated (ρ=0.05) compared with controls. There was no significant difference in the liver levels for the small and large fish. The levels found in gills of exposed fish were significantly elevated compared with controls, and the levels found in small fish were significantly higher than those found in large fish. In bile, only the levels found in small fish were significantly elevated compared with controls (and large fish). The total chromium levels found in muscle of exposed fish were significantly higher than those of the controls, but no significant difference was seen between the large and small fish. Overall, no correlation between chromium levels and body weight could be determined in the study (Flos et al, 1983).

Table 3.10 Uptake of chromium (VI) by goldfish of different size

Exposure group/weight	Mean total chromium concentration (mg/kg dry weight)			
	Gill	Liver	Bile	Muscle
Control (2-12 g)	42±15	55±26	143±83	11±4
Large fish (6-12 g)	93±22	143±68	192±94	40±14
Small fish (2-4 g)	163±75	214±99	345±152	47±24

Mears and Eisler (1977) carried out a survey of total chromium levels in livers of marine fish (bluefish (*Pomatomus saltatrix*); tautog (*Tautoga onitis*); and tilefish (*Lopholatilus chamaeleonticeps*) collected off the New Jersey coast. The total chromium concentrations found in the livers were found to decrease with fish body length in female bluefish and male tautog, but no significant correlations (at the ρ=0.05 level) were seen in the total chromium concentrations in liver of fish of different sizes in the male bluefish, female tautog or male and female tilefish samples. As this was a field study, it is likely that the majority of chromium measured was chromium (III).

Giesy Jr. and Wiener (1977) analysed fresh water fish for levels of total chromium. The fish were taken from a lake where the average total chromium concentration of the water column was 0.35 µg/l. The mean whole body concentrations found in the fish (on a dry weight basis) were 0.16 mg/kg in bluegill (*Lepomis macrochirus*), 0.09 mg/kg in blueback herring (*Alosa aestivalis*), 0.28 mg/kg in brook silverside (*Labidesthes sicculus*), 0.19 mg/kg in golden shiner (*Notemigonus crysoleucas*) and 0.15 mg/kg in chain pickerel (*Esox niger*). Based on the measured concentrations of total chromium found in the water and fish, whole body BCFs in the range 260-800 l/kg on a dry body weight basis can be estimated (the mean dry weight/wet weight ratio of the fish was given as 0.22, so the fresh weight BCF values were 57-176 l/kg). Analysis of the stomach contents of chain pickerel indicated that this species was feeding mainly on bluegill. The authors concluded that, based on the measured concentrations in bluegill and chain pickerel, no bioaccumulation of total chromium was occurring through this food chain. As this was a field study, it is likely that much of the chromium present in the organisms in this study was as chromium (III).

Invertebrates

USEPA (1980) reported bioconcentration factors (BCFs) of between 125 and 200 l/kg for chromium (VI) in salt water with oyster (*Crassostrea virginica*), polychaete worm (*Neanthes arenaceodentata*) and blue mussel (*Mytilus edulis*) for exposures of 84-150 days. BCFs for chromium (III) in blue mussel (*M. edulis*) and soft shell clam (*Mya arenaria*) were generally lower at between 86 and 155 l/kg. Similar BCFs of 109-126 l/kg were determined by Shuster Jr. and Pringle (1969) for chromium (III) (as chromic nitrate) in oyster (*Crassostrea virginica*) exposed to 0.05 and 0.10 mg Cr/l using a flow-through sea water system (salinity 31‰) over 20 weeks.

Wang et al. (1997) studied the uptake of chromium (VI) by marine mussels (*Mytilus edulis*). The routes considered were direct uptake from water, feeding on alga/phytoplankton and feeding on sediments. Mussel bioconcentration factors (BCF) were derived by measuring the rate of uptake and rate of depuration of ^{51}Cr (as sodium chromate; total concentration 2-200 nmol/l ≡ 0.1-10 µg Cr/l) from seawater (salinity 28‰). For uptake via the water phase, a BCF (on a dry weight mussel basis) of 9,100 l/kg was determined for chromium (VI). The corresponding BCF for chromium (III) was 2,800 l/kg. Assimilation efficiencies were also determined for mussels fed on phytoplankton or sediment containing chromium (VI). The assimilation efficiency for

chromium (VI) was 1.1-10.4% from phytoplankton (the assimilation efficiency for chromium (III) was lower at around 0.2-1.1%). In the experiments with sediments, the added chromium (VI) was found to be rapidly reduced to chromium (III) and so the assimilation efficiency of chromium (VI) could not be determined. The efflux rate constant of chromium (VI) from the mussels was found to be around 0.01 d^{-1}. The authors used a kinetic model to analyse the bioaccumulation in mussels in the field and concluded that the major route of uptake of chromium (VI) is likely to be via the dissolved phase or via ingested food. This contrasted with the situation with chromium (III) where uptake via sediments was predicted to be the major route of uptake.

In an earlier study (Wang and Fisher, 1996), the effect of food quality on the assimilation efficiency of chromium in mussels (*Mytilus edulis*) fed on varies species of algae was investigated. Seven alga species (*Alexandrium tamarense, Chlorella autotrophica, Nannochloris atomus, Phaeodactylum tricornutum, Prorocentrum micans, Tetraselmis maculata* and *Thalassiosira pseudonana*) were spiked with ^{51}Cr (oxidation state not stated) and fed to mussels (shell length 3 cm) for 30 minutes (>90% of the food particles were ingested over this period). The pH of the seawater used in the experiments was around 8. After this feeding time, the retention of the ^{51}Cr in the mussels was studied for 4 days. In this experiment, the assimilation efficiency was defined as the proportion of ingested metal retained after completion of digestion and gut evacuation (after approximately 72 hours). The results of the experiment indicated that >98% of the ingested ^{51}Cr was excreted in faeces by 24 hours, indicating the chromium had a low potential for uptake and accumulation by mussels from food. The chromium assimilation efficiencies were all low (0.2-1.3%) for the 7 algal food species tested.

The uptake of chromium by mussels (*Mytilus edulis*) has also been studied by Walsh and O'Halloran (1997). Groups of 20 mussels were exposed to various forms of chromium (concentration 50 µg Cr/l) over 4 weeks (solutions renewed every 3 days) in salt water (34.5‰) containing <5 mg/l of suspended solids. The exposure period was followed by a 48 hour depuration period (to ensure that no particulate chromium was present in the digestive tract) before the organisms were analysed for total chromium concentrations. The chromium species used in the experiment included potassium dichromate (chromium (VI)); and three forms of chromium (III): particulate Cr $(OH)_3$ and soluble chromium (III) complexes with protein (typical of complexes found in leather tannery effluent) and citrate. The results are shown in **Table 3.11**. The authors found that significant uptake of chromium (VI) from solution occurred in the digestive gland, gill and kidney.

Table 3.11 Uptake of chromium by mussels (Walsh and O'Halloran, 1997)

Organ	Mean organ total chromium concentration on a dry weight basis (exposure concentration 50 µg Cr/l except for control)				
	Cr(VI) ($K_2Cr_2O_7$)	Cr(III) ($Cr(OH)_3$)	Cr(III)-citrate complex	Cr(III)-protein complex	Control (no added Cr)
Muscle	1.55±1.4 mg/kg	3.0±0.7 mg/kg	0.26±0.2 mg/kg	48±21 mg/kg*	3.0±2.8 mg/kg
Gill	10.5±3.4 mg/kg*	8.4±2.1 mg/kg*	2.1±1.1 mg/kg	169±90 mg/kg*	1.7±1.6 mg/kg
Mantle	3.8±1.8 mg/kg	2.4±0.5 mg/kg	2.3±2.6 mg/kg	74±65 mg/kg*	2.1±1.7 mg/kg
Kidney	7.4±2.9 mg/kg*	5.3±0.9 mg/kg*	3.4±0.9 mg/kg	117±60 mg/kg*	3.9±1.5 mg/kg
Digestive gland	12.9±5.2 mg/kg*	18.4±3.5 mg/kg*	5.1±0.9 mg/kg*	475±236 mg/kg*	2.9±1.9 mg/kg

Note * indicates statistically significant difference from controls at $p<0.05$ level

A similar pattern of uptake of total chromium has been seen in mussels (*Mytilus edulis*) from an estuary receiving wastewater from a leather tannery. The tannery processed around 4,000 hides per week and discharged around 85 kg of chromium/day, after primary precipitation treatment, to an estuary. The chromium present in the plant effluent consisted entirely of chromium (III) species. Mussels from around the plant had elevated levels of total chromium (levels in the gills were around 400-1,000 mg/kg dry weight; compared with levels of up to 6 mg/kg dry weight in gills of mussels from a reference site), with the levels found generally decreasing in the various tissues in the following order: gills>kidney>digestive gland>mantle>adductor muscle. A depuration half-life of 16-18 weeks was estimated for total chromium in gills and digestive gland, with longer half-lives estimated for other tissues. The majority of the chromium found was associated with the particulate fractions (rather than the cytosolic) fractions of the cells of gills and digestive glands. The authors concluded that two uptake patterns were occurring: over the short-term, uptake by ingestion dominated, resulting in high concentrations in the digestive gland; over the long-term, preferential uptake and accumulation in the gills and kidney occurs (Walsh and O'Halloran, 1998).

Chassard-Bouchaud et al. (1989) carried out a detailed microanalytical study of the distribution and chemical form of chromium (III) in mussels (*Mytilus edulis*) after exposure to chromium chloride in seawater (36‰) for 2 weeks. The uptake of chromium (III) was thought to occur via the gills in this study, with the main storage occurring in muscle. The digestive gland was thought to play a very minor role in the accumulation. The target organelle was the lysosome, where the metal was associated in an insoluble form with phosphorus and sulphur. Excretion of chromium (III) from the organism was thought to occur mainly via the kidney.

Chipman (1966) investigated the uptake of chromium (VI) (as $Na_2\ ^{51}CrO_4$) and chromium (III) (as $^{51}CrCl_3$ or ^{51}Cr-EDTA chelate) from natural sea water (pH 8.05) by the clam *Tapes decussatus*, a representative of a detritus and particle feeding organism. In the experiments with chromium (III), a large proportion (80%) of the $^{51}CrCl_3$ was found in the particulate phase immediately after addition to the seawater. The clams were shown to remove the chromium (III)-containing particles from solution by filter-feeding, and the peak levels of ^{51}Cr found in the clams occurred within the first day of exposure. The level of chromium (III) in the clams then decreased with time during the 9-day exposure period as the clams excreted the ingested chromium (III)-containing particles and the amount of chromium (III) present in the sea water decreased. There was some evidence that the chromium (III) present in solution was adsorbed onto the surfaces of the clam (e.g. shells, gills, mantle etc.), but there was no evidence of uptake into the body tissues of chromium (III) from solution. In the experiments with chromium (III)-EDTA complex (where 99.75% of the chromium added was in solution), slight uptake of the chromium (III) was seen in shells and soft tissues over the 13-day exposure period, the concentrations found did not reach those present in the water i.e. BCF<1. In the chromium (VI) experiments, rapid uptake into body tissue was seen, with only a small amount of the chromium (VI) being found in the shells. The results are shown in **Table 3.12**. After 20 days exposure, the concentration in body tissue was around 28 times that found in the water, although it is clear from the results that a steady state had not been reached within this time period. The depuration of the chromium (VI) from the clams was studied over a 39-day period. The results indicated that the rate of loss of the ^{51}Cr from the clams was essentially the same as that for radioactive decay and so the depuration rate could not be determined.

Table 3.12 Uptake of chromium (VI) by clams (*Tapes decussatus*) from seawater

Body part	Exposure period (days)	Concentration in clam at various initial exposure concentrations (µg/kg)		
		3 µg Cr/l	10 µg Cr/l	100 µg Cr/l
Shell	5	7.0	5.1	5.0
	10	15.5	13.6	9.8
	15	21.5	18.0	16.0
	20	27.3	26.0	18.0
Tissue	5	37.4	55.8	775
	10	44.2	129.4	1,879
	15	80.7	231.8	2,750
	20	84.0	275.1	2,470

As part of a 2-generation assay test on a marine worm (Polychaeta, *Neanthes arenaceodentata*) a dose-dependent accumulation of chromium (VI) was found. Juvenile worms (~1 cm in length) were exposed to various concentrations of chromium (VI) (2.6-38.2 µg/l as potassium dichromate) in filtered natural seawater at 18-24°C, salinity 33-35‰ and pH 8.1 using a static renew procedure (renewal every 3 weeks). At the highest chromium (VI) exposure level, 38.2 µg/l, the whole body tissue concentration of total chromium for the first generation was 8,278 µg/kg wet weight (BCF = 217 l/kg) after 158 days exposure, and 6,030 µg/kg wet weight (BCF = 158 l/kg) after 157 days exposure for the second generation (Oshida and Word, 1982).

The uptake of chromium (VI) (as $Na_2{}^{51}CrO_4$) and chromium (III) (as $^{51}CrCl_3$) by barnacles (*Balanus* sp.) collected from a polluted estuary has been studied in laboratory experiments. The barnacles were exposed in sea water both with and without suspended particles (water filtered through 0.45 µm membrane). In the experiments with suspended particles, the barnacles were added to the system after equilibrium between the chromium in the dissolved and particulate phase had been reached (after 24 hours for chromium (III) and after 7 days for chromium (VI)). In filtered seawater a BCF of 543 l/kg on a dry tissue weight basis was determined for soft tissues for chromium (VI) after 27 days exposure, based on the total chromium concentration in the organism. The half-life for depuration of total chromium from the organism was estimated at 70 days. In the experiments with chromium (VI) in seawater containing 0.05 g/l of suspended particles, around 2% of the total chromium added to the test solution was associated with the particulate phase, and a BCF of 380 l/kg on a dry weight basis was determined for soft tissues after 61 days, with a depuration half-life for the adsorbed chromium of 180 days. In the experiments with chromium (III), maximum uptake was seen after 15-20 days, coinciding with the complete removal of the radioactive particles (the chromium (III) formed a precipitate in the seawater solution) from solution by the barnacles. No evidence for accumulation of chromium (III) in the soft tissues of the organisms was seen (the chromium (III) passed through the digestive system without absorption (van Weerelt et al., 1984).

A comparison of the accumulation of chromium (VI) (as $Na_2{}^{51}CrO_4$) by direct uptake from water with uptake from food (^{51}Cr adsorbed onto *Chlamydomonas* sp after five days incubation) has been carried out using the American oyster *Crassostrea virginica* over 110 hours exposure in artificial seawater. More ^{51}Cr was found to be accumulated by direct adsorption from the water than by ingestion of the algae and the rates of uptake by the two routes were also found to differ. The elimination of the ^{51}Cr from the organisms was slow, with no elimination being detected

over 5 days. The Na_2CrO_4 concentration in direct adsorption experiments was $6.62 \cdot 10^{-4}$ mg/l (Preston, 1971).

A model of biota sediment accumulation factors (BSAF) relating the ratio of metal concentrations in 2 marine bivalves (*Crassostrea virginica* and *Mytilus edulis*) to sediment metal concentrations indicates total chromium has the smallest BSAF at 0.01 (Thomann et al., 1995).

Crayfish, *Procambarus clarkii*, were exposed over 96 hours at 19.5°C to chromium (VI) (as sodium chromate) at concentrations ranging from 10 to 500 mg Cr/l. The tissue concentrations of total chromium found after exposure are shown in **Table 3.13**. The amount of chromium accumulated increased with increasing exposure concentration in all tissues, with the concentration of total chromium in gland > gills > hepatopancreas > muscle. However, the relative accumulation rates decreased with increasing chromium (VI) concentrations in the water (Hernandez et al., 1986). From the data reported in **Table 3.13**, BCFs of around 4.3-7.4 l/kg can be estimated for based on the dry whole body weight values.

Table 3.13 Accumulation of chromium in crayfish exposed to chromium (VI)

Exposure concentration	Mean total chromium concentration in organisms (mg/kg dry weight)				
	Gills	Hepatopancreas	Gland	Muscle	Whole body
Control	13.1±1.6	1.0±0.4	38.2±5.0	0.4±0.2	52.7
10 mg Cr(VI)/l	67.2±17.0	20.3±3.5	37.5±9.2	1.8±0.4	126.8
37 mg Cr(VI)/l	89.4±13.3	55.9±25	147±42	3.9±1.2	296.2
136 mg Cr(VI)/l	230±69	189±99	286±88	7.3±1.5	712.3
500 mg Cr(VI)/l	541±125	462±102	1,170±202	32.0±3.0	2205

Stackhouse and Benson (1989) studied the effects of humic acid on the bioaccumulation of chromium (VI) (as potassium dichromate) and two forms of chromium (III) (as chromic chloride and a Cr-lignosulphonate complex) by Daphnia magna. In the experiment, 7-day old Daphnia were exposed to a chromium concentration of 10 mg Cr/l for 96 hours (solutions renewed every 24 hours) and the animals were then analysed for the presence of total chromium. The water used in the study had a hardness of 92 mg/l as $CaCO_3$ and a pH of 8, and contained varying concentrations of humic acids (0, 0.5, 5 and 50 mg/l). After 96 hours exposure, the total chromium concentration in the chromium (VI)-exposed organism was between 58.5 and 67.8 mg Cr/kg dry weight at humic acid concentrations between 0 and 5 mg/l, and 52.1 mg Cr/kg dry weight at a humic acid concentration of 50 mg/l. These concentrations allow bioconcentration factors of 4,810-6,380 l/kg dry weight to be estimated for chromium (VI) (the background level of total chromium in the Daphnia was 4 mg/kg dry weight). In the chromium (III) uptake experiments, the humic acid had a much more marked effect in reducing the amount of chromium accumulated in the Daphnia (in the experiments with $CrCl_3$, the concentration in Daphnia was reduced from 105.9 mg Cr/kg dry weight when no humic acid was present (BCF~10,190 l/kg dry weight) to 32.8 mg Cr/kg dry weight at a humic acid concentration of 50 mg/l (BCF~2,880 l/kg dry weight)).

Algae and aquatic plants

The uptake of chromium (VI) from water by 4 species of phytoplankton (*Chlorella autotropica, Prorocentrum minimum, Tetraselmis levis* and *Thalassiosira pseudonana*) has been studied by Wang *et al* (1997). Cells of each species (initial concentration $2\text{-}8 \cdot 10^4$ cells/ml) were exposed to ^{51}Cr (VI) (as sodium chlorate; concentration 0.3 nmol/l) in seawater. Steady state concentrations

were obtained after 3-10 days exposure (when the cell growth had reached the stationary phase. The concentration factors (on a cell dry weight basis) were 500 l/kg for *C. autropica*, 420 l/kg for *P. minimum*, 190 l/kg for *T. levis* and 470 l/kg for *T. pseudonana*. The equivalent concentration factors for chromium (III) were around a factor of 100-1,000 higher (12,000-130,000 l/kg). Cellular fractionation showed that >98% of the chromium (III) present on the cells was adsorbed onto the cell wall/membrane.

Jouany et al. (1983) determined the uptake of chromium (VI) (as potassium dichromate) by the freshwater alga *Chlorella vulgaris* as part of a 96h-toxicity study. The exposure concentrations used were 100-900 µg Cr (VI)/l, and the concentration factors determined were in the range 612-988 l/kg (based on the total chromium content of algae on a dry cell weight basis).

The uptake of both chromium (III) (as chromium potassium sulphate, Cr (III)-EDTA complex or Cr (III)-glycine complex) and chromium (VI) (as potassium dichromate) by the fresh water green alga *Chlorella pyrenoidosa* and a wild strain of *Chlorella* have been studied by Meisch and Schmitt-Beckmann (1979). In the experiments, algal cultures were exposed to chromium concentrations of 0.5 and 1 mg Cr/l in nutrient medium for 5 days. After the exposure period, the total chromium concentrations in the dry algal cells were determined. The concentration factors for *C. pyrenoidosa* (on a dry cell weight basis) were around 256-390 l/kg for chromium (VI) and 558-580, 11-12 and 224-254 l/kg for the three chromium (III) species. Slightly lower concentration factors (220 l/kg for chromium (VI)) were obtained in the wild *Chlorella* strain.

Aksu et al. (1990) investigated the uptake of chromium (VI) (as potassium dichromate) by dead cells of *Chlorella vulgaris*. The maximum rate of uptake of chromium (VI) by the cells was found to occur over the temperature range 35-50^{o}C and a pH of 1-2, however, these results have limited applicability to the environment.

Other bioconcentration factors of 2,300-29,000 l/kg have been reported for natural algal populations exposed to chromium (VI) concentrations of 0.01-0.4 mg/l for 2-4 weeks (Braunschweiler et al., 1996) and BCFs of 20-215 l/kg have been estimated for chromium in alga collected in the river Rhine (Janus and Krajnc, 1990; as quoted in Braunschweiler et al., 1996).

Kähkönen and Manninen (1998) studied the uptake of chromium (VI) (as sodium chromate) by the aquatic plant *Elodea canadensis*. The plants were exposed to chromium (VI) for 24 hours in filtered lake water (pH 7.2-9.1). The mean initial exposure concentrations used in the experiment were 150, 800 and 2,090 µg Cr/l and these concentrations were found to remain reasonably constant throughout the exposure period. The concentration of total chromium found in the plants at the end of the experiments was 5.5 mg/kg dry weight in the control plants, and 8.3, 35 and 84 mg/kg dry weight in plants exposed to the 150, 800 and 2,090 µg Cr/l solutions respectively. Based on these data, bioconcentration factors (on a dry plant weight basis) of approximately 19-38 l/kg can be estimated.

Bacteria

The uptake of chromium (III) (10-400 mg/l ≡ 2.7-106 mg Cr(III)/l, as chromic sulphate) and chromium (VI) (10-400 mg/l ≡ 3.7-141 mg Cr(VI)/l, as potassium dichromate) by suspended cells (0.4 mg dry weight cells/ml of solution) of *Pseudomonas aeruginosa* has been studied over 24-30 hours. The uptake of chromium by the cells was found to increase with chromium concentration up to a concentration of around 200 mg/l, after which the concentration in the cells no longer increased with exposure concentration. The ratio of concentration of chromium in cells (mg Cr/kg)/concentration of chromium in water (mg Cr/l) were of the order of 100-340 l/kg for

chromium (VI) and 1,000-3,800 l/kg for chromium (III). The uptake of chromium (VI) was found to decrease with increasing pH over the range 3.0-4.5, whereas the uptake of chromium (III) was found to increase with pH over the same range. Similar levels of uptake were seen with both biologically active and metabolically inhibited cells (Nair and Krishnamuruthi, 1991b).

Gaur and Bhattacherjee (1991) studied the accumulation of chromium (III) and chromium (VI) by *Escherichia coli*. Solutions of K_2CrO_4, $K_2Cr_2O_7$ or $Cr_2(SO_4)_3$ (chromium concentration 192-1,154 μmol/l ≡ 10-60 mg Cr/l) in peptone water were inoculated with 0.1 ml of bacterial culture ($4 \cdot 10^9$ colony forming units/ml) and incubated for 24 hours at 37°C. No evidence of uptake of chromium (III) was seen in the experiment. The potassium chromate was found to be highly toxic to the micro-organisms at the concentrations tested. The ratio of the concentration of chromium in cells (mg Cr/kg)/concentration of chromium in water (mg Cr/l) was around 0.005-0.014 l/kg. Potassium dichromate was found to be less toxic, and in this case the ratio of the concentration of chromium in cells (mg Cr/kg)/concentration of chromium in water (mg Cr/l) was similar at around 0.009-0.035 l/kg.

Aksu *et al* (1990) found that chromium (VI) could be adsorbed onto dead cells of the activated sludge bacterium *Zoogloea ramigera*. The highest adsorption rate was found to occur from solutions of pH 1-2 at 25°C.

Discussion of bioconcentration data from water

For the risk assessment, a reliable value for the BCF in fish is needed. The available data indicate that the bioconcentration factor for chromium (VI) in fish is relatively low at around 1 l/kg. Once in the organism, reduction of chromium (VI) to chromium (III) appears to occur, resulting in an accumulation of total chromium in the organisms to a factor of approximately 100 times the original concentration in water. Uptake of chromium (III) directly from water is likely to be very low due to the limited water solubility and strong adsorption to sediment under most conditions found in the environment.

Thus for the risk assessment, the following BCFs will be used:

a) to estimate the concentration of chromium (VI) in fish;

$$\frac{[Cr(VI)]_{fish}\ mg/kg}{[Cr(VI)]_{water}\ mg/l} = BCF_{Cr(VI)} = 1\ l/kg$$

b) to estimate the concentration of chromium (III) in fish resulting from uptake and subsequent reduction of chromium (VI);

$$\frac{[Cr(III)]_{fish}\ mg/kg}{[Cr(VI)]_{water}\ mg/kg} = BCF_{Cr(VI)\text{-}Cr(III)} = 100\ l/kg$$

The uptake of chromium by aquatic organisms may be pH dependent, but insufficient information is available to take any possible variation in the BCF into account. Any pH dependence may be related to differences in solubility and speciation of the chromium in solution and this is taken into account to some extent in the consideration of bioavailability (e.g. adsorption, solubility) of the various forms elsewhere in the assessment.

For chromium (VI) in solution at pHs found in the environment the two main species are likely to exist are the monovalent hydrochromate anion ($HCrO_4^-$) which will dominate at lower pHs and the dichromate anion ($Cr_2O_7^{2-}$), which will dominate at higher pHs and higher chromium concentrations. It has been postulated that, due to its higher negative charge, the mobility of the

dichromate anion across biological membranes is impaired relative to that of the hydrochromate anion (Walsh and O'Halloran, 1997; Nair and Krishnamurthi, 1991b).

The uptake of chromium by other organisms appears to be higher than seen for fish, although few if any of the experiments distinguish between chromium (VI) and chromium (III) concentrations in the organisms. Similar to the situation for fish, it is possible that once taken up by the organism, chromium (VI) is reduced to chromium (III) in the tissues, resulting in a build up of chromium (III) and hence an overestimate for the true bioconcentration factor for chromium (VI). BCFs of up to around 9,100 l/kg (on a mussel dry weight basis) for chromium (VI) and 2,800 l/kg (on a mussel dry weight basis) for chromium (III) have been determined in mussels, and BCFs of around 500 l/kg (on a cell dry weight basis) for chromium (VI) and 12,000-130,000 l/kg (on a cell dry weight basis) for chromium (III) have been determined in algae. Transfer of chromium via the alga $\Rightarrow$ bivalve, and sediment $\Rightarrow$ bivalve food chains appears to be relatively low.

Uptake from soil (porewater)

The equilibrium partitioning of total chromium between soil and earthworms has been investigated by Janssen et al. (1997b). In the experiments, earthworms (*Eisenia andrei*) were exposed to samples of 20 soils that where known to contain various heavy metals. Soil samples (~1 kg) were placed in covered glass jars and acclimated to the experimental temperature of 20^{o}C for 24 hours. Groups of 10 animals (approximately 21-24 weeks old) were then placed in each exposure vessel. After 3 weeks exposure the animals were collected and analysed for the presence of total chromium (after the animals had voided their gut contents). Bioconcentration factors (BCFs) were determined as: total metal concentration in worm (mmol/kg dry weight)/total metal concentration in solid phase (mmol/kg dry weight). The uptake of total chromium by the earthworms was generally found to be small, with bioconcentration factors in the range 0.03-0.53 being determined. The authors investigated the effects of various soil parameters, and also the possible species present in the soil pore water, on the uptake of total chromium. No significant correlation was found for the uptake of chromium by earthworm with any of the soil (e.g. pH, organic matter content, iron and aluminium oxyhydroxide contents, clay content) and soil pore water properties (metal speciation, dissolved organic carbon, ionic strength), although some correlation of BCF with soil organic matter content was found in soils with a pH>5. Overall, from the soils studied, it appears that the BCF for earthworm is relatively independent of the soil properties, and that the total concentration of chromium in earthworm is governed mainly by the total concentration present in the soil. The results were thought to be consistent with uptake being via the pore water phase.

Van Gestel et al. (1993), as part of an earthworm reproduction test, also reported low bioconcentration factors for chromium by earthworms. In this experiment chromium (III) nitrate was added to artificial soil and 9.5-15.5 week old earthworms were incubated in the soil for 3 weeks at 20^{o}C. The bioconcentration factors determined (on a [mg/kg dry worm]/[mg/kg dry soil] basis) were 0.031-0.047 at exposure concentrations of 10-100 mg Cr/kg dry soil, and 0.016-0.019 at 320-1,000 mg Cr/kg dry soil. At the end of a three week recovery period, where the earthworms were placed in clean soil, the total chromium levels had returned to background levels. The elimination half-life for total chromium was estimated at 51-109 days for the lowest exposure groups and 5-7 days for the highest exposure groups.

Sharma (1997) studied the uptake and distribution of chromium in maize (*Zea mays* L, Cv. Ganga 5) grown in refined sand under glass house conditions. Thirty days after sowing, sodium dichromate was added to the plants in the daily nutrient solution at concentrations of 0.05-1 mM

and the concentration of total chromium present in various parts of the plant were determined after 46 days growth. The chromium uptake was found to be concentration dependent and greatest in the roots. The approximate concentrations (taken from a graph given in the paper) of total chromium found in the plant are shown in **Table 14**.

Table 3.14 Uptake of chromium by maize (Sharma, 1997)

Chromium (VI) concentration in	Concentration of total chromium in plant (mg Cr/kg dry weight)		
Nutrient solution (mg Cr(VI)/l)	Roots	Young leaves	Old leaves
0	n.d.	n.d.	n.d.
10.4	~150	~10	~30
26	~900	~20	~80
52	~1,000	~40	~100
104	~2,000	~600	~500

The uptake of chromium (VI) (as chromium trioxide) and chromium (III) (as chromic chloride) by barley (*Hordeum vulgare*) and rape (*Brassica napus*) has been studied in nutrient culture as part of a toxicity study. The plants (2 week old for barley; 3 week old for rape) were grown in a mineral solution (solution pH=5.0) containing chromium (concentration 10, 30, 50 or 100 mg Cr/l) for between 1 and 14 days. After the exposure period, plants were harvested and the leaves and stems were analysed for the concentration of total chromium. Effects on growth of the plants, particularly the roots, were seen at all concentrations tested. In the plants exposed to chromium (III), the peak concentration of total chromium reached 400 mg/kg dry weight (leaves) and 200 mg/kg dry weight (stems) in barley and 100 mg/kg dry weight (leaves) and 400 mg/kg dry weight (stems) in rape after 4-6 days exposure to chromium (III) at 100 mg/l. Exposure of the plants to chromium (VI) in solution resulted in plant concentrations around 1-2 orders of magnitude higher than seen for chromium (III). The concentrations of total chromium found in leaves of both plants were in the range 3,000-5,000 mg/kg dry weight when exposed to a chromium (VI) concentration of 100 mg/l. At this high chromium (VI) concentration significant toxic effects (growth reduction) were seen. At lower chromium (VI) concentrations (e.g. 10 mg/l) the levels found in leaves were around 100 mg/kg dry weight (Hauschild, 1993).

Otabbong (1990) looked at the effects of $Si(OH)_4$ on the uptake of chromium (VI) (as chromium trioxide) by ryegrass (*Lolium perenne*). Two soils were used in the experiment. One soil had a pH of 5.2 and a clay and humus content of 36.1% and 7.0% respectively, and the second had a pH of 6.9 and a clay and humus content of 54.3% and 3.4% respectively. The soil was spiked with chromium (VI) at a concentration of 50 mg/kg dry weight and then sowed with seeds. After 30 days growth, the roots and shoots were analysed for the presence of total chromium. Plant growth in the chromium (VI) exposed soil was slightly inhibited when compared with the control plants, but the addition of $Si(OH)_4$ caused a severe reduction in growth. The concentrations of total chromium in shoots and leaves of the chromium (VI) exposed plants are shown in **Table 3.15**. Using the data for the chromium experiments (without the added $Si(OH)_4$, soil-plant concentration factors (defined as concentration of total chromium (corrected for control) in plant (mg/kg dry weight)/concentration of chromium (VI) added to soil (mg/kg dry weight) of $1.4 \cdot 10^{-4}$ and $2.6 \cdot 10^{-3}$ for shoots and 0.0122 and $3.9 \cdot 10^{-3}$ for roots.

Table 3.15 Uptake of chromium (VI) by ryegrass

Exposure concentration	Total chromium concentration in plant (µg/kg dry weight)	
	Shoots	Roots
Soil I (pH 5.2; 36.1% clay content; 7% humus content)		
Control soil (no added Cr(VI)	13	43
Cr(VI) - 50 mg/kg dry weight	20	654
Cr(VI) - 50 mg/kg dry weight; Si - 25 mg/kg dry weight	74	1,685
Soil II (pH 6.9; 54.3% clay content; 3.4% humus content)		
Control soil (no added Cr(VI))	17	21
Cr(VI) - 50 mg/kg dry weight	149	214
Cr(VI) - 50 mg/kg dry weight; Si - 25 mg/kg dry weight	169	242

3.1.1.3 Summary of behaviour of chromium (VI) in the environment

The processes that are important in determining the fate and distribution of chromium in the environment include: redox transformations, precipitation and dissolution, and adsorption/desorption (Rai et al., 1989). Some of these processes are discussed in detail in the previous Sections. This Section discusses the processes that are of particular importance for each environmental compartment (air, surface water, sediment, soil, groundwater) and the likely chromium species to be found in each compartment as a result of these processes.

Chromium exists in the environment in a number of valence states. Chromium (VI) and chromium (III) are the most stable (Bartlett, 1991). However, in the environment, kinetic and other non-equilibrium factors mean that chromium (III) species dominate in nature, with high levels of chromium (VI) species generally only found as a result of man-made pollution. Although chromium (VI) is thermodynamically stable only under oxidising conditions, the kinetics of reduction to chromium (III) under certain conditions can be slow (see Section 3.1.1.2.1).

Ionic equilibria for chromium (VI)

Chromium (VI) is a strong oxidising agent and as a result only exists as oxygenated species in the environment. For the dichromates, the actual species present in solution depends on the pH according to the following equilibria (Losi et al., 1994; Katz and Salem; Palmer and Wittbrodt; Cotton and Wilkinson, 1976):

$H_2CrO_4 \Leftrightarrow H^+ + HCrO_4^-$ $pKa_1 = -0.6; 0.74; 0.86$

$HCrO_4^- \Leftrightarrow H^+ + CrO_4^{2-}$ $pKa_2 = 5.9; 6.49; 6.51$

Based on these equilibria alone, at very low pH (e.g. near 0) the dominant species in solution would be the fully protonated form (H_2CrO_4). At pHs between 0 around 6-6.5, the dominant chromate species in solution would be $HCrO_4^-$, and at pHs above around 6-6.5 the main chromate species in solution would be CrO_4^{2-}.

In addition to the above equilibria, the chromate ion is in equilibrium with the dichromate ion according to the following equilibria (Losi, 1994; Katz and Salem, 1993):

$2CrO_4^{2-} + 2H^+ \Leftrightarrow Cr_2O_7^{2-} + H_2O$ $\qquad \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2} = K_{eq} = 3.98 \times 10^{14}$

$2HCrO_4^- \Leftrightarrow Cr_2O_7^{2-} + H_2O$ $\qquad \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} = K_{eq} = 33$

In addition, there are the following base-hydrolysis equilibria:

$Cr_2O_7^{2-} + OH^- \Leftrightarrow HCrO_4^- + CrO_4^{2-}$

$HCrO_4^- + OH^- \Leftrightarrow CrO_4^{2-} + H_2O$

Overall, the available information indicates that at very low pH values (<1) the main species in solution is H_2CrO_4, at higher pHs between around 2 and 6, $HCrO_4^-$ and $Cr_2O_7^{2-}$ will both be present in equilibrium, and at higher pHs (>7) the main species present will be CrO_4^{2-}. Thus at environmental pHs the species found in solution will be a mixture of $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-}, irrespective of the form in which the chromium (VI) enters solution.

Ionic equilibria for chromium (III)

The predominant forms of chromium (III) present in solution are Cr^{3+} at very low pH, then with increasing pH, $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$ and finally $Cr(OH)_4^-$ at very high pH. The species $Cr(OH)_2^+$ is thought to occur only over a very narrow pH range (approximately pH 6.27-6.84; Palmer and Wittbrodt, 1991).

In solution, the equilibrium between chromium (III) ions and chromium hydroxide lays well over to the side of the relatively insoluble hydroxide at pH>5 according to the following equilibrium (Losi et al., 1994):

$Cr^{3+} + 3H_2O \Leftrightarrow Cr(OH)_3\,(s) + 3H^+ \quad K_{eq} = 1 \cdot 10^{-12}$

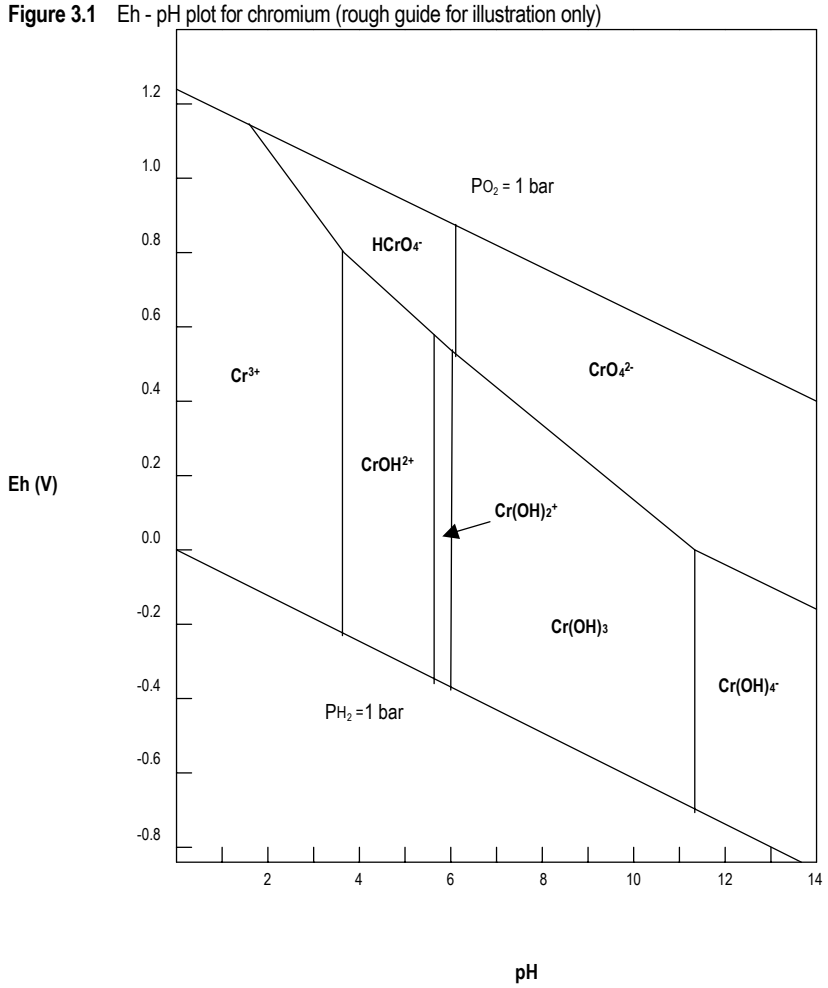
This means that at pHs >5 chromium (III) can be expected to precipitate out of solution as the insoluble hydroxide, often in conjunction with iron. However, complexation of chromium (III) ions with organic matter (such as citric acid, diethylenetriaminepentaacetic acid (DTPA), fulvic acid) can result in increased solubilisation of chromium (III) at higher pHs (Palmer and Wittbrodt, 1991).

Dominant forms of chromium in the environment

Based on the ionic equilibria of the various chromium (III) and chromium (VI) species in aqueous solution and the known oxidation-reduction potentials, diagrams can be constructed to indicate the dominant form of chromium likely to be present in a system at a given redox potential (Eh) and pH. An example of such a diagram is shown in **Figure 3.1** (Palmer and Wittbrodt, 1991; Rai et al., 1989) (note that this plot is intended for illustration only and should not be interpreted as an exact representation of the species present).

Based on this information, the most likely forms of chromium in the various environmental compartments can be deduced.

Figure 3.1 Eh - pH plot for chromium (rough guide for illustration only)



Atmosphere

Chromium (VI) compounds are not volatile and so are found in the atmosphere associated with aerosols or particulate matter. In the atmosphere, chromium (VI) can be reduced to chromium (III) if suitable reductants are present, however it is likely that in most situations, chromium (VI) will be relatively stable under the conditions present in the atmosphere. The chromium present on particulate matter and in aerosols can be transported to land surfaces via wet and dry deposition.

Surface water

Chromium (VI) and chromium (III) are the most stable oxidation states of chromium at the redox potential (E_h) and pH range of natural waters. The prevalent species present at equilibrium depends both on the pH and E_h of a given system (see **Figure 3.1**).

The major dissolved species of chromium (III) are Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_3^0$ and $Cr(OH)_4^-$. Of these species, Cr^{3+} only exists in significant amounts at pH <3.6-3.8 and similarly, $Cr(OH)_4^-$ is prevalent only at high pH (pH > c.a. 10-11.5). Between these pH values, $CrOH^{2+}$ is though to be the dominant species up to a pH of around 6.3-6.5, and $Cr(OH)_3^0$ is the dominant species in solution at pH between 6.3-7 and 10-11.5. Polymeric species such as $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$ and

$Cr_4(OH)_6^{6+}$, although they exist, are never significant in the environment. Overall, chromium (III) species show a minimum solubility between pH 7-10 (Richard and Bourg, 1991; Rai et al., 1987). Over this range, the solubility of Cr $(OH)_3$ is $\sim 10^{-6.84}$ mole/l (≡ 7.5 µg Cr/l) (Rai et al., 1989; Richard and Bourg, 1991). The chromium (III) ion acts as a hard Lewis acid and so readily forms complexes with ligands such as hydroxyl, sulphate, ammonium, cyanide, sulphocyanide, fluoride and chloride, as well as natural and synthetic organic ligands.

At pHs from around 5-6 up to around 12, the solubility of chromium (III) in aqueous systems is limited by the formation of Cr $(OH)_3$. If iron, particularly Fe (III), is also present, the chromium (III) can also form insoluble iron complexes of the form $Cr_xFe_{1-x}(OH)_{3,\ the}$ solubility of which decreases with decreasing chromium (III) fraction, but all are less soluble than Cr $(OH)_3$. The mixed chromium/iron hydroxides also have a lower free energy of formation than for Cr $(OH)_3$ and so are expected to preferentially form (Rai et al., 1989). This reaction is particularly important when chromium (VI) is reduced to chromium (III) by iron (II) (which itself is oxidised to iron (III)) (Palmer and Wittbrodt, 1991).

The major dissolved species of chromium (VI) are $HCrO_4^-$ and CrO_4^{2-}. The relative proportion of these two species depends on the pH of the system$^-$ (Richard and Bourg 1991). Although these two species could dimerise to form dichromate anions (e.g. $HCr_2O_7^-$ or $Cr_2O_7^{2-}$) the equilibrium is such that the process only becomes significant at high chromate concentrations (e.g. >0.08 mol/l ≡ 0.4 g Cr/l) (Rai et al., 1989). The chromium (VI) species present in the environment are much more soluble than the chromium (III) forms, however, a relatively insoluble barium salt ($BaCrO_4$ or mixed sulphate/chromate salt) could be formed if barium ions are present (Rai et al., 1989). Formation of such salts could limit the solubility of chromium (VI) in the environment.

A significant proportion of total chromium in aquatic systems is associated with the solid phase. For example, around 90% of the total chromium transported in the River Po (Italy) was found to be associated with the particulate but at least 85% of the soluble or dissolved chromium (~10% of total chromium) was found as chromium (VI) (cited in Katz and Salem, 1994).

Reduction of chromium (VI) to chromium (III) may also occur to some extent in surface waters, particularly where oxygen-deficient conditions exist. Iron (II) and organic matter-rich environments favour the reduction processes (Richard and Bourg, 1991).

Chromium (III) is not readily, or rapidly, oxidised to chromium (VI) under most conditions found in the environment, but can be by oxidised by naturally occurring manganese oxides (Rai et al., 1989; Richard and Bourg, 1991). The extent of chromium (III) oxidation is limited by anionic adsorption of chromium (VI) to the mineral surface in acidic solutions and by precipitation of Cr $(OH)_3$ in neutral to alkaline solutions (Eary and Rai, 1987). The rate of reaction is slower than the reduction of chromium (VI), possibly explaining why the distribution of chromium (VI) and chromium (III) in natural waters often deviates from thermodynamic predictions (Eary and Rai, 1987).

Adsorption of chromium (VI) to suspended and bottom sediment exhibits typical anionic sorption behaviour where the adsorption occurs to positively charged sites on mineral particles (Katz and Salem, 1994). The adsorption of chromium (VI) to particulate matter decreases with increasing pH and when competing dissolved anions are present (Richard and Bourg, 1991). On the other hand, chromium (III) exhibits a typical cationic sorption behaviour, where adsorption occurs onto negatively charged sites on the mineral surface or onto organic matter. The adsorption of chromium (III) increases with pH but decreases when competing cations are

present (Richard and Bourg, 1991), however, in general, the adsorption of chromium (III) to particulate matter is much higher than that of chromium (VI) under the same conditions.

Groundwater

Chromium (VI) reduction occurs in solutions, particularly where the oxygen concentration is low or reducing conditions exist, over a wide range of pHs, indicating that chromium introduced into groundwater as chromium (VI) will be reduced to chromium (III) by the residual amounts of Fe (II) commonly contained in oxide and silicate materials. In such environments, dissolved total chromium concentrations will be limited by the solubility of $(Cr,Fe)(OH)_3(s)$ over the pH range of natural waters (4 to 9) (Eary and Rai, 1989).

Ferrous iron contained in naturally occurring minerals (e.g., hematite, biotite) is an important inorganic reductant for chromium (VI) to chromium (III) in groundwater. Chromium (VI) reduction by iron (II) ions in solution is nearly instantaneous, but when the iron (II) source is contained within weathering minerals, the rate of reduction is dependent on the dissolution rates of the iron (II) contents of these minerals, which is increased at low pH or by high concentrations of anions that complex iron (II). Following reduction, chromium (III) may precipitate as $(Cr,Fe)(OH)_3$, which limits the concentration of dissolved chromium to less than 10^{-6} M between pH 4 and 12. Chromium (VI) reduction by dissolved iron (II) has been demonstrated to occur even in oxygenated solutions. Overall, the rates of chromium (VI) reduction are fastest at pH <4, independent of pH over the range 6 to 9, and slower at pH>9 (Eary and Rai, 1989).

The presence of manganese oxides in groundwater would indicate the potential oxidation of chromium (III) to the more soluble chromium (VI). In the absence of significant concentrations of manganese oxides, the oxidation of aqueous chromium (III) is unlikely to occur and all the chromium (III) present will be adsorbed and relatively immobile (Eary and Rai, 1987).

Sediment

The same processes that govern the distribution of chromium in natural waters, such as redox potential, precipitation and adsorption also govern the distribution of chromium in sediments.

Chromium (VI) exists mainly as oxoanions in the environment and is expected to be highly mobile under aerobic conditions. Under alkaline conditions, chromium (VI) is not readily sorbed and remains highly mobile. In acidic oxidised sediments with a high content of iron and manganese oxides or clay minerals, chromium (VI) should be adsorbed more strongly onto the sediment as the higher net positive charge present in acidic sediment should provide more or stronger sites for adsorption of the chromium (VI) anions. The adsorption is thought to occur with the mineral fraction, especially those with exposed hydroxyl groups on their surface such as iron and aluminium oxides and montmorillonite. Decreasing pH results in increasing protonation of the mineral surface and hence increasing adsorption of the chromium (VI)-containing anions (Rai et al., 1989). However, other anions present in natural systems such as SO_4^{2-} can also compete with the adsorption of chromium (VI), resulting in lower adsorption of chromium (VI) than might be expected (Palmer and Wittbrodt, 1991). Overall, chromium (VI) anions can be considered to be mobile in sediments in the environment, except possibly under highly acidic conditions.

Reduction of chromium (VI) to chromium (III) is expected to occur in anaerobic sediments. Strong adsorption of the insoluble chromium (III) species formed to sediment is likely at pHs found typically in the environment. At very low pH (<5) more soluble chromium (III) cationic

species may be formed, which may be more mobile in sediments at these pHs. In general, once chromium (III) is scavenged from the water column, it becomes part of the sediment matrix and is thus less available for uptake from biota.

Chromium (III) may be oxidised by naturally occurring manganese oxides in sediments to give chromium (VI) (Rai et al., 1989; Richard and Bourg, 1991). The extent of chromium (III) oxidation is limited by anionic adsorption of chromium (VI) to the mineral surface in acidic solutions and by the formation of insoluble Cr $(OH)_3$ in neutral to alkaline solutions (Eary and Rai, 1987).

Soil

The behaviour of chromium (VI) in soils is likely to be similar to that in sediment. Adsorption to the soil matrix is expected to increase with increasing acidity of the soil, but under neutral to alkaline conditions, chromium (VI) is expected to be highly mobile in soil, and may leach into lower anaerobic layers where reduction to chromium (III) would be expected to occur. In the environment, iron oxides are the primary site of adsorption for chromium (VI) in acidic to neutral soils, with some contribution also from minerals with aluminium-OH groups (Rai et al., 1989).

Since adsorption of chromium (VI) appears to be electrostatic in nature, this implies that once the available adsorption sites are occupied (either by chromium (VI) or other anions) then no further adsorption can take place and increased mobility may occur.

Chromium (VI) added to soil will remain mobile only if its concentration exceeds both the adsorbing and reducing capacities of the soil (Bartlett and Kimble, 1976). In the presence of organic matter, chromium (VI) is reduced rapidly to chromium (III). Reduction is likely to be slower in soils with low organic matter contents.

Similar to the case with sediment, chromium (III) is expected to be rapidly and strongly adsorbed onto soil, particularly by iron and manganese oxides, clay minerals and sand. About 90% of added chromium has been found to be adsorbed onto clay minerals and iron oxides in 24 hours. The adsorption of chromium (III) onto soil follows the pattern typical of cationic metals and increases with pH and the organic matter content of the soil and decreases when other competing (metal) cations are present. Certain dissolved organic ligands may also reduce the adsorption of chromium (III) to the solid phase by forming complexes which enhance the solubility of chromium (III) in the aqueous phase (Richard and Bourg, 1991). Oxidation of chromium (III) to chromium (VI) could also occur to a limited extent in soils rich in manganese dioxide.

3.1.1.4 Natural sources

Chromium is the 21st most common element in the earth's crust. As a result, chromium is a natural constituent of many rocks, soils, sediments and waters, and the atmosphere (as a result of wind blown dust). The ranges of levels associated with various phases are shown in **Tables 3.16** to **3.20**. The levels given usually refer to the concentration of total chromium and give no indication of the form or (bio)availability of the chromium found.

The most important chromium-containing minerals are chromite ($(Mg,Fe)O(Cr,Fe,Al)_2O_3$), crocoite ($PbCrO_4$), melanochroite, vanquelinite, uvarovite and pyrope (Bencko, 1985). The chromium content of rocks varies from an average of around 20 mg/kg for granitic rocks up to 1,800 mg/kg in ultra basic and serpentine rocks.

The chromium concentration of soils varies greatly from traces up to 250 mg/kg or more (Bencko, 1985). In most soils, chromium occurs at concentrations between 2 and 60 mg/kg. In soils and sediments, the highest concentrations of chromium tend to be associated with the finest grain size (Richard and Bourg, 1991). Only a fraction of the total chromium present in soil is available for plants. Although chromium is not thought to be an essential element for plants, all plants appear to contain chromium at levels up to 0.19 mg/kg wet weight (WHO, 1988).

The concentrations of chromium in rivers and freshwaters are usually between 1 and 10 µg/l (although levels in lakes in Scandinavia tend to be lower than this). In oceans, the chromium concentrations are typically reported to be in the range 0.1-5 µg/l (Bencko, 1985) and generally <1 µg/l (WHO, 1988).

Table 3.16 Natural levels of chromium found in waters

Sample type	Total chromium concentration (µg Cr/l)	Reference
Freshwater		
River	0.52 typical; 0-114 range	Richard and Bourg (1991)
Lake	<0.1-1.7 range	Richard and Bourg (1991)
Groundwater	<1 typical; 0.5-208 range	Richard and Bourg (1991)
Tap water	0.4 typical; 0-36 range	Richard and Bourg (1991)
Freshwaters (general)	1.0 typical; 0.1-6.0 range	Losi et al (1994)
Marine		
Seawater	0.16 typical; 0.0052-0.83 range	Richard and Bourg (1991)
	0.3 typical; 0.2-50 range	Losi et al (1994)
Interstitial water (marine sediment)	0.052-0.34 range	Richard and Bourg (1991)

Table 3.17 Natural levels of chromium found in sediment

Sample type	Total chromium concentration (mg Cr/kg)	Reference
Freshwater		
River sediment	0-104 range	Richard and Bourg (1991)
River suspended matter	187 typical	Richard and Bourg (1991)
Sandy sediment	26 typical; 16-36 range	Richard and Bourg (1991)
Clayey sediment	62 typical; 36-83 range	Richard and Bourg (1991)
Marine		
Coastal suspended matter	0.5-11 range	Richard and Bourg (1991)
Deep sea clay	94 typical; 57-109 range	Richard and Bourg (1991)
Marine sediment	10-36 range	Richard and Bourg (1991)
Marine sediment	32 ppm (18.5-565 ppm range)	Carral et al (1995)

Table 3.18 Natural levels of chromium found in rocks and minerals

Sample type	Total chromium concentration (mg Cr/kg)	Reference
Granite	21 typical; 1-26 range	Richard and Bourg (1991)
	20-35 average	Losi et al. (1994)
Sandstone	36 typical; 10-99 range	Richard and Bourg (1991)
	20-35 average	Losi et al. (1994)
Shale	88 typical; 88-400 range	Richard and Bourg (1991)
Carbonate	10 typical; 1-16 range	Richard and Bourg (1991)
	20-35 average	Losi et al. (1994)
Clay	120 typical; 31-588 range	Richard and Bourg (1991)
Basaltic igneous rock	220 average	Losi et al. (1994)
Ultramafic rock	1,800 average	Losi et al. (1994)
Continental crust	125 typical; 80-200 range	Losi et al. (1994)
Grey soil (derived from basalt)	172 mean; 95-249 range (Total metal) 16 mean; 7.5-25 range (Extractable metal)	Crockett (1998)
Red soil (derived from scoria)	317 mean; 154-480 range (Total metal) 5.0 mean; 2.9-7.1 range (Extractable metal)	Crockett (1998)

Table 3.19 Natural levels of chromium found in soils

Sample type	Total chromium concentration (mg Cr/kg)	Reference
Soil	99 typical; 1-3,016 range	Richard and Bourg (1991)
Soil	40 typical; 10-150 range	Losi et al. (1994)
Soils derived from serpentinitic materials	up to 125,000	Losi et al. (1994)
Baseline concentration levels	25.7 mean; 1.17-119 range	Tack et al. (1997)

Table 3.20 Natural levels of chromium found in the atmosphere

Location	Total chromium concentration (µg Cr/kg)	Reference
Antarctica, Greenland and Norwegian Arctic	$5.0 \cdot 10^{-6}$ - $1.2 \cdot 10^{-3}$	Losi et al. (1994)
Cloudwater samples, San Pedro Hill USA	0.78 –2.24	Siefert et al. (1998)

Chromium concentrations in air are generally in the range 10-50 ng/m^3 in urban areas, with lower levels (annual means <10 ng/m^3) found in rural areas. Most of the chromium in air is associated with the particulate phase (Bencko, 1985).

There is a natural cycle for chromium from rocks and soils to water, biota and air, and back to soil (WHO, 1988). It has been estimated that of the total input of chromium into the environment, 70% comes from man made emissions such as metal use (60%), general ore and metal production (3%) and combustion sources (7%), whilst 30% comes from the natural cycle such as weathering of rocks and soils (15%) and extraction from soils by plants (15%), with <1% coming from volcanic emissions (Merian, 1984).

It is estimated that around 100,000 tonnes/year of chromium are extracted from soil by plants, with a similar amount entering the environment from weathering of rocks and soils (Merian, 1984). In contrast to these figures, the global natural mobilisation of chromium by weathering has been estimated as around 36,000 tonnes/year (Bertine and Goldberg, 1971).

3.1.1.4.1 Natural levels in EU countries

The information in this section was supplied by member states as comments on the preliminary draft of the risk assessment.

Germany

A review of heavy metal concentrations in unpolluted waters in Germany gave the mean values in **Table 3.21** (LAWA, 1997).

Table 3.21 Mean levels of chromium in unpolluted German waters

Source	IKSR (1989)	IKSR (1989)	Wachs (1989, 91)	Salomons & Förster (1984)	Merian (1984)
	Soluble	Total	0,45 µm filtered		
Cr (µg/l)	0.5	4.7	<0.1	0.5	1

A typical mean natural background concentration for natural water of 2.5 µg/l Cr-total has been derived for Germany on the basis of various studies (LAWA, 1997). This concentration is made up of 0.5 µg/l for the dissolved fraction and c. 2.0 µg/l for the particulate fraction (assuming 25 mg/l suspended matter, with no further correction or normalisation for other parameters). As a water quality criterion for aquatic communities, four times this background concentration (10 µg/l Cr-total) is used (as a 'Zielvorgabe') in Germany.

For suspended matter a natural background concentration of 80 mg Cr/kg is given for Germany (LAWA, 1997) (range 40-160 mg/kg). The report states that this mean background concentration may be over-estimated.

During 1977 - 1983 a full-coverage survey on heavy metals was performed in the Western part of Germany. The objective was to find new ore deposits using hydrogeochemical prospecting methods (Fauth et al., 1985). The chromium concentrations in creek sediments ranged between 5 mg/kg (detection limit) and 5,700 mg/kg. The median (50 percentile) was 54 mg/kg.

Chromium occurs in the oxide and silicate minerals of early magmatic differentiates; thus it is considerably more concentrated in silica-poor rocks (e.g. gabbro and basalt) than in silica-rich rocks (e.g. granite and gneiss). High concentrations are associated with the basalts of the mountain ranges of Vogelsberg, Westerwald, and Rhön.

Elevated chromium concentrations are also observed in other areas in which silica-poor igneous rocks crop out rather extensively, e.g. in the Frankenwald, Fichtelgebirge, and Eifel areas, and in the Harz mountains. In many of the cases where isolated anomalous chromium concentrations were found it is thought that anthropogenic contamination is probable.

The Netherlands

The following natural background concentrations for chromium are used (Crommentuijn et al., 1997):

- standard soil / sediment: 100 mg/kg dry wt
- standard surface water (freshwater): 0.17 µg/l (dissolved concentration)
  1.6 µg/l (total concentration)
- groundwater: 2.4 µg/l (dissolved concentration)

The values for soil/sediment are similar to the upper range of values found in ambient soil in relatively unpolluted areas. Hence some influence from human activities (for example, through deposition) cannot be excluded. The real natural background concentration may therefore be lower.

The International Rhine Committee uses a natural background of 80 mg/kg dry wt for chromium in suspended matter in the river Rhine, based on the concentration in the < 20 µm fraction of unpolluted sediment (IRC, 1993; cited in Van den Berg and Zwolsman, 2000). Based on this and a value for $Kp_{susp.}$ of 218,000 l/kg derived for the period 1992-1998 (as noted in Section 3.1.1.2.2), Van den Berg and Zwolsman (2000) derived a natural background in Rhine water of 0.4 µg/l for dissolved chromium and (using a suspended matter concentration of 26 mg/l) 2.5 µg/l for total chromium. Using a factor of 1.5 between metal levels in suspended matter and sediment, a natural background concentration of 80 mg/kg dry wt for suspended matter corresponds to 50 mg/kg dry wt for sediment.

Norway, Sweden and Finland

A very comprehensive study was performed in 1995 in Norway, Sweden and Finland with regard to heavy metal concentrations in lakes. Nearly 3,000 lakes were sampled. The study found a median Cr concentration of 0.070 µg/l in Norway, 0.13 µg/l in Sweden and 0.29 µg/l in Finland respectively (Skjelkvåle et al., 1999).

3.1.2 Aquatic compartment (incl. sediment)

3.1.2.1 Calculation of predicted environmental concentrations in water

Estimates of the emission rates to water have been made in Section 3.1.1.1. It is clear from the comments from individual manufacturers and processors that their wastewaters are treated before release. The treatment generally involves the reduction of chromium (VI) to chromium (III) and the removal of chromium (III) by precipitation as insoluble hydrated oxides, although other techniques are also in use. From the information available it is not possible to estimate how widespread the use of this or other clean-up processes are, although in view of the controls on chromium emissions in place in most countries some form of treatment would be expected. Also it is not possible to derive any realistic figures for the efficiency of the process, although from a number of the examples provided this can be greater than 99%.

In view of these uncertainties it has been decided to calculate the PECs in two ways. The first will assume that all the chromium remains in the form of chromium (VI) when released - this will clearly be an extreme worst-case assumption. The second method will assume that all the chromium is in the form of chromium (III) before release. For discharges to WWTP, the fate of

chromium has been estimated in Section 3.1.1.2.3 as follows: for chromium (VI), 50% to sludge and 50% in water; for chromium (III), 80% to sludge and 20% to water.

3.1.2.1.1 Production

Specific information has been provided by the producers. In addition to the information from Section 3.1.1.1.1, they have also provided information on flow rates and the receiving waters. The resulting concentrations in water are as follows (all as chromium (VI) unless noted):

Site 1: 2.1 µg/l
Site 2: 0 µg/l
Site 3: <0.02 mg/l (total chromium)

3.1.2.1.2 Use

Local concentrations

The local concentrations have been calculated by assuming that the releases are in the form of chromium (VI) or chromium (III). For the latter, the suspended sediment sorption coefficients derived in Section 3.1.1.2.2 are large enough to have an effect on the dissolved concentrations. As the sorption coefficients vary between acid and alkaline conditions, concentrations for both conditions have been estimated. The default sizes for the WWTP and dilution from the TGD have been used. The results are in **Table 3.22**.

Table 3.22 Calculated local concentrations in water from chromium use

Process	Emission to WWTP (kg/day as Cr)	Clocal as Cr (VI) (mg/l)	Clocal as Cr (III) (mg/l)	
			acid	Alkaline
Pigment production	11	0.28	0.076	0.02
Cr_2O_3 production	12	0.30	0.083	0.022
Chrome tanning salts	14	0.35	0.097	0.025
Wood preservative formulation	6.9	0.17	0.048	0.013
Wood preservative application	0.18	0.0045	0.0012	0.00033
Metal treatment formulation	3.7	0.093	0.026	0.0067
Electroplating	4.3	0.11	0.030	0.0078
Passivating	3.5	0.088	0.024	0.0064
Anodising	0.73	0.018	0.005	0.0013
Brightening	4.4	0.11	0.030	0.008
Mordant dyeing	0.014	0.00032	0.0001	0.00003

In addition to the generic or default information used above, a number of sites provided specific information on releases. The concentrations calculated for these sites are in **Table 3.23**.

Table 3.23 Concentrations in water from specific sites

Process	Concentration (μg/l)	Comments
Pigment production	0	No release of Cr (VI). Cr (III) removed by precipitation
Tannery using dichromate on site	42	as Cr (III)
Chromium metal production	0.6 as Cr (VI) 0.16 or 0.04 as Cr (III)	
Chromium dioxide production	<5 as Cr (VI)	

Braunschweiler et al. (1996) calculated a concentration of chromium in surface water from the release of chromium from preservative-treated wood. The scenario used was of a pond with treated wood at its edge such that there was 1 m^3 of wood to 100 m^3 of water. The wood was assumed to have a chromium content of 1.764 kg/m^3; the fraction of the chromium expected to leach to water in the first year was 0.14. The fraction of the chromium associated with particulates was taken as 0.75, and it was assumed that 50% of the water in the pond would be changed over the year. The resulting concentration of chromium in the water was 309 μg/l (including a contribution from the background). The leaching rate of 0.14 was considered to be a realistic worst case; a further calculation with a 'typical' rate of 0.05 was also carried out, giving a water concentration of 108 μg/l.

RIVM have carried out similar calculations for a situation where the treated wood is at the edge of a ditch (personal communication, with summary of information from confidential reports). The dimensions of the ditch were assumed to be 5 m wide and 1.5 m deep, with a flow rate of 375 m^3/day. Two scenarios were used, one with 100 m of treated wood edging the ditch and the second with 1 km of treated wood. The flow rate meant that water traversed the lengths of treated wood in 2 days and 20 days respectively. Calculations were performed for two temperatures. The results are presented in **Tables 3.24** and **3.25**.

Table 3.24 Maximum concentrations and concentrations in water after 28 days for ditch scenario

Concentration in ditch water with 1 km long facing [μg/l]		Concentration in ditch water with 100 m long facing [μg/l]		Conditions	
20-day (max.)	28-day	2-day (max.)	28-day	Temperature	pH
27.4	18.3	5.4	2.4	8 ^{0}C	7
41.4	25.1	9.3	3.4	20^{0}C	7

Table 3.25 Water and sediment concentrations after 1 year for ditch scenario (based on different estimates)

Water [μg/l]	Sediment [mg/kg]	Conditions
3.4 – 9.5	655 – 1,810	pH 7; T = 8 ^{0}C
5.3 – 11.6	1,010- 2,210	pH 7; T = 20 ^{0}C

Effluent concentrations

In addition to the surface water concentrations, the assessment uses the concentrations in the effluent from the WWTP to assess the possibility of impacts on the functioning of WWTPs. The required concentrations are in **Table 3.26**.

Table 3.26 Concentrations in effluents from WWTPs

Process	Ceff as Cr (VI) (mg/l)	Ceff as Cr (III) (mg/l)
Pigment production	2.75	1.1
Cr_2O_3 production	3.0	1.2
Chrome tanning salts	3.5	1.4
Wood preservative formulation	1.7	0.69
Wood preservative application	0.045	0.018
Metal treatment formulation	0.93	0.37
Electroplating	1.1	0.43
Passivating	0.88	0.35
Anodising	0.18	0.073
Brightening	1.1	0.44
Mordant dyeing	0.004	0.0014

Sediment concentrations

Sediment concentrations have been calculated using the methods in the Technical Guidance. Two values for the sediment sorption coefficients were derived in Section 3.1.1.2.2, for acid and alkaline conditions, for both chromium (VI) and chromium (III). The results are in **Table 3.27**.

Table 3.27 Calculated local concentrations in sediment

Process	Clocal as Cr (VI) (mg/kg)		Clocal as Cr (III) (mg/kg)	
	acid	alkaline	acid	alkaline
Pigment production	120	12	495	1,304
Cr_2O_3 production	130	13	540	1,423
Chrome tanning salts	152	15	630	1,660
Wood preservative formulation	75	7.5	310	818
Wood preservative application	2.0	0.2	8.1	21
Metal treatment formulation	40	4.0	166	439
Electroplating	47	4.7	193	510
Passivating	38	3.8	157	415
Anodising	7.9	0.79	33	87
Brightening	48	4.8	198	522
Mordant dyeing	0.15	0.015	0.63	1.7

Sediment concentrations have also been estimated from the pond water concentrations calculated above. Taking the concentration of 108 μg/l as chromium (III) the resulting levels in sediment are 2.8 g/kg or 28 g/kg for acid or alkaline conditions respectively.

3.1.2.2 Measured levels in water and sediment

There is a large body of information on the total levels of chromium in various water and sediment systems. In terms of this risk assessment, these levels of total chromium are of limited value as they give no information on the form and bioavailability of the chromium found. This Section reviews the measured levels where some degree of speciation has been carried out, and the levels of total chromium associated with various industrial uses, as these are likely to be the most useful for consideration in the risk assessment (**Tables 3.28-3.30**).

Table 3.28 Measured levels in water

Location	Comments	Chromium level (µg Cr/l)			Reference
		Cr(VI)	Cr(III)	Total	
Freshwater					
Shark River, USA	Samples filtered (0.4 µm) -Cr(III) separated by iron (III) hydroxide precipitation, Cr(VI) determined by difference	nd	0.009 ±0.0002	0.009 ±0.002	Kaczynski and Kieber (1993)
Cape Fear River, USA		-	0.003 ±0.0006	-	
Singletary Lake, USA		0.0002 ±0.0003	0.009 ±0.013	0.006 ±0.005	
Greenfield Lake USA		0.0007 ±0.002	0.002 ±0.002	0.002 ±0.003	
Stream water - mid-Wales – remote from industry	Total dissolved chromium (samples filtered (0.45 µm)) - major source thought to be from rainwater - yearly averages 1983-1995			<0.2-8	Neal et al. (1996)
Devil's Swamp, USA SuperFund site	Samples filtered (1µm and 0.1 µm))			0.3	Bundy and Berzins (1998)
Delta Ebro River, Spain				20	Schuhmacher et al. (1995)
Tweed Basin, UK				0.5	Neal et al. (1997)
River Nidd, UK				0.6	
River Ouse, UK				0.5	
River Aire				2.5	
Vietnam	Near Kraft Pulp and Paper mill			72.6	Kim Oanh et al. (1995)
Groundwater					
Well water, Poland		0-1.6	0-1.75	0-3.0	Siepak et al. (1996)
Rainwater					
Mid-Wales – remote from industry	Total dissolved chromium - yearly averages 1983-1995			0.2-8	Neal et al. (1996)

Table 3.28 continued overleaf

Table 3.28 continued Measured levels in water

Location	Comments	Chromium level (µg Cr/l)			Reference
		Cr(VI)	Cr(III)	Total	
Marine					
Florida Bay, USA	Samples filtered (0.4 µm) -Cr(III) separated by iron (III) hydroxide precipitation, Cr(VI) determined by difference	0.0006 ±0.0004	0.010 ±0.003	0.012 ±0.003	Kaczynski and Kieber (1993)
Straits of Florida, USA		0.010 ±0.004	0.006 ±0.003	0.016 ±0.003	
Masonboron Inlet, USA		0.004 ±0.008	0.006 ±0.003	0.009 ±0.007	
Estuary, downstream from tannery, Ireland	Dissolved concentrations	<3	12.2		Walsh and O'Halloran (1996b)
	Dissolved + particulate			145	
Wastewater					
Tannery effluent, Ireland	Dissolved concentration	<3	3,400	3,400	Walsh and O'Halloran (1996b)

Table 3.29 Measured levels in sewage sludge

Location	Comments	Chromium level (mg Cr/100g sludge dry weight)			Reference
		Cr(VI)	Cr(III)	Total	
UK 1996/7	Sewage sludge used for agricultural purposes			2.4 (median) 1.2 (10%ile) 15.8 (90%ile)	Environment Agency (1999)
Sindh province, Pakistan	Domestic sewage sludge			1.2-5.4	Ansari et al. (1997)
	Industrial sewage sludge			1.8-2.3	
USA	Sewage sludge used for agricultural purposes			15.2 mg/kg dry weight	Surampalli et al. (1994)

Table 3.30 Measured levels in sediment

Location	Comments	Chromium level (µg Cr/g dw)			Reference
		Cr(VI)	Cr(III)	Total	
Freshwater					
Lake Piaseczno, Poland	Bottom lake sediments			9-24 mg/kg dw Mean 16 mg/kg	Górniak et al.(1993)
Devil's Swamp USA				8.75	Bundy and Berzins (1998)
Ebro River Delta, Spain				15.43	Schuhmacher et al (1995)
Galicia region, Spain	Estuarine river basin samples – Granite lithology.			30 ppm	Carral et al. (1995)

Table 3.30 continued overleaf

Table 3.30 continued Measured levels in sediment

Location	Comments	Chromium level (µg Cr/g dw)			Reference
		Cr(VI)	Cr(III)	Total	
	Estuarine river basin samples –Schist-gneiss lithology.			54 ppm	
Mediterranean coastal region, Israel	Estuarine river samples, 131 sample sites			4.4-93 ppm	Herut et al. (1995)
State of Mina Gerais, Brazil	Upstream from tannery effluent. 6 rivers, 2 sites per river			14.2 – 340	Jordão et al. (1997)
	Downstream from tannery effluent. 6 rivers, 3-4 sites per river			24.1-2,878	
Vietnam	Near to Kraft Pulp and Paper mill			67.4	Kim Oanh (1995)
Mexico	Receives untreated wastewater			Up to 2.7	Mendoza et al. (1996)

Neal et al. (1996) reported the results of a 13 year study (starting May 1983) looking at atmospheric inputs of soluble chromium (via rainwater) into freshwater streams in the Plynlimon catchment. The study area was located in mid-Wales and is considered to be a rural upland site >100 km from major industrial centres. After collection, all water samples were filtered (0.45 µm) before being analysed for total soluble chromium. The mean yearly chromium concentration in rainfall ranged between around 0.2µg/l-~8 µg/l. In general, the concentration found in rainfall was found to decrease as the weekly volume collected increased. A similar range of concentrations were generally found in the stream waters collected from the area, with the highest concentrations generally corresponding with the lowest flows. The major source of chromium in the rainwater could not be identified in the study.

Walsh and O'Halloran (1996a and 1996b) determined the concentration of chromium (VI) and chromium (III) in the effluent from a tannery. The tannery used chromium (III) salts in the processes and discharged their untreated effluents into an estuary after high tide each day. At the end of the tanning process, the concentration of total dissolved chromium present in the drums (chrome waste stream) was 2.8-4.6 g/l (pH of solution 4.1-4.6). After adjustment of the pH to 9.0 the total dissolved chromium concentration had fallen to 20-140 mg/l. The mean dissolved chromium (VI) concentration in these pH-adjusted solutions was 26.6 µg/l. Before discharge, this waste stream was mixed with the sulphide waste stream (contains high concentrations of BOD, dissolved protein, salt and sulphide at high pH (>11) as a result of initial fleshing and liming stages of the process). Although this stream contained relatively low-levels of total dissolved chromium (0.02-0.07 mg/l, when this was mixed with the chrome waste stream an enhancement of the total soluble chromium concentration in the combined waste stream was observed. This was thought to be due to binding of chromium (III) to the protein. Another consequence of mixing the two waste streams was that the sulphide-containing effluent was effective in reducing the chromium (VI) into chromium (III), and no chromium (VI) could be detected in the combined effluent. The mean dissolved concentrations of chromium (III) in the effluent were 2.0 mg/l as complexes with organic compounds and 1.4 mg/l as protein complexes. A large proportion of the chromium (III) in the effluent was associated with particulate matter in

the effluent. In the receiving estuary, the levels of total dissolved chromium peaked at 12.2 µg/l about 45 minutes after discharge. Again, no dissolved chromium (VI) was detected (detection limit 3 µg/l) and the dissolved chromium (III) was mainly as complexes with organic matter (51%) or protein (49%). The protein complex was thought to be relatively short lived in the estuary (probably precipitated). The dissolved fraction of chromium was around 8% of the total chromium content found at the site (145 µg/l), indicating that >90% of the total chromium present in the estuary was associated with the particulate phase. The highest concentration of total chromium in sediment from the estuary was 117 mg/kg.

A survey of the levels of copper, chromium and arsenic in sediments close to a wood treatment plant in California has been carried out in 1992. The plant had been in operation since 1942 and the levels found were 12-60 mg Cr/kg dry weight. The highest levels were found to be localised in one or two areas (Haywood et al., 1996).

Weis et al. (1993a) analysed marine sediments close to bulkheads made of CCA treated wood for copper, chromium and arsenic. The bulkheads were from a variety of estuarine (salinity 20-30%) locations in New Jersey and New York, United States, and ranged in age from several months to several years. At all sites, the sediments adjacent to the bulkheads consisted mainly of sand, with very low percentages of silts and clays. Further away from the bulkheads, the percentage of fine-grained (<63 µm) sediments (silts and clays) progressively increased, along with an increase in organic carbon. It was found that the metals were associated mainly with the fine-grained silts and clays, and as a result, although the concentrations of metals in this phase decreased markedly with distance from the bulkheads, the total concentrations in sediment increased with distance from the bulkhead (up to 5 m) due to the increasing fraction of silts and clays present in the sediment with distance. Results for one site are shown in **Table 3.31** (note: the figures have been read from graphs in the original reference). For all sites higher concentrations were generally found in poorly flushed areas rather than open water environments. The highest concentrations of all were found next to the newest bulkhead (up to ~100 mg/kg chromium in the fine particulate (fines) phase).

Table 3.31 Levels of chromium in marine sediment near CCA treated bulkheads (Weis et al., 1993a)

Location	Distance from bulkhead	Fines %	Concentration Cr in sediment (mg/kg)	
			total	Fines
Shelter Island, USA	0 m	~4	~5	~107
	1 m	~7	~5	~53
	3 m	~34	~20	~57
	5 m	5~6	~30	~53

A similar study has also been undertaken by Wendt et al. (1996). Here, sediments at ten well flushed tidal creeks which contained wooden docks (it is not clear if all the docks were CCA treated) were sampled. The results are shown in **Table 3.31**. When the levels of copper, chromium and arsenic were normalised to the level of aluminium in sediment (a method used in order to correct for differences in the type of sediment found at each site), none of the mean levels close to the docks was significantly different from the levels further away and the control sites.

Table 3.32 Mean levels of chromium in well flushed tidal creeks containing wooden docks (Wendt et al., 1996)

Location	Mean sediment concentration Cr (mg/kg dry weight)
<1 m from docks	41.1±3.2
> 10 m from docks	32.4±3.4
control site	34.8±2.6

3.1.2.3 Comparison of measured and predicted levels

Levels of chromium in water measured at remote locations can be very low, <0.01 μg/l for both chromium (VI) and chromium (III). Other total chromium measurements in non-specific surface waters are around 0.5 μg/l. There are no measured levels related to specific industrial activities apart from tannery operations, which are not considered in the assessment as they use chromium (III) compounds. It is of interest that the concentration of total chromium in receiving waters at the tannery site reached ~12 μg/l, which is of the same order as the estimated concentrations based on chromium (III), but lower than those based on chromium (VI). The tannery wastewater also appeared to be treated to remove chromium by precipitation.

There are a few measurements of levels of chromium in sludges from WWTPs, with no indication of specific industrial activities responsible. These levels are 2-3 orders of magnitude lower than those estimated for chromium (VI) or chromium (III).

Natural levels in sediments can range from 0-100 mg/kg as total chromium. There are also measurements from less remote areas which show similar concentrations. Levels measured near to a wood treatment plant, at 12-60 mg Cr/kg, agree with the calculated values for chromium (III) for wood preservative application. Most of the other measured sediment levels relate to the use of treated wood. The sediment levels calculated for a pond containing treated wood are somewhat higher than those measured in estuarine sediments; as these situations are potentially very different it is difficult to draw any conclusions from this comparison.

The measured levels available do not differ markedly from the calculated values based on total chromium, with the noted exception of the sludge levels. Great care has to be taken in interpreting the measured data. For example, in the sediment data reported by Weis et al. (1993a), chromium was associated with fine sediments, and the distribution of chromium concentrations was governed by the amount of fine sediments in the whole sediment samples. In the study by Wendt et al. (1996), concentrations of 30-40 mg/kg were measured, of similar order to those calculated, but these were not significantly different from control samples once normalised to the aluminium content.

Overall, it is considered that the available measured levels data are not sufficient in extent or specificity to replace the calculated values, and hence the assessment will be based on the concentrations calculated above.

3.1.3 Air

3.1.3.1 Predicted environmental concentrations

As discussed in Section 3.1.1.1, emissions to air of the chromium chemicals are expected to be low. Where they do occur the low vapour pressure of the substances means that they will be associated with the particulate or aerosol phases.

Emission rates to air were derived for two processes in Section 3.1.1.1. The resulting concentrations in air have been estimated using the methods of the Technical Guidance, and the results are in **Table 3.33**.

Table 3.33 Predicted local concentrations in air

Process	Emission rate as chromium	Concentration in episode	Annual average concentration	Comment
Production	19 kg/day	5.2 μg/m^3	4.3 μg/m^3	Based on largest release from actual sites
Metal treatment formulation	3.1 kg/day	0.86 μg/m^3	0.71 μg/m^3	

Deposition rates have been calculated from the emission rates using the methods in the Technical Guidance. There are no indirect emissions from WWTPs. The fraction of substance associated with aerosols was set to 1 as the vapour pressure of these substances is very low. The resulting deposition rates, Dair in mg/kg soil/day, are in **Table 3.34**.

Table 3.34 Deposition rates from air (Dair, mg/kg/day)

Process	Dair for arable land	Dair for grassland
Production	$4.4 \cdot 10^{-4}$	$8.8 \cdot 10^{-4}$
Metal treatment formulation	$1.5 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$

3.1.3.2 Measured levels in air

Levels of total chromium in air have been measured at a location approximately 500 metres downwind from a major production site. The average level measured in 1996, from 23 samples at approximately 2 week intervals, was 44 ng/m^3 (standard deviation 25 ng/m^3, range 1-99 ng/m^3). At the same site the measured average soluble chromium deposition rate was 0.09 mg/m^2/day (equivalent to $5.3 \cdot 10^{-4}$ mg/kg/day to grassland).

Kocková et al. (1996) measured the concentration of heavy metals in dry and wet depositions at some localities in the Morava River basin in the Czech Republic. The annual deposition rate of chromium, measured as total chromium, was reported as 0.0294, 0.0320 and 0.0338 kg/ha/year.

3.1.3.3 Comparison of measured and calculated levels

There are limited measurements of chromium in air to compare with the calculated levels. The concentration measured at a production site was 44 ng/m^3, two orders of magnitude lower than the calculated value of 4.3 μg/m^3. This may be due in part to the different distances from the

source - the calculation assumes 100 metres whereas the measurements were at 500 metres. The measured levels are taken to be more representative.

The deposition rates for local sites calculated above are equivalent to 0.19-0.51 kg/ha/year; the values are similar to that measured at a production site, but an order of magnitude or so higher than those measured in the Czech Republic.

3.1.4 Soil

3.1.4.1 Predicted concentrations in soil

3.1.4.1.1 Local concentrations

The routes by which chromium can enter the terrestrial environment are through sludge application and through deposition from air. It should be noted that there are restrictions on the application of sludges containing metals to soils in many countries. This has not been taken into account in the calculations below. The fate of chromium in the WWTP was described in Section 3.1.2 and was considered to depend on the form of the chromium (as chromium (VI) or chromium (III)). As a result, two concentrations of chromium in sewage sludge have been calculated for each process. These are presented in **Table 3.35**. The values obtained are around two orders of magnitude higher than measured levels in sludges applied to agricultural soils in the UK. In Germany the chromium content in sewage sludge used in agriculture was monitored as 52, 52 and 46 mg/kg dry weight in 1995, 1996 and 1997 respectively (WA II 4, 1999).

Table 3.35 Calculated concentrations in sludge (g/kg dry weight)

Process	Csludge as Cr (VI)	Csludge as Cr (III)
Pigment production	7.7	12
Chromium oxide production	8.5	14
Tanning salts production	9.9	16
Wood preservative formulation	4.9	7.8
Wood preservative application	0.13	0.20
Metal treatment formulation	2.6	4.2
Electroplating	3.0	4.8
Passivating	2.5	3.9
Anodising	0.51	0.82
Brightening	3.1	5.0
Mordant dyeing	0.01	0.016

Thus far the calculations of environmental concentrations have assumed that the chromium is either in the form of chromium (VI) or of chromium (III). This was done to take account of the uncertainty of the extent of conversion from (VI) to (III) immediately following release. From Section 3.1.1.2.1 chromium (VI) is reduced to chromium (III) by organic matter and this process occurs reasonably readily in soils. Studies on the effects of chromium (VI) compounds on soil processes (Section 3.2.1) show that the chromium (VI) is reduced over a period of around two weeks. It is therefore assumed that the chromium present in soil following application is in the form of chromium (III).

Chromium is not biodegradable and not volatile, so the only removal route from soil is through leaching. Values for the soil-water partition coefficient were derived in Section 3.1.1.2.2, and found to vary with the pH of the soil. Based on these values the following rates for leaching from soil have been calculated using the methods in the Technical Guidance (**Table 3.36**).

Table 3.36 Values for k_{leach} (day^{-1})

Soil type	Chromium (VI)		Chromium (III)	
	Acid	Alkaline	Acid	Alkaline
Arable	$3.2 \cdot 10^{-5}$	$7.5 \cdot 10^{-4}$	$2 \cdot 10^{-6}$	$1.1 \cdot 10^{-7}$
Grassland	$6.4 \cdot 10^{-5}$	$1.5 \cdot 10^{-3}$	$4 \cdot 10^{-6}$	$2 \cdot 10^{-7}$

Chromium (VI) is more mobile, but the rapid reduction to chromium (III) means that the values for chromium (III) are more applicable. These indicate that there is effectively no removal of chromium in this form through leaching, and so the estimated fraction remaining after one year is ~1. Therefore the concentrations after 10 years of application are 10 times those after the first application. The resulting concentrations after 10 years are in **Table 3.37**. Concentrations arising from aerial deposition have also been estimated using the methods in the Technical Guidance, and these are included in the Table. Only one process, metal treatment formulation, has releases to air and to sludge; for this process the concentrations are combined.

Table 3.37 Predicted local concentrations in soil

Process	Chromium concentration (as Cr (III), mg/kg)	
	Arable soil	Grassland
Production[a]	2.0	3.6
Pigment production	182	73
Chromium oxide production	199	80
Tanning salts	232	93
Wood preservative formulation	114	46
Wood preservative application	3.0	1.2
Metal treatment formulation[b]	61	25
Electroplating	71	29
Passivating	58	23
Anodising	12	4.8
Brightening	73	29
Mordant dyeing	0.23	0.093

a from aerial deposition
b from combined aerial deposition and sludge application (air contribution <5%)

For wood preservative application, a direct release to industrial soil was calculated as 1.8 kg/day. If this is assumed to occur over an area of 100 · 100 m and over a depth of 0.1 m, the concentration after one year of releases is calculated as 0.32 g/kg wet weight, and 3.2 g/kg after 10 years.

3.1.4.2 Measured levels in soils

The following **Tables** (**3.38-3.42**) present the results of measurements on the levels of chromium in soil. Most are reported as total chromium and do not distinguish between the oxidation states. Most also relate to levels arising from the use of wood preservatives.

Lund and Fobian (1991) studied the concentrations of copper, chromium and arsenic in soils at the sites of two wood preservation plants in Denmark. At one site, treatment of wood began in 1920, where copper sulphate was used as the impregnation agent. Later, in the mid 1940s, salts of arsenic, fluorine and chromium were used until the plant was closed in 1968. The soil at the site is an Alfisol. At the second site, treatment of wood began in 1922 and until the 1950's copper sulphate was the main impregnating agent, which was replaced by CCA treatments. The plant at this site was closed in 1982. The soil at this site is classified as a Spodosol. The soil samples were collected during 1985-86. Elevated levels of chromium were found in the A horizons (down to a depth of 25-50 cm). The highest concentrations measured were around 3,380 mg Cr/kg. The results indicated that the three elements were bound strongly in the layers with high organic matter content. Chromium was effectively immobilised in the surface layers.

Table 3.38 Measured levels in soil

Location	Comments	Chromium level (dry weight)			Reference
		Cr(VI)	Cr(III)	Total	
Agricultural soil					
Germany: Baden-Württemberg Brandenberg Bremen Rheniland-Pfalz	Topsoil, A horizon			50%ile/90%ile: 36/60 4/7 13/37 29/51	LABO (1998)
Sindh province, Pakistan	Humus rich soil			4.2 (mg Cr/100g soil)	Ansari et al. (1997)
Rural developing district, Mexico	Receives untreated wastewater from Mexico City			Up to 0.9 (mg Cr/100g soil)	Mendoza et al. (1996)
Soil near industrial activity					
Basilicata region, Italy				0.1-0.2 ppm dry weight	Caggiano et al. (1998)
Flemish region of Belgium.	Contaminated soil.			322 (34-615) (mg Cr/100g soil	Tack et al. (1997)
Singapore	Roadside soil from heavy traffic area.			Mean 30.2-40.4 μg/g	Zhou et al. (1997)
	Residential area			Mean 26.7 μg/g	
	Nature reserve area			Mean 12.9 μg/g	
	Golf course area			Mean 37.0 μg/g	
	Industrial area			Mean 63.2 μg/g	
UK	Near to chromium compound production site	n.d at 0.5 mg/kg		73% of samples below 100 mg/kg. 12.5 % of samples below 20 mg/kg Mean 148 mg/kg High 1,680 mg/kg Background 20 mg/kg.	IPEH (1997)
USA	Concentration in sludge amended agricultural soil			Range 11.8-37.5 mg/kg	Surampalli et al. (1994)

Table 3.39 summarises the levels chromium in soils sampled near to wood preservation plants.

Yeates et al. (1994) determined the levels of copper, chromium and arsenic in soil that had been contaminated by surface runoff from a wood treatment plant. Samples of plants growing on the site (mainly ryegrass and white clover) and earthworms were also analysed. The soil was a silty loam with an organic carbon content of 6-7% in the upper 5 cm. Four types of site were sampled, high, medium and low contamination and a control (background) site. The results of the analyses are given in **Table 3.40**. The concentrations of metals in soil at contaminated sites declined markedly with depth, approaching the background levels at a depth of 20-30 cm for even the most contaminated sites. The levels in plants and earthworms correlated with the levels in soil.

Table 3.39 Levels of chromium in soil close to wood treatment plants

Location	Concentration Cr (mg/kg)	Reference
Surface layer (0-40 cm) from preservation plants in Sweden		Bergman (1983) in Vihavainen (1989)
Surface layer (0-5 cm) from Finnish impregnation plant	1.0-2.4	Mälkki et al. (1988)
Five impregnation plants, Finland. Highest levels found in surface layer (0-5 cm)	0.5-2,970	Seppänen (1988) in Vihavainen (1989)
26 samples from 6 Swedish preservation plants. Concentrations refer to soluble content	8-4,906	Bergholm (1990)
Surface layer (0-5 cm) from area used to stack freshly treated timber, United Kingdom	530-37,000	Grant and Dobbs (1977)
Surface layer (0-5 cm) from near preservative solution mixing tanks, United Kingdom	4,500-24,000	Grant and Dobbs (1977)
Surface layer (0-5 cm) from random on-site areas, United Kingdom	420-2,200	Grant and Dobbs (1977)
Surface layer (0-5 cm) from off-site soil from area of natural drainage from site, United Kingdom	22-45,000	Grant and Dobbs (1977)

Table 3.40 Levels of chromium in soil, plants and earthworms at a site contaminated by surface runoff from a wood treatment facility (Yeates et al., 1994)

Site	Soil depth (cm)	Soil concentration (Cr mg/kg dry wt)	Plant concentration (Cr mg/kg dry wt)		Earthworm concentration (Cr mg/kg)	
			Leaves	Roots	*Lumbricus rubellus*	*Apporrectodea rosea*
Control	0-5 5-10 10-20 20-30	47.3 45.3 44.3 47.3	2.4	8.7	2.9	2.9
Low	0-5 5-10 10-20 20-30	148 83.8 61.0 56.0	2.8	23.2	9.8	2.9
Medium	0-5 5-10 10-20 20-30	382 93.0 79.0 66.0	5.2	62.3	no samples	no samples
High	0-5 5-10 10-20 20-30	739 132 83.5 86.0	7.9	39.8	no samples	no samples

The levels of copper, chromium and arsenic in soil under decks made from CCA treated timber have been determined in North-eastern United States. In the field study, 85 soil samples were taken from below 7 decks ranging in age between 4 months to 15 years. Control soil samples were collected at minimum of 5 m from the decks. All soils were classified as sandy loam and the top 5 cm was sampled. The results are shown in **Table 3.41**. At each site, the average levels found in soil under the decks were higher than the levels in the control soil (statistically significant at $p<0.025$, except for chromium at the 2 year old site). The levels were also found to increase with age of the deck. The 15 year old deck was painted 1 year after construction and again about 8 years later, which may have reduced leaching at this site. When the distribution of

the metal with depth was looked at, the concentrations of copper and chromium quickly reduced with depth, approaching the control levels at a depth of around 14-15 cm (Sitwell and Gorny, 1997).

Table 3.41 Levels of chromium in soil under CCA treated decks (Stilwell and Gorny, 1997)

Deck age (years)	Concentration of chromium (mg/kg dry soil)	
	Range	average
0.3	20-31	26
2	16-73	26
5	27-68	42
7	34-95	58
7	26-138	64
8	31-154	59
15	16-33	23
Control	11-30	20

The leaching and subsequent movement in soil of copper, chromium and arsenic from CCA treated stakes (Southern pine) over 30 years has been studied (DeGroot et al., 1979). The stakes were treated with CCA at a level of 10.6 kg/m^3 (CCA Type I) or 8.8 kg/m^3 (CCA type II) on an oxide basis and were placed in an acid sandy soil. The average rainfall for the area is 1.6 m and the climate was subtropical (Mississippi). The concentrations of chromium measured in soil around the stakes (both directly below and in the top 15 cm of soil taken at various distances from the stakes), along with the background levels, are shown in **Table 3.42**.

Table 3.42 Concentrations of chromium in soil near to CCA treated stakes after 30 years (DeGroot et al., 1979)

Location	Concentration of chromium (mg/kg)		
	background	after 30 years	
CCA treatment		**I**	**II**
Depth below stake:			
0-15 cm	3.8	25.1	22.9
15-30 cm	7.5	8.2	7.4
30-45 cm	6.9	9.2	6.2
45-61 cm	7.1	9.4	7.1
Distance from stake:			
7.6 cm	3.8	9.4	8.2
15.2 cm	3.8	6.4	4.7
22.8 cm	3.8	6.2	5.3

3.1.4.3 Comparison of measured and predicted levels

Strictly a comparison of the measured and calculated levels cannot be carried out as the calculated levels do not include any anthropogenic or natural background contributions. This is more significant than for water. The main comparisons in this section are with measurements at

sites using chromium (VI) compounds, where local inputs are expected to be relatively more important.

Background levels of chromium in soil can vary considerably; values of 99, 40 and 26 mg/kg have been suggested as typical, but the range is up to 125,000 mg/kg.

Measurements near to a production site did not find chromium (VI) at a detection limit of 0.5 mg/kg. The mean value for total chromium was 148 mg/kg dry weight, 130 mg/kg wet weight. This is higher than the concentrations estimated from aerial deposition based on emission data from the same site, although these were based on chromium (VI) emissions and not on total chromium.

Measured levels in sludge amended agricultural soil of 12-38 mg/kg have been found, which are in the same range as some of the predicted values, although some of the calculated values are higher.

Levels in soil at wood treatment plants range from 1 mg/kg to 37 g/kg, with high levels in older samples, probably before the widespread introduction of concrete surfaces to collect drips. The calculated level in soil from direct release to soil is 3.2 g/kg, which is of the same order.

As with water, there are few measured data which can be related to the calculated values, and few which identify the oxidation state of the chromium. As a result the calculated values for the soil concentrations will be used in the assessment. In addition, the measured values from the production site and from release from treated wood will also be used.

3.1.4.4 Groundwater

The Technical Guidance document suggests that in the first instance the concentration in soil pore water can be used as an estimate of the concentration in groundwater. Soil porewater concentrations have been calculated from the concentrations in soil in **Table 3.37** according to the methods of the TGD, and the results are in **Table 3.43**. Concentrations have been calculated for arable and grassland, for both acidic and alkaline conditions.

There is evidence that chromium is not mobile in soils. The calculated leaching rates in Section 3.1.4.1.1 are very low. Measurements of concentrations in soil around treated wood poles (Section 3.1.4.2) showed a rapid decrease with depth below the poles and with distance from them. Levels in soil contaminated with run-of from a wood treatment facility also showed a rapid decline with depth. It is therefore expected that actual groundwater concentrations will be much lower than those calculated for pore water concentrations above.

Table 3.43 Calculated concentrations of chromium in soil pore water (μg/l)

Process	Arable soil		Grassland	
	Acid	Alkaline	Acid	Alkaline
Production	2.8	0.15	5.1	0.27
Pigment production	258	14	103	5.5
Chromium oxide production	282	15	113	6.0
Chrome tanning salts	329	18	132	7.0
Wood preservative formulation	162	8.6	65	3.5

Table 3.43 continued overleaf

Table 3.43 continued Calculated concentrations of chromium in soil pore water (μg/l)

Wood preservative application	4.2	0.2	1.7	0.09
Metal treatment formulation	74	3.9	31	1.7
Electroplating	101	5.4	40	2.2
Passivating	82	4.4	33	1.8
Anodising	17	0.9	6.9	0.37
Brightening	103	5.5	41	2.2
Mordant dyeing	0.33	0.018	0.13	0.007

3.1.5 Non-compartment specific exposure

This section deals with the exposure of predators to food organisms containing chromium taken up from the relevant environmental compartment. It also considers levels in biota, which may be relevant to indirect exposure of humans through the environment.

3.1.5.1 Calculated levels in fish and earthworms

Bioconcentration factors for fish were derived in Section 3.1.1.2.4. The values were:

1 l/kg for chromium (VI)
100 l/kg for chromium (III) related to chromium (VI) in water

Bioconcentration factors for mussels were also presented in the same section. Values of 9,100 l/kg for chromium (VI) and 2,800 l/kg for chromium (III) have been measured on a dry weight basis. Assuming a dry-weight/wet weight ratio of 0.2, the adjusted BCF values are 1,820 and 560 l/kg for chromium (VI) and (III) respectively.

A number of values for uptake in earthworms were also presented in the same section. Three ranges of values were included: 0.03-0.53; 0.031-0.047; and 0.016-0.019. Taking the mean of the middle of each range gives a value of 0.11 kg/kg. This value has been used to estimate concentrations in worms.

The concentrations estimated in fish, mussels and worms are presented in **Table 3.44**.

Table 3.44 Predicted concentration in fish and earthworms

Process	Fish (mg/kg)		Mussels (mg/kg)		Earthworms (mg/kg)	
	Cr (VI)	Cr (III)	Cr (VI)	Cr (III)	Arable	Grass
Production	0.002[a]	0.2[a]	3.8[a]	7.8[b]		16[c]
Pigment production	0.28	28	500	42	20	8.0
Chromium oxide production	0.30	30	550	46	22	8.8
Chrome tanning salts	0.35	35	640	54	26	10
Wood preservative formulation	0.17	17	310	27	13	5.0
Wood preservative application	0.005	0.5	8.2	0.7	0.32/352[d]	0.13
Metal treatment formulation	0.093	9.3	170	14	6.7	2.7
Electroplating	0.11	11	200	17	7.8	3.1

Table 3.44 continued overleaf

Table 3.44 continued Predicted concentration in fish and earthworms

Process	Fish (mg/kg)		Mussels (mg/kg)		Earthworms (mg/kg)	
	Cr (VI)	Cr (III)	Cr (VI)	Cr (III)	Arable	Grass
Passivating	0.088	8.8	160	14	6.4	2.6
Anodising	0.018	1.8	33	2.8	1.3	0.53
Brightening	0.11	11	200	17	8.0	3.2
Mordant dyeing	0.0004	0.04	0.64	0.06	0.03	0.01

a based on chromium (VI) emissions from site 1
b based on total chromium emissions to water from site 3
c based on mean measured level in soil
d first value from sludge application, second value from direct release to soil

3.1.5.2 Indirect exposure of humans through the environment

The methods used in the Technical Guidance to estimate the concentrations in plants and food animals depend largely on the octanol-water partition coefficient. As this parameter does not have any meaning for the substances considered in this assessment then these methods cannot be used in the usual way. Information is available on levels in plants from laboratory experiments and also from measurements on plants growing in contaminated areas. These will be used to indicate potential exposure through this route.

3.1.5.3 Measured levels in biota

3.1.5.3.1 Levels in animals

Some other information on levels in aquatic organisms is included in Section 3.1.1.2.4 on bioaccumulation.

Chiffoleau and Bonneau (1994) measured the concentration of chromium in two species of mussels (*Mytilus edulis* and *Mytilus galloprovincialis*) and oysters (*Crassostrea gigas*) from the coast of France. Samples for analysis were collected and cleaned and depurated in seawater from the sampling station. The soft tissues were removed from their shells, ground, homogenised and freeze dried. Samples of the freeze-dried tissue were digested using concentrated HNO_3 at 80ºC and then diluted. The samples were analysed by an atomic absorption spectrophotometer. The concentration of total chromium in the species sampled was as follows: *Mytilus edulis* mean 2.07 μg/g dry weight, range 0.71-4.23 μg/g dry weight; *Mytilus galloprovincialis* mean 1.75 μg/g dry weight, range 0.30-3.38 μg/g dry weight; *Crassostrea gigas* mean 1.00 μg/g dry weight, range 0.45-2.34 μg/g dry weight.

Tong et al. (1974) measured the concentration of trace metals in freshwater trout (*Salvelinus namaycush*). They found that chromium concentrations increased with trout age, the correlation between age and concentration being statistical significant (r = 0.65; P = 0.05). The highest concentration measured was 90 ppb fresh weight in 12 year old fish.

A series of studies have investigated the concentrations of copper, chromium and arsenic in marine ecosystems growing on or near CCA treated wood which was used in the construction of bulkheads and floating docks in the United States (Weis and Weis, 1996).

Weis and Weis (1992) collected algae from docks and bulkheads made from CCA treated wood in a marine bay (Old Fort Pond, Southampton, United States). The wood was around 3 years old. Control samples were collected from areas remote from the CCA treated wood. The concentrations of all three metals in the algae from the docks were significantly higher than those from control samples. When snails (*Nassarius obsoletus*) were fed the algae from the docks and control sites for 4 weeks, although some mortality occurred, the snails fed on the CCA-exposed alga did not show elevated concentrations of copper, chromium or arsenic over those found for the snails fed the control algae. Samples of oysters (*Crassostrea virginica*) and fiddler crabs (*Uca panacea* or *Uca pugilator*) were also collected from and around CCA treated structures (a dock in open water, a bulkhead in a restricted canal and control sites, mainly in Pensacola Beach, Florida or Shelter Island, New York). All three metals showed significantly higher levels than controls in *Uca pugilator* samples from Shelter Island. The results are shown in **Table 3.45**.

In another study, samples of alga (*Ceramium* sp.), barnacle (*Balanus eburneus*) and mussel (*Brachydontis recurvis*) were collected from a 7 year old CCA treated dock in open water, a canal lined with CCA treated wood and pilings (some of which were 1 year old) in the Pensacola Beach area. Elevated levels of the metals were found in most organisms when compared to controls. These elevated levels were statistically significant for all three metals in barnacles from the canal (Weis et al., 1993b). The results are shown in **Table 3.45**.

In a further study by the same authors (Weis and Weis, -1992) samples of snails (*Thais haemastoma floridana*), juvenile spot (*Leiostomus xanthurus*), pinfish (*Lagodon rhomboides*) and polychaetes (*Neanthes succinea*) were collected from similar sites and analysed for concentrations of copper, chromium and arsenic. In all species, the levels of chromium were not significantly different from that of controls. These results are also shown in **Table 3.45**.

A similar study has also been undertaken by Wendt et al. (1996). Here, oysters from ten well flushed tidal creeks which contained wooden docks (it is not clear if all the docks were CCA-treated) were sampled. The results are shown in **Table 3.46**. Only the concentration of copper was found to be statistically significantly higher in samples taken from close to the docks compared to samples taken from >10 m away from the docks and control samples.

Table 3.45 Levels of chromium in marine ecosystems near to CCA treated wood (Weis and Weis, 1992; Weis and Weis, 1993; Weis et al., 1993b)

Species	Site	Cr Concentration
Alga *Enteromorpha intestinalis*	Floating docks, Old Fort Pond Control site	6.3 mg/kg dry wt. 2.6 mg/kg dry wt.
Alga *Ulva lactuca*	Floating docks, Old Fort Pond Control site	13.3 mg/kg dry wt. 4.0 mg/kg dry wt
Alga *Cerium sp.*	Open water dock Control site	not detected not detected
Barnacle *Balanus eburneus*	Canal bulkhead (new wood) Canal bulkhead Control site	~27 mg/kg wet wt ~1.6 mg/kg wet wt. no data
Mussel *Brachydontis recurvis*	Canal bulkhead Control site	0.55 mg/kg wet wt not detected

Table 3.45 continued overleaf

Table 3.45 continued Levels of chromium in marine ecosystems near to CCA treated wood

Species	Site	Cr Concentration
Oyster *Crassostrea virginica*	Floating dock Canal bulkhead Control site	not detected not detected not detected
Fiddler crab *Uca panacea*	Near piling Near bulkhead Control	~14 mg/kg dry wt. ~14 mg/kg dry wt. ~14 mg/kg dry wt.
Fiddler crab *Uca pugilator*	Near bulkhead Control	~11 mg/kg dry wt. ~4 mg/kg dry wt.
Snail *Thais haemastroma floridana*	Near bulkhead Control	no data
Polychaete worm *Neanthes succinea*	Near bulkhead Control	no data
Juvenile spot *Leiostomus xanthurus*	CCA wood lined canal Control	~0.26 mg/kg wet wt not detected
Pinfish *Lagadon rhomboides*	CCA wood lined canal Control	not detected ~0.3 mg/kg wet wt

Table 3.46 Mean levels of chromium in well oysters from flushed tidal creeks containing wooden docks

Location	Mean oyster concentration (Cr mg/kg dry weight)
<1 m from docks	not detected
> 10 m from docks	1.5±1.5
Control site	not detected

Carral et al. (1995) measured the concentration of total chromium in intertidal organisms from the Galacia region of Spain. The average concentration and range of concentrations observed in were as follows for the following species: *Mytilus galloprovinciallis* 6 (3-26) ppm; *Scrobicularia plana* 21 (1-508) ppm; *Cerastoderma edule* 10 (11-100) ppm; *Nereis diversicolor* 17(3-409) ppm.

3.1.5.3.2 Measured levels in plants

A study of hexavalent and total chromium levels in plants grown near to a chromium compound manufacturer is reported (IPEH, 1997). In the study hexavalent chromium was not detected in plant samples taken from near the production site (detection limit 1 mg/kg wet wt). The mean concentration of total chromium in pasture plants was 38.7 mg/kg wet wt and the maximum concentration of total chromium was 52 mg/kg wet wt. The mean concentration of total chromium was 5.1 mg/kg wet wt in blackberries, 1.0 mg/kg wet wt in redcurrents, 0.5 mg/kg wet wt in apples and 0.2 mg/kg wet wt in rosehips. For produce grown on allotments near the site the range of total chromium levels was 0.2-0.7 mg/kg wet wt. For cereal crops grown on agricultural land near the site the mean concentration of total chromium was 9 mg/kg wet wt and the maximum concentration was 14 mg/kg.

Carrel et al. (1995) measured the concentration of total chromium in intertidal organisms from the Galacia region of Spain. The average concentration and range of concentrations observed were as follows for the following species: *Ascophyllum nodosum* 17 (3-97) ppm; *Enteromorpha*

sp. 20 (2-173) ppm; *Fucus spiralis* 3 (1-54) ppm; *Fucus ceranoides* 5 (1-159) ppm; *Ulva sp.* 4 (2-51) ppm; *Zostera noltii* 3(1-70) ppm.

López et al. (1995) measured the concentration of chromium in the fresh asparagus (*Asparagus officinalis* L.). The mean level of chromium was 0.517 mg/kg dry weight.

Larsen et al. (1992) studied the uptake of arsenic and chromium by leaf and root vegetables grown near to a combined saw mill and wood preservation plant in Denmark. The wood preservative used was a paste consisting of 34% As_sO_5, 27% CrO_3 and 15% CuO in water. Waste from the plant was incinerated and the smoke from the oven was passed through a multi-cyclone, cooled and filtered before release to the environment. Plants (kale, lettuce, carrots and potatoes) were grown in experimental plots located between 250 and 1,400 m from the source, in the region where modelling indicated maximum fall-out. The edible parts of the plants were sampled for the presence of arsenic and chromium. The results of the analyses are shown in **Table 3.47**.

The concentrations given for lettuce and kale were taken before rinsing the vegetables. Rinsing with water was found to reduce the concentrations by an average of 50% for chromium in kale and 84% for chromium in lettuce. The general background level of chromium in soils was thought to be around 13 mg/kg dry weight respectively. The levels of chromium in vegetables were found to be elevated in areas influenced by emissions from the wood treatment facility. Empirical modelling using the data indicated that the main route of contamination of kale was from atmospheric deposition, but that uptake by carrots and potatoes was by a combination of atmospheric deposition and uptake from the soil.

The levels of copper, chromium and arsenic in leaf, stems and fruit of grape plants grown near CCA treated southern pine posts have been determined by Levi et al. (1974). The posts (minimum diameter 5 inches) were pressure treated with CCA type C preservative to give an average retention of 0.6 pcf (pounds per cubic foot) on an oxide basis. Half the posts were kiln dried immediately after treatment and the rest were placed in the ground without drying. The posts were sunk to a depth of 18 inches and year old grape plants (*Vitis rotundifolia*) were placed 3 inches from the posts in 1970. The soil at the site was a sandy loam of pH 6.0-6.5 and the average annual rainfall was 52 inches. Samples of leaves, stems and fruit were collected over 3 years. No chromium was found in any of the samples collected (detection limit were 0.2 mg/kg dry weight for chromium).

Table 3.47 Concentrations of total chromium in vegetables grown near a wood preservation plant (Larsen et al., 1992)

Distance from source (km)	Concentration (Cr mg/kg dry weight)				
	Soil	Kale	Lettuce	Carrot	Potato
2.3	11	-	0.041	<0.01	<0.01
2.3	13	0.30	0.068	<0.01	0.012
1.5	26	0.083	0.058	<0.01	<0.01
1.4	15	0.021	0.016	<0.01	0.024
1.05	30	0.030	0.023	<0.01	0.012
0.85	12	0.021	0.041	0.012	<0.01
0.85	15	0.071	0.020	0.012	0.01
0.85	10	0.036	0.017	<0.01	<0.01
0.85	15	0.032	0.013	<0.01	<0.01

Table 3.47 continued overleaf

Table 3.47 continued Concentrations of total chromium in vegetables grown near a wood preservation plant(Larsen et al, 1992)

Distance from source (km)	Concentration (Cr mg/kg dry weight)				
	Soil	Kale	Lettuce	Carrot	Potato
0.83	10	<0.01	-	0.012	0.014
0.50	15	0.028	0.039	<0.01	<0.01
0.50	15	0.021	0.032	<0.01	<0.01
0.45	14	0.15	0.027	<0.01	<0.01
0.35	12	0.011	0.036	<0.01	<0.01
0.30	14	0.049	0.032	<0.01	0.014
0.25	75	0.19	1.0	<0.01	0.015
0.15	22	0.083	0.20	<0.01	<0.01
0.10	22	0.26	0.015	<0.01	<0.01
0.10	32	0.041	0.13	<0.01	0.012

The concentrations of copper, chromium and arsenic in tomato plants grown up CCA treated stakes have been measured (Jin and Preston, 1994). The plants were grown in containers of soil containing 4 southern yellow pine stakes (10·38·300 mm) that had been CCA treated at a nominal retention of 6.4 kg/m^3. Three different drying regimes were used for the treated wood, undried (used wet), 48 hours air drying and 2 week air drying. The concentrations of chromium found in the roots of the plants grown near the treated wood were found to be only slightly elevated when compared with background levels. The results are shown in **Table 3.48**.

Table 3.48 Concentrations of chromium in roots of tomato plants grown near CCA treated stakes (Jin and Preston, 1994)

Drying conditions	Concentrations in roots (Cr mg/kg)	Concentrations in soil around roots (Cr mg/kg)	Concentrations in soil next to wood (Cr mg/kg)
Used wet	46.3	289.8	226.4
48 hours	45.6	292.8	219.4
2 weeks	32.2	183.0	211.1
background	34.5	170-258	177-193

3.1.5.4 Comparison of measured and calculated levels in biota

There are few measured levels in biota that can be compared with the concentrations estimated above. From Section 3.1.1.2.4, levels of 33 mg chromium in fish of average weight 140 g were found downstream of an unspecified pollution source. This corresponds to a concentration of 240 mg/kg (wet weight). In the notes above, mussels in a tannery effluent contained 400-1,000 mg/kg dry weight, or 80-200 mg/kg wet weight assuming dry weight of 0.2. These values are an order of magnitude higher than those estimated. This may be because the estimates are based on releases of chromium (VI) and not total chromium.

Other levels in organisms appear to indicate background concentrations of 0.1-0.4 mg/kg.

The predicted values will be used in the assessment of secondary poisoning.

3.2 EFFECTS ASSESSMENT: HAZARD IDENTIFICATION AND DOSE (CONCENTRATION) - RESPONSE (EFFECT) ASSESSMENT

Chromium, as chromium (III) compounds, is an essential element in animal nutrition, functioning mainly in glucose metabolism and also possibly fat metabolism. It is considered to be non-essential for plant growth, although it is essential for some microbes, possibly as a cofactor for specific enzyme systems. Chromium (VI) compounds are not thought to be nutritionally useful forms of chromium. Due to the high mobility (bioavailability) in biological systems and powerful oxidising properties of chromium (VI) compounds, these are considered to be much more toxic to biological systems than the chromium (III) forms (Losi et al., 1994).

The hexavalent chromates of concern in this assessment include compounds that yield both dissolved chromate and dichromate ions. The equilibrium between these ions varies with pH (see Section 3.1.1.3), therefore the ecotoxicology for the hexavalent chromates has been reviewed based on the assumption that the toxic mode of action will be a result of the dissolved chromium (VI), regardless of the original chromium compound. In order to do this, the effect concentrations have been converted where appropriate to give the results in terms of mg chromium (VI) rather than in terms of mg of the original compound. This is consistent with the way many toxicity results for chromium are expressed. However, in a few cases, it is not always clear if the results in a given paper are expressed on a chromium (VI) or total compound basis. In these cases, the latter has been assumed and the results have been converted to mg chromium (VI). These studies are indicated in the comments in the Appendices. None of these studies are included in the summary tables in the main text. All concentrations in the tables in this section are expressed as chromium.

All of the ecotoxicity data for the substances under consideration reviewed for this assessment are summarised in Appendices I to V. The studies have been given a validity marking according to the criteria set out in **Table 3.49**.

Table 3.49 Validity criteria for aquatic toxicity tests

Validity marking	Validity criteria
I	The method is, or is very similar to, the current recommended test guidelines. The test is well reported and most important experimental details are given.
II	The method used in essentially similar or compatible with the current recommended test guidelines. The test is well reported but there may be some aspects of the test for which information is not given.
IIIa	Insufficient data reported to make a judgement on the validity.
IIIb	Some part of the method deviates significantly from what would normally be expected in the current recommended test guidelines, making the significance of the result difficult to interpret. Examples may be tests carried out at very high or low temperatures, results where effects were seen but the statistical significance is uncertain, inappropriate concentrations tested.
IV	Result is clearly invalid or not relevant.

The marking refers to the quality of the study (i.e. how well the study was carried out) and not necessarily the usefulness of the result in risk assessment. The current OECD test guidelines were taken as the basis for the comparison. This is relatively straightforward where a standard organism or method was used. Where other organisms were used, a judgement has been made as to whether the method used is appropriate to the type of organism, by considering the guidelines for similar organisms. Where the method differs from the guidelines, a judgement has been made

on the significance of the differences. This means that some studies which are marked as IIIb may in fact be suitable for use in the risk assessment, especially where guidelines do not exist for the type of organism. Any such instances are identified in the text. Otherwise the data included in the tables and used in the assessment come from categories I and II. General comments about the relative toxicity of different chromium ions and the effects of water properties take some of the other quality data into account.

The validation of the studies has also looked into whether the level of chromium present in the dilution water, and hence control solutions, has been determined or reported. Since chromium is present in most natural waters this may mean that the control organisms were also exposed to chromium in the test. Only a few of the available studies have actually determined the level of chromium present. This has usually been determined by atomic adsorption methods and so determines both chromium (III) and chromium (VI). As discussed earlier in the assessment, the majority of chromium in the environment away from local sources of release will exist as chromium (III) and so it would be expected that any chromium present in the dilution waters used in the tests would also be chromium (III). The level of total chromium found in the dilution waters, when detected, is usually very low (typically around 1 μg/l or less). Tests using artificial dilution waters, which are usually made up from distilled or deionised water, would be expected to have very low concentrations of chromium present.

Overall, the level of chromium (VI) present in the dilution water, if any, is unlikely to be large enough to make any significant difference to the results obtained.

It should be noted that tests carried out using measured chromium exposure concentrations will include a contribution from any chromium present in the dilution water, whereas those using nominal concentrations would not. In almost every case where measured concentrations have been determined the values are very close to the nominal concentrations and are certainly within the 80% criteria recommended in the current test guidelines.

3.2.1 Aquatic compartment (incl. sediment)

Under the conditions of the aquatic tests it is expected that the chromium will remain predominantly in the form in which it is added. The limited data available on conditions that influence bioavailability do not support the development of quantitative relationships. As tests are usually carried out under conditions of high availability, it is recognised that there may be an over-estimate of the toxicity under other conditions. The PEC values do depend on the environmental properties, so to some degree the issue of availability is incorporated into the PEC part of the calculations.

3.2.1.1 Toxicity to algae and aquatic plants

The available toxicity data for algae and aquatic plants are summarised in **Table 3.50**. The results for three aquatic plant species from studies marked IIIb have also been included. These do not meet the full criteria for I or II, as they are from semi-field tests with some variation in the conditions such as temperature. However, they are well-reported and are considered to be sufficiently reliable to be included. Details of these (as for all tests) are in the relevant appendix.

Table 3.50 Summary of toxicity to algae and aquatic plants

Species	Endpoint (g) – growth (b) - biomass	Value (mg/l)	Reference
Algae - freshwater			
Chlamydomonas sp	10 d NOEC (g)[c]	0.5	Cairns Jr. et al. (1978)
Chlorella vulgaris	72 h IC_{50} (g)	0.47	Jouany et al. (1982)
Chlorella pyrenoidosa	96 h NOEC (b)	0.1	Meisch and Schmitt-Beckmann (1979)
Chlorella sp (wild)	96 h NOEC (b)	0.1	Meisch and Schmitt-Beckmann (1979)
Lyngbya (blue-green)	18 d NOEC (g)[c]	0.1	Cairns Jr. et al. (1978)
Microcystis aeruginosa (blue-green)	96 h NOEC (g)	0.35	Sloof and Canton (1983)
Scenedesmus pannonicus	96 h NOEC	0.11	Sloof and Canton (1983)
Scenedesmus subspicatus	72 h EC_{50} (g)	4.6	Kuhn and Pattard (1990)
	72 h EC_{10} (g)	0.64	
	72 h EC_{50} (b)	0.13	
	72 h EC_{10} (b)	0.032	
Selenastrum capricornutum	72 h IC_{50} (g)	0.99	Nyholm (1991)
	72 h IC_{10} (g)	0.11	
	96 h EC_{50} (b)	0.217	Greene et al. (1988)
	72 h EC_{50} (g)	0.233	Christensen et al. (1983) Christensen and Nyholm (1984)
	72 h EC_{10} (g)	0.01	
Algae - brackish water			
Thalassiosira pseudonana	EC_{50}	0.341	-l Riedel(1984)
Aquatic plants – freshwater			
Lemna gibba	8 d NOEC (g)	0.1[b,d]	Staves and Knaus (1985)
Lemna minor	7 d NOEC (g)	0.11	Sloof and Canton (1983)
Spirodela polyrhiza	8 d NOEC (g)	0.1[b,d]	Staves and Knaus (1985)
Spirodela punctata	8 d NOEC (g)	0.5[a,b,d]	Staves and Knaus (1985)

a NOEC calculated as LOEC/2 from paper, effect of 14%; (b) - biomass; (g) – growth
b sodium chromate tested; all others used potassium dichromate. All concentrations as Cr.
c duration of test too long for inclusion in PNEC derivation.
d study rated as IIIb

Potassium dichromate is recommended as a reference substance in the algal inhibition test (Method C.3; EEC, 1992). A ring test involving 16 laboratories determined the mean 72h-EC_{50} values for *Scenedesmus subspicatus* and *Selenastrum capricornutum*. The mean and range of the values obtained (for the two species combined) are shown below on both a $K_2Cr_2O_7$-concentration basis (EEC, 1992) and also converted to the equivalent chromium concentration.

Endpoint	mean value	range
EC_{50}(growth rate)	0.84 mg $K_2Cr_2O_7$/l	0.6-1.03 mg $K_2Cr_2O_7$/l
	≡0.30 mg Cr/l	≡0.21-0.36 mg Cr/l

EC_{50}(biomass)	0.53 mg $K_2Cr_2O_7$/l ≡0.19 mg Cr/l	0.20-0.75 mg $K_2Cr_2O_7$/l ≡0.071-0.26 mg Cr/l.

Most of the algal toxicity data have been generated with potassium dichromate. Where comparison is possible, the toxicity of sodium chromate or sodium dichromate, when expressed on a total chromium basis, does not appear to be significantly different from that of potassium dichromate. This is as would be expected if the equilibria between the chromate and dichromate anions are established in the test medium. Little information is available for ammonium dichromate and chromic acid, but it would be expected that their toxicity would be similar to that of the other chromates/dichromates, when expressed on a total chromium concentration basis.

The available EC_{50} values for algae and plants range from 0.13 to 4.6 mg/l Cr; NOEC values are in the range 0.01 to 0.64 mg/l Cr.

With marine algae, salinity and sulphate ion concentration have been shown to be important factors in determining the toxicity of chromium (VI). The toxicity of chromium (VI) is generally highest at low salinities (<2‰) and low sulphate ion concentrations (Riedel, 1984 and 1985; Frey et al., 1983). At higher salinities, marine alga appears to be of similar or slightly lower sensitivity as freshwater algae.

Riedel (1985) studied the uptake of chromium (VI) (as potassium dichromate) by the marine diatom *Thalassiosira pseudonana* at low salinities (0.32-3.2‰) and sulphate ion concentrations. It was found that the rate of uptake of chromium (VI) was approximately linear with time, proportional the aqueous chromium (VI) concentration and inversely proportional to the aqueous sulphate concentration. The concentration of chromium (VI) that inhibited cell growth also inhibited sulphate uptake.

3.2.1.2 Toxicity to invertebrates

The available toxicity data for invertebrates for acute and longer term exposures are summarised in **Tables 3.51** and **3.52** respectively. For acute data, the lowest valid (class I or II) values from the appendices which relate to standard test durations and life stages are included in the table. For chronic data, all of the values in classes I or II are included. Potassium dichromate, sodium dichromate and sodium or potassium chromate are represented in the data.

Table 3.51 Summary of acute toxicity to invertebrates

Species	Endpoint	Value (mg/l)	Reference
Freshwater			
Crustaceans			
Ceriodaphnia sp	48 h LC_{50}	0.03	Dorn et al. (1987)
Ceriodaphnia dubia	24 h LC_{50}	0.053	Hickey (1989)
Ceriodaphnia pulchella	24 h LC_{50}	0.196	Hickey (1989)
Ceriodaphnia reticulata	48 h EC_{50}	0.195[a]	Elnabarawy et al. (1986)
Crangonyx pseudogracilis	96 h LC_{50}	0.42	Martin and Holdrich (1986)
Daphnia carinata	24 h EC_{50}	0.423	Hickey (1989)
Daphnia magna	48 h EC_{50}	0.035 0.112[a], 0.05[b]	Stephenson and Watts (1984) Elnabarawy et al. (1986) Trabalka and Gehrs (1977)

Table 3.51 continued overleaf

Table 3.51 continued Summary of acute toxicity to invertebrates

Species	Endpoint	Value (mg/l)	Reference
Daphnia obtusa	48 h EC_{50}	0.061	Coniglio and Baudo (1989)
Daphnia pulex	48 h EC_{50}	0.063 0.122[a] 0.18[c]	Dorn et al. (1987) Elnabarawy et al. (1986) Jop et al. (1987)
Macrobrachium lamarrei	96 h LC_{50}	0.65	Murti et al. (1983)
Simocephalus vetulas	24 h EC_{50}	0.154	Hickey (1989)
Insects			
Chironomus tentans	48 h LC_{50}	11.8	Khangarot and Ray (1989a)
Molluscs			
Biomphalaria glabrata	96 h LC_{50}	37.3	Bellavere and Gorbi (1981)
Goniobasis levescens	48 h LC_{50}	2.4	Cairns Jr. et al. (1976)
Lymnaea acuminata	96 h LC_{50}	5.97	Khangarot et al (1982)
Lymnaea emarginata	48 h LC_{50}	34.8	Cairns Jr. et al. (1976)
Physa integra	48 h LC_{50}	0.66	Cairns Jr. et al. (1976)
Polychaetes			
Acolosoma haedlyi	48 h LC_{50}	8.6	Cairns Jr. et al. (1978)
Enchytreaus albidus	96 h LC_{50}	0.67	Roembke and Knacker (1989)
Rotifers			
Philodina acuticumis	48 h LC_{50}	29	Cairns Jr. et al. (1978)
Philodena roseola	96 h LC_{50}	5.5[b]	Schaefer and Pipes (1973)
Saltwater			
Crustaceans			
Allorchestes compressa	96 h LC_{50}	5.56	Ahsanullah (1982)
Artemia sp	24 h LC_{50}	13.7	Vanhaeke and Persoone (1981)
Artemia salina	24 h LC_{50}	7.8 7.9[b] (48 h)	Persoone et al. (1989) Kissa et al. (1984)
*Callinectes sapidus**	96 h LC_{50}	34	Frank and Robertson (1979)
Cancer magister	96 h LC_{50}	3.44	Martin et al. (1981)
Corophium volutator	96 h LC_{50}	4.4	Bryant et al. (1981)
Mysidopsis almyra	48 h EC_{50}	5.13	Dorn et al. (1987)
Mysidopsis bahia	48 h EC_{50}	2.03 6.0[c]	Lussier et al. (1985) Jop et al. (1987)
*Nitocra spinipes**	96 h LC_{50}	5.7	Lindén et al. (1979)
Palaemonetes pugio	96 h LC_{50}	4.86[b]	Conklin et al. (1983)
Praunus fluxuosus	96 h LC_{50}	10	McLusky and Hagerman (1987)
Tisbe holothuriae	48 h LC_{50}	8.1[b]	Moraitou-Apostolopoulou and Veriopoulos (1982)

Table 3.51 continued overleaf

Table 3.51 continued Summary of acute toxicity to invertebrates

Species	Endpoint	Value (mg/l)	Reference
Molluscs			
Crassostrea gigas	48 h EC_{50}	4.54	Martin et al. (1981)
Mathoma balthica	96 h LC_{50}	29	Bryant et al. (1984)
Rangia cuneata	96 h TL_m	14	Olson and Harrel (1973)
Polychaetes			
Capitella capitata	96 h LC_{50}	5.0[a]	Reish et al. (1976)
Neanthes arenaceodentata	7 d LC_{50}	1.63	Mearns et al. (1976)
Nereis diversicolor	96 h LC_{50}	7.5	Bryant et al. (1984)
Rotifers			
*Branchionus plicatilis**	24 h LC_{50}	51.6	Persoone et al. (1989)

Notes All results are from tests with potassium dichromate except:
a sodium dichromate;
b sodium chromate;
c potassium chromate.
All concentrations as Cr. * - tested in brackish water

Table 3.52 Summary of chronic toxicity to invertebrates

	Species	Endpoint	Value (µg/l)	Reference
Crustacean	*Ceriodaphnia dubia*	7-day NOEC (survival)	8.4	De Graeve et al. (1992)
		7-day NOEC (reprod)	4.7	De Graeve et al. (1992)
	Daphnia carinata	14-day NOEC (reprod)	50	Hickey (1989)
	Daphnia magna	21-day NOEC (mortality)	18	Kuhn et al. (1989)
		21-day NOEC (reprod)	18	Kuhn et al. (1989)
		21-day NOEC (mortality)	35	Sloof and Canton (1983)
		21-day NOEC (reprod)	35	Sloof and Canton (1983)
		21-day NOEC (survival)	200	Van Leeuwen et al. (1987)
		21-day NOEC (growth)	60	Van Leeuwen et al. (1987)
		21-ay NOEC (yield)	350	Van Leeuwen et al. (1987)
		14-day NOEC (reprod)	25	Hickey (1989)
		14-day NOEC (reprod)	0.5[a]	Elnabarawy et al. (1986)
Coelenterate	*Hydra littoralis*	11-day NOEC (reprod)	35	Dannenberg (1984)
	Hydra oligactis	21-day NOEC (growth)	1,100	Sloof and Canton (1983)
Insect	*Culex pipiens*	25-day NOEC (survival)	1,100	Sloof and Canton (1983)
		25-day NOEC (development)	1,100	Sloof and Canton (1983)
Mollusc	*Lymnaea stagnalis*	40-day NOEC (reprod)	110	Sloof and Canton (1983)
		40-day NOEC (mortality)	3,500	Sloof and Canton (1983)
		7-day NOEC (hatchability)	350	Sloof and Canton (1983)

Results are from tests with potassium dichromate except for a - sodium dichromate. All concentrations as Cr.De Graeve et al., 1992: this paper reported the results of a ring test, in which 18 determinations of the NOEC values were made. See Appendix C for details. The values in the table here are the geometric mean of the NOEC values reported for each endpoint. Where the value reported was given as <. Half of the limit value has been used in calculating the means (recognising that the actual level of effect was not reported in this paper).

Potassium dichromate is recommended as a reference substance in the acute toxicity to Daphnia test (Method C.2; EEC, 1992). A ring test involving 129 EC_{50} determinations from 46

laboratories determined the mean 24h-EC_{50} value as 1.5 mg $K_2Cr_2O_7$/l (EEC, 1992). This is equivalent to an EC_{50} of 0.53 mg Cr/l, expressed on a concentration of chromium basis.

The toxicity of chromium (VI) to invertebrates in short-term tests appears to depend on water properties such as hardness, pH and temperature. Persoone et al. (1989) noted decreasing EC_{50} values for Daphnia magna with decreasing hardness and with increasing temperature. Although the conditions included some which were outside those recommended, checks were carried out to make sure that they did not cause mortality or stress in the controls. Longer term tests appear to show less influence of the properties on toxicity, but there are few if any studies where the properties have been varied. It may be noted that there are no long-term studies in low hardness waters (<50 mg $CaCO_3$/l).

For some invertebrates, toxicity data is available for more than one of the chromium (VI) compounds included in this assessment. The limited available information indicates that, when expressed on a total chromium concentration, there are no significant differences between the toxicity of sodium chromate, sodium dichromate and potassium dichromate (allowing for differences in water properties). This is as would be expected if the equilibria between the chromate and dichromate anions are established in the test medium. Little information is available for ammonium dichromate and chromic acid, but it would be expected that their toxicity would be similar to that of the other chromates/dichromates, when expressed on a total chromium concentration basis.

Very sharp dose-response curves have been noted in some studies with invertebrates. De Graeve et al. (1992) reported the results of a ring-test on the 7-day test with Ceriodaphnia dubia. The overall mean NOEC values for survival and reproduction (see footnote to **Table 3.52**) were 8.4 and 4.7 µg/l respectively. The overall mean 7-day LC_{50} values for the same endpoints were 14.3 and 14.6 µg/l respectively (ratios of 1.7 and 3.1).

As well as effects on survival and reproduction of invertebrates, sublethal effects of exposure to chromium (VI) have been reported. Adult grass shrimp, *Palaemonetes pugio*, were exposed to levels of chromium (VI) (as sodium chromate) ranging from 0.5 to 4.0 mg/l over 28 days. Approximately 41% of surviving shrimp possessed cuticular lesions, usually associated with articulations of the appendages and abdomen, after exposure to 0.5 mg/l. Increasing exposure concentrations lead to a proportionate increase in the loss of limbs such that nearly 50% of limbs were lost at the highest exposure concentration. It was proposed that the organisms experienced chromium-induced exoskeletal deficiencies resulting in a viaduct for pathogenic organisms and direct chromium influx that perpetuated lesion development (Doughtie et al., 1983).

3.2.1.3 Toxicity to fish

The toxicity of chromium (VI) to fish has been extensively studied. The results are reported in Appendices I to V. The available acute values are summarised in **Table 3.53**; the data are taken from the appendices, selecting tests with standard durations and life stages. The lowest value for each species is included in the table, but several values are included where different substances were tested with the same species. The NOEC values are summarised in **Table 3.54**. In both tables the data are from classes I and II.

The acute toxicity of chromium (VI) to fish appears to be dependent on the water hardness and also pH. Higher toxicity has generally been seen in soft water and at more acidic pHs, particularly those <6.5. This dependence appears to follow a similar pattern to the uptake of

chromium (VI) by fish (see Section 3.1.1.2.4), where it has been postulated that at lower pHs, the main form of chromium (VI) in solution is the monovalent $HCrO_4^-$ ion, which has been postulated as having a higher mobility across cell membranes than the divalent chromium (VI) oxyanions found at higher pH.

For some fish species, toxicity data are available for more than one of the chromium (VI) compounds included in this assessment. The available information indicates that, when expressed on a total chromium concentration, there are no significant differences between the toxicity of sodium chromate, sodium dichromate and potassium dichromate (allowing for differences in water properties). This is as would be expected if the equilibria between the chromate and dichromate anions are established in the test medium. Little information is available for ammonium dichromate and chromic acid, but it would be expected that their toxicity would be similar to that of the other chromates/dichromates, when expressed on a total chromium concentration basis.

Table 3.53 Summary of acute toxicity to fish

Species	Endpoint	Value (mg/l)	Reference
Freshwater			
Brachydanio rerio	96-hour LC_{50}	58.5	Bellavere and Gorbi (1981)
Carrasius auratus	96-hour LC_{50}	37.5	Pickering and Henderson (1966)
Channa punctatus	96-hour LC_{50}	45.2	Saxena and Parashari (1983)
Colisa fasciatus	96-hour LC_{50}	20.8[c]	Srivastava et al. (1979)
Ictalurus punctatus	24-hour LC_{50}	58	Cairns Jr. et al (1978)
Lebistes reticulatus	96-hour TL_m	30	Pickering and Henderson (1966)
Lepomis macrochirus	96-hour LC_{50} 48-hour TL_m 96-hour LC_{50}	110 213[a] 120[b]	Trama and Benoit (1960) Turnbull et al. (1954) Cairns Jr. and Scheier (1958)
Morone saxitalis	96-hour LC_{50}	28[b]	Palawski et al. (1985)
Notemigonus crysoleucas	96-hour LC_{50}	55	Hartwell et al. (1989)
Oncorhynchus mykiss	96-hour LC_{50}	63.6 69[a] 13[d]	Brown et al. (1985) Benoit (1976) Van Der Putte et al (1981b)
Pimephales promelas	96-hour TL_m 96-hour LC_{50} 96-hour TL_m	17.6 33.2[a] 45.6[b]	Pickering and Henderson (1966) Benoit (1976) Pickering and Henderson (1966)
Salvelinus fontinalis	96-hour LC_{50}	59	Benoit (1976)
Saltwater			
*Alburnus alburnus**	96-hour LC_{50}	84.8	Lindén et al. (1979)
Chelon labrosus	48-hour LC_{50}	47.2	Taylor et al. (1985)
Citlerichthys stigmaeus	96-hour LC_{50}	30	Mearns et al. (1976)
Cyprinodon variegatus	96-hour LC_{50}	25 21.4[b]	Jop et al. (1987) Dorn et al. (1987)
*Gasterosteus aculcatus**	96-hour LC_{50}	33 35[b]	Jop et al. (1987)
Limanda limanda	96-hour LC_{50}	47	Taylor et al. (1985)

Notes: all results are from tests with potassium dichromate except: a - sodium dichromate; b - potassium chromate; c - chromium trioxide; d- sodium chromate. All concentrations as Cr. * - tested in brackish water

Some studies have looked at the effects of chromium (VI) on different ages of fish. Van Der Putte et al. (1981b) observed increased sensitivity in younger fish, with LC_{50} values of 7.6 mg/l at 4 months rising to 45 mg/l at 9 months.

As well as effects on survival, growth and reproduction, chromium (VI) (mainly as potassium dichromate) has been shown to cause a variety of sublethal haemotological, pathological, physiological and behavioural effects. These effects are detailed below.

In experiments with the freshwater fish *Channa punctatus*, 10 mM and 1.0 mM of chromium (VI) (as potassium dichromate, equivalent to 520 and 52 mg Cr/l) significantly decreased the rate of absorption of xylose (a sugar) by the intestine over 1 hour, whereas 0.01 mM and 0.001 mM (equivalent to 0.52 and 0.052 mg Cr/l) significantly increased the rate of absorption of xylose over the same period (Sastry and Sunita, 1983a).

Table 3.54 Summary of chronic toxicity to freshwater fish

Species	Life stage	Endpoint	Value (mg/l)	Reference
Catastomus commersoni	Egg/fry	30-day NOEC (g)	0.923[a]	Sauter et al. (1976)
		60-day NOEC (g)	0.29[a]	Sauter et al. (1976)
Esox lucius	Egg/fry	20-day NOEC (s)	0.538[a]	Sauter et al. (1976)
Ictalurus punctatus	Egg/fry	30-day NOEC (g)	0.15[a]	Sauter et al. (1976)
		30-60-day NOEC (g)	0.305[a]	Sauter et al. (1976)
Oncorhynchus mykiss	Egg/fry	60-day NOEC (g)	0.051[a]	Sauter et al. (1976)
		60-day NOEC (s)	0.384[a]	Sauter et al. (1976)
	Alevin-juvenile	8-m NOEC (g)	0.1[a]	Benoit (1976)
		8-m NOEC (m)	0.2[a]	Benoit (1976)
Oryzias latipes	Embryo/larval	40-day NOEC (m)	3.5	Sloof and Canton (1983)
		40-day NOEC (g)	35	Sloof and Canton (1983)
Pimephales promelas	Larval	7-day NOEC (g)	1.1	De Graeve et al. (1991)
		7-day NOEC (s)	4.2	De Graeve et al. (1991)
	4-week	412-day NOEC (s)	1	Pickering (1980)
		9-w LOEC (g)	<0.018*	Pickering (1980)
		412-day NOEC (g)	3.95	Pickering (1980)
		NOEC (r)	>3.95	Pickering (1980)
	egg/larvae	60-day NOEC (s)	1	Pickering (1980)
		60-day NOEC (g)	1	Pickering (1980)
	larvae	30-day NOEC (g)	0.05[a]	Broderius and Smith Jr. (1979)
		30-day NOEC (m)	>3.06[a]	Broderius and Smith Jr. (1979)
Poecilia reticulata	3-4 week	28-day NOEC (m)	3.5	Sloof and Canton (1983)
		28-day NOEC (g)	3.5	Sloof and Canton (1983)
Salvelinus fontinalis	Embryo/juvenile	8-m NOEC (g)	0.01[a]	Benoit (1976)
		8-m NOEC (m)	0.2[a]	Benoit (1976)
Salvelinus namaycush	Egg/fry	60-day NOEC (g)	0.105[a]	Sauter et al. (1976)
		60-day NOEC (s)	0.82[a]	Sauter et al. (1976)

Notes: all results are from tests with potassium dichromate except:
a - sodium dichromate.
All concentrations as Cr. (s) - survival; (m) - mortality; (g) - growth; (r) - reproduction
* - the authors viewed this result as a temporary effect and did not consider it significant in deriving a maximum allowable concentration. The value has not been included in the derivation of a mean NOEC for growth later in the RAR.

In another series of experiments with *Channa punctatus,* fish were exposed to sublethal concentrations of chromium (VI) (as potassium dichromate) of 2.6 mg Cr/l for 15 and 30 days at

a pH of 7.4. At the end of the experiment, the fish were dissected and various organs were analysed. At both exposure levels, fish were found to be hyperglycemic and hyperlactemic (elevated blood glucose levels and a decrease in liver glycogen content was seen). An elevation of the activity of enzymes involved in glycolysis and the Kreb's cycle was also seen in muscles and liver, indicating that the metabolic rate of the exposed fish was higher than that of controls (Sastry and Tyagi, 1982; Sastry and Sunita, 1982 and 1984). Similar results were found in a 120 day exposure to the same concentration (Sastry and Sunita, 1983b).

An experiment was carried out with the freshwater fish *Tilapia sparrmanii* in order to determine the effect of chromium on blood coagulation at acidic (pH 5), physiological (pH 7.4) and alkaline (pH 9) pHs. Fish were exposed to 0.098 mg/l of potassium dichromate (i.e. 0.034 mg Cr (VI)/l) over 96 hours. Fish exposed to chromium contracted thrombocytopenia (a blood disease caused by a shortage of thrombocytes present in blood) with an increase in water pH (Van Pittius et al., 1992).

Gill and Pant (-1978) found that acute (12 and 24 hours) and chronic exposure (30 and 60 days) of the freshwater fish *Barbus conchonius* to potassium dichromate (chromium concentration 41.2 mg Cr (VI)/l for acute exposures, 0.687 and 1.03 mg Cr (VI)/l for chronic exposures) in hard water (395 mg/l as $CaCO_3$, pH 7.1), resulted in anomalies in peripheral blood and tissues of fish. Pathological changes were also observed in gills, kidneys and liver of chromium-exposed fish.

A study was carried out to assess the avoidance behaviour of rainbow trout (*Oncorhynchus mykiss*) pre-exposed to sublethal levels of chromium (VI) (as potassium dichromate). Fish were pre-exposed to chromium (VI) concentrations ranging from 0.01 to 3.0 mg Cr (VI)/l. An avoidance threshold of 0.028 mg Cr (VI)/l was determined for fish not pre-exposed to chromium (VI), while avoidance thresholds for pre-exposed fish increased linearly with the level of pre-exposure. A level of 0.8 mg Cr (VI)/l was proposed as a critical pre-exposure level for short term recovery of normal chemoreceptive capacity (Anestis and Neufeld, 1986).

Vaile and Calamari (1984) studied the immune response in rainbow trout (*Oncorhynchus mykiss*) exposed to chromium (VI) (as potassium dichromate) over a 4-month exposure period. Fish were exposed to 0.05 ('safe' concentration) and 0.200 ('effect' concentration) mg Cr (VI)/l. The kinetics of antibody production against human red blood cells were monitored. Chromium (VI) was ineffective at reducing the humoral immune response, that is, there was no evidence of sublethal effects of the metal on the immune system of fish at the levels tested.

Bogé et al. (1988) investigated effects of chromium (VI) as potassium dichromate on enzymatic activities and transport processes of intestinal brush border membrane (alkaline phosphatase and maltase activities, glycine adsorption) of rainbow trout (*Oncorhynchus mykiss*). The experiments were carried out by perfusion for 30 minutes of solutions containing either 141 or 14 mg Cr (VI)/l. The higher concentration was lethal to trout over 24 hours exposure. Chromium (VI) exposure lead to a severe decrease of alkaline phosphatase activity growing more severe with increasing chromium (VI) concentration and with time. An approximate 50% inhibition of activity was observed after 30 min with the 141 mg Cr (VI)/l exposure and after 90 min with 14 mg Cr (VI)/l exposure. Enzyme activity remained low after removal of chromium, indicating no recovery of initial activity. No effect of chromium on maltase activity was observed. Chromium (VI), this time as sodium dichromate, was an inhibitor of glycine absorption in trout at high concentrations: 90% inhibition at 14.1 g Cr (VI)/l whereas concentrations of 1.4 g Cr (VI)/l caused no effect.

Temmink et al. (1983) investigated the mechanism of toxicity of chromium (VI) as sodium chromate in fingerling rainbow trout (*Oncorhynchus mykiss*). Fingerling trout were exposed to 3.2 mg Cr (VI)/l at pH 6.5 for up to 11 days to induce hyperplasia of the gill epithelium. Hyperplasia disappeared in gills of those fish that survived exposure and recovered in control conditions for 0.5 to 4 weeks. The toxic effect of chromium (VI) was thought to occur by a three step process with the first step being degeneration and eventual death of the epithelial cells - the plasma membrane being the primary target for oxidative action of chromium (VI) (Temmink et al., 1983).

Singh and Sivalingam (1982) investigated the effects of heavy metals, including chromium (VI) (as potassium dichromate), on the activity of the liver enzyme catalase of *Sarotherodon mossambicus*. High concentrations of chromium (VI) caused inhibition of catalase activity. Catalase activity was inhibited by 21% and 37% at concentrations of 30 mg Cr (VI)/l and 40 mg Cr (VI)/l, respectively.

Brown trout (*Salmo trutta*, 1 year old), and mirror carp (*Cyprinus carpio*, 3+ years old) were exposed to low-levels of potassium dichromate, 1.01 mg Cr (VI)/l over 266 days (38 weeks). The humoral antibody response to MS2 bacteriophage was followed using a 50% viral neutralisation assay method. Immuno-suppression was observed in both fish species. Total suppression of the immune response was observed in the carp exposed to chromium (VI) and these fish also showed symptoms of acute toxicosis (moribund within 11 weeks). Other sublethal effects seen in the study included a significant loss in weight in exposed fish compared with controls. (O'Neill, 1981).

Jana and Sahana (1988) reported no change in the levels of free amino acids in muscle or protein in kidney or testis of fish (*Clarias batrachus*) exposed to sodium chromate (5 mg Cr (VI)/l for 14 days at pH 8.5. A small decrease in the dry weight of certain organs (muscle, liver, kidney, stomach, intestine, testis and ovary) was noted in exposed fish when compared with controls.

Kranz and Gercken (1987) investigated whether sublethal concentrations of potassium dichromate (0.175 and 0.7 mg Cr (VI)/l) induce changes in the occurrence of splenic melano-macrophage centres (MMC) in juvenile plaice (*Pleuronectes platessa*) after 27 days exposure. Macrophages are cells of the immune system which, amongst others, remove foreign particles and effete or damaged cells from an organism. Chromium accumulated to a level of 0.4 mg/kg at both exposure concentrations. Exposure to both levels of chromium (VI) caused a continuous increase in the frequency of splenic MMC in plaice, although the average size of the MMC decreased, therefore the total area did not increase (Kranz and Gercken, 1987).

3.2.1.4 Other aquatic organisms

The toxicity to other aquatic organisms is summarised in **Table 3.55**. Further details of the tests carried out are given in the appropriate Appendix (A-E).

Table 3.55 Summary of toxicity to other organisms

Species	Life stage	Endpoint	Value (mg/l)	Reference
Freshwater amphibians				
Bufo melanostictus	Tadpole	96-hour LC_{50}	49.3	Khangarot and Ray (1987a)
Rana hexadactyla	Frog	96-hour LC_{50}	100	Khangarot et al. (1985)
Rana cyanophlyctia	Frog	96-hour LC_{50}	81 85[a] 43[b]	Joshi and Patil (1991)
Xenopus laevis	Frog	100-day NOEC (g) 100-day NOEC (m) 100-day NOEC (d)	1.1 0.35 1.1	Sloof and Canton (1983)

Notes all results are from tests with potassium dichromate except:
a - sodium dichromate;
b - sodium or potassium chromate.
All concentrations as Cr. (m) - mortality; (g) - growth; (d) - development.

Only a limited comparison is possible between the toxicities of the various chemicals, but the available values, when expressed on a total chromium basis, do not appear to be significantly different from each other.

3.2.1.5 Micro-organisms

The toxicity data for chromium (VI) to micro-organisms are reported in Appendices I to IV and summarised in **Table 3.56**. Note that the data included in the appendices and the table cover a range of micro-organism types, and are not limited to those relevant to the assessment of a wastewater treatment plant.

Table 3.56 Summary of toxicity to micro-organisms

	Species	Endpoint	Value (mg/l)	Reference
Activated sludge	mixed	3-hour IC_{50}	30[a]	Klecka and Landi (1985)
Bacteria	*Bacillus subtilis*	10-hour EC_{50}	0.11	Ogawa et al. (1989)
	Escherichia coli	24-hour EC_{50}	3.5 0.42[b]	Gaur and Bhattacherjee (1991)
	Photobacterium phosphoreum	30-minute EC_{50}	21 27 200[c]	Tarkpea et al. (1986) Krebs (1983) Krebs (1983)
	Pseudomonas fluorescens	7-day NOEC	0.11	Sloof and Canton (1983)
	Vibrio harveyi	50-minute EC_{50}	2.2	Thomulka and Lange (1997)
Protozoan	*Chilomonas paramecium*	19-25-hour NOEC	1.0	Cairns Jr. et al. (1978)
	Colpidium campylum	24-hour IC_{50}	2.8	Dive et al. (1990)
	Microregma heterostoma	28-hour NOEC	0.21	Bringmann and Kuhn (1959)

Notes: all results are from tests with potassium dichromate except for a - sodium dichromate and b - sodium chromate. c - solutions were pH neutralised. All concentrations as Cr.

Ross et al. (1981) reported that an influent concentration of 10 mg Cr (VI)/l reduced the efficiency of a model activated sludge plant by 5%, as measured by effluent chemical oxygen demand. The same or similar results were also found by Barth et al. (1967) using a pilot scale activated sludge sewage treatment plant. In this study, chromium (VI) (form unknown) was added into the influent to the sewage treatment plant, and the plant was allowed to acclimate for 2 weeks before data on the functioning of the plant were obtained. The plant was then run for a further 60 days and the quality of the final effluent from the plant (in terms of biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity and suspended solids) was compared with that from an identical plant receiving domestic sewage only. It was found that once above a threshold concentration where the efficiency of the treatment plant was affected, there was no further deterioration in performance of the plant until very high concentrations of chromium (VI) were reached. The threshold concentration of chromium (VI) identified in the study was 10 mg Cr/l as a continuous concentration in plant influent. The study also investigated the effects of pulses of higher concentrations of chromium (VI) on the treatment plant. It was found that a chromium (VI) concentration of 500 mg/l (as a four hour dose) in influent had no noticeable effect on the performance of the plant (as measured by COD removal).

There is evidence that some species of micro-organism are much more tolerant to chromium (VI) than others. It has been reported that a strain of *Pseudomonas aeruginosa* was able to grow in the presence of 428 mg Cr (VI)/l (as potassium chromate), and another *Pseudomonas* species was tolerant to 5,356 mg Cr (VI)/l (as potassium chromate). Similarly species of *Athrobacter* and *Agrobacter* could tolerate chromium (VI) concentrations up to 400 mg Cr (VI)/l and 100 mg Cr (VI)/l (as potassium dichromate) respectively. Gram positive bacteria are generally more resistant to chromium (VI) than gram negative bacteria (Coleman, 1988).

Miranda and Castillo (1998) investigated the resistance of 172 motile *Aeromonas* sp. (associated with sewage treatment processes) isolated from Chilean raw drinking water supplies, irrigation waters and runoff waters receiving sewage to chromium (VI) (source not stated). In the experiment, a Minimal Inhibitory Concentration (MIC) was determined using a growth media containing yeast extract, peptone and agar. The chromium (VI) concentration tested ranged between 5-700 mg/l and MICs in the range 20-300 mg/l were determined. Around 2-5% of the strains tested were considered by the authors to be resistant to chromium (VI) (MIC>100 mg/l), and 50% of the strains tested had MICs in the range 40-80 mg/l.

Ross et al. (1981) looked at the effect of chromium (VI) (as potassium dichromate) and chromium (III) (as chromic chloride) on the growth of a mixed bacterial population isolated from soil. Aqueous soil extracts were used in the experiment (pH 6.5) using both non-aerated and aerated cultures at 23-33^{o}C for up to 48 hours. A difference in sensitivity between gram negative and gram positive bacteria was found in the study. The growth of all gram negative bacteria was found to be almost completely inhibited by 10-11 mg Cr (VI)/l. A concentration of 1 mg Cr (VI)/l had no effect on most gram positive bacteria, whereas significant growth inhibition was seen with some gram negative bacteria at the same concentration. Analysis after 48 hours indicated that around 80% of the chromium present was still as chromium (VI). The experiments with chromium (III) showed that it was much less toxic to the bacteria, with higher growth rates than controls being seen with some species at a concentration of 10 mg Cr (III)/l and only a small amount of growth inhibition being seen at a concentration of 100 mg Cr (III)/l.

3.2.1.6 Sediment organisms

There are very few studies that have investigated the toxicity of chromium (VI) to organisms in the sediment phase. The two tests included here do not involve organisms which live in intimate contact with sediments, and so are not particularly relevant to an assessment of the risk to sediment organisms.

Dave (1992) investigated the toxicity of chromium (VI) (as potassium dichromate) and chromium (III) (as chromium potassium sulphate), spiked onto sediment, to 4-5 day old *Daphnia magna.* The experiment was carried out by mixing 5 g of sediment with a solution of either chromium (III) or chromium (VI) (total volume of 50 ml), and allowing the suspension to equilibrate and settle for 3 days at 20^{o}C. The toxicity test was carried out by adding 20 *Daphnia* to each suspension, and mortality was monitored after 24 and 48 hours exposure. The 48-hourEC_{50} values were found to be 195 mg/kg dry weight for chromium (III) and 167 mg/kg dry weight for chromium (VI), based on the amounts added to the dry sediment. The sediment used in this experiment had a background total chromium concentration of 92 mg/kg dry weight.

In a study using marine sediment, Gardner et al. (1992) showed that oysters (*Crassostrea virginica*) developed tumours when exposed for 30 days to the overlying water containing 20 mg/l suspended sediment for 30 days. In the study, the marine sediment was spiked with chromium (VI) (as potassium chromate) at levels of 1,460 and 14,600 mg/kg dry weight, however, 10 other known or suspected carcinogens were also added to the sediment during the test, and so the effects seen cannot be attributed directly to the chromium (VI) alone.

3.2.1.7 Predicted no effect concentration (PNEC) for the aquatic compartment

3.2.1.7.1 Water

Overview of aquatic toxicity data

Short-term and long-term ecotoxicological data on the effects of hexavalent chromium compounds are available for a wide variety of organisms (freshwater and marine fish, invertebrates, algae, plants, amphibians), lifestages (juveniles, adults, fry, larvae, tadpoles, eggs, etc.), endpoints (LC_{50}s, EC_{50}s, NOECs, LOECs based on mortality, reproduction, hatching, etc.), and test conditions (see Appendices A to E). The results are expressed as the concentrations of chromium (VI), for ease of comparison among the five hexavalent compounds. In general, the majority of ecotoxicological information is available for potassium dichromate, as it is a reference toxicant. Few results are available for chromic acid and ammonium dichromate.

The results indicate that the acute toxicity of chromium (VI) is dependent on a number of factors, including pH, water hardness, salinity and temperature. In general, chromium (VI) toxicity is increased with decreased pH (i.e. 8.0 to 6.0), increased temperature (i.e. 15 to 25^{o}C) and decreased water hardness (>100 to <100 mg/l as $CaCO_3$) or salinity (<2%). The values in parenthesis are general values for fish and aquatic invertebrates and will vary according to individual species' optimum environmental requirements. It should be noted that there are also studies which show little change in toxicity with changes in water properties. From the available data there does not appear to be any difference among the sensitivity of organisms to the nature of the chromium (VI) ion in short-term tests.

The acute toxicity values are plotted in **Figures 3.2-3.4**. **Figure 3.2** shows the distribution of results in the four main groups of algae, invertebrates, fish and amphibians, and combines freshwater and saltwater data. **Figure 3.3** shows the relative sensitivities of freshwater and saltwater organisms. **Figure 3.4** shows the distribution of the freshwater results, with the invertebrates separated into the separate orders or phyla.

In the acute tests, aquatic invertebrates are the most sensitive test species to chromium (VI), making up the vast majority of the upper half of the ranking (**Figure 3.2**). There are a large number of invertebrate results, so there are species which are of a much lower sensitivity as well. The smaller number of algal results also appears in the upper half.

The comparison between freshwater and saltwater organisms (**Figure 3.3**) shows that the former appear to be more sensitive. Decreasing salinity appears to lead to increased toxicity; this can be seen in the results of particular studies included in the appendices; for example, Bryant et al. (1984) with *Corophium volutator* and *Macoma balthica*, and Persoone et al. (1989) with *Branchionus plicatilis*. Where saltwater organisms have been tested in water of low salinity (<2%), their sensitivity appears to become comparable with that of freshwater organisms.

The more detailed breakdown of the invertebrate species (**Figure 3.4**) for freshwater organisms shows that the most sensitive group of invertebrates are cladocerans, such as *Ceriodaphnia dubia* and *Daphnia magna*. The single amphipod result lies within the range of the cladocerans, as do two of the three algal species. All of the values for fish are higher than the cladoceran and amphipod values.

The summary tables of freshwater chronic toxicity values presented earlier contained several values for some species, covering a range of endpoints. These have been combined into the values given in **Table 3.57**. For species where more than one value was available for an end point, the geometric means of the values for survival/mortality, reproduction, and growth/development were calculated to produce one value per endpoint. Then for all species the lowest value between these endpoints was selected as the NOEC for the species. The table includes notes on data selection where there was a choice.

The freshwater chronic toxicity values are plotted in **Figure 3.5**, again separating the invertebrates into their component groupings.

The long-term studies available do not appear to show any clear dependence of toxicity on the properties of the water. There are indications that toxicity may be higher in lower hardness waters, but there are few if any studies which allow the comparison to be made for the same species at different levels of hardness, or other properties. The range of water hardness values in the studies included in **Table 3.57**, where these were reported, is 24 - 250 mg/l as $CaCO_3$. Most of the reported values are below 50 mg/l. The pH in the tests was generally between 7.5 and 8.5. Although relationships between hardness and toxicity have been described for divalent metal cations, the fact that the chromium species here are oxoanions means that their toxicity may be less influenced by water properties. As no relationships can be established, the toxicity data will be treated together. It should be noted that the calculated concentrations do depend on the environmental properties.

Table 3.57 Data used for PNEC derivation

	Species	NOEC (mg Cr/l)	Notes
Blue-green algae	*Microcystis aeruginosa*	0.35	
Algae	*Chlorella pyrenoidosa*	0.1	
	Chlorella sp (wild)	0.1	
	Scenedesmus pannonicus	0.11	
	Selenastrum capricornutum	0.033	Geometric mean of EC_{10} (g)
Macrophytes	*Lemna gibba*	0.1	
	Lemna minor	0.11	
	Spirodela polyrhiza	0.1	
	Spirodela punctata	0.5	
Crustaceans	*Ceriodaphnia dubia*	0.0047	Reproduction value
	Daphnia carinata	0.05	
	Daphnia magna	0.019	Geometric mean of reproduction values
Coelenterates	*Hydra littoralis*	0.035	
	Hydra oligactis	1.1	
Insect	*Culex pipiens*	1.1	Survival/growth NOEC
Mollusc	*Lymnaea stagnalis*	0.11	Reproduction value
Fish	*Catastomus commersoni*	0.29	Longer growth value
	Esox lucius	0.538	
	Ictalurus punctatus	0.15	30-d growth NOEC
	Oncorhynchus mykiss	0.07	Geometric mean of growth NOECs
	Oryzias latipes	3.5	Survival NOEC
	Pimephales promelas	0.68	Geometric mean of growth NOECs
	Poecilia reticulata	3.5	Growth/mortality NOEC
	Salvelinus fontinalis	0.01	Growth NOEC
	Salvelinus namaycush	0.105	Growth NOEC
Amphibian	*Xenopus laevis*	0.35	Mortality NOEC

Assessment factor approach

According to the standard assessment factor approach, the PNEC is derived from the lowest NOEC available. The lowest NOEC included in the preceding sections is 4.7 μg/l, for reproduction of the cladoceran *Ceriodaphnia dubia*. As there is a large amount of long-term effect data on a wide range of aquatic organisms, an assessment factor of 10 is used, giving a PNEC by this method of 0.47 μg/l.

Figure 3.2 Acute toxicity data (fresh and saltwater)

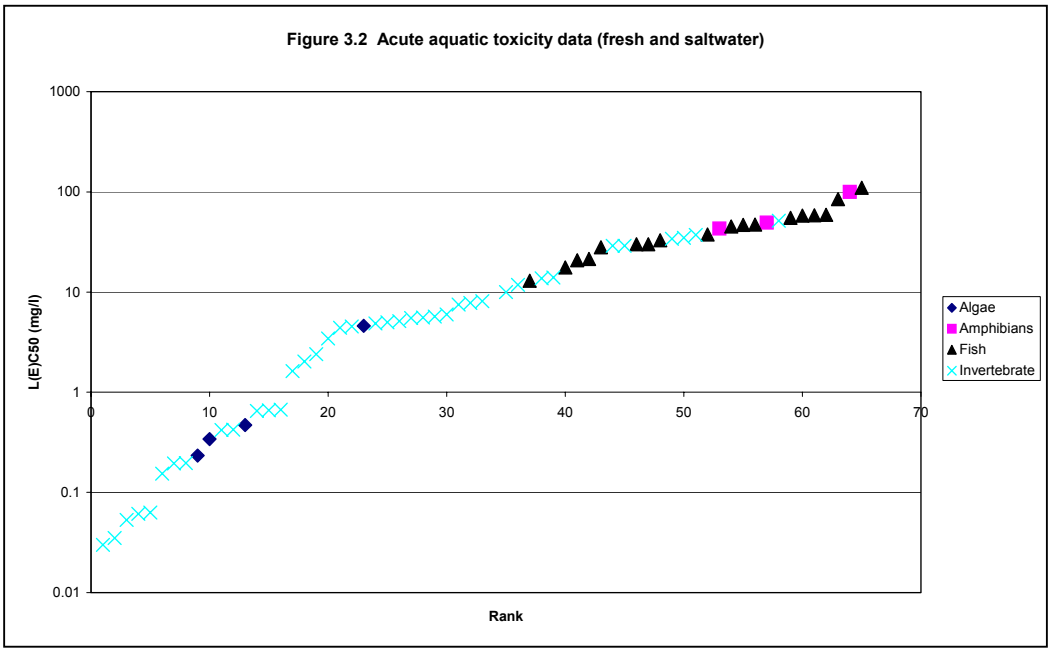


Figure 3.3 Acute aquatic toxicity – fresh v salwater

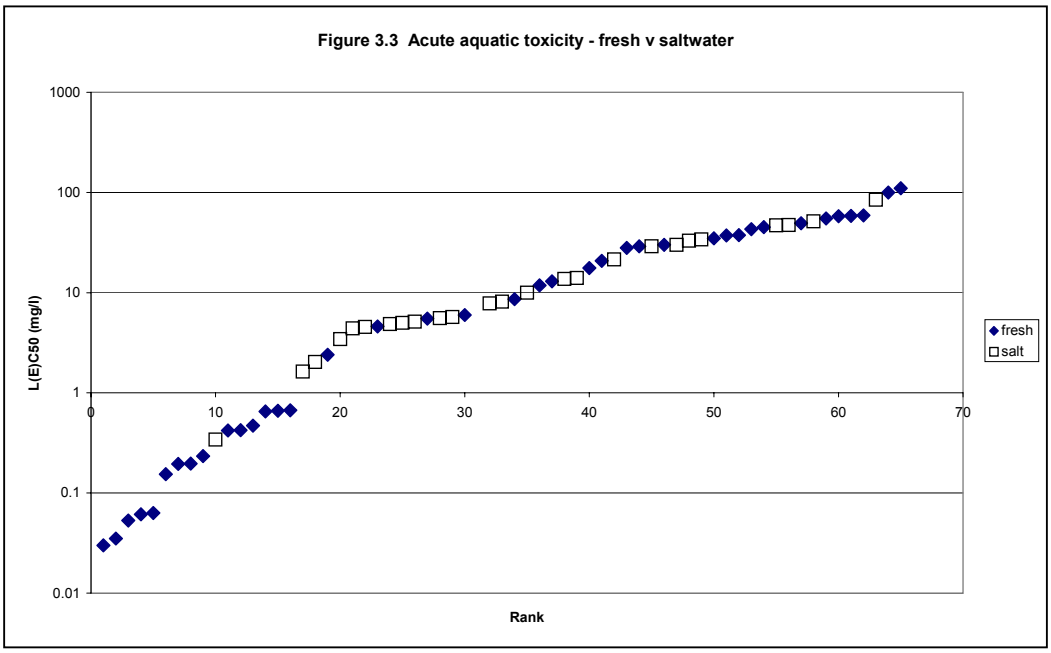


Figure 3.4 Acute aquatic toxicity - freshwater

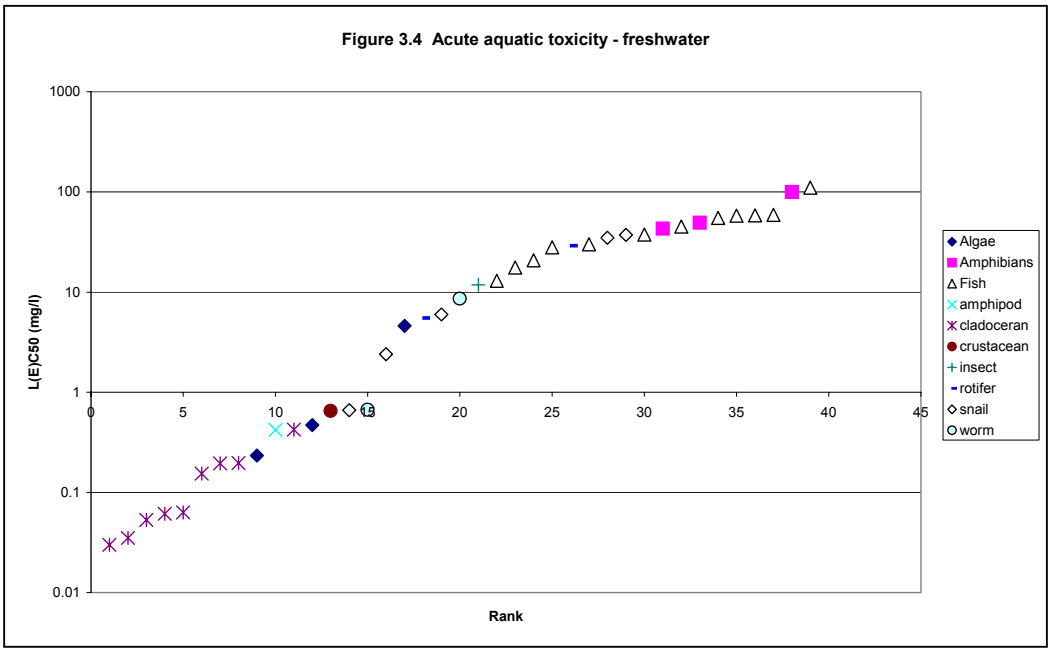
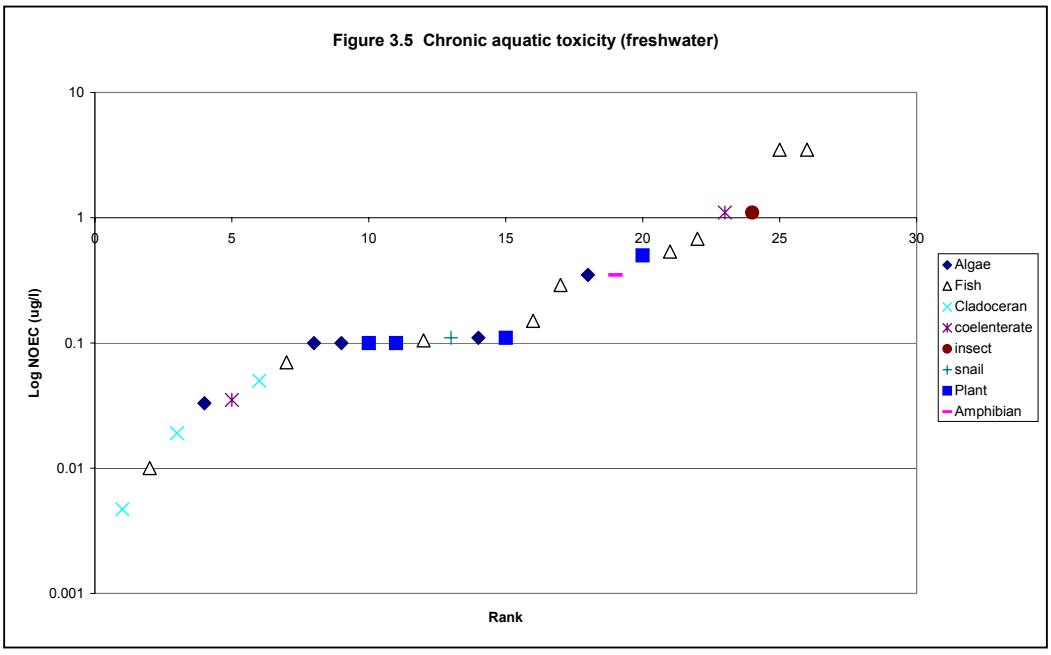


Figure 3.5 Chronic aquatic toxicity (freshwater)



Statistical extrapolation approach

According to the TGD, the effects assessment can also be supported by a statistical extrapolation method if the data base is sufficient for its application. A workshop on the use of statistical extrapolation for the derivation of PNEC values in case of data-rich substances was held in London in January 2001 in the framework of the EU Existing Substances programme. This workshop was specifically aimed at the use of statistical extrapolation for the derivation of PNEC values for the metals zinc, cadmium and hexavalent chromium, since for these metals large chronic databases are available. The workshop recommended the inclusion of statistical extrapolation in the derivation of PNEC values for these metals, provided the chronic database meets certain requirements (EU, 2001). The data set for chromium is discussed below in relation to these requirements.

There is a considerable amount of ecotoxicological information available on the toxicity of the five hexavalent chromium compounds to aquatic organisms (Appendices I-V, summarised in the preceding sections). There are 28 NOEC (or derived NOEC) values available for calculating a HC_5 for chromium (VI) from a wide range of aquatic taxa including: fish, crustacea, algae, aquatic plants, insects, molluscs, amphibians, and coelenterates. These values can be matched against the criteria used by the US EPA which were adopted at the workshop, with the addition of algae and aquatic plants. This is done in **Table 3.58**. (Only one species is included against each criterion, but the data set contains more examples).

Table 3.58 Criteria for species representation

Criterion	Species
The family Salmonidae in the class Osteichthyes	*Oncorhychus mykiss*
A second family in the class Osteichthyes, preferably a commercially or recreationally important warm water species (e.g. bluegill, channel catfish, etc.)	*Pimephales promelas*
A third family in the phylum Chordata (may be in the class Osteichthyes or may be an amphibian, etc.)	*Esox lucius*
A planktonic crustacean (e.g. cladoceran, copepod, etc.)	*Ceriodaphnia dubia*
A benthic crustacean (e.g. ostracod, isopod, amphipod, crayfish)	
An insect (e.g. mayfly, dragonfly, damselfly, stonefly, caddisfly, mosquito, midge, etc.)	*Culex pipiens*
A family in a phylum other than Arthropoda or Chordata (e.g. Rotifera, Annelida, Mollusca, etc.)	*Hydra littoralis*
A family in any order of insect or any phylum not already represented	*Xenopus laevis*
Algae	*Selenastrum capricornutum*
Aquatic plant	*Lemna gibba*

The one gap in the data set is for a benthic crustacean. One amphipod (*Crangonyx pseudogracilis*) is present in the selected data set for acute values, and is less sensitive than the cladocerans included. There are other non-selected values in the overall acute data set which would indicate similar or lower sensitivity to cladocerans. There are also several other representatives for some of the groups indicated in the criteria above. Hence the absence of this specific group is not considered to make the data set unrepresentative.

The number of available NOEC values (28) is significantly more than the minimum requirements discussed at the workshop. The tests from which the values come cover a range of chronic endpoints, including growth, reproduction and survival, and cover sensitive life stages for longer lived-organisms (e.g. fish) and multiple life cycles for shorter-lived species (e.g. cladocerans). Multiple data values for the same species and endpoint have been combined as agreed at the workshop (see above).

A further consideration for the use of the method is whether the data fit to the expected distribution. The data set in **Table 3.57** has been tested against a log-normal distribution, as preferred at the workshop. The resulting observed and expected frequencies and cumulative frequencies are plotted in **Figures 3.6** and **3.7** respectively.

The Kolmogorov-Smirnov test does not reject the null hypothesis, that the data come from a log-normal distribution, at the 1%, 5% or 10% levels. It is clear from the plots that there is a preponderance of values towards the centre of the distribution, but with values also at some distance from it, giving relatively long tails.

Overall the data set is considered suitable for use in the extrapolation method. The lower 5% value from the species distribution (HC_5) has been calculated according to the following equation for a log-normal distribution (Wagner and Lokke, 1991) as preferred at the workshop.

$$HC_5 = 10^{(x_m - k_m s_m)}$$

where:
HC_5 = lower 5% limit of species distribution
m = the number of test species (here 26)
x_m = sample mean of log NOEC data for m species (here 2.19)
k_m = the one-sided extrapolation constant for a normal distribution (here 1.67)
s_m = the sample standard deviation of log NOEC values for m species (here 0.70)

The resulting value for the 50% confidence level in the HC_5 (HC_5-50%) is 10.2 μg/l. The value for the 95% confidence level (HC_5-95%) is 3.8 μg/l.

Having obtained these results the application of a possible assessment factor to derive the PNEC value has to be considered. The data set used in the extrapolation covers a wide range of aquatic species and a range of chronic endpoints. It includes the types of organism indicated to be the most sensitive in acute tests, and there do not appear to be any groups of sensitive organisms which are missing from the data set. The organisms cover a range of trophic levels and feeding strategies, including primary producers, herbivores, fish which consume algae and invertebrates, fish which consume other fish, and detritivores.

Figure 3.6 Chromium chronic aquatic toxicity data distribution

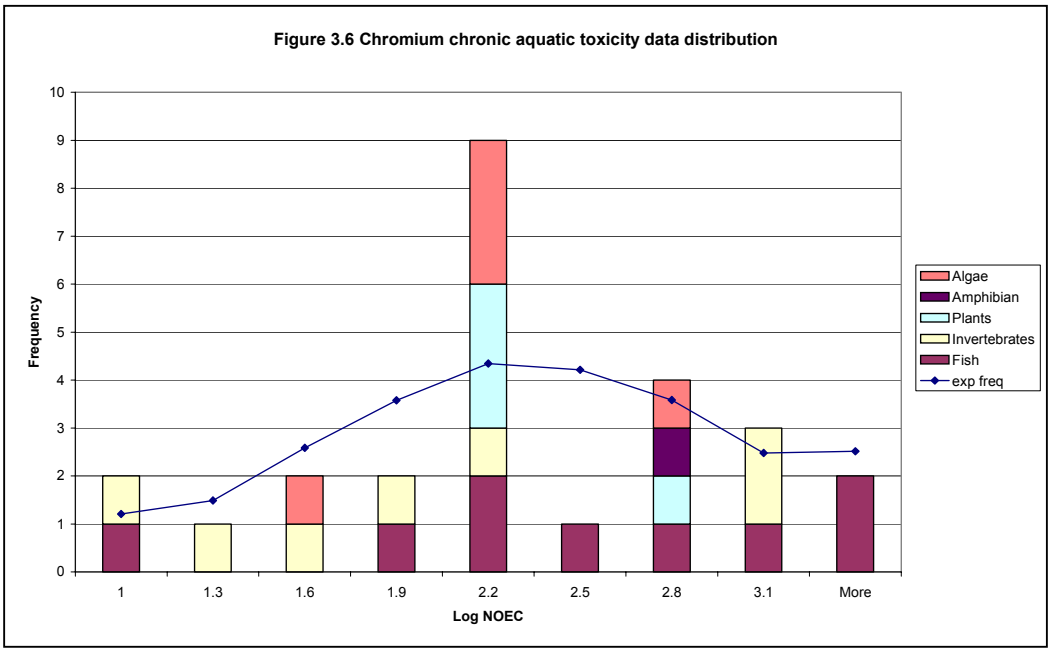
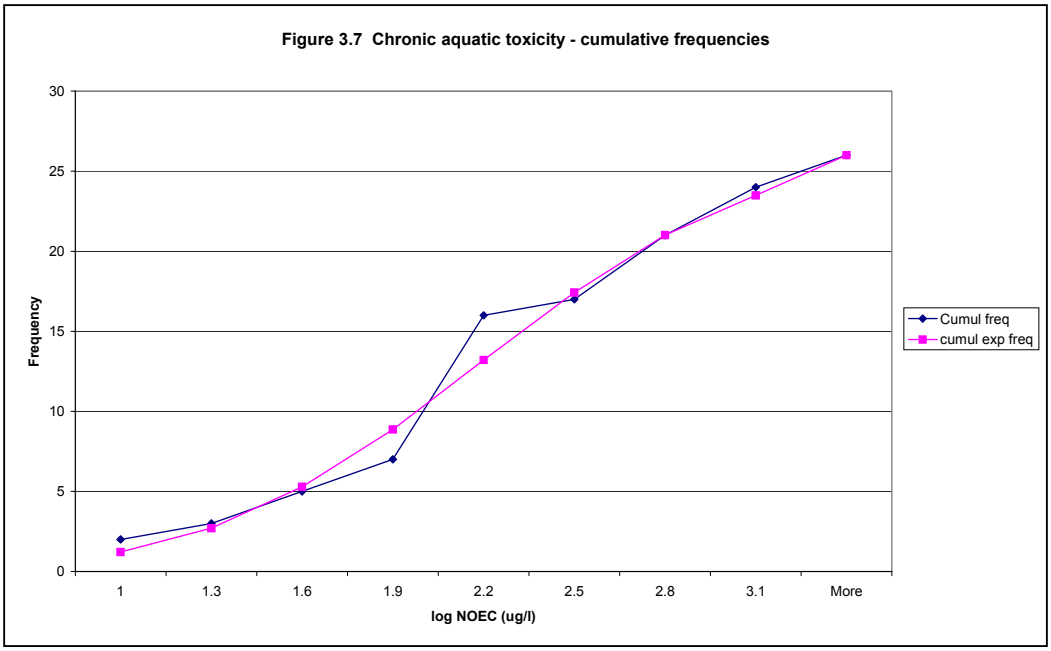


Figure 3.7 Chronic aquatic toxicity – cumulative frequencies



Against these points, there are a relatively large number of results for fish (although they cover different types) and only one each for insects or molluscs. There are also no results from mesocosm or field studies to compare to the derived values. There are two values included in the data set which lie below the HC_5-50% value, one for the cladoceran *Ceriodaphnia dubia* and the other for the fish *Salvelinus fontinalis*. In the case of *Ceriodaphnia dubia*, the NOEC for reproduction was 4.7 µg/l; from the same report the NOEC for survival was 8.4 µg/l. These values come from a ring test and are derived from 18 individual results (as noted below **Table 3.52**). In the same study the 50% effect concentration for survival and reproduction over 7 days was 14 µg/l, indicating a steep dose-response. The NOEC for Salvelinus fontinalis is 10 µg/l, which is virtually the same as the $HC_{5\text{-}50\%}$ value.

The considerations above suggest that a small assessment factor could be applied to the extrapolated value to give a more protective PNEC. The choice of assessment factor to be used with the HC_5 makes little or no difference to the overall result of the assessment, but a factor of 3 was accepted during Technical Meeting discussions as a reasonable compromise between member states that expressed a view. This gives a PNEC of 3.4 µg/l.

The HC_5s calculated here for chromium (VI) are similar to the HC_5s calculated by Emans et al. (1993) for total chromium of 4.9 µg/l and 4.6 µg/l, based on the methods of Aldenberg and Slob (1993) and Wagner and Lokke (1991), respectively. The $HC_{5\text{-}50\%}$ value calculated here is virtually the same as that reported by Okkerman et al. (1991) for potassium dichromate, according to the method of van Straalen and Denneman (1989) (they reported a value of 29 µg/l for potassium dichromate, the value for chromium would be 10 µg/l). Crommentuijn et al. (1997) calculated a value of 6.4 µg/l for freshwater organisms by the Aldenberg and Slob method, and 8.5 µg/l for a mixed freshwater and saltwater data set.

In saltwater, chromium (VI) would be expected to be less toxic than indicated by these values, except perhaps at very low salinities.

Since chromium (VI) is converted to chromium (III) under some conditions in the environment, the possible effects of chromium (III) should also be considered in the assessment. The toxicity of chromium (III) to aquatic organisms is briefly summarised in Appendix F. From the available data, it can be seen that chromium (III) appears to be less toxic than chromium (VI) in waters of medium hardness (>50 mg $CaCO_3$). In lower hardness waters the acute toxicity increases; there are also indications that NOEC values decrease with decreasing hardness. There are insufficient data to carry out an HC_5 calculation for chromium (III). From the freshwater data reported in Appendix F, long-term NOEC values are 0.05 mg/l for fish and 0.047 mg/l for invertebrates, and >2 mg/l for algae (although an EC_{50} of 0.32 mg/l is reported for another species). The fish and invertebrate values relate to hardness levels of 26 and 52 mg/l respectively. Applying an assessment factor of 10 to the lowest available NOEC gives a tentative PNEC for chromium (III) of 4.7 µg/l for soft water. This is similar to that derived for chromium (VI) above, but the two values are not directly comparable as they are based on very different data sets. However, this may indicate that in low hardness waters the two forms may not be very different in effect. The NOEC from the same invertebrate study at a hardness of 100 mg/l was 0.129 mg/l, which would give a 'PNEC' of 13 µg/l. The data indicate that chromium (III) may have reduced toxicity at greater hardness levels, but as with chromium (VI) the evidence is limited (these comments relate to chronic toxicity).

The PNEC is at the lower end of the range of published criteria/standards for the protection of aquatic life. For example, the UK Environmental Quality Standard for total chromium in freshwater ranges from 5 to 50 µg/l (dependent on water hardness) and in saltwater it is 15 µg/l.

It should also be noted that the PNEC for chromium (III) refers to the dissolved water concentration. In laboratory tests, water soluble forms of chromium (III) have generally been used. However, in the environment, chromium (VI) is likely to be reduced to forms of chromium (III) with limited water solubility, which will be associated mainly with the particulate (sediment and suspended matter) phases of the water compartment.

In summary, the PNEC values for the surface water compartment are 3.4 µg/l for chromium (VI) and 4.7 µg/l for chromium (III).

3.2.1.7.2 Sediment

There is insufficient data available to derive a PNEC from studies on sediment dwelling organisms. According to the Technical Guidance Document, an equilibrium partitioning approach can be used in the absence of experimental data. However, such an approach for chromium (VI) should be considered very tentative in nature as chromium (VI) is likely to be reduced to chromium (III) under the conditions found in most sediments, and the chromium (III) formed is likely to be of much lower water solubility (and bioavailability).

For chromium (VI), a $PNEC_{water}$ of 3.4µg/l has been derived. For chromium (III) a worst-case PNEC of 4.7µg/l was derived.

According to the Technical Guidance Document, the $PNEC_{sediment}$ can be estimated from:

$$PNEC_{\text{sediment}} = \frac{K_{\text{susp-water}}}{RHO_{\text{suso}}} \times PNEC_{\text{water}} \times 1000$$

where RHO_{susp} = density of suspended matter = 1,150 kg/m^3

From Section 3.1.1.2.2, the following values for $K_{susp\text{-}water}$ were derived:

Chromium (VI) $K_{susp\text{-}water}$ = 500 m^3/m^3 (acid conditions); $K_{susp\text{-}water}$ = 50 m^3/m^3 (neutral/alkaline conditions)

Chromium (III) $K_{susp\text{-}water}$ = 7,500 m^3/m^3 (acid conditions); $K_{susp\text{-}water}$ = 75,000 m^3/m^3 (neutral/alkaline conditions)

Using these values, the $PNEC_{sediment}$ can be estimated as follows:

For chromium (VI), $PNEC_{sediment}$ = 1.5 mg/kg wet weight for acid conditions, and 0.15 mg/kg wet weight for other conditions.

Similarly, for chromium (III), $PNEC_{sediment}$ = 31 mg/kg wet weight for acid conditions and 307 mg/kg wet weight for other conditions.

A recent report (Environment Canada, 1997) has derived draft guideline values for chromium based on the results of numerous field surveys. In the approach taken, the data on sediment characteristics and the presence or absence of benthic species was investigated to look for associations between total chromium concentrations and any adverse effect seen. Such an

approach cannot prove that a given effect was caused by a given chromium concentration, since it relies on field data where exposures are likely to be to a wide range of substances. Using this approach, a draft threshold effect level (level below which adverse effects are expected to occur rarely) of 37.3 mg/kg dry weight for freshwater sediments and 52.3 mg/kg dry weight for marine sediments was derived for total chromium. The corresponding draft probable effect level (the level above which adverse effects are expected to occur frequently) was estimated to be 90 mg/kg dry weight for freshwater sediments and 160.4 mg/kg dry weight for marine sediments (again for total chromium).

Given that the vast majority of chromium (VI) entering into sediment will be converted to chromium (III), the $PNEC_{sediment}$ of 31 mg/kg wet weight (which is equivalent to around 80 mg/kg on a dry weight basis) is in reasonable agreement with the draft effect levels derived by Environment Canada (1997).

3.2.1.7.3 Wastewater treatment plants

There are a number of studies that indicate the chromium (VI) is toxic to single species of bacteria. However, it is also clear that many bacteria are tolerant of high concentrations of chromium (VI). Both single species and mixed population tests can be used to derive a PNEC for wastewater treatment plants. The available data were summarised in **Table 3.56**. From these data those which are relevant to the assessment of the wastewater treatment plant have been selected, and are listed in **Table 3.59** with the appropriate assessment factor and resulting PNEC.

Table 3.59 PNEC values for micro-organisms

Species	Endpoint	Value (mg/l)	Assessment factor	PNEC (mg/l)
Chilomonas paramecium	NOEC	1.0	1	1
Colpidium campylum	IC_{50}	2.8	10	0.28
Microregma heterostoma	NOEC	0.21	1	0.21
Activated sludge	IC_{50}	30	100	0.3

The lowest of the PNEC values in the table is 0.21 mg/l, and this will be used in the risk characterisation.

There is evidence from studies on pilot-scale activated sludge plants that once acclimated to the presence of chromium (VI), plants can tolerate up to 10 mg Cr (VI)/l in the influent, with only minor reductions in efficiency seen at substantially higher concentrations. This observation indicates that the PNEC derived above may be overprotective of wastewater treatment plants that regularly receive, and are therefore acclimated to, chromium (VI) in the influent.

Chromium (III) appears to be much less toxic to micro-organisms than chromium (VI). A concentration of 10 mg/l promoted growth in some species of bacteria, and 100 mg/l produced only a small amount of growth inhibition. The study did not provide a formal NOEC; it is proposed to use 10 mg/l as the PNEC for chromium (III).

3.2.2 Terrestrial compartment

Coleman (1988) reported that the amount of chromium "available" to plants and other soil flora is usually low (e.g. 0.1-1% of the total). This means that in terms of determining a PNEC for the chromium (VI) species of interest, the background concentration of total chromium in soil can be ignored as this is likely to make only a minor contribution to the toxicity seen.

Once released into soil, it is likely that much of the chromium (VI) present will be reduced to chromium (III). Toxicity data are available for chromium (VI) in soil, but it is also likely that in these experiments the majority of the chromium present will be converted to chromium (III) during the test.

3.2.2.1 Toxicity data for chromium (VI)

A specific set of validity criteria was not developed for soil tests in the same way as was done for the aquatic tests. The nature of the medium and the types of tests mean that the results are more variable. The Rapporteur has tried to give a view of all of the data considered relevant for the discussion of toxicity in soil, even where the individual studies may not be used directly in determining a PNEC value. The creation of a set of criteria to include or exclude studies from the assessment would probably lead to the exclusion of tests which provide some useful indications of levels of effect. This does not mean that we use studies with only one exposure concentration as the basis for the PNEC, but such studies can provide supporting evidence. It should be noted that studies involving exposure through nutrient solution are included in this section, especially for plants, as they allow exposure to chromium (VI) to be performed. However these studies are not representative of exposure in the environment and are not used in deriving a PNEC.

3.2.2.1.1 Plants

Miller et al. (1980) studied the effects of sodium dichromate on germination and growth of green beans (*Phaseolus vulgaris*) and sweetcorn (*Zea mays*) in greenhouse studies. The soil used in the study was a silt loam (organic carbon content 8.1%, pH 6.0-6.2) and 1.8 kg of soil was placed into a pot and planted with 8 seeds. These seedlings were thinned to 6 per pot after germination and the plants grown on for 56 days. At the end of the period, the dry weight yields of crop were determined and compared with that obtained with controls. Two concentrations of $Na_2Cr_2O_7$ were used in the study, 2.05 g/1.8 kg of dry soil and 12.3 g/1.8 kg dry soil. These concentrations are equivalent to total chromium concentrations of 452 mg Cr/kg dry soil and 2,710 mg Cr/kg dry soil respectively. At the higher exposure concentration, the growth of the crops was severely reduced (10% of controls for beans and 4% of controls for sweetcorn). At the lower exposure concentration, crop growth (yield) was slightly reduced from that of controls (80% of control for beans and 85% of control for sweetcorn; reduction in growth only statistically significant ($p=0.01$) for beans), and so the exposure concentration of 452 mg Cr/kg dry soil can be considered as a LOEC for beans and a NOEC for sweetcorn. The authors postulated that at least some of the effects seen may have been due to a "salt" effect, due to the high concentrations of sodium also present, but that chromium itself was also toxic to the plants. The effects seen in the study included slowed germination, bluish curled bean leaves and red-tinted and white tipped corn leaves.

Pestemer et al. (1987) reported the results of the OECD Terrestrial Plant Growth Test for potassium dichromate and compared these to results obtained from field studies. The soil used in

the laboratory test was a sandy soil of pH 6 and organic carbon content 1.5%. In all 15 plant species were used in the test (*Sinapis alba* L., *Brassica napus* L. ssp. napus, *Brassica rapa* ssp rapa, *Brassica chinensis, Raphanus sativus* L., *Vicia sativa* L., *Phaseolus aureus Roxb. vigna radiata* L., *Trifolium pratense* L., *Trigonella meliotus-coerulea* L., *Lolium perenne* L., *Avena sativa* L., *Triticum aestivum* L., *Sorghum vulgare* Pers., *Lepidium sativum* L. *and Lactuca sativa* L.). The EC_{50} values determined for potassium dichromate were either 100 mg/kg soil (for 9 species) or 10 mg/kg soil (for 6 species). On a total chromium basis, these EC_{50} values are equivalent to 35.3 mg Cr/kg soil or 3.53 mg/kg soil. The NOEL for the laboratory studies was determined as 0.35-3.53 mg Cr/kg soil. In field studies using the same plant species, stimulation of plant growth or no effects were generally seen at concentrations of 10 and 100 mg/kg of potassium dichromate over the cropping period of the plant. The exception to this was that a slight decrease in growth (<30% effect) was seen at 3.53 mg Cr/kg soil with *Sinapis alba* L., *Brassica napus* L, and *Raphanus sativus* L, but at higher concentrations of 35.3 mg Cr/kg soil, growth stimulation was seen with these species.

Guenther and Pestemer (1990) found similar results for growth of seedlings exposed for 10-14 days to chromium (VI) (as potassium dichromate) in a sandy loam soil. The following results were reported for chromium (VI): *Avena sativa* 14d-EC_{50} = 30 mg Cr/kg dry soil for growth; *Brassica rapa* 10d-EC_{50} = 8.25 mg Cr/kg dry soil for growth (the 10d-EC_{50} for this species was 4.96 mg Cr/kg dry weight when grown in vermiculite); *Lepidum sativum* 3d-EC_{50} = 30 mg Cr/kg soil for germination.

Otabbong (1990) reported that a soil concentration of 50 mg Cr (VI)/kg dry soil (as chromium trioxide), caused a slight to moderate inhibition of growth of ryegrass (*Lolium perenne*) over 30 days.

Adema and Henzen (1989) carried out studies on seed germination and growth (OECD 208) using chromium (VI) (as potassium dichromate) in nutrient solution, a loam soil (1.4% organic matter, pH 7.5) and humic sand (3.7% organic matter, pH 5.1). The species tested included lettuce (*Lactuca sativa*), tomato (*Lycopersicum esulentum*) and oats (*Avena sativa*). The test was carried out from planting the seeds until 14-days after germination occurred. The results of the study are shown in **Table 3.60**.

Dua and Sawhney (1991) found that chromium (VI) (as potassium dichromate), when added to growth media at a concentration of 52 mg/l, caused the depression in activity of several enzymes associated with germination in seeds of pea (*Pisum sativum*).

Roy and Mukherji (1982) investigated the effects of chromium (VI) (as potassium dichromate) on the germination of mungbean *Phaseolus aureus*. A chromium (VI) concentration of 208 mg Cr/l in the growth medium was found to give a reduction in hypocotyl length, root length, wet weight and dry weight after 5 days of germination. Stimulation of enzyme activity was seen at concentrations up to 624 mg Cr/l. Chromium (III) (as chromic sulphate) was also tested under the same conditions and this was shown to be slightly less toxic than chromium (VI), although the reduction in root length seen was similar to that found with chromium (VI).

Table 3.60 Results of OECD 208 plant growth test (Adema and Henzen, 1989)

Species	Exposure medium	Effect concentration (expressed as Cr (VI))
Avena sativa	Nutrient solution	NOEC = 0.12 mg/l
		EC_{50} = 1.4 mg/l
	Loam soil	NOEC = 3.5 mg/kg dry weight
		EC_{50} = 7.4 mg/kg dry weight
	Humic sand	NOEC = 11 mg/kg dry weight
		EC_{50} = 31 mg/kg dry weight
Lactuca sativa	Nutrient solution	NOEC = 0.04 mg/l
		EC_{50} = 0.16 mg/l
	Loam soil	NOEC = 0.35 mg/kg dry weight
		EC_{50} = 1.8 mg/kg dry weight
	Humic sand	NOEC = >11 mg/kg dry weight
		EC_{50} = >11 mg/kg dry weight
Lycopersicum esculentum	Nutrient solution	NOEC = 0.11 mg/l
		EC_{50} = 0.29 mg/l
	Loam soil	NOEC = 3.2 mg/kg dry weight
		EC_{50} = 6.8 mg/kg dry weight
	Humic sand	NOEC = 10 mg/kg dry weight
		EC_{50} = 21 mg/kg dry weight

Turner and Rust (1971) studied the effects of chromium (VI) (as potassium dichromate) on growth of two soybeans (*Glycine max* L. Merr.) both in nutrient media and soil. In the nutrient media studies, 9-day old plants grown in nutrient solution (pH 6) containing chromium (VI) at concentrations of 0.05-5 mg Cr (VI)/l. After 5 days the plants were assessed for symptoms of toxicity and analysed for the presence of 10 essential elements. A slight, but not statistically significant (p=0.05) increase in the yield of tops was seen at 0.05-0.1 mg Cr (VI)/l, while concentrations of 0.5 mg Cr (VI)/l and above caused a significant reduction in yield of tops and concentrations of 1.0 mg Cr (VI)/l and above caused a significant reduction in yield of roots. A similar pattern was seen in the concentrations of Ca, K, P, Fe, Mn, and Mg found in the plants. The visual symptoms of toxicity seen in the experiment were wilting of the plants at high doses, and interveinal chlorosis in older leaves. In the soil experiments, potassium dichromate was added to 15-day old plants grown in pots of soil (loam) at doses of 5, 10, 30 and 60 mg Cr (VI)/kg soil. Three days after treatment, the yields of tops and roots were determined. Plants receiving 10 mg Cr (VI)/kg soil showed severe wilting similar to seen in the nutrient solution experiments, and plants receiving 30 and 60 mg Cr (VI)/kg soil died. All treatments significantly reduced the yield of tops.

The ability of chromium (VI) (as chromium trioxide) and chromium (III) (as chromic chloride) to induce stress in barley (*Hordeum vulgare*) and rape (*Brassica napus*) has been studied in nutrient culture. The plants (2 week old for barley; 3 week old for rape) were grown in a mineral solution (solution pH=5.0) containing chromium (concentration 10, 30, 50 or 100 mg Cr/l) for between 1 and 14 days. After the exposure period, plants were harvested and inspected for signs

of stress. Green leaf material was analysed for the presence of polyamines (produced by the plant when under stress). The growth of plants was found to be significantly reduced at chromium (VI) concentrations of 50 mg/l and above for barley and 30 mg/l and above for rape. No reduction in growth was seen at any of the lower concentrations. In contrast to this, on exposure to chromium (III), growth was significantly reduced only in barley exposed to 100 mg/l. Root length was found to be significantly reduced in all chromium (VI) treatments, whereas chromium (III) caused a significant decrease in root length in barley only at concentrations of 30 mg/l and above. Stress of the plants, as measured by polyamine production and by visual inspection, followed a similar concentration related pattern as the growth parameters. The effects seen were consistent with the toxic effect of chromium (VI) being connected with disturbance of the normal function of the root (Hauschild, 1993).

Liu et al. (1992) studied the effects of chromium (VI) (as potassium dichromate) and chromium (III) (as chromic nitrate) on root growth, cell division and chromosome morphology of *Allium cepa* grown in nutrient media for 96 hours. A chromium (VI) concentration of 208 mg Cr/l was found to cause an almost complete inhibition in root growth over the 96 hour test period. Chromium (III) was found to be of similar toxicity to root growth as chromium (VI). A small reduction in growth (the significance of which is unknown) was also seen at the lowest concentration of chromium (VI) tested (0.021 mg/l). Miotic irregularities were also seen in the test.

3.2.2.1.2 Earthworms

Soni and Abbasi (1981) studied the effects of chromium (VI) (as potassium dichromate) on the mortality of earthworms (*Pheretima posthuma*). Adult earthworms were kept in beakers containing paddy-field soil treated with chromium (VI). Three sets of experiments were carried out starting in May (Set I), June (Set II) and July (Set III), with the soil being renewed every three weeks. Although the results were found to be variable, the time required for 100% mortality was found to decrease with increasing chromium concentration. The overall estimated times for 100% mortality were 56-116 days at 10 mg Cr/kg soil, 27-109 days at 20 mg Cr/kg soil, 27 to 85 days at 40 mg Cr/kg soil, 27-78 days at 60 mg Cr/kg soil, 6-56 days at 80 mg Cr/kg soil and 5 days at 100 mg Cr/kg soil. Mortalities in the controls were 1.25-2.5% after 61 days.

A toxicity test has been carried out with chromium (VI) (as potassium dichromate) using the terrestrial annelid *Enchytraeus albidus*. An artificial soil was used in the test (10% sphagnum moss, 20% kaolin, 70% quartz; pH 6.5, moisture content 35%). The endpoints monitored included mortality and biomass production. The 28-day LC_{50} determined in the test was 146 mg Cr (VI)/kg dry soil (Roembke, 1989; Roembke and Knacker, 1989).

Roembke (1989) also reported the results of an OECD207 earthworm, acute toxicity test carried out by Cabridenc (1984) using *Eisenia fetida* and potassium dichromate. The 14-day EC_{50} was determined as 792 mg Cr (VI)/kg dry soil.

3.2.2.1.3 Soil processes

Ross et al. (1981) investigated the effects of both chromium (VI) (as potassium dichromate) and chromium (III) (as chromic chloride) on the microbial activity of soil. Two soils were used, a loam (pH 6.4) and a fine sandy loam (pH 5.9). In the experiments, 1 kg dry weight of soil and either chromium (VI) (concentration 10 or 100 mg Cr (VI)/kg dry soil) or chromium (III)

(concentration 100 mg Cr (III)/kg dry soil) was added. The soils were wetted to give water contents of 25% (loam) or 20% (sandy loam), and then the soils were incubated for 22 days in the dark at 25°C. At intervals, the amount of CO_2 evolved from the soils was determined, along with the amount of chromium (VI) present in the soil. Microbial activity in the control experiments was found to be higher than all chromium-treated soil. The differences between the three chromium treatments in the amount of CO_2 evolved/day were small. Chromium (VI) was found to be rapidly reduced to chromium (III) in the experiments (about 75% of the chromium (VI) added in the 100 mg/kg treatment was not extractable after 3 days incubation). A small amount of chromium (VI) was also found in the chromium (III) experiments after 3 days in the loam soil, but this had disappeared by 13 days.

Ueda et al. (1987) investigated the effects of chromium (VI) (as sodium chromate) and organic amendments on the composition and activity (as measured by CO_2 evolution) of microbial flora in soil. In the study, chromium (VI) was added at concentrations of 10, 20, 50 and 100 mg Cr (VI)/kg dry soil to alluvial soil (total carbon content 1.1%), along with an organic amendment (dried rice straw and/or fresh cow manure), and incubated at 28°C in the dark for 20 days. Separate experiments were also carried out to look at the reduction of chromium (VI) to chromium (III) in the test system. The chromium (VI) added to the soil was found to be rapidly reduced to chromium (III), and the reduction was fastest in the soil amended with rice straw and cow manure. Only traces of extractable chromium (VI) were found in the soil after 14 days. The chromium (VI), at an initial concentration of 10 mg Cr (VI)/kg dry soil did not suppress the evolution of CO_2 from the soil system, whereas a slight suppression in CO_2 evolution was seen at a concentration of 20 mg Cr (VI)/kg dry soil, with a marked decrease occurring at 50 and 100 mg Cr (VI)/kg dry soil. When the composition of micro-organisms present in the soil was investigated, it was found that although the total number of micro-organisms present were approximately the same in soil exposed to 100 mg Cr (VI)/kg dry soil as compared with the control soil, the population of fungi had increased and the population of actinomycetes had decreased in the exposed soil compared with the control soil.

The effects of chromium (VI) (as sodium chromate) and chromium (III) (as chromium chloride) on soil nitrification and ammonification have been studied by Ueda et al. (1988). The soil used in the study was a loam with a total carbon content of 1.1% and a pH of 6.2-6.5. Ammonium sulphate was added to the soil at 250 mg/kg to act as the nitrogen source in the nitrification experiments and urea was added to the soil at 250 mg/kg in the ammonification experiments. The chromium compounds were added to the soil at concentrations of 10, 100 and 1,000 mg/kg dry weight (equivalent to 3.2, 32.1 and 321 mg Cr (VI)/kg soil) and the soil was incubated in the dark at 28-30°C for 4 weeks. Chromium (VI) was found to inhibit nitrification at all three concentrations. At the lowest concentration, a slight reduction in nitrification was seen over the first 2 weeks exposure, but after this period the soil recovered to control levels. Almost complete inhibition of nitrification occurred at the two highest exposure concentrations, and this persisted throughout the 4 week experiment at the highest dose. Chromium (III) was found to be much less toxic with partial inhibition of nitrification occurring only at the highest exposure concentration (~330 mg Cr (III)/kg soil). Chromium (VI) was much less toxic to ammonification, with only partial inhibition of ammonification occurring over the first 3 days at the highest concentration tests (321 mg Cr (VI)/kg soil). Overall, the LOEC from this study is around 3.2 mg Cr (VI)/kg soil. A similar transient inhibition of soil nitrification was reported by James and Bartlett (1984) using potassium dichromate at a concentration of 100 µM (~10.4 mg/l) in soil suspensions.

The rapid transformation of chromium (VI) to chromium (III) noted in some of the above studies indicates that data on chromium (III) toxicity to soil processes is probably more relevant to the assessment (see Section 3.1.3.2).

3.2.2.1.4 Other studies

Al-Hakkak and Hussain (1990) studied the effects of chromium (VI) (as potassium dichromate) on development and fertility of eggs of the fig moth (*Ephestia cautella*). In the experiment 250 eggs of 0-48 hour old embryos were placed in jars containing 100 g of a mixture of food spiked with chromium (VI) at concentrations of 50, 100, 150 and 200 mg/kg food (it is not clear if the concentrations refer to those of total chromium (VI) or of $K_2Cr_2O_7$). After 1 week exposure, the percentage of eggs hatched was determined and after a further 2 weeks exposure, a layer of cotton wool was added to the jars for pupation. After a further 1 week (i.e. 4 weeks in total) the number of pupae present was counted. Significant effects on the number of pupae, number of adults and the number malformed were found at an exposure concentration of 100 mg/kg food, and a significant effect on the number of eggs hatched was seen at 100 mg/kg food. Thus the NOEL for this study is 50 mg/kg food. No effects were seen with chromium (III) (as chromic sulphate) at the same exposure concentrations.

The teliospore germination of *Neovossia horrida* and *N. indica* was enhanced at concentrations of potassium dichromate of 100, 200 and 500 mg Cr/l after 7 days germination. These fungi cause Karnal bunt, a disease of rice and wheat (Krishna and Singh 1982; Kumar and Singh 1987).

3.2.2.1.5 Toxicity data for chromium (III)

In addition to some of the studies above, where comparative toxicity of chromium (VI) and chromium (III) was determined, some studies have investigated the toxicity of chromium (III) alone. These studies are reported here.

Van Gestel et al. (1993) carried out an OECD 21-day earthworm reproduction test using *Eisenia andrei* in artificial soil at 20^{o}C. The source of chromium used in the experiment was chromium (III) nitrate. Reproduction was found to be significantly reduced at chromium concentrations of 100 mg Cr/kg dry soil and above, while growth was significantly reduced only at a concentration of 1,000 mg Cr/kg dry soil. The NOEC from the study was 32 mg/kg dry soil. At the end of the three week exposure period, the earthworms were placed in clean soil for a further 21 days. At the end of this period, the reproduction of the earthworms had virtually recovered to that of the control organisms.

Moulinier and Mazoyer (1968) reported the results of plant toxicity tests using two forms of chromium (III), chromic oxide and chromic sulphate. Two soils were used in the test, the first had a pH of 5.5 and the other had a pH of 8.3. Wheat (variety *Florence-Aurore*) and tomatoes (variety *John Moran*) were grown in the soil spiked with various concentrations of chromium (III) (10-500 mg Cr/kg soil for wheat; 20-1,000 mg Cr/kg soil for tomatoes). Chromium (III), in the form of chromic sulphate, was shown to reduce the yields of wheat at concentrations of 200 mg Cr/kg and greater in the acid soil, and around 100 mg Cr/kg soil and greater in the alkaline soil. No effects were seen with chromium (III) in the form of the insoluble oxide. The paper concluded that chromium (III) in the form of chromic sulphate may adversely affect the yields of wheat and tomatoes. The reduction in yield was concurrent with a lower phosphate

concentration in the plants. The toxic effects seen were found to be suppressed by the addition of either calcium carbonate or monobasic calcium phosphate to the soil.

Crommentuijn et al. (1997) reviewed the toxicity of chromium (III) to soil processes. The results of 51 determinations were reported, covering arylsulphatase, nitrification, N-mineralisation, phosphatase, respiration and urease. The test results ranged from 1.0 mg/kg dw to 3,332 mg/kg dw (both values being for arylsulphatase). All studies used soluble chromium (III) compounds, largely chromic (III) chloride. For this risk assessment, data were selected from this survey, taking values where a NOEC was obtained directly or where the LOEC related to an effect level of 20% or less (and using LOEC/2 as the NOEC). A total of 37 values were obtained, and a further selection was made giving preference to longer exposure times in the same studies, resulting in a final data set of 30 values. The statistical extrapolation method has been used to derive an HC_5-50% value of 5.9 mg/kg. The selected data and distribution plots are included in Appendix G.

3.2.2.2 Estimated PNEC for the terrestrial compartment

A substantial amount of information is available for the toxicity of chromium (VI) to terrestrial organisms. In the environment, it is likely that chromium (VI) will be reduced to chromium (III) in soil, and it is also likely that such conversion would have taken place in many of the toxicity tests.

For chromium (VI), long-term toxicity data are available for three trophic levels (plants, earthworms and soil processes/micro-organisms), with plants generally being the most sensitive species (although a clear NOEC has not been determined for earthworms, the EC_{50} values are generally higher than those found in the plant experiments). The lowest NOEC from these studies is around 0.35 mg/kg dry weight of soil for plants. According to the Technical Guidance Document, an assessment factor of 10 is appropriate and so the $PNEC_{soil}$ can be estimated as 0.035 mg/kg dry weight. Using the water content of soil from the Technical Guidance Document of 11.8% by weight (20% by volume), this is equivalent to a $PNEC_{soil}$ of around 0.031 mg/kg on a wet weight of soil basis.

Chromium (III) has generally been shown to be less toxic than chromium (VI) to soil organisms. One exception to this may be on the effects seen in some experiments using growth media (no soil) where reduction in root growth was seen at similar concentration as found for chromium (VI). Since chromium (III) adsorbs more strongly onto soil than chromium (VI) (see Section 3.1.1.2.2), it would again be expected that in soils, chromium (III) would be less toxic than chromium (VI). From the available data, the NOEC for chromium (III) to plants is of the order of 100 mg Cr/kg soil, with a NOEC of 32 mg Cr/kg dry soil being reported for earthworms, and a NOEC/LOEC of ~100-330 mg Cr/kg soil also being reported. Applying an assessment factor of 10 to the lowest of these NOECs gives a PNEC for chromium (III) of approximated 3.2 mg Cr/kg dry soil, which is equivalent to a PNEC of around 2.8 mg/kg on a wet weight of soil basis. This value is also lower than the HC_5 value for soil processes which was calculated in Section 3.2.2.1.5.

According to the Technical Guidance Document, an equilibrium partitioning approach can also be used in the derivation of the $PNEC_{soil}$. However, such an approach for chromium (VI) should be considered very tentative in nature as chromium (VI) is likely to be reduced to chromium (III) under the conditions found in most soils, and the chromium (III) formed is likely to be of much lower water solubility (and bioavailability).

For chromium (VI), a $PNEC_{water}$ of 3.4 µg/l has been derived. For chromium (III) a worst-case PNEC of 4.7 µg/l was derived.

According to the Technical Guidance Document, the $PNEC_{soil}$ can be estimated from:

$$PNEC_{soil} = \frac{K_{soil\text{-}water}}{RHO_{soil}} \times PNEC_{water} \times 1000$$

where RHO_{soil} = density of soil = 1,700 kg/m^3

From Section 3.1.1.2.2, the following values for $K_{soil\text{-}water}$ were derived:

Chromium (VI) $K_{soil\text{-}water}$ = 75 m^3/m^3 (acid conditions); $K_{soil\text{-}water}$ = 3.2 m^3/m^3 (neutral/alkaline conditions)

Chromium (III) $K_{soil\text{-}water}$ = 1,200 m^3/m^3 (acid conditions); $K_{soil\text{-}water}$ = 22,500 m^3/m^3 (neutral/alkaline conditions)

Using these values, the $PNEC_{soil}$ can be estimated as follows:

For chromium (VI), $PNEC_{soil}$ = 0.15 mg/kg wet weight for acid conditions, and 0.006 mg/kg wet weight for other conditions.

Similarly, for chromium (III), $PNEC_{soil}$ = 3.3 mg/kg wet weight for acid conditions and 62 mg/kg wet weight for other conditions.

The $PNEC_{soil}$ estimated for chromium (III) for acidic conditions using the equilibrium partitioning method is in very good agreement with the values obtained above using the available toxicity data. For the risk assessment the PNECs obtained from experimental data will be used. Thus the $PNEC_{soil}$ for chromium (VI) is taken as 0.031 mg/kg wet weight. The $PNEC_{soil}$ for chromium (III) is taken to be 2.8 mg/kg wet weight.

For the risk characterisation the $PNEC_{soil}$ for chromium (III) is used, as the concentrations of chromium in soil are calculated as chromium (III).

It should be noted that the PNEC for chromium (III) is derived from experiments where a highly soluble (and hence bio available) form of chromium (III) has been tested. In the environment, chromium (VI) is likely to be reduced to forms of chromium (III) of limited solubility and bioavailability, where it is unlikely that the concentration of "dissolved" and hence available chromium (III) will reach the levels where effects might be expected. This is seen in experiments with both soil and aquatic organisms when a form of chromium (III) with low water solubility has been tested.

Similarly, it is clear from Section 3.1.1.4, that there are many natural soils where the levels of total chromium are above the PNECs derived here. Again, the main form of the chromium needs to be considered. In natural soils, the majority of chromium will be present as low solubility chromium (III) complexes, where bioavailability is again limited. The PNECs derived are not appropriate for such situations.

3.2.3 Atmosphere

Chromium (VI) in the atmosphere is unlikely to contribute to abiotic effects such as global warming, ozone depletion in the stratosphere, ozone formation in the troposphere or acidification. Levels of chromium (VI) in particulates and aerosols in the atmosphere are unlikely to be of concern due to the very low atmospheric emissions arising from human activity.

3.2.4 Secondary poisoning

Chromium (VI) has been shown to be taken up by a wide range of organisms from water, sediment and soil. For fish, although uptake does occur, the bioconcentration factors for chromium (VI) are usually very low (~1 l/kg).

The toxicity of chromium (VI) to birds has been studied by several authors.

Biswas (1985) reported an 18 day-LD_{50} value for chromium (VI) (as potassium dichromate) of 300 ppm for chick embryos. In the experiment, embryonated eggs were inoculated with solutions of potassium dichromate and it is not clear from the paper if the LD_{50} refers to the concentration of chromium in the solution given to the eggs or to the dose of chromium given to the eggs.

Huu Chanh and Chanvatte (1967) investigated the toxicity of chromium (VI) (as sodium chromate) to pigeon (*Columba domestica*) and chicken (*Gallus gallus*), by intravenous injection of solutions of the chemical. The 60-minute lethal dose was found to be 101.9-111.3 mg/kg body weight for pigeon and 105.4-107.6 mg/kg body weight for chicken.

The toxicity of chromium (VI) (as sodium chromate) has been studied in a 1-year feeding study using chickens (*Gallus gallus*). In the study, the chickens were fed parboiled rice containing 0.7 mg Cr/kg rice. The estimated average daily intake of chromium (VI) from the treated rice was 40.9 µg/bird. The control chickens were fed non-spiked rice, and the background daily exposure to total chromium from this rice was around 3.5 µg/bird. No effects were seen over this time period on body weight, organ weights or haematological parameters, and no gross or histological changes attributable to the exposure were found in liver, spleen, kidneys, heart, lungs and gonads. Similar results were found in experiments with mice (Rao et al., 1983).

The available mammalian toxicity data are reviewed in Section 4. The most relevant results from these data are a no observed adverse effect level (NOAEL) of 20 mg Cr (VI)/kg body weight/day for effects on the testes in mouse (oral gavage route) and a LOAEL of 20 mg Cr (VI)/kg body weight/day for developmental effects in mice (drinking water route). For the purpose of this assessment the 20 mg/kg bw value is used, recognising that in one of the studies effects were seen at this level. Converting the NOAEL to a concentration in food (conversion factor from the TGD is 8.3) gives a NOEC in food of 166 mg/kg. As this is a chronic test an assessment factor of 10 is appropriate. Hence the PNEC for secondary poisoning is 17 mg Cr (VI)/kg food.

In the absence of a review of mammalian data, a PNEC for secondary poisoning for chromium (III) has not been derived

3.3 RISK CHARACTERISATION

Chromium is a naturally occurring element, and as such there are natural background levels in the environment. The measured data show that these levels can vary widely. As a result it is not possible to determine a representative background concentration to which the releases from industrial activity would add. Therefore the assessment is carried out on the additional concentration resulting from industrial activity involving the five chromium (VI) substances only. This needs to be kept in mind when considering risk management measures, as other sources may need to be considered in particular circumstances.

3.3.1 Aquatic compartment (incl. sediment)

In the preceding sections estimates have been made of the concentrations in the freshwater aquatic environment resulting from the production and use of chromium (VI) compounds, and of the predicted no-effect concentrations for both chromium (VI) and chromium (III). In this section these results are compared by calculating the Clocal/PNEC ratios for each area of release.

3.3.1.1 Water

3.3.1.1.1 Risk characterisation using PNECs derived from statistical extrapolation

The PNEC value for chromium (VI) in water has been estimated as 3.4 μg/l. For chromium (III), one PNEC (4.7 μg/l) was derived, but two concentrations (for acid and alkaline conditions) were estimated for each use area. Hence there are two sets of ratios for chromium (III). The resulting Clocal/PNEC ratios are in **Table 3.61**.

Table 3.61 Clocal/PNEC ratios for water

Process	Chromium (VI)	Chromium (III)	
		Acid	Alkaline
Production[a]	0.62	3.8	2.0
Pigment production	82	16	4.3
Chromium oxide production	88	18	4.7
Tanning salts	103	21	5.3
Wood preservative formulation	50	10	2.8
Wood preservative application	1.3	0.26	0.07
Metal treatment formulation	27	5.5	1.4
Electroplating	32	6.4	1.7
Passivating	26	5.1	1.4
Anodising	5.3	1.1	0.28
Brightening	32	6.4	1.7
Mordant dyeing	0.09	0.02	0.01

Note: a - chromium (VI) values for site 1; chromium (III) values for site 3 assuming all release as chromium (III)

A concentration of 108 µg/l in pond water was calculated for leaching from preservative treated wood. Taking this to be in the form of chromium (III) gives a Clocal/PNEC ratio of 23. A different calculation of leaching from treated wood at the edge of a ditch gave peak and 28-day concentrations higher than the PNEC values for chromium (VI) and chromium (III) for a 1 km length of fence. The maximum concentration for a 100 m fence was also above the two PNECs, but values after 28 days were below both values. Concentrations calculated for one year after application exceeded the PNECs in some cases.

All the ratios based on chromium (VI) are greater than 1 with the exception of production and mordant dyeing. In most cases the ratios are significantly above 1. The ratios based on chromium (III) are almost all greater than 1, but are not as large as those for chromium (VI) (production is an exception to this as the calculation is based on a different release). These calculations assume that all the chromium is reduced to chromium (III) before release to wastewater, but do not include any removal before this, for example through precipitation. The ratios based on chromium (III) are higher for the acidic environment than for the alkaline environment, reflecting the greater degree of removal by sorption in the latter. This may indicate that there may be more concern for the acidic type of environment. Concentrations calculated for specific sites involved in some of the processes (see **Table 3.23**) give ratios less than 1 for pigment production and chromium metal production, and above one for a tannery using dichromate on site, and chromium dioxide production (although this latter is a limit value of <5 µg/l).

The PNEC values for chromium (VI) are derived from a large database of long term studies, and so the PNECs are unlikely to be revised to a great degree through new data on toxicity. Any revision of the Clocal/PNEC ratios would therefore need to be through changes to the predicted concentrations. Information from specific sites indicates that methods to remove chromium before discharge are generally employed, but does not allow general conclusions to be drawn on the efficiency of such processes or the actual extent to which they are in use. The overall conclusion for the risk assessment is therefore that risk management measures are needed. From the information provided, such measures may already be in use in many locations.

The overall conclusion is based on the worst-case of the three Clocal/PNEC ratios calculated for each use area. The conclusions for the surface water compartment are therefore:

Conclusion (ii) There is at present no need for further information and or testing, and no need for risk reduction measures beyond those already in place.

This conclusion applies to production (two sites only) and to use in mordant dyeing.

Conclusion (iii) There is a need for limiting the risks: risk reduction measures which are already being applied shall be taken into account.

This conclusion applies to the other production site and to all other uses covered in the assessment.

3.3.1.1.2 Risk characterisation using PNEC derived from assessment factors

This applies only to the concentrations of chromium (VI), as the assessment above for chromium (III) already uses a PNEC derived using assessment factors. The PNEC for chromium (VI) using assessment factors is 0.47 µg/l. From **Table 3.26**, only the concentration from use in mordant dyeing is below this value. Thus all of the site-specific concentrations included are above the PNEC. It is unlikely that further information would remove the concern for all of these sites, and

so the conclusions would be the same as those above. This section is for information only, since the PNEC derived by statistical extrapolation is the preferred approach.

3.3.1.2 Sediment

For sediment, both the Clocal values and the PNECs have been derived through use of the equilibrium partitioning method. Based on this the ratios for sediment will be the same as those for water, and so are not repeated here. However, the high degree of sorption to the solid phase expected in sediment means that possible uptake from the solid phase also needs to be considered (the equilibrium partition approach only considers uptake from the water phase). The TGD indicates that an extra factor of 10 should be applied to the PEC/PNEC ratio when the log K_{ow} value is above 5 or where the substance shows corresponding sorption or binding behaviour. Using the default TGD parameter values, a log K_{ow} value of 5 corresponds to a Kp_{susp} of 1,400. The Kp_{susp} values for chromium (VI) and chromium (III) (see Section 3.1.1.2.2) are above this value, with the exception of the chromium (VI) value in alkaline conditions. Hence an extra factor of 10 should be applied to the ratios in **Table 3.59** to determine the ratios for sediment. The result is that all scenarios have a ratio above one with the exception of mordant dyeing.

As the effect concentration is not derived from results with sediment organisms, it would be possible to refine the PNEC through sediment tests. Therefore the conclusion for sediment is:

Conclusion (i) There is a need for further information or testing.

There may be value in trying to establish whether sediment organisms have a similar sensitivity to chromium as do aquatic organisms. The conclusion can be applied to all of the use areas, as sediment organism-based PNEC could change the ratios based on the equilibrium partitioning approach. However, no further testing is proposed at present, since any measures to reduce the water concentrations will also have an impact on the sediment levels. The issue could perhaps be revisited once the risk reduction measures have been proposed.

3.3.1.3 Wastewater treatment

Two effluent concentrations were calculated for each use area, for chromium (VI) and chromium (III). A PNEC for chromium (VI) for micro-organisms has been derived, as 0.21 mg/l, and a value of 10 mg/l for chromium (III). The resulting Clocal/PNEC ratios are in **Table 3.62** (on-site treatment plants (if any) at the three production sites have not been assessed).

Table 3.62 Clocal/PNEC ratios for WWTPs

Process	Chromium (VI)	Chromium (III)
Pigment production	13	0.1
Chromium oxide production	14	0.1
Tanning salts	17	0.1
Wood preservative formulation	8.1	0.07
Wood preservative application	0.2	0.002
Metal treatment formulation	4.4	0.04
Electroplating	5.2	0.04
Passivating	4.2	0.04
Anodising	0.86	0.007
Brightening	5.2	0.04
Mordant dyeing	0.02	0.0001

The ratios based on no reduction of chromium (VI) are mostly greater than 1 (exceptions are wood preservative application, anodising and mordant dyeing), whereas those based on chromium (III) are all less than 1. The widespread use of the hexavalent chromium compounds means that many wastewater treatment plants will receive effluent containing chromium from these processes. As the performance of wastewater treatment plants is monitored regularly this implies that they are not receiving such high concentrations of chromium (VI) as have been calculated in this assessment. This may again be due to clean up of the wastewater on the processing site before release to sewer, or to possible acclimation to higher chromium (VI) levels.

The conclusion for wastewater treatment is

Conclusion (ii) There is at present no need for further information and or testing, and no need for risk reduction measures beyond those already in place.

This conclusion applies to the use in wood preservative application, anodising and use in mordant dyeing.

Conclusion (iii) There is a need for limiting the risks: risk reduction measures which are already being applied shall be taken into account.

This applies to the other uses of chromium (VI) substances covered by this assessment. As with water, measures to reduce the concentrations are likely to be already in use at many locations.

3.3.2 Air

There are no data on the toxicity of chromium to organisms in the environment through air exposure. As chromium is considered to be associated with particulates in the air, it would be expected that any emissions to air would settle out to soil. Calculated levels in air are very low. No abiotic effects are expected from chromium (VI) in the atmosphere. The conclusion for air is therefore

Conclusion (ii) There is at present no need for further information and or testing, and no need for risk reduction measures beyond those already in place.

3.3.3 Terrestrial environment

The calculations for the levels of chromium in soil have considered all the chromium to be in the form of chromium (III). Concentrations have been calculated in arable and grassland soils. One PNEC for soil was derived from experimental results for chromium (III), and this has been used to compare to the Clocal values. The ratios are presented in **Table 3.63**.

Table 3.63 Clocal/PNEC ratios for soil

Process	Arable soil	Grassland
Production[a]		0.7
Pigment production	65	26
Chromium oxide production	71	29
Tanning salts	83	33
Wood preservative formulation	41	16
Wood preservative application[b]	1.1/1,143	0.4
Metal treatment formulation	22	8.9
Electroplating	25	10
Passivating	21	8.2
Anodising	4.3	1.7
Brightening	26	10
Mordant dyeing	0.08	0.03

Note: a - based on measured concentration
b - second ratio is for direct release to soil, not related to soil type
Production and regional concentrations not dependent on soil type (arable or grassland)

Measured levels in soils close to treated wood in use were presented in Section 3.1.4.2. These give PEC/PNEC ratios of 1.5-19.

The ratios are all greater than 1, with the exception of use in mordant dyeing. The removal rate for chromium from soil is virtually zero (and has been treated as zero in the calculations). This means that continuing input to soil would eventually bring all ratios to greater than 1. In Section 3.2.2 it was noted that the available fraction of chromium in soil (available to plants and fauna) was generally low, at 0.1-1%. This could indicate that as the soils age the chromium is converted into insoluble forms which then are not available to have an effect on organisms. If a factor of 1% were applied to the ratios above then all but the direct release to soil from wood preservative treatment on acid soil would give a ratio less than 1. Thus the ratios above may over-estimate the effects of the chromium.

For comparison, an ecological assessment based on surveys of species at locations close to a major production site found little evidence for any effects of chromium even though measured levels of total chromium in the soil were up to 1,000 mg/kg (all as chromium (III), as chromium (VI) was not detectable). Some of the species present were noted as being sensitive to environmental stress; the overall assemblage of plant and animal species was not considered to

be atypical of the surrounding region. This also indicates that the above ratios probably over-estimate the potential for effects from chromium in soil.

The major route to soil included in the calculations is through sludge application. The specific information provided by users indicates that sludges are generally disposed of to landfill. Any clean up measures used before release to sewer would also reduce the amount of chromium available to absorb to sludge and so be applied to land. As with the aquatic compartment, some information on these aspects is available for individual sites, but no overview of the situation across the EU. The conclusion is that risk reduction measures are needed to reduce inputs of chromium to soil. Measures to achieve this may already be in place in many areas.

The overall conclusion is based on the worst-case of the three Clocal/PNEC ratios calculated for each use area. The conclusions for the terrestrial compartment are therefore:

Conclusion (ii) There is at present no need for further information and or testing, and no need for risk reduction measures beyond those already in place.

This conclusion applies to production and to the use in mordant dyeing.

Conclusion (iii) There is a need for limiting the risks: risk reduction measures which are already being applied shall be taken into account.

This conclusion applies to all other uses covered in the assessment.

It should be noted that the PNEC for chromium (III) is derived from experiments where a highly soluble (and hence bioavailable) form of chromium (III) has been tested. In the environment, chromium (VI) is likely to be reduced to forms of chromium (III) of limited solubility and bioavailability, where it is unlikely that the concentration of "dissolved" and hence available chromium (III) will reach the levels where effects might be expected. This is seen in experiments with both soil and aquatic organisms when a form of chromium (III) with low water solubility has been tested.

Similarly, it is clear from Section 3.1.1.4, that there are many natural soils where the levels of total chromium are above the PNECs derived here. Again, the main form of the chromium needs to be considered. In natural soils, the majority of chromium will be present as low solubility chromium (III) complexes, where bioavailability is again limited. The PNECs derived are not appropriate for such situations.

3.3.4 Non-compartment specific exposure

Concentrations in fish and worms were calculated in Section 3.1.5.1 (**Table 3.45**). A PNEC of 17 mg Cr (VI)/kg food was calculated in Section 3.2.4. The toxicity studies from which the PNEC is derived involved application through gavage or drinking water, so there would be little conversion of chromium (VI) to chromium (III). Scenarios where the concentration of chromium has been calculated as chromium (III) are not realistic for comparison with this PNEC. Therefore ratios have only been calculated for scenarios where chromium (VI) in organisms has been estimated. These are for fish and mussels for aquatic food chains. The earthworm food chain is not considered as the chromium levels in soil have been calculated as chromium (III). The resulting Clocal/PNEC ratios are presented in **Table 3.64**. Note that in contrast to usual TGD practice, the local concentrations (rather than the local-regional average) have been compared directly with the effect level.

Table 3.64 Clocal/PNEC ratios for non-compartment specific exposure

Process	Fish-based food chain	Mussel-based food chain
Production	<0.001	0.22
Pigment production	0.016	29
Chromium oxide production	0.018	32
Chrome tanning salts	0.02	38
Wood preservative formulation	0.01	18
Wood preservative application	<0.001	0.48
Metal treatment formulation	0.005	10
Electroplating	0.006	12
Passivating	0.005	9.4
Anodising	0.001	1.9
Brightening	0.006	12
Mordant dyeing	<0.001	0.038

The results are all less than 1 for the fish-based chain, and mostly greater than 1 for the mussel-based chain. The TGD standard assessment would use the fish results, which indicate that there is no concern for secondary poisoning. The mussel values have been included for information, but appear to show that there may be accumulation of chromium in certain organisms to levels which may cause concern. The BCF value used for mussels comes from a salt water organism, while the water concentrations are for freshwater. At this stage the evidence is not considered sufficient to reach a conclusion of concern.

The conclusion for non-compartment specific exposure is therefore:

Conclusion (i) There is a need for further information or testing.

Further work could be done to test whether the mussel-based food chain is of concern, for example through further investigation of the uptake of chromium into organisms other than fish, characterisation of the nature of the chromium in organisms and consideration of the toxicity of chromium in other forms to organisms consuming prey containing chromium. However it should be noted that reductions in the emissions of chromium (VI) to water will reduce the estimated levels in biota as well.

At present it is not proposed to carry out any further work, but to await the development of risk reduction measures.

4 HUMAN HEALTH

4.1 HUMAN HEALTH (TOXICITY)

4.1.1 Exposure assessment

4.1.1.1 General aspects

Definitions and limitations

In this document, unless otherwise stated, the term exposure is used to denote personal exposure as measured or otherwise assessed without taking into account the effect of any personal protective equipment (PPE) which might be in use. This definition permits the effects of controls other than PPE to be assessed and avoids the problem of trying to quantify the actual protection provided by PPE in use.

This general discussion summarises the important issues arising from the exposure assessments and brings together measured exposure data and predictions from the EASE (Estimation and Assessment of Substance Exposure) model. EASE is a general purpose predictive model for workplace exposure assessments. It is an electronic, knowledge based, expert system which is used where measured exposure data are limited or not available. The model is in widespread use across the European Union (EU) for the occupational exposure assessment of new and existing substances.

All models are based upon assumptions. Their outputs are, at best, approximate and may be wrong. EASE is only intended to give generalised exposure data and works best in an exposure assessment when the relevance of the modelled data can be compared with and evaluated against measured data.

EASE is essentially a series of decision trees. For any substance, the system asks a number of questions about the physical properties of the substance and the circumstances of its use. For most questions, the EASE user is given a multiple-choice list from which to select the most appropriate response. Once all the questions have been answered, the exposure prediction is determined absolutely by the choices made. EASE can be used to estimate inhalation and dermal exposure - dermal exposure is assessed as the potential exposure rate to the hands and forearms (a total skin area of approximately 2,000 cm^2). The dermal model is less developed than the inhalation model, and its outputs should be regarded as no more than first approximation estimates.

The output ranges generated by EASE for inhalation exposure relate to steady-state conditions, and estimate the average concentration of the substance in the atmosphere over the period of exposure. The model will not directly predict short term exposures, but predictions of values for these circumstances are possible by interpreting and modifying the output data using professional judgment. Although short term exposures may be predicted by EASE in this way, such modifications to the model output should be regarded with caution.

Some information has been made available through the manufacturers and users of the five chromates, but detailed information regarding sampling techniques, frequency and duration of exposure were not always provided.

Where real exposure data is not available or scant, EASE has been used to predict exposures. Details of the reasoning behind any assumptions made during the course of EASE predictions are made clear in the relevant sections.

Overview of exposure

The total number of people occupationally exposed to the five chromates is not known, but due to their widespread use it is expected to be thousands. Most of the data used in this assessment have been either supplied by industry or taken from HSE's National Exposure Database (NEDB). No data were available from any of the other Competent Authorities, except that data supplied by Institut National de Recherché et de Securite (INRS), taken from Cross et al. (1997) have been included where appropriate.

Occupational exposure to the five chromates is discussed in 9 sections:

- manufacture of the five chromate compounds;
- manufacture of other chromium-containing compounds;
- copper chrome arsenate (CCA) use;
- metal treatment;
- manufacture of magnetic tapes;
- manufacture of montan wax;
- manufacture of vitamin K;
- during use as a mordant in wool dyeing and
- catalyst manufacture.

There are reports in the literature of other uses for these five chromium (VI) compounds, for example as an oxidant in the dyeing of cotton, in photography, in drilling muds, as a corrosion inhibitor in cooling water, and in the manufacture of activated carbon. These uses have either been discontinued or are being phased out due to the availability of substitutes and a recognition of the adverse health effects of these chromium (VI) compounds.

Occupational exposure limits

There are a number of countries with exposure limits for chromates and these have been tabulated below.

These limits are provided for information and not as an indication of the level of control of exposure achieved in practice in workplaces in these countries.

Table 4.1 Occupational Exposure Limits for the five chromates

Country	Compound	Limit (mg/m^3 as Cr)	Type of Limit	Source
UK	Cr(VI) compounds	0.05	8-hour TWA (MEL)	EH40/99[1]
Germany	production of soluble Cr(VI) compounds other Cr(VI) compounds	0.1 0.05	8-hour TWA (TRK)	MAK Values[2]
USA ACGIH	Water soluble Cr(VI) compounds	0.05	8-hour TWA (TLV)	ACGIH[3]
USA OSHA	Cr(VI) compounds	0.1 (as CrO3)	STEL/ceiling (PEL)	Cross et al. (1997)
USA NIOSH	Cr(VI) compounds	0.001	TWA (REL) 10-hour workday 40-hour workweek	Cross et al. (1997)
Netherlands	Soluble Cr(VI) compounds	0.025 0.05	8-hour TWA STEL	Cross et al. (1997)
Sweden	Chromates and chromic acid	0.02 0.06	8-hour TWA STEL	Cross et al. (1997)
Finland	Cr(VI) compounds	0.05	TWA	Cross et al. (1997)
Japan	Cr(VI) compounds – carcinogenic forms Cr(VI) compounds	0.01 0.05	8-hour TWA 8-hour TWA	Cross et al. (1997)
France	Cr(VI) compounds	0.05 0.1	8-hour TWA STEL	Cross et al. (1997)

ACGIH American Conference of Governmental Industrial Hygienists
MEL Maximum exposure limit
NIOSH National Institute for Occupational Safety and Health
PEL Permissible exposure limit
OSHA Occupational Safety and Health Administration
REL Recommended exposure limit
STEL Short term exposure limit
TLV Threshold limit value
TRK Technical exposure limit
TWA Time weighted average

4.1.1.2 Occupational exposure

4.1.1.2.1 Occupational exposure during the manufacture of the five chromate compounds

Figures available from the UK and German producers indicate that the number of people potentially exposed to chromium (VI) during manufacture is approximately 330 (personal communication industry). No information was made available by the Italian manufacturing site.

At Company 1 the manufacturing process for the five chromate compounds is predominantly an enclosed one, with exposures only likely during packing of product and during maintenance. All staff wear overalls, glasses or goggles and chemical resistant gloves.

All packing stations have local exhaust ventilation (LEV) at the discharge point, those for sodium dichromate and chromium trioxide are fully automatic and all the packer has to do is check that the system is working properly and sort out any problems. Those for potassium dichromate and ammonium dichromate, although automated to some degree, require that the packer is more involved with the process. They have to place the bag or keg on the filling plant and set the process in motion. In any 8 hour shift, most production staff, including packers, will spend approximately 5 hours on the plant (not all this time will be spent on tasks which could lead to exposure).

The amount of time spent on the plant is variable for the maintenance staff; it depends on the nature of the problem. All maintenance work is covered by a permit-to-work system. Respiratory protective equipment (RPE) is worn by maintenance staff; the standard used depends on the nature of the work to be undertaken. For example, where the work will take place in an area that it is not possible to thoroughly clean before entry, e.g. inside dust conveyors then a higher standard of RPE will be worn than if the area had been cleaned. Disposable overalls are also worn over normal work clothes for particularly dirty jobs.

HSE data

HSE has data on chromium (VI) compound manufacture from 1986 to 1990 and they are shown in **Table 4.2**.

Table 4.2 Personal occupational exposure during the manufacture of chromate compounds (HSE data)

Activity	Number of samples	Range (mg/m^3 Cr (VI))	Arithmetic mean (mg/m^3 Cr (VI))	Geometric mean (mg/m^3 Cr (VI))
Packing/unpacking	10	nd - 0.07	0.016	0.0093
Impregnating	8	0.011 - 0.14	0.042	0.028
Kilning	85	0.001 - 0.12	0.01	0.0046
Leaching plant	72	0.01 - 0.05	0.006	0.0031
Crystal plant	59	0.001 - 0.54	0.03	0.0098
Evaporation	56	0.001 - 0.05	0.0091	0.0043
Chromic acid plant	69	0.001 - 0.13	0.0089	0.0038
Potassium dichromate plant	34	0.002 - 0.08	0.019	0.011
Chromium trioxideplant	21	0.001 - 0.01	0.0036	0.0026
Chrome tan plant	15	0.001 - 0.005	0.002	0.0017
General plant	12	0.001 - 0.05	0.01	0.006

These data are not used to derive the reasonable worst case as they are greater than 10 years old and there is a sufficient quantity of newer data to use.

Industry data

Inhalation exposure data supplied by industry are shown in **Table 4.3**.

The data supplied by Company 1 relates to the years 1994 to 1997. Individual sampling times were variable but were usually between 2 to 4 hours. Another manufacturer (Company 2) also supplied exposure data. No information was given regarding sampling times. It was noted that

for some tasks at this plant a respirator (particle filter P3) is obligatory. No information was given as to exactly what the tasks entailed.

Table 4.3 Personal occupational exposure during the production of the five chromium (VI) compounds (Industry data)

Company	Plant	Job	Number of samples	Range (mg/m^3)	Arithmetic mean (mg/m^3 Cr(VI))	Geometric mean (mg/m^3 Cr(VI))
1	PPA	Maintenance staff	95	0.0001 - 0.78	0.015	0.004
1	PPA	Operator	352	0.0001 - 0.16	0.006	0.004
1	PPA	Team Leader	78	0.001 - 0.05	0.006	0.004
1	PPA	All PPA staff	525	0.0001 - 0.78	0.007	0.004
1	CCP	Maintenance staff	71	0.001 - 0.063	0.01	0.006
1	CCP	Operator	385	0.00001 - 0.22	0.009	0.005
1	CCP	Packer	302	0.001 - 0.11	0.01	0.006
1	CCP	Team leader	118	0.001 - 0.054	0.008	0.005
1	CCP	All CCP staff	876	0.00001 - 0.22	0.01	0.005
2	Rotary kiln	surveillance, sampling and cleaning	16	0.001 - 0.075	0.018	0.006
2	Filtration	surveillance sampling and cleaning	6	0.003 - 0.036	0.015	0.009
2	drying of filtration residue	surveillance, sampling and cleaning	12	0.001 - 0.035	0.012	0.006
2	drying by evaporation	surveillance, sampling and cleaning	6	0.005 - 0.76	0.14	0.02
2	crystallisation and drying	surveillance sampling and cleaning	7	0.004 - 0.044	0.018	0.01

PPA: primary process area, stages of manufacture from raw material through to manufacture of sodium chromate and sodium dichromate
CCP: crystal chromic acid plant, includes manufacture of other chromium (VI) compounds

A reasonable worst case (RWC) for manufacture of 0.02 mg/m^3 is taken forward to the risk characterisation. This was derived from the 90^{th} percentile of the data from all the jobs at Company 1. Company 1 data were used as they were more recent and had more contextual information provided with them to aid evaluation.

Modelled dermal exposure data

As the five chromates are manufactured in largely enclosed processes, the only opportunities for dermal exposure arise during packing of both solid and liquid products or during maintenance.

Enough information was available to allow EASE modelling of dermal exposure to be carried out on packing operations.

For packing of both solid and liquid products, the most appropriate EASE scenario was non-dispersive use with direct handling, with incidental contact. This results in a prediction of 0-0.1 mg/cm^2/day dermal exposure.

It was not possible to carry out EASE modelling for maintenance activities as there was insufficient information available.

4.1.1.2.2 Occupational exposure during the manufacture of other chromium containing chemicals

Manufacture of pigments and dyes

There are two categories of chromium pigments: those that remain as chromium (VI), e.g. lead, strontium and zinc chromates and those which are made by reduction to chromium (III).

Sodium dichromate is the compound most used in the manufacture of chromium (VI) pigments. Exposure to sodium dichromate only occurs at the beginning of the process, as once the reactants have been mixed and heated, the chromium (VI) exposure is to lead, strontium or zinc chromate and therefore not relevant to this assessment. In the process liquid sodium dichromate is pumped from storage tanks to the mixer to which the other reactants are also added. The resulting precipitate/slurry is then filtered, dried and bagged.

Sodium dichromate and potassium dichromate are used in the manufacture of chromium (III) base colours for use in ceramic and glass decoration. They are used to make crimson and pink colours. Production is on a campaign basis using up to 100 kg per day of potassium dichromate crystals and sodium dichromate powder. They form approximately 2% of the batch weight and are scooped out of the container onto scales and then added to the mixer to be blended with the other constituents. The mixture is then transferred to a kiln where the chromium (VI) is converted to chromium (III).

Green chromium (III) oxide pigment is manufactured by tipping approximately 25 kg sodium dichromate on to a weighing machine by hand and then adding to a mixer with water and boric acid. The resulting paste is re-weighed into bags and taken to the furnace. After calcinations the solid is predominantly chromium (III) oxide. Any residual chromium (VI) is washed out with boiling water and the pigment is then filtered and packed. No sampling data were available for this process.

Industry data

A German Trade Association representing inorganic pigment producers (Verband der Mineralfarbenindustrie) indicated that, in their opinion, there would be no inhalation exposure to sodium dichromate possible during the manufacture of chromium (VI) pigments. They report that this view was confirmed by air sampling, but did not supply any data.

The majority of results in **Table 4.4** are from a company who used to manufacture dyestuffs. The plant to which these results relate is now longer in use. The samples were all taken between 1985 and 1991. There is no information as to specific details of the tasks carried out, or reasons why some results are very high or what control measures were in use.

The last set of results relate to chromium (III) pigments made for the ceramic and glass industries.

Table 4.4 Personal occupational exposure data from companies manufacturing dyestuffs (industry data)

Industry	Task	Sampling time (minutes)	Results (mg/m³ Cr(VI))	Control
Manufacture of dyestuffs	charging to pan	300 240 120 320 250	0.008 0.002 <0.005 <0.005 <0.005	no information given
Manufacture of dyestuffs	charging to process	205 330	0.78 <0.005	no information given
Manufacture of dyestuffs	process duties	240	<0.005	no information given
Manufacture of dyestuffs	sodium dichromate charging	390 390 60 210	1.4 0.5 <0.25 <0.036	no information given
Manufacture of chromium (III) pigments for ceramics and glass industries	all process duties	480	0.01 0.01 0.02	LEV

HSE data

Data from HSE's NEDB are shown in **Table 4.5**. They are the results from samples taken over different time periods.

Table 4.5 HSE data for personal occupational exposure during manufacture of pigments and dyes

Industry	Task	Number of samples	Range (mg/m³ Cr VI)	Arithmetic mean (mg/m³ CrVI)	Geometric mean (mg/m³ CrVI)	Control
Paints, varnishing and printing inks manufacture	mixing	13	0.003 - 0.088	0.022	0.012	15% used LEV
Dyestuffs and pigment manufacture	mixing	7	ND - 0.31	0.096	0.034	86% used LEV
	paint production	4	0.039 - 0.15	0.09	0.07	

Published data

Cross et al. (1997) quote data supplied by INRS for the production of dyes and pigments. From nine samples the range of exposure was 0.0003 to 0.04 mg/m^3 Cr (VI), with an arithmetic mean of 0.016 mg/m^3 and a geometric mean of 0.009 mg/m^3. Seven of the samples were collected when LEV was provided.

A value of 0.5 mg/m^3 has been taken forward as the RWC based on discussion at the Technical Meeting. For short term exposures a value of 1.5mg/m^3 will be taken forward. A value of 3 times the long term RWC is used as there are no real short term data.

Modelled dermal exposure data

Dry ingredients, containing chromium (VI) are weighed and charged to mixers before conversion to chromium (III) takes place. These activities can take place with or without LEV. The same activities take place in the manufacture of chromium (VI) pigments. No exposure assessment will be carried out for the other tasks in the manufacture of chromium (VI) pigments once the reaction has taken place. The EASE scenario which best fits the situation is non-dispersive use with direct handling and intermittent contact. The prediction for this scenario is 0.1-1 mg/cm^2/day dermal exposure.

4.1.1.2.3 Occupational exposure during manufacture of chromium (III) sulphate (tanning salts)

Chromium tan salts can be made by reacting sodium dichromate with sulphur dioxide gas in an enclosed process. The sodium dichromate is pumped in from another part of the plant and it is all reacted to form chromium (III) salts.

Alternatively liquid sodium dichromate and sodium chromate can be used to make chromium (III) sulphates of varying basicity by reacting them with a reducing sugar. The liquids are delivered by tanker and discharged into storage vessels from which they are pumped to the reaction vessel. Therefore exposure is only likely during discharge to the storage vessel. No sampling data were available from this company.

Industry data

All data provided, shown in **Table 4.6**, are from one company. Samples were taken during the manufacture of chromium (III) sulphate and chromium (III) oxide. This company also manufactures the five chromium compounds on site.

Table 4.6 Personal occupational exposure during manufacture of chromium (III) sulphate salts (industry data)

Activity	Number of samples	Range of results (mg/m^3 Cr (VI))	Arithmetic mean (mg/m^3 Cr(VI))	Geometric mean (mg/m^3 Cr(VI))
Dryer	1	0.00001		
Maintenance staff	36	0.00001 - 0.018	0.003	0.002
Operator	35	0.001 - 0.025	0.005	0.003
Packer	31	0.00001 - 0.01	0.002	0.002
Team leader	12	0.001 - 0.024	0.004	0.003
All staff	115	0.00001 - 0.025	0.004	0.002

The 90th percentile of all the available data is 0.007 mg/m^3 and this is taken forward as the RWC.

Modelled dermal exposure data

Where chrome tan salts are made on the same site as manufacturing of the five chromate compounds, exposures are likely to be very low because the process is enclosed and when the chrome tan salts are packed they are in the form of chromium (III).

Exposures during tanker emptying are likely to be intermittent and of short duration. During filling of storage tanks by coupled line, air will enter the tanker as it empties, thus releases are unlikely. Exposure is only likely during these tasks when the line is uncoupled, which is estimated to take about 1 minute.

Using this scenario it is possible to use EASE to predict dermal exposures. The EASE scenario that best describes this short term exposure is non-dispersive use with direct handling with incidental contact. This gives a prediction of 0 - 0.1 mg/cm^2/day.

4.1.1.2.4 Occupational exposure during manufacture of wood preservation products

There are two different types of CCA product; liquid and paste which are made by blending with other components in a batch process. The paste has a slightly higher solid content than the solution and contains slightly more chromium trioxide. Chromium trioxide flake is supplied from pre-weighed intermediate bulk containers (IBCs), which are tipped into an enclosed mixing vessel. The chromium trioxide in IBCs is lifted to the reactor charge holes by a traversing hoist. LEV is used when the chromium trioxide is tipped into the reactor. The hoist is controlled remotely with one operator nearby to line the IBC up before tipping takes place. This operator moves away when the tipping is in process. Approximately 9,000 kg of chromium trioxide flake is used per batch and on average 3 batches a day are prepared. The ingredients are mixed for approximately 1 hour before the product is transferred by gravity feed through a control meter to containers.

Products may be packed in IBCs or drums. Drums are filled through a dedicated batching flow meter on an automatic filling line with LEV. IBCs are filled via an IBC filling scale equipped with a batch controller which stops product flow once a predetermined weight has been loaded, with LEV at the filling point.

Industry data

Inhalation exposure data shown in **Table 4.7** are for operators who carry out all jobs on the process. The results are for total chromium rather than chromium (VI). Although they will be an overestimate of actual exposures, most of what was measured will be chromium (VI) and the results given can be viewed as worst-case exposures.

Table 4.7 Industry data for personal occupational exposure during manufacture of CCA

Work area	Number of samples	Sampling time (minutes)	Range of results (mg/m^3 Cr)	Arithmetic mean (mg/m^3 Cr)	Geometric mean (mg/m^3 Cr)
CCA paste	24	50 - 570	0.0008 - 0.06	0.01	0.005
CCA solution	41	120 - 430	0.0002 - 0.021	0.005	0.003
Packing	1	270	<0.01		
All jobs	66	50 - 570	0.0002 - 0.06	0.007	0.004

The 90th percentile of all of this data is 0.01 mg/m^3 and this value has been taken forward as the RWC.

Modelled dermal exposure data

Dermal exposures could occur during the tipping of chromium trioxide flake into the reactor and during drum filling of liquid product. The EASE scenario which best fits these tasks is non dispersive use with direct handling and incidental contact. Although tipping of the CrVI flake and drum filling occurs on average three times per day, incidental contact was used to model exposures as the operator monitors progress of the process remote from the machines which carry out these tasks and is only likely to be exposed once per day. This results in a prediction of 0 - 0.1 mg/cm^2/day dermal exposure.

4.1.1.2.5 Occupational exposure during manufacture of chromium metal

This process involves the weighing, mixing and firing of chromium (III) oxide, aluminium powder, alloying additions, oxidising and conditioning agents. Potassium dichromate is one of the oxidising agents. A number of methods are used to reduce exposure to potassium dichromate: automated weighing equipment with LEV; an enclosed area for mixing; an enclosed automated feed system; firing takes place in enclosed chambers with high power fume extraction, the initial cooling after firing takes place in extracted chambers, final cooling in ventilated enclosed corridor and pots stripped in enclosed extracted plant. Exposure to chromium (VI) is only likely at the start of the process, particularly during weighing.

Exposure data for this process are summarised in **Table 4.8**. No information is available as to sampling time.

Table 4.8 Personal occupational exposure during manufacture of chromium metal (industry data)

Year	Job	Results (mg/m3 Cr (VI))	Control	Source
1993 - 1996	Weighman	0.011 0.001 0.003 0.004 nd nd	automated system + LEV	Industry
1993 - 1996	Smelter	0.002 0.001 nd nd 0.018 0.006	enclosure + LEV	Industry
1993 - 1996	Rammer	0.001 0.001 nd nd nd 0.012	not known	Industry
1993 - 1996	Stripper	nd 0.016 0.001 0.009 nd 0.002	enclosure + LEV	Industry
1981	Weighing	0.02	LEV	HSE

Table 4.8 continued overleaf

Table 4.8 continued Personal occupational exposure during manufacture of chromium metal (industry data)

Year	Job	Results (mg/m3 Cr (VI))	Control	Source
not known	production of chromium metal (48 samples)	nd - 0.02 mean - 0.004 geometric mean - 0.0021	LEV	Cross et al. (1997) (from industry)

nd - none detected

A RWC of 0.01 mg/m^3, based on professional judgement, is carried forward to the risk characterisation.

Modelled dermal exposure data

Dermal exposure can be modelled for weighing out of potassium dichromate, with non dispersive use and no direct handling as the most appropriate scenario. This results in a prediction of very low dermal exposure.

4.1.1.2.6 Occupational exposure during formulation of metal treatment products

Formulators of metal treatment products buy in the chromates they use and make them into proprietary mixtures. This is done for both dry and liquid mixes and is usually carried out on a batch basis. They usually make a wide range of metal finishing blends, the exact contents of which tend to be kept secret.

Industry data

Table 4.9 shows occupational exposure to different chromates used in the formulation of metal treatment products.

At Company 1 all of the results are from essentially the same type of process, dry mixing of powders without any chemical reaction taking place. An operator slits open and tips 25 kg sacks of chemicals into a chute under LEV which leads to a mixer. After mixing for a few minutes the mixer is emptied via a chute at the base of the mixer and packed into 50 kg drums. The exit from the mixer is also under LEV.

The results shown were from "worst-case" mixes in that the products were chosen because they contained about 98% w/w chromium (VI) and it was assumed that the operators were producing batches of this all day. This is rarely the case in practice; typically chromium-containing products would be mixed for half a day twice a week. Therefore in normal production exposures would be lower than this. Operators wear a protective suit, safety shoes, safety glasses, gloves and a particulate respirator when carrying out this work.

Company 2 uses chromium trioxide flake in two different processes. In process 1 chromium trioxide is added to reactors either by manual scooping or by tipping the contents of 14 · 25 kg tins into the reactor man lid. The addition is done slowly, taking a maximum of 30 minutes. Products containing chromium trioxide are made in this way, on average, once a month. In process 2, chromium trioxide solution is produced by the manual addition of approximately 5 kg chromium trioxide flake to a reactor containing water, via a man lid as in process 1. The chromic acid solution is heated and mixed with slurried starch to produce a reduced chromic acid (RCA) solution. The RCA stock is used as the basis for another chromium based metal finishing product. On average an RCA solution will be made on the plant once per week. Operators wear a

disposable particulate respirator when tipping chromium trioxide flake as well as gloves, overalls and glasses.

Company 3 uses predominantly chromium trioxide, with much smaller amounts of potassium dichromate and sodium dichromate to make both dry and liquid blends with other base chemicals. Powder mixes are produced in a vertical ribbon blender, which has LEV both at the mixer lip level and at the bagging off device. The tank is covered with a lid during the mixing process. Liquid mixes are carried out in 4,000 l conical bottomed steel vessel with mechanical agitation and LEV at tank lip level. The process consists of dissolving various chemicals in water to produce an aqueous mixture for sale. PPE for operators consists of chemical goggles, gauntlets, acid resistant work wear and single canister respirator during solid loading operations.

Company 4 uses predominantly chromium trioxide with much smaller amounts of sodium dichromate and potassium dichromate for the manufacture of liquid passivate concentrates. The dry chromates and other constituents are blended in a tank with water and then dispensed into containers. Usually, three lots of 25 kg of chromium trioxide are used per batch. There is LEV above the tank and at the pouring off area. PPE worn during the process is overalls, boots, gloves, hats, respirator or face shield and chemical goggles.

At Company 5, solid chromium trioxide is dissolved in water and then mixed with other ingredients in a mixing tank, which is under pressure and has LEV. Operators are exposed to chromium (VI) for approximately 15 minutes per day when emptying the drums containing chromium trioxide and during filling of containers. PPE worn during the process are chemical goggles, rubber or PVC gloves and a half mask respirator.

Table 4.9 Personal occupational exposure to chromates during formulation of metal treatment products (industry data)

Company	Date	Chemical/process	Result (mg/m^3 Cr (VI))	Sampling time	Control
1	1996	dry mixing of powders including sodium dichromate	0.15	8-hour TWA	LEV(not working)
1	1996	dry mixing of powders including sodium dichromate	0.019	8-hour TWA	LEV
1	1997	dry mixing including strontium chromate and chromium trioxide	0.016	8-hour TWA	LEV
1	1997	dry mixing including strontium chromate and chromium trioxide	0.012	8-hour TWA	LEV
1	1997	dry mixing including chromium trioxide	0.008	8-hour TWA	LEV
1	1997	dry mixing including chromium trioxide	0.008	8-hour TWA	LEV
2	1993	addition of chromium trioxide flake to reactor slowly	<0.02	60 minutes	none
2	1993	addition of chromium trioxide flake to reactor slowly	<0.02	60 minutes	none
2	1995	addition of chromium trioxide flake to reactor slowly	<0.02	60 minutes	LEV
2	1995	addition of chromium trioxide flake to reactor slowly	<0.02	60 minutes	LEV

Table 4.9 continued overleaf

Table 4.9 continued Personal occupational exposure to chromates during formulation of metal treatment products (industry data)

Company	Date	Chemical/process	Result (mg/m³ Cr (VI))	Sampling time	Control
2	1996	charging of chromium trioxide to reactor	<0.002	125 minutes	not known
3	1994	all tasks in manufacture of dry mix	<0.002	121 minutes	LEV
3	1994	addition of raw materials and filling off of a batch of powdered salts	<0.002	47 minutes	LEV
4	1994 - 1997	manufacture of passivate concentrate	none detected in 8 samples	8-hour TWA	LEV
5	1995	all tasks in process	0.022 (not known if total Cr or Cr VI)	284 minutes	LEV
5	1995	all tasks in process	0.006 (not known if total Cr or Cr(VI))	409 minutes	LEV

HSE data

HSE has two data points on its NEDB from 1989. Both are for short term sampling of 10 minutes (weighing out of sodium dichromate) and 15 minutes (mixing) respectively. For weighing out the result were 0.475 mg/m^3, with the 8-hour TWA calculated as 0.01 mg/m^3. For mixing, the result was 0.04 mg/m^3, with a calculated 8-hour TWA of 0.00125 mg/m^3. LEV was in use during both tasks.

A RWC of 0.02 mg/m^3, based on professional judgement, is taken forward to the risk characterisation.

Modelled dermal exposure data

During dry handling of ingredients and bagging of product the most appropriate EASE scenario is non dispersive use with either direct handling with incidental contact or direct handling with intermittent contact, depending on levels of process activity. This results in predictions of 0 - 0.1 mg/cm^2/day and 0.1 - 1 mg/cm^2/day, respectively.

During wet blending and drum filling, the most appropriate EASE scenario is non- dispersive use and direct handling with intermittent contact. This results in a prediction of 0.1 - 1 mg/cm^2/day.

4.1.1.2.7 Occupational exposure during CCA use

Wood is treated with preservative to prevent infestation with fungi and wood-boring insects. In industrial pre-treatment, preservative products are applied as fluids before wood is used for the first time and is usually through impregnation in vessels using combinations of vacuum and pressure.

Wood is loaded into cylindrical treatment vessels, a vacuum may be applied and then the vessel is filled with preservative automatically. The vessel is held at 1 - 1.4 · 10^{-6} Pa for several hours.

Following pressure release and draining a further vacuum may be applied or steam introduced (accelerated fixation). Wood is then removed to storage.

An operator is likely to have greatest inhalation exposure at the end of the treatment cycle when the door is opened and the treated wood is pulled out and removed to the drip area. Exposures can also occur when the concentrated CCA paste is diluted for use manually. Concentrated CCA is delivered either as paste in 100 kg kegs or in solution in 1,000 litre IBCs or by road tanker.

There are a number of other tasks through which wood pre-treatment process operators can become contaminated with CCA:

- wood is placed onto a bogie for loading into the treatment vessel, and is strapped down to prevent its flotation when fully immersed in preservative. Unless freshly cleaned, these bogies and restraining straps are likely to be contaminated.
- as the bogie is unloaded, residual preservative fluid dislodges from wet surfaces to work clothing.
- residues will also dislodge during routine maintenance activities, such as when the operator wipes the vessel door seals to remove material that impairs sealing, or checks the density of working solutions.
- over time, preservative can spread further from the treatment vessel, into the work environment; and contact with contaminated surfaces occurs as operators work in the treatment zone, drive lift trucks, or move wet wood.

The basic equipment issued to wood treatment operators include overalls, protective rubber gloves or gauntlets and boots or Wellingtons. Goggles and/or full face visors are often worn for mixing and when entering the treatment vessel. RPE is also provided in many places, and is used mainly when entering the treatment vessel, not when opening the door.

Industry data

No UK industry data were made available for this assessment.

HSE data

Between 1996 and 1998 HSE carried out surveys at 54 sites, to measure potential dermal and inhalation exposure of operators to preservative fluids used in industrial wood pre-treatment. The survey strategy involved sampling one process operator per site, where possible during two treatment cycles. A treatment cycle is taken to be from when the wood is strapped to the bogies, and then placed in the treatment chamber to when it is removed from the treatment vessel and placed in storage. All the sampling equipment was worn during these cycles, except that on the second cycle the operator would be provided with new nitrile protective gloves and with new sampling gloves to wear inside them. Only one of the surveys included a CCA dilution operation during the sampling period. Maintenance operations were not surveyed.

Details of the survey methods are given in Garrod et al. (in press). Dermal exposures were calculated by relating the amount of active substance on a sampling pad to the relevant exposed part of the body. Results for amounts deposited on work wear and hands and feet were calculated and then added together. It was assumed that 10% on the amount of the work clothing would get on to the skin. Exposures were calculated as mg chromium (VI) on the skin, not as dose. Results for both dermal and inhalation exposure are given in **Table 4.10**.

A company also supplied some data for personal inhalation exposures during CCA use. During 1992 and 1993 measurements of 0.021 mg/m^3, 0.004 mg/m^3, 0.039 mg/m^3 and 0.002 mg/m^3

were reported. They all had sampling times of 2 hours except for the first result which was taken over 4 hours.

Table 4.10 Personal occupational exposure during use of CCA (HSE data)

Reference number	Number of cycles	Dermal exposure (mg Cr(VI))	Inhalation exposure (mg/m3Cr(VI))
E160	2	5.98	none detected
E161	2	3.21	none detected
E162	2	3.76	none detected
E163	2	8.78	none detected
E164	5	21.56	none detected
E165	5	12.11	none detected
E166	2	1.847	none detected
E167	2	1.781	none detected
E168	2	9.59	none detected
E169	1	41.71	none detected
E170	1	19.68	-
E244	1	10.79	0.004
E245	2	15.13	0.006
E246	2	1.904	0.001
E247	2	13.96	0.009
E248	2	2.525	0.001
E249	2	2.44	none detected
E250	2	13.93	0.003
E251	2	7.39	0.008
E252	2	6.81	0.002
E253	2	9.02	0.001
E254	2	2.855	none detected
E255	2	6.55	0.001
E256	2	1.896	0.002
E257	1	3.87	none detected
E258	2	1.781	0.005
E259	2	2.519	0.004
E260	2	5.153	0.002
E261	1	4.5	0.001
E262	2	2.566	0.001
E263	2	8.23	0.009
E264	2	1.37	0.001
E265	2	7.15	0.001

Table 4.10 continued overleaf

Table 4.10 continued Personal occupational exposure during use of CCA (HSE data)

Reference number	Number of cycles	Dermal exposure (mg Cr(VI))	Inhalation exposure (mg/m3Cr(VI))
E266	2	13.53	0.001
E267	2	8.84	0.003
E268	2	4.96	0.003
Number of samples		36	35
Range	1 - 5	1.37 - 41.71	none detected - 0.009
Mean		8.05	0.002
Median	2	6.26	0.001
Geometric mean		5.66	0.001

The inhalation RWC of 0.006 mg/m^3, derived from the 90th percentile of the data given above, is taken forward to risk characterisation. The dermal RWC of 16.5 mg CrVI, derived from the 90th percentile of the data given above, is taken forward to the risk characterisation.

4.1.1.2.8 Handling wet treated wood

Contact with Cr (VI) from treated wood could occur if it was still wet after the impregnation process and went on sale in that state. This is considered to represent foreseeable misuse, since the CCA treated wood should be dry before it is sold (in the UK this is a condition of the approval of the use of the preservative under The Control of Pesticides Regulations, 1986). Wet treated wood will contain a high percentage of Cr (VI), (Coggins et al., 1979).

An estimate of exposure can be derived for a scenario in which wet treated wood is bought and used to erect a fence. In such a scenario, it is anticipated that a worker could handle wet wood between the supply depot and road vehicle, and again between the vehicle and the installation site. There are no measured data for such a scenario and therefore the exposure estimate is based on a series of assumptions.

Assumptions:

- the task is "single occasion" - it is done once and not repeated;
- loading, unloading and carrying treated fence posts and rails takes 30 minutes;
- the area of skin exposed to surface deposits is 2,000 cm^2 - hands and forearms;
- the dislodgeable chromium residue on the wood is 14.5 μg/cm^2 (see below), which, as a worst-case scenario, is present as 100% Cr(VI);
- the transfer coefficient is 1,000 cm^2/hour (information provided by the NL CA);
- there is no more than 20% transfer from contaminated skin to food or cigarettes;
- finger - food/cigarette contact area is at most, 40 cm^2;
- there is no potential for exposure by inhalation by carrying damp wood.

Justifications:

- the value for dislodgeable Cr is taken from a study by Coggins and Hiscocks (1979). In this study, wood was swabbed to remove any Cr from the wood surface immediately after treatment. It is recognised that the conditions of this study are extreme in relation to the situation that would occur during handling of wet wood, but for the purposes of the risk characterisation this value will be used;

- a transfer coefficient is assumed because only a proportion of the surface deposits will be removed during handling;
- uptake of Cr(VI) via the skin is 4% maximum (Wahlberg and Skog, 1963);
- there are no aerosols of Cr (VI) created, and it is not volatile.

Dermal exposure

$$\text{Dermal Exposure} = \frac{\text{Dislodgeable residue } (\mu g / cm^2) \times \text{Transfer Coefficient } (cm^2 / h)}{\text{Skin Surface Area Potentially Exposed } (cm^2)} \times \text{Contact time (h)}$$

thus

$$\text{Dermal Exposure} = \frac{14.5\ (\mu g / cm^2) \times 1000\ (cm^2 / h)}{2000\ (cm^2)} \times 0.5\ (h) \quad = \quad 3.62\ \mu g\ Cr(VI) / cm^2$$

Therefore the total amount of Cr (VI) on the skin is 2000 × 3.62 = 7250 µg Cr (VI).

Taking account of 4% dermal absorption this would lead to a body burden of 4.14 µg Cr (VI)/kg for a 70 kg worker.

Oral exposure

Cr (VI) exposure	=	finger food contact area × dermal exposure
	=	40 cm^2 · 3.62 µg Cr(VI)/cm^2
	=	145 µg Cr(VI)

It is assumed that 20% is transferred from the skin and is ingested = 29 µg.

For a 70 kg worker, this exposure is equivalent to 0.414 µg/kg, which, assuming 5% absorption via the oral route (see Section 4.1.3.1), gives rise to a body burden of 0.02 µg/kg.

Total body burden from this scenario (dermal and oral combined) is 4.162 µg/kg.

Observations

Wood preserved with CCA preparations must be stored at the treatment site until it is dry and before release to the market. Consequently, the likelihood of this scenario is remote. If exposure should occur, the above estimates represent an extreme worst-case situation. It is expected that the presence of CCA preservative on the skin would be noticeable and it is likely that any excess would be wiped off. Similarly, it is assumed that all of the chromium available is present as Cr (VI); in reality, some if not most will have been reduced to Cr (III). Given this, no formal risk characterisation will be carried out but should this exposure situation occur in practice there would be concerns for human health.

4.1.1.2.9 Occupational exposure during metal treatment

The metal treatment industry can be split into two basic types: electrolytic and passive. Exposures will vary between the two types as the use of an electric current in the bath leads to the formation of mist. Airborne chromium (VI) in the form of a mist is a direct result of the plating process and is produced by the generation of hydrogen bubbles at the cathode. Mist formation does not occur during passive treatment of metals and so inhalation exposures during this process will be very low. Inhalation exposure can occur in both types of process when

chromate solutions are made up from either chromate crystal or powder for addition to the treatment bath. These tasks are usually performed by the plater, as and when necessary.

There are three forms of exposure control widely used in the chrome plating industry, either singly or in combination: LEV, mist suppressants and chroffles. LEV is usually used in the form of lip extraction sited at the top of the plating bath. The problems with this type of control can be corrosion of metal parts, due to the acidic and oxidising environment, and lack of maintenance of the system. For the LEV to work most effectively there should be covers over the baths. These are rarely used as they often impede the process.

There are many different mist suppressants on the market for use in chrome plating situations. They are added to the bath, usually by the plater, and work by repressing the emission of mist. Good mist control can be achieved using these chemicals, provided adequate levels of the suppressant are used. The decision as to when to add more suppressants is usually taken by the plater when the thickness of the foam blanket is reduced. The timing for addition is determined by eye rather than by measurement.

Chroffles can only have a small effect in reducing aerosol formation. Their main purpose is to retain heat in the plating solution. They have the disadvantage that they can come out of the bath with the work piece and consequently spread plating solution around the work area.

In the UK Regulation 10(2)/Schedule 5 of the Control of Substances Hazardous to Health Regulations 1999 requires that "spray given off from vessels at which an electrolytic chromium process is carried on, except trivalent chromium" should be monitored every 14 days. The typical way in which this is carried out is to take static samples above the bath for approximately one hour. Therefore very little personal exposure data is available from the UK for chrome plating processes. The static measurements can be described as worst-case estimates for personal exposures as platers very rarely spend much of their time standing next to the plating bath when the current is on.

Dermal exposure, in both electrolytic and passive processes can occur during the handling of objects after their removal from the bath as well as from splashes. The extent of this depends on the level of automation used. Dermal exposures can also occur during handling and use of chromium trioxide flake or neat solutions, especially when it is being added to water and the solution added to the bath. Also, when steel strips are plated or passivated, dermal exposure could occur following a breakage of the strip which has to be re-threaded.

HSE data

Data held on HSE's NEDB are given in **Table 4.11**. HSE also has other sampling data for chrome plating, which were collected during a project looking at the use of different sampling filters in chrome plating works. During this project simultaneous personal and static sampling was carried out at a number of different workplaces. These data are given in **Table 4.12**.

Table 4.11 Occupational inhalation exposures during chrome plating from NEDB

Type of sample	Number of samples	Range of results (mg/m^3 Cr(VI))	Geometric mean (mg/m^3 Cr(VI))
Personal	24	0.01 - 0.05	0.016
Static	72	0.01 - 1.96	0.05

Table 4.12 Comparative data of static and personal sampling during chrome plating

Plating process	Process type	Plating time (minutes)	Current used (amps)	Control	Static 8-hr TWAs (mg/m^3 Cr(VI))	Personal 8-hr TWAs (mg/m^3 Cr(VI))
Decorative	automatic	4	800	mist suppression	0.0001 0.0002 0.0002 0.0002 0.0001	0.0003 0.0002 0.0001
Decorative	semi-automatic	2	1000	mist suppression	0.001 0.0006	0.0001 0.0005
Decorative	semi-automatic	2	600 - 800	mist suppression	0.0028 0.0038 0.0004 0.0002	0.00005
Decorative	semi-automatic	2	800 – 1,200	mist suppression	0.0002 0.0003	0.0005
Decorative	semiautomatic	1.5	800 – 1,200	mist suppression	0.0006 0.0004	0.0001
Decorative	hand	5	800 – 1,000	LEV	0.0002 0.0002 0.0002	0.0004 0.001 0.0027
Decorative	automatic	5	up to 1,400	LEV	0.0008 0.0007 0.0009 0.0006	0.0004 0.0004 0.0004 0.0002
Hard	semi-automatic	120	2,400 – 6,000	mist suppression	0.004 0.004 0.005 0.008 0.006 0.004 0.003	0.0002
Hard	semi-automatic	60	1,100 – 3,900	mist suppression	0.138 0.143 0.04 0.034 0.017 0.021 0.167 0.184 0.584 0.653	0.02
Hard	hand	15 - 120	100 - 200	mist suppression	0.0005 0.0005 0.0002 0.0002 0.0003 0.0004	0.0003 0.00005

Table 4.12 continued overleaf

Table 4.12 continued Comparative data of static and personal sampling during chrome plating

Plating process	Process type	Plating time (minutes)	Current used (amps)	Control	Static 8-hr TWAs (mg/m3 Cr(VI))	Personal 8-hr TWAs (mg/m3 Cr(VI))
Hard	semi-automatic	240	14,000	LEV	0.001 0.004 0.00005 0.00005 0.007 0.009 0.04	0.00005 0.00005 0.00005
Hard	semi-automatic	80	3,100	LEV	0.13 0.14 0.0009 0.0001	0.0006

The total number of static samples taken was 57, with a range of 0.0005 to 0.653 mg/m^3. The arithmetic mean of the static sampling results was 0.04 and the geometric mean was 0.002 mg/m^3. The total number of personal samples taken was 23, with a range of 0.00005 to 0.02 mg/m^3. The arithmetic mean of these samples was 0.001 mg/m^3 and the geometric mean was 0.0002 mg/m^3.

Industry data

In the UK when the static sampling results are less than 0.05 mg/m^3, the actual number is rarely recorded. It is usual to record as less than 0.05 mg/m^3, to show compliance with the MEL. Therefore the industry data quoted below comes from very few companies.

Table 4.13 Occupational inhalation exposure during metal treatment (industry data)

Industry	Type of sample	Number of samples	Range of results (mg/m^3 Cr(VI))	Arithmetic mean (mg/m^3 Cr(VI))	Geometric mean (mg/m^3 Cr(VI))
Chrome plating	static	590	0.02 CrO_3 (90th percentile)		
Chrome plating	personal	95	0.035 CrO_3 (90th percentile)		
EECS	personal	69	<0.001 - 0.002	0.0006	0.0006
EECS	static	74	<0.001 - 0.0003	0.006	0.0007
Passivation	personal	42	<0.001	0.0005	0.0005
Passivation	static	118	<0.001 - 0.09	0.004	0.001

Published data (from Cross et al., 1997)

Table 4.14 shows published exposure data for metal treatment, taken from Cross et al. (1997).

Table 4.14 Published exposure data for metal treatment

Industry	Type of sample	Number of samples	Range of results (mg/m³ Cr(VI))	Arithmetic mean (mg/m³ Cr(VI))	Geometric mean (mg/m³ Cr(VI))
hard chrome plating (+ production of chromium metal)	static	330	none detected - 0.021	0.002	0.0016
*treatment and coating of metals	personal	104	0.0001 - 0.04	0.0028	0.0008
*treatment and coating of metals	static	145	0.00003 -3.19	0.12	0.0025

* data supplied by INRS for soluble Cr (VI).

The RWC of 0.02 mg/m^3, based on the 90th percentile of all of the available data, is taken forward to risk characterisation.

Modelled dermal exposure data

Dermal exposure during metal treatments is likely to occur when bath solutions are made up and added to the treatment bath for both electrolytic and passive processes. There is also the possibility of dermal exposure from handling of treated articles and splashes from drag-out.

Also when steel strips are plated or passivated, dermal exposure could occur following a breakage of the strip which has to be re-threaded. The most appropriate EASE scenario for this task is non-dispersive use and direct handling with intermittent contact. This gives a prediction of 0.1 - 1 mg/cm^2/day dermal exposure.

Sufficient information is available to allow modelling of exposure data for mixing of solutions and adding of solutions to the treatment bath. The most appropriate EASE scenario for mixing of chromic acid solution is non-dispersive use and direct handling with incidental contact. This results in a prediction 0 - 0.1 mg/cm^2/day.

The most appropriate EASE scenario for adding solution to the treatment bath is non-dispersive use with direct handling and incidental contact. This results in a prediction of 0 - 0.1 mg/cm^2/day dermal exposure.

The most appropriate EASE scenario for dermal exposure during drag out is non-dispersive use and direct handling with extensive contact. This results in a prediction of 1-5 mg/cm^2/day.

4.1.1.2.10 Occupational exposure during manufacture of magnetic tapes

Chromium dioxide (CrO_2) is used to make magnetic tapes. This is made by reacting chromic acid with chromium (III) oxide in an autoclave. This is done at 350°C and 300 bar pressure. Chromium dioxide is black/brown in colour and has a composition between CrO_3 and Cr_2O_3. The operations likely to lead to exposure are charging of reagents and packing.

No further information has been made available by the one EU company making this product.

Industry data

The company has reported inhalation exposures in the range 0 to 0.0084 mg/m^3, with an average exposure of 0.002 mg/m^3. This data is based on 40 samples taken between 1979 -1998. The 90th

percentile of results is 0.005 mg/m^3. No indication of whether or not these are 8-hr TWAs are given.

Modelled data

Very little information is available on the process. However, if it is assumed that dermal exposures will occur through breaching of a closed system then EASE can be used to predict dermal exposure. EASE predicts dermal exposure to be 0.1 – 1 mg/cm^2/day for breaching of a closed system with non dispersive use and direct handling.

4.1.1.2.11 Occupational exposure during manufacture of montan wax

Little information was made available by the one company carrying out this process on what tasks are undertaken by people working on this process, as this information was confidential. We were informed that as the chromium (VI) compound is continuously electrochemically regenerated and is produced in a closed system then there would be no exposure.

Modelled exposure data

There is likely to be little exposure to chromium (VI) once the compound has been reduced in the process and therefore exposure is only likely when chromium (VI) is added and if sampling occurs during the process before the reduction takes place. Although very little information is available it is possible to predict exposures providing certain assumptions are made. If it is assumed that sodium dichromate is used and sampling from the enclosed process takes place 2 times per 8 hour shift and each time exposure lasts for 2 minutes, making a total of 4 minutes exposure per shift.

If $1 \cdot 10^{-6}$kPa is used as the vapour pressure EASE predicts inhalation exposure for breaching of closed system to be 0 –1 mg/m3 both with and without LEV. Taking into account the amount of time exposure occurs this gives a predicted exposure for sampling from the closed system of 0-0.004mg/m^3. The highest predicted EASE value of 0.004 mg/m^3 is taken forward to the risk characterisation as the RWC.

EASE predicts dermal exposure to be 0.1-1 mg/cm^2/day for breaching of a closed system with non dispersive use and direct handling.

4.1.1.2.12 Occupational exposure during vitamin K manufacture

Liquid sodium dichromate is used as an oxidant for beta-methyl-naphthalene in the manufacture of vitamin K. It is reported by industry that the process is totally enclosed and all of the chromium (VI) is converted to chromium (III) sulphate during the process. The only potential exposure is when the tanker is unloaded. No sampling data are available for this process.

Modelled exposure data

Exposures during tanker emptying are likely to be intermittent and of short duration. During filling of storage tanks by coupled line, air will enter the tanker as it empties, thus releases are unlikely. Exposure is only likely during these tasks when the line is uncoupled, which is estimated to take about 1 minute.

Using this scenario it is possible to use EASE to predict dermal exposures. The EASE scenario that best describes this exposure is non-dispersive use with direct handling with incidental contact. This gives a prediction of 0-0.1 mg/cm^2/day

Inhalation exposures will be negligible as sodium dichromate does not have a vapour pressure. The most appropriate EASE scenarios for this task are non dispersive use and direct handling with dilution ventilation. If a vapour pressure of $1 \cdot 10^{-6}$kPa is assumed then EASE predicts exposures to be 0 – 0.0025 mg/m^3 taking the time exposed (1 minute per 8-hour shift) into account. The highest predicted EASE value of 0.0025 mg/m3 is taken forward as the RWC to the risk characterisation

4.1.1.2.13 Occupational exposure during use as a mordant in wool dyeing

Sodium dichromate is used to improve the fastness of dark coloured (black, navy, maroon) dyes. In this process the solid sodium dichromate is weighed out, mixed with water and then added to the dye vat either manually or is pumped from the mixing container. The wool is then passed through the dye vat and when dyeing is complete rinsed with clean water and dried.

The quantities used are not large, from 30 g to 2 kg per addition to the bath, depending on the process requirements. PPE (gloves, apron, glasses, overalls) is worn to protect the skin from exposure. RPE is sometimes also worn, particularly for weighing operations. Weighing and addition of sodium dichromate solution usually takes place in either a downdraught booth or using LEV. Once the sodium dichromate is in solution then inhalation exposures will be negligible as sodium dichromate solution has no vapour pressure.

Industry data

Very few companies sample specifically for chromium (VI) as it is a minor component of their dyeing process. One company has measured inhalation exposures to total dust during weighing operations, where weighing occurs approximately 5 times per shift, as 0.33 mg/m^3 8-hour TWA. Only a small proportion of this will be sodium dichromate.

HSE data

HSE has 3 data points for this type of process on its NEDB. They are all from 1987 and at the same company. The dye pod operator, who weighed out the sodium dichromate, had an exposure of 0.042 mg/m^3 8-hour TWA. The dyer, who weighed out the dyes, had an exposure of 0.002 mg/m^3 8-hour TWA. The drying machine operator had an exposure of less than 0.001 mg/m^3 8-hour TWA. No LEV was provided at any part of the process. The dyer and the dye pod operator both wore respirators, overalls and rubber gauntlets.

Modelled inhalation exposure data

If sodium dichromate is weighed out approximately 5 times per shift, each time taking 1 minute, then exposure to dry sodium dichromate will last for 5 minutes per day. The most appropriate EASE scenarios for this task are dry manipulation with and without LEV. This results in predictions of 2 - 5 mg/m^3 with LEV and 5 - 50 mg/m^3 without LEV. When the time taken to carry out this task is taken into account this results in predictions of 0.02 - 0.05 mg/m^3 8-hour TWA, with LEV and 0.05 - 0.52 mg/m^3 8-hour TWA, without LEV.

A RWC of 0.5 mg/m^3, based on the higher value EASE prediction due to paucity of real data, is taken forward to the risk characterisation. For short term exposures a RWC of 1.5 mg/m^3 will be used. This is based on 3 times the long term RWC exposure.

Modelled dermal exposure data

Dermal exposure during mordanting is likely to occur when the sodium dichromate solution is made up and added to the dye vat.

Sufficient information is available to allow modelling of exposure data for mixing of solutions and adding of solutions to the dye vat. The most appropriate EASE scenario for mixing of sodium dichromate solution is non-dispersive use and direct handling with intermittent contact. This results in a prediction of 0.1 -1 mg/cm^2/day.

The most appropriate EASE scenario for adding solution to the dye vat is non-dispersive use with direct handling and incidental contact. This results in a prediction of 0 - 0.1 mg/cm^2/day.

4.1.1.2.14 Occupational exposure during catalyst manufacture

Sodium dichromate solution is metered into an enclosed reaction vessel with the other reactants to produce an iron/chrome nitrate solution. In the process the chromium (VI) is converted to chromium (III) and the reaction is not considered complete until no chromium (VI) is detected. The mixed nitrate solution then goes through a process of precipitation, filtration, drying, calcining, powder compaction and pelletising.

Exposures to chromium (VI) therefore can only occur when the solution is unloaded into storage tanks and during sampling of the reaction mix to check whether or not the reaction is complete. Inhalation exposures in both cases are likely to be minimal as sodium dichromate has no vapour pressure.

Industry data

Data provided by one company, for the years 1995 to 1997, indicate inhalation exposure for production operators to total chromium is in the range 0.001 to 0.09 mg/m^3, for 22 samples. They report that chromium (VI) is likely to be 10% or less of the total chromium. Therefore actual exposures are likely to be in the range 0.0001 to 0.009 mg/m^3 Cr (VI). The geometric mean is 0.0006 mg/m^3 Cr (VI) and the arithmetic mean is 0.001 mg/m^3 Cr (VI). The RWC of 0.005 mg/m^3, based on professional judgement, is taken forward to the risk characterisation.

Modelled dermal exposure data

Dermal exposure could occur when the chromium (VI) solution is transferred to storage tanks and during sampling of the process.

Exposures during tanker emptying are likely to be intermittent and of short duration. During filling of storage tanks by coupled line, air will enter the tanker as it empties, thus releases are unlikely. Therefore exposure is only likely during these tasks when the line is uncoupled, which is estimated to take about 1 minute.

Using this scenario, it is possible to use EASE to predict dermal exposures. The EASE scenario that best describes exposure during unloading is non-dispersive use with direct handling with incidental contact. This gives a prediction of 0 - 0.1mg/cm^2/day

The EASE scenario which best describes QC sampling from the process is breached closed system, i.e. non-dispersive use. With no direct handling of QC samples dermal exposure is predicted to be very low. Where there is handling of QC samples, the most appropriate EASE scenario is direct handling with intermittent contact. Dermal exposure is predicted to be 0.1-1 mg/cm^2/day. No information is available regarding handling of QC samples.

4.1.1.2.15 Inhalation exposure (general discussion)

The results on which this assessment is based are summarised in **Table 4.15**. The reasonable worst-case exposures are based on the 90th percentile of available measured data with professional judgement used where limited data are available. The discussion follows the order in which previous sections have appeared.

The manufacturing process for the five chromates is largely enclosed with breaching for bagging of product and some maintenance activities. The measured exposure data indicate that inhalation exposures for operators are usually very low, with those for maintenance staff and packers slightly higher. Exposures during the manufacture of the five chromates range from none detected to 0.78 mg/m^3. A reasonable worst-case exposure is 0.02 mg/m^3, based on the 90th percentile of the industry data for 1994-1997 for Company1.

There are two types of chromium pigments: those that remain as chromium (VI) and those which are reduced to chromium (III). For both types, exposures usually occur during weighing and mixing of ingredients. Once they have been mixed and reacted then there is no further exposure to any of the five chromates involved in this assessment. The range of exposures is quite large, from none detected to 1.4 mg/m^3. It seems likely that the high exposures were obtained when LEV was not in use. A reasonable worst-case exposure of 0.5 mg/m^3 was agreed at the Technical Meeting. For short term exposures a RWC is 1.5 mg/m^3.

Chrome tanning salts are made either by reacting sodium dichromate with sulphur gas in an enclosed process or by reacting sodium dichromate and sodium chromate with a reducing sugar. In both cases liquid chromates are used and exposures will be low as there is little potential for exposure except when liquid chromate is discharged from a road tanker into a storage vessel. The range of exposures is 0.00001 - 0.025 mg/m^3. A reasonable worst-case exposure is 0.007 mg/m^3, based on the 90th percentile of the available data.

Copper chrome arsenate wood preservation products are manufactured using chromium trioxide flake. Exposure can occur during weighing and mixing of reactants and during packing of the finished product. However, use is made of remote working and automatic filling lines to reduce exposures. The range of exposures reported by industry is 0.0002 to 0.06 mg/m^3. A reasonable worst-case exposure is 0.01 mg/m^3, based on the 90th percentile of the available data.

Potassium dichromate is used as an oxidising agent in the manufacture of chromium metal. Exposure to chromium (VI) is only likely at the start of the process, particularly during weighing, before it is converted to chromium (III). Exposures range from none detected to 0.02 mg/m^3. A reasonable worst-case exposure is 0.01 mg/m^3, based on professional judgement.

Both dry and liquid metal treatment formulations are produced, the exact contents of which tend to be kept secret. Essentially, this use of chromates is one of mixing without any reactions taking place. Exposures will occur during weighing and mixing of ingredients and during packing of the final product. The results range from none detected to 0.15 mg/m^3. The highest result was obtained when the LEV was not working. Other results at the same plant when the LEV was

working indicate that in general exposures were much lower (less than 0.02 mg/m^3). A reasonable worst-case exposure would be 0.02 mg/m^3, based on professional judgement.

Inhalation exposures during use of CCA for the preservation of wood are likely to be highest when the treatment vessel's doors are opened at the end of the cycle and the treated wood is pulled out and removed to the drip area. HSE data for this process indicated that exposures are in the range of none detected to 0.009 mg/m^3. A reasonable worst-case exposure would be 0.006 mg/m^3, based on the 90th percentile of available data.

Occupational exposure to chromium (VI) during metal treatment can be from either electrolytic or passive processes. When electric current is used airborne chromium (VI) in the form of mist is generated. This mist is not generated with passive processes and so inhalation exposures during passive metal treatment will be very low. Exposure will also occur in both types of process when chromate solutions are made up and added to the treatment bath. Exposures for electrolytic metal treatment range from less than 0.001 to 0.05 mg/m^3. A reasonable worst-case exposure is 0.02 mg/m^3, based on the 90th percentile of available data.

Chromium dioxide is used to make magnetic tapes and is made by reacting chromic acid with chromium (III) oxide. The operations likely to lead to exposure are charging of reagents and packing. Reported inhalation exposures range from 0 to 0.0084 mg/m^3. A reasonable worst-case exposure is 0.005 mg/m^3, based on the 90th percentile of available data.

There is little information available on chromium (VI) inhalation exposures during the manufacture of montan wax and vitamin K. However, exposures during both of these processes are likely to be very low as they are mostly enclosed. A RWC exposure for montan wax manufacture is 0.004g/m^3, based on the highest value EASE prediction. A RWC exposure for vitamin K manufacture is 0.0025 mg/m3, based on the highest value EASE prediction.

Exposures to sodium dichromate during its use as a mordant in wool dyeing occur during weighing and mixing with water. Once it is in solution inhalation exposure will be negligible as sodium dichromate solution has no vapour pressure. There are few measured exposure data which range from 0.001 to 0.042 mg/m^3. A reasonable worst-case exposure is 0.5 mg/m^3 is taken forward to the risk characterisation, based on the highest value of the EASE prediction. For short term exposures a RWC of 1.5 mg/m^3 will be used.

Exposures to chromium (VI) during catalyst manufacture occur when sodium dichromate solution is unloaded into storage tanks and during sampling of the reaction process. Data provided by one company show chromium (VI) exposures to be in the range 0.0001 to 0.009 mg/m^3. A reasonable worst-case exposure is 0.005 mg/m^3, based on professional judgement.

Table 4.15 Summary table of occupational inhalation exposure data used in this exposure assessment

Industry	Number of samples	Range of exposures (mg/m³)	Geometric mean (mg/m³)	Reasonable worst case (mg/m³)	Source
manufacture of the 5 chromates	1,889	nd - 0.78	0.004	0.02	measured data
manufacture other Cr containing chemicals					
-dyestuffs	39	nd - 1.4	0.02	0.5 (8 hours) 1.5 (short term)	measured data judgement
-chrome tan	115	0.00001 - 0.025	0.002	0.007	measured data
- CCA manufacture	66	0.0002 - 0.06	0.004	0.01	measured data
manufacture Cr metal	73	nd - 0.02	0.002	0.01	measured data
-formulation metal treatment products	25	nd - 0.15	0.01	0.02	measured data
CCA use	35	nd - 0.009	0.001	0.006	measured data
metal treatment					
-electrolytic	315	<0.001 - 0.05	0.01	0.02	measured data
-passivation	42 (personal results only)	<0.001		0.001	measured data
manufacture of magnetic tapes	40	0 - 0.0084	0.002	0.005	measured data
manufacture of montan wax		no information available but exposures likely to be low due to the nature of the process		0.004	*EASE*
manufacture of vitamin K		little information available but inhalation exposures likely to be low as sodium dichromate liquid has no vapour pressure		0.0025	*EASE*
use as a mordant in wool dyeing	3	0.001 - 0.042	0.015	0.5	measured data
catalyst manufacture	22	0.0001 - 0.009	0.0006	0.005	measured data

nd - none detected

4.1.1.2.16 Dermal exposure (general discussion)

EASE was used to predict dermal exposures during the manufacture of the five chromates. For CCA. For CCA use where measured data were available. **Table 4.16** summarises the dermal exposure data.

In the manufacture of the five chromate compounds dermal exposures were predicted to be 0 to 0.1 mg/cm^2/day during packing operations. It was not possible to predict dermal exposures during maintenance operations because of lack of information. PPE is worn during all manufacturing stages. PPE, properly selected and worn will significantly reduce exposure.

In the manufacture of other chromium-containing chemicals dermal exposures most often occur during weighing and charging of reactants to vessels. In the manufacture of dyestuffs dermal exposure is predicted to be 0.1-1 mg/cm^2/day. In chrome tan manufacture dermal exposures are predicted to be 0-0.1 mg/cm^2/day. When CCA is manufactured dermal exposures are predicted to be 0-0.1 mg/cm^2/day. Dermal exposures are predicted to be very low during manufacture of chromium metal. During formulation of metal treatment products dermal exposure is predicted to

be either 0-0.1 mg/cm^2/day or 0.1-1 mg/cm^2/day, depending on the level of process activity. PPE is worn during the tasks involved in the manufacture of all chromium-containing compounds. PPE, properly selected and worn will significantly reduce exposure.

Measured data for the amount of chromium (VI) on the skin were available for dermal exposures during CCA use. Dermal exposure can occur at a number of stages in the wood treatment process, particularly when the bogie containing the treated wood is unloaded, during maintenance of the treatment vessel and from contact with contaminated surfaces. Exposures ranged from 1.37 - 41.71 mg chromium (VI) on the skin. A reasonable worst-case exposure is 16.5 mg chromium (VI) on the skin, based on the 90th percentile. PPE is worn during all tasks involved in this process. PPE, properly selected and worn will significantly reduce exposure.

In metal treatment dermal exposures are likely to be similar for both electrolytic and passive processes. They can occur during making up of treatment solutions, adding the solution to the treatment bath, from drag out and splashing and when re-threading treated steel strips. EASE predicted dermal exposures to be 0 to 0.1 mg/cm^2/day during mixing of solutions and adding to the treatment bath, 0.1 to 1 mg/cm^2/day during re-threading of steel strips and 1 to 5 mg/cm^2/day from drag out. PPE may be worn for these tasks. PPE, properly selected and worn will significantly reduce exposure.

In the manufacture of magnetic tapes and montan wax dermal exposure to Cr VI is only likely to occur during sampling of a closed system. The EASE prediction for this task is 0.1-1 mg/cm^2/day. PPE may be worn for this task. PPE, properly selected and worn will significantly reduce exposure.

In the manufacture of vitamin K dermal exposure to liquid sodium dichromate is only likely to occur during road tanker unloading. The EASE prediction for this task is 0 to 0.1 mg/cm^2/day. PPE may be worn for this task. PPE, properly selected and worn will significantly reduce exposure.

When sodium dichromate is used as a mordant in wool dyeing dermal exposure can occur during weighing, making up of solutions and during addition of the solution to the dyeing vat. The prediction for all of these tasks is 0 to 0.1 mg/cm^2/day. PPE is worn for all of these tasks. PPE, properly selected and worn will significantly reduce exposure.

In catalyst manufacture dermal exposure to sodium dichromate solution occurs during unloading of the liquid to storage tanks and during sampling of the process. The prediction for unloading of sodium dichromate is 0.1 to 1 mg/cm^2/day. During sampling of the process dermal exposure is predicted to be very low with no direct handling and 0.1 to 1 mg/cm^2/day with direct handling. PPE may be worn for these tasks. PPE, properly selected and worn will significantly reduce exposure.

Table 4.16 Summary table of occupational dermal exposure data used in this assessment

Industry	Range of exposures ($mg/cm^2/day$)	Geometric mean ($mg/cm^2/day$)	Reasonable worst case ($mg/cm^2/day$)	Source
Manufacture of the five chromates	0 - 0.1			EASE
manufacture other Cr containing chemicals -dyestuffs -chrome tan -CCA manufacture -manufacture Cr metal -formulation of metal treatment products	 0.1 - 1 0 - 0.1 0 - 0.1 very low 0 - 0.1/ 0.1 - 1			 EASE EASE EASE EASE EASE
CCA use	1.37 - 41.71 mg Cr VI on skin	5.66 mg C rVI on skin	16.5 mg C rVI on skin	measured data
metal treatment -mixing of solutions -adding to bath -drag out -re-threading steel strip	 0 - 0.1 0 - 0.1 1 - 5 0.1 - 1			EASE
manufacture of magnetic tapes	0.1 -1			EASE
manufacture of montan wax	0.1 –1			EASE
manufacture of vitamin K	0 - 0.1			EASE
use as a mordant in wool dyeing	0.1 - 1			EASE
catalyst manufacture -unloading -process sampling	 0 - 0.1 very low / 0.1 - 1			EASE

4.1.1.3 Consumer exposure

Chromium (VI) compounds are not known to be included in greater than residual concentrations in products available directly to the consumer. They are present at residual concentrations in copper chrome arsenate (CCA) treated wood, which can be handled by consumers. The residual concentration may vary depending on a number of factors; for the purposes of this exposure assessment, a conservative estimate of the concentration of Cr (VI) in CCA preservative will be used. Assessment of this aspect of the use of CCA-treated wood may be considered under the Biocidal Products Directive (98/8) in the future. However, since that Directive is not yet implemented, an assessment is included here.

Toxicokinetic studies indicate that the extent of absorption varies between different exposure routes. Based on the evaluation of these studies (see Sections 4.1.2 and 4.1.3.1) an absorption factor of 5% is used to estimate body burden via the oral route. An absorption factor of 25% has been used for estimates of body burden via inhalation exposure. Information on the rate of dermal absorption suggests that it is limited. For workers, it is assumed that skin contact is minimised because of the corrosive and irritant properties of the Cr (VI) compounds themselves. However, these properties may not be expressed at the very low concentrations present in Cr (VI)-containing products that consumers use. Therefore exposure via the dermal route has been incorporated into the body burden estimates and the maximum rate reported in the toxicokinetics studies has been used to set an absorption factor of 4%.

4.1.1.3.1 Handling CCA treated wood

Chromium (VI) is used in CCA wood preservatives (see Section 2.3.1.3) to prevent decay of wood used outdoors. In the EU, these preservatives are applied by vacuum pressure impregnation, which is an entirely industrial process. During impregnation the Cr (VI) undergoes reduction to Cr (III). After impregnation the wood is dried and any remaining Cr (VI) runs off or is reduced to Cr (III). There is no measured data about exposure from residual Cr (VI) to consumers from CCA treated wood; the only data are from occupational use. Samples collected in joinery workshops where treated wood was cut showed undetectable levels of Cr(VI) (Nygren et al., 1992).

However, some studies have suggested that residual levels of Cr (VI) could remain in treated wood and therefore modelled exposure estimates have been calculated. Estimates have also been calculated for the worst-case scenario of a consumer wrongly being sold wood that is still damp from treatment.

The type of operation a consumer might carry out would include putting up fence posts or sawing, sanding/drilling treated wood. The use of CCA treated wood by consumers is also likely to be infrequent, probably only occurring on a few days per year.

Installing a fence made of dried preserved wood

This task would involve cutting preserved wood posts and rails and fixing them in position.

Assumptions:

- the task is single occasion - it is not repeated
- cutting wood takes 30 minutes and installing the fence takes 3 hours
- breathing rate = 1.25 m^3/hour
- the wood is dry - wood density = 0.8 tonnes/m^3
- size of posts = 2 m long · 10 cm diameter; 8 posts used
- size of rails = 2 m long · 10 cm wide · 2 cm cross-section; 35 rails used
- 5 mg/m^3 inhalable wood dust is created by sawing (machine or manual hand tool)
- uptake by inhalation occurs during sawing only
- 5% of sawdust deposits on skin and 20% of the available chromium dislodges
- 4% uptake via the skin (Wahlberg, Skog, 1963)
- there is no uptake by ingestion
- sawdust volume is a 1 mm layer from the cross-sections of posts and rails

The value of 5 mg/m^3 inhalable wood dust is a worst-case value derived from data measured in woodworking industries. Across a range of workshops total inhalable dust was measured at 1.0 to 4.8 mg/m^3 for wood cutting machine operators (Jones and Smith, 1986). This value is consistent with other data presented in the literature where in scenarios that could be assumed to fit with the conditions of a consumer building a fence such as joinery or carpentry, dust levels at or around 5mg/m^3 have been measured (Scheeper et al., 1995, Rapp et al., 1997). HSE surveys showed wood cutting machine operators to be exposed to dust levels between 0 to 11 mg/m^3 (75th percentile just below 6 mg/m^3, unpublished). However, the scenarios in these surveys are less relevant to the consumer setting, and the values reported are likely to exceed the dust levels experienced by a consumer.

In addition sawing by consumers working outdoors is unlikely to produce exposures as high as 5 mg/m^3 total inhalable dust during the work period, with hand sawing producing much lower

exposures. However as there is a lack of actual data for consumer exposure overall, a value of 5mg/m^3 will be used as a worst-case estimate of exposure.

Inhalation exposure

The concentration of Cr(VI) in wood dust will be taken as 0.26% as reported in the literature (Arsenault, 1977).

Consequently the concentration of 5 mg wood dust/m^3 results in a concentration of Cr (VI) of 13 µg/m^3.

If a consumer works for 30 minutes inhaling 5 mg/m^3 of wood dust in a volume of 0.63 m^3 (1.25 m^3/hour · 0.5 hours), the consumer will inhale 3.12 mg of wood dust containing 8.12 µg Cr(VI) (or 0.12 µg/kg, assuming a 70 kg consumer).

Assuming that all of the Cr (VI) leaches and that 25% of this will be absorbed, the final body burden from inhalation exposure will be 0.029 µg/kg.

Dermal exposure

weight of sawdust produced = wood density · volume of wood dust (1 mm layer from the cross-sections of posts & rails)

$$= 0.8 \text{ tonnes/m}^3 \cdot (7.9 \cdot 10^{-3} \text{ m}^2 \cdot 0.001 \text{ m} \cdot 8 + 2 \cdot 10^{-3} \text{ m}^2 \cdot 0.001 \text{ m} \cdot 35)$$

$$= 106 \text{ g wood dust.}$$

This contains 276 mg Cr(VI) (Cr(VI) content = 0.26%).

Amount of Cr(VI) on skin = Cr(VI) from wood dust x percentage of dust landing on skin · rate dislodging on to skin

$$= 276 \cdot 5\% \cdot 20\%$$

$$= 2.76 \text{ mg}$$

For a 70 kg adult this equates to 39.4 µg/kg with a body burden via the dermal route of 1.6 µg/kg (based on an absorption factor of 4%).

Total body burden carried forward to the risk characterisation will be 1.63 µg/kg.

Observations:

Wood dust inhalation at 5 mg/m^3 (with exposure to Cr (VI) at 13 µg/m^3) is a worst-case estimate. As the chromium becomes fixed in wood, it is increasingly present as Cr(III). In addition, dry, coarse wood dust adheres poorly to skin.

<u>Handling wet treated wood</u>

It is possible that a consumer could come into contact with Cr (VI) from treated wood that is still wet after impregnation with CCA. However, since all CCA treated wood should be dry before it is sold (in the UK this is a condition of the approval of the use of the preservative under The Control of Pesticides Regulations, 1986), this scenario should be extremely unlikely in practice. For this reason, no formal exposure assessment will be performed for this scenario.

Children playing on wooden equipment

Wooden playing structures may be installed in children's outdoor play areas and may be treated with CCA products to prolong the lifetime of the wood. It is assumed that the apparatus used by children will be made of dry wood and that at least two weeks will have passed between the CCA-treatment and installation ready for a child's use and thus most if not all of the Cr (VI) will have reduced to Cr (III). This exposure scenario looks at the potential transfer of chromium content from the surface of the wood onto the skin based on a 5-year old child playing on a wooden surface. A value of 30 mg/m^2 (3 μg/cm^2) for dislodgeable chromium has been reported in the literature (Coggins and Hiscock, 1979). This is an extreme worse-case scenario, showing the maximum dislodgeable amounts of chromium 24 days after treatment. Given that a child's exposure will mainly occur more than 24 days after the wood has been treated, this represents a very worst-case scenario, and this should be taken into account in considering the outcome of the risk characterisation. From the literature (Cruz, 1995, Coggins, 1979) it can be assumed that the average percentage of Cr (VI) in total chromium will be 3% at this stage of use as most of the Cr (VI) has been reduced to Cr (III).

Assumptions:

- Transfer coefficient is 1,000 cm^2/hr (information provided by the NL CA);
- Palmar surface area for a child at 5 years of age is 65 cm^2 (Lee, 1990, information provided by NL CA);
- Contact time with CCA-treated wood is 0.42 hours/day (Sell, 1989, Schwab, 1992, and California Air Resources, 1987, information provided by NL CA);
- The contribution of Cr (VI) to the total chromium content is 3%; and
- The average weight for 5 yr olds is 17.75 kg (female) and 18.25 kg (male). (DRV COMA report, 1991: 50th centile weights for 5 year olds). The 17.75 kg value for females will be used in this scenario, as it will give a more conservative result.

Dermal Exposure

$$\text{Dermal Exposure} = \frac{\text{Dislodgeable residue } (\mu g / cm^2) \times \text{Transfer Coefficient } (cm^2 / h)}{\text{Palmar Surface Area } (cm^2)} \times \text{Contact time (h)}$$

$$\text{Dermal Exposure} = \frac{3\ (\mu g / cm^2) \times 1000\ (cm^2 / h)}{65\ (cm^2)} \times 0.42\ (h) \quad = \quad 19.38\,\mu g / cm^2 \quad \sim \quad 20 \mu g / cm^2$$

Therefore assuming that all available skin makes contact with the wood the total amount of Cr on the skin would be 65 · 20 = 1,300 μg chromium.

If 3% of this was Cr (VI) and the skin then took up 4%, this would give an internal exposure of 1.5μg of Cr (VI). For a 17.75 kg child this would give a body burden of 0.08 μg/kg.

Oral Ingestion

Assumptions:

- The entire hand of the child will be in contact with food or placed in their mouth;
- 20% is transferred from the skin and is ingested;

Cr (VI) ingested = Palmar Surface Area · Dermal Exposure · 3% · 20%
= 65 · 20 · 3% · 20%

= 1,300 · 3% · 20%µg Cr(VI)
= 8 µg.

For a 17.75 kg child this exposure is equivalent to 0.02 µg/kg if an absorption rate of 5% is assumed (see Section 4.1.3.1).

Total body burden from this scenario (oral plus dermal) would be 0.1 µg/kg of Cr (VI).

4.1.1.3.2 Leather goods

All tanning within the EU is carried out using basic trivalent chromium (III) sulphate. Basic trivalent chromium sulphate manufactured within the EU contains no measurable Cr (VI) (Cross et al., 1997). Consequently there is no consumer exposure to Cr (VI) from leather goods based on leather tanned within the EU.

4.1.1.3.3 Chromium pigments

Chromate pigments are used in paints and metal primers, and as colorants in rubber, paper and inks. Pigments are derived mainly from zinc and lead chromates which fall outside the scope of this review. Although some pigments can be manufactured from sodium dichromate the resulting pigments are Cr (III) based and any residual Cr (VI) is removed by washing during manufacture (see Section 2.2.1.2). Chromium (III) pigments can subsequently be used in consumer products but fall outside the scope of this review.

4.1.1.3.4 Stainless steel goods

Chromium is present at up to 30% in stainless steels. Although occupational exposure to Cr (VI) can occur during the manufacture of stainless steels once the finished product is marketed no exposure to Cr (VI) is possible. The chromium is part of the steel as chromium metal and in any case is not available for exposure being totally bound up in the steel which by its very nature is corrosion resistant. Consumer exposure to Cr (VI) is therefore non-existent from this source.

4.1.1.3.5 Dyestuffs

Some Cr (VI) compounds are used as a mordant in dyeing wool. It is added to fix the dye and during the process the chromium is totally reduced to Cr (III) and reducing agents may be added to facilitate this. Dyed wool garments are washed during and after treatment and the finished wool does not contain any Cr (VI) (see Section 2.2.6). There is, therefore, no consumer exposure to Cr (VI) from wool garments.

4.1.1.3.6 Products derived from vitamin K

Sodium dichromate is used in the manufacture of vitamin K derivatives of which are used in animal feeds and some drugs. During the production of vitamin K all the Cr (VI) is reduced to Cr (III) sulphate (see Section 2.2.5). The chromium sulphate is a saleable by-product. Derivatives of vitamin K produced by organic synthetic methods are used in some drugs (anti-coagulants).

There is, therefore, no consumer exposure to Cr (VI) from drugs derived from the use of sodium dichromate in this process.

4.1.1.3.7 Montan waxes

These are polyhydric alcohol esters make by an oxidative reaction that can involve sodium dichromate (see Section 2.2.4). They are used in various plastics including food packaging.

These are produced in a process that involves continuous regeneration of Cr (VI). However, when the process is completed, only Cr (III) is left (see Section 4.1.1.2.10). The waxes are free of any Cr contamination and hence consumer exposure is nil.

4.1.1.4 Indirect exposure via the environment

Releases of chromium (VI) from any sources are expected to be reduced to chromium (III) in most situations in the environment (see Section 3.1.1.2.1) so the impact of chromium (VI) as such is likely to be limited to the area around the source. Therefore this assessment focuses on the local impact of emissions from the production and use of the five chromium (VI) compounds. The wider background emissions of chromium from other sources are not considered for risk assessment. Hence the concentrations calculated in this assessment are local ones (as Clocal), and the assessment is based on the added risk which they may present.

Section 3.1 describes the release and behaviour of chromium in the environment, and contains estimates of concentrations in the various environment compartments. For some of the compartments, concentrations were estimated based on the assumption that release occurred as Cr (VI) or as Cr (III). For other compartments, particularly soil, it was concluded from the properties of chromium that it would be effectively found only as Cr (III). In order to assess indirect exposure to Cr (VI) only those compartments where Cr (VI) concentrations were estimated have been included. These are water and fish, and for two process steps air. The values are included in **Table 4.17** It is likely that these will over-estimate the actual indirect exposure as conversion of Cr (VI) to Cr (III) is expected to occur under the vast majority of environmental conditions.

Table 4.17 Concentrations of chromium (VI) in environmental media

Process	Water (mg/l)	Air (μg/m³)	Fish (mg/kg)
Production	0.002	4.3	0.002
Pigment production	0.28		0.28
Cr_2O_3 production	0.30		0.30
Chrome tanning salts	0.35		0.35
Wood preservative formulation	0.17		0.17
Wood preservative use	0.0045		0.0045
Metal treatment formulation	0.093	0.71	0.093
Electroplating	0.11		0.11
Passivating	0.088		0.088
Anodising	0.018		0.018
Brightening	0.11		0.11
Mordant dyeing	0.0003		0.0003

The above concentrations have been used to estimate uptake from the environment (**Table 4.18**).

Table 4.18 Uptake of chromium (VI) from environmental media

Process	Water (mg/day)	Air (mg/day)	Fish (mg/day)	Total	
				(mg/day)	(μg/kg bw/day)
Production	0.004	0.086	0.0002	0.090	1.3
Pigment production	0.19		0.032	0.22	3.1
Cr_2O_3 production	0.60		0.035	0.64	9.1
Chrome tanning salts	0.70		0.04	0.74	11
Wood preservative formulation	0.34		0.02	0.36	5.1
Wood preservative use	0.009		0.005	0.01	0.14
Metal treatment formulation	0.19	0.014	0.011	0.20	2.9
Electroplating	0.22		0.013	0.23	3.3
Passivating	0.18		0.01	0.19	2.7
Anodising	0.036		0.002	0.04	0.57
Brightening	0.22		0.013	0.23	3.3
Mordant dyeing	0.0006		0.00003	0.000063	0.009

Assumptions in calculating uptake:

- Water consumption 2 l/day
- Fish consumption 0.115 kg/day
- Inhalation rate 20 m^3/day
- Bioavailability through inhalation 100%
- Adult body weight 70 kg.

Toxicokinetic studies indicate that absorption of chromium (VI) compounds is limited via all routes and a factor of 5% has been used elsewhere in this document to calculate body burdens following oral exposure. However, there is no information available upon which to base the use of a different oral absorption factor for humans than for animals. Therefore, the risk characterisation for exposure via the environment (see Section 4.1.3.4) will use the daily intake figures presented above, without conversion to body burden. Although there is exposure via inhalation for two scenarios, the total body burden from these is less than that from the scenario with the highest environmental exposure, manufacture of chrome tanning salts.

4.1.1.5 Combined exposure

For a combined exposure, consideration should be given to a consumer who is also potentially exposed via the environment. A worst-case scenario would be someone living in the vicinity of a plant producing chrome tanning salts, and thus potentially exposed to 0.011 mg/kg/day, with further exposure as a result of installing a fence using CCA treated wood (1.63 µg/kg). This would lead to a total exposure of 0.013 mg/kg, and this value will be taken forward to the risk characterisation.

4.1.2 Effects assessment (Hazard identification and dose (concentration) - response (effect) relationship)

Introduction

The toxicological database for chromium (VI) (Cr(VI)) is generally extensive. Sodium chromate, dichromates of sodium, potassium and ammonium, and chromium (VI) trioxide, the substances covered in this review, are all highly water-soluble hexavalent compounds.

Chromium (VI) trioxide in solution produces chromic acid, concentrated solutions of which are highly acidic. Hence, of the five Cr(VI) compounds covered by the assessment, there are site-of-contact issues related to low pH that are a consideration for chromium (VI) trioxide but not for the other four.

Beyond this, the five Cr(VI) compounds will all readily dissolve in aqueous environments in the body, to release chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) ions. These two ions will co-exist, in equilibrium, regardless of the particular Cr (VI) compound involved. The chromate/dichromate ions produced from all five compounds will behave similarly in biological tissues and hence, other than the additional property of acidity and its potential influence on toxicity for chromium (VI) trioxide, the five can be treated as a common group. Furthermore, toxicological observations made with other chromium (VI) compounds that can similarly readily dissociate to produce chromate/dichromate ions in solution can be legitimately made use of in predicting the toxicity of these five compounds.

Chromium (VI) compounds have been the subject of an extensive review for use by DG-EMPL's SCOEL in a regulatory context. This 'Criteria Document' was produced by the Institute of Occupational Health (IOH), Birmingham, UK, in 1997 (Fairhurst S and Minty CA, 1989). The health effects of chromium compounds were also comprehensively reviewed by HSE in 1989 in Toxicity Review No.21 (Cross et al., 1997). These two reviews have been taken to provide a firm foundation for the assembly of this assessment; health effect information covered in the reviews is summarised below. Relevant additional data which have become available since the reviews were published are summarised in more detail.

Also, the relevant entry from the HSE published compendium "Asthmagen?" (1997), which provides critical assessments of the evidence for agents implicated in occupational asthma, ("Asthmagen?", 1997). In each compendium entry a critical appraisal of original papers has been made and a decision reached as to whether the substance meets the revised EU criteria (1996) for classification as a respiratory sensitiser (a cause of asthma) and labelling with R42.

This report refers extensively to these 3 reviews throughout the following Effects Assessment. These reviews are provided as accompanying documents to this report and available as an weblink in the references chapter.

4.1.2.1 Toxicokinetics

Data on toxicokinetics are covered in the sections of the HSE Review on pages 8-21 and the IOH Review on pages 104-124. No relevant studies have become available over and above those covered by these previous reviews.

Information has come from studies in rats, mice, guinea pigs and rabbits. Following inhalation or intratracheal instillation of highly water-soluble Cr (VI) compounds, approximately 20-30% of the chromium dose was rapidly absorbed into the bloodstream, apparently much of this still in the hexavalent state. Some chromium was also removed from the lung by mucociliary clearance into the gastrointestinal tract. The residual chromium remaining in the lung was cleared much more slowly, with significant amounts remaining in the lung for several weeks. In animals, gastrointestinal uptake of chromium following oral administration of highly-soluble Cr (VI) was generally poor due to reduction of Cr (VI) to Cr (III) in stomach. When food was given ad libitum, only 1-3% of orally administered Cr (VI) was absorbed in rats and mice; the amount increased if food had been withdrawn for 16-48 hours. In contrast, one study reported at least 18% absorption in unstarved guinea pigs receiving potassium chromate orally. It has been reported that insulin-dependent diabetic patients absorbed significantly more ^{51}chromium than non-diabetic subjects (IPCS, 1988).

Dermal absorption of highly water-soluble Cr (VI) compounds in guinea pigs varied between <1% and 4% of the applied aqueous dose, depending on the chromium concentration.

Once absorbed into the bloodstream, a substantial proportion of Cr (VI) is initially taken up by the erythrocytes via a specific transport mechanism. Inside the erythrocyte, Cr (VI) is rapidly reduced to Cr (III) by glutathione, becoming irreversibly bound to haemoglobin for the lifespan of the cell. Cr (VI) is also reduced to Cr (III) in plasma. Ascorbic acid, cysteine and cytochrome P450 enzymes can also reduce Cr (VI). Extra-cellular reduction to Cr (III) prevents cellular uptake.

Chromium is cleared rapidly from the plasma but persists in the erythrocytes for several weeks. Systemically absorbed chromium is distributed very widely and rapidly, initially a proportion remaining in the Cr (VI) state. In experimental animal studies, the level of chromium in most

tissues decreased gradually from the first day post-exposure. However, the chromium content of the spleen showed a time-dependent increase over several weeks, due to clearance of senescent chromium-laden erythrocytes. Parenteral administration studies in pregnant rats (intravenous, intraperitoneal, subcutaneous) and mice (intravenous) using water-soluble ^{51}Cr (VI) compounds have shown that radioactivity in the bloodstream can cross the placenta and be distributed within the embryo. No data are available on potential excretion into milk.

Inhaled or intratracheal instilled Cr (VI) is excreted in urine and faeces in similar amounts (in the range 20-70% of administered dose). When orally administered, most appears in faeces, due to poor gastrointestinal tract absorption. Chromium in urine and faeces is in the form of Cr (III) complexes, with glutathione for example. During the first 7 days following parenteral administration of readily water-soluble chromates, 35-60% of the chromium was excreted in the urine and 14-28% in the faeces. Repeated daily exposure to highly water-soluble Cr (VI) compounds by inhalation, oral or subcutaneous administration produced accumulation of chromium in many organs and tissues. In the case of the inhalation route, high levels were found in lungs, spleen, duodenum, kidneys, liver and testes.

In terms of available human data, results from volunteer studies indicate that only poor absorption occurs in the gastrointestinal tract (2-9%). However, it is known from the literature that diabetic patients may absorb up to 4 times more chromium from the gastrointestinal tract than healthy individuals (IPCS, 1988). Workers in chromate production, chromium plating and SS-MMA welding with occupational exposure to highly water-soluble Cr (VI) compounds had elevated blood and urine chromium levels. In addition, chromate production workers (who also had exposure to poorly-soluble chromium) had very high levels of chromium in the lungs and higher than normal chromium levels in several other tissues; these increases were still apparent a considerable number of years after exposure ceased. The increased body burden in these studies was probably the result of absorption via the respiratory tract since absorption of highly water-soluble Cr (VI) through intact skin is limited in humans.

4.1.2.1.1 Summary of toxicokinetics

There is a reasonably good database available on the toxicokinetics of the Cr (VI) compounds under review, although there are relatively few human data. The available data indicate that generally the Cr (VI) compounds covered by this document are likely to behave in a similar manner in respect of toxicokinetics, and that the kinetic behaviour of these substances would be similar in those species studied, including humans.

Following inhalation exposure, animal studies have shown that 20-30% of the administered Cr (VI) is absorbed via the respiratory tract. Highly water-soluble Cr (VI) is poorly absorbed via the gastrointestinal tract (only 2-9% of the dose was absorbed in human studies) due to reduction to the relatively poorly absorbed Cr (III). Only limited dermal absorption takes place through intact skin, with 1-4% Cr (VI) from an aqueous solution crossing the skin in guinea pig studies.

According to results of animal testing, chromium derived from these compounds can remain in the lungs for several weeks after inhalation exposure and also becomes bound to haemoglobin in erythrocytes for the lifespan of the cells. Cr(VI) becomes reduced to Cr(III) after entering the body due to the influence of reducing agents, for example glutathione. Distribution is widespread even after a single dose and includes transfer of absorbed Cr (VI) across the placenta. Excretion occurs in urine and faeces. Repeated exposure leads to accumulation of chromium in several tissues, particularly the spleen because of uptake of senescent erythrocytes.

4.1.2.2 Acute toxicity

Data on acute toxicity are covered in the sections of the HSE Review on pages 23-26 and 48-50 and the IOH Review on pages 125-128 and 194-197. Additional acute toxicity data on chromium (VI) trioxide have become available over and above those covered by these previous reviews and are included below.

In terms of acute inhalation toxicity, potassium dichromate aerosols (mass median aerodynamic diameter 1-2 microns) were toxic when inhaled by rats, deaths occurring following a 6-hour exposure to 37 mg/m^3 (13 mg Cr (VI)/m^3) and above. There were no deaths at 31 mg/m^3 (11 mg Cr(VI)/m^3). Decreased body weight gain and increased lung weight were observed following 2-hour exposure to 20 mg/m^3 (7 mg Cr(VI)/m^3). LC_{50} values of 99 mg/m^3 (potassium dichromate) (35 mg Cr(VI)/m^3), 200 mg/m^3 (sodium and potassium dichromate) (70 mg Cr(VI)/m^3), 200 mg/m^3 (ammonium dichromate) (83 mg Cr(VI)/m^3) and 104 mg/m^3 (sodium chromate) (33 mg Cr(VI)/m^3) have been reported for male rats with a 4-hour aerosol exposure period. Signs of toxicity included reduced body weight, respiratory distress and irritation of the respiratory tract. Lung oedema, inflammation and tracheal epithelium necrosis were seen in rats following inhalation of 28 mg/m^3 sodium chromate (9 mg Cr(VI)/m^3) for 24 hours; minimal lung effects (reduction in glycoprotein secretion in the trachea) were seen at 8 mg/m^3 (3 mg Cr(VI)/m^3) for 24 hours. Intratracheal instillation of potassium dichromate at 1.14 mg (0.4 mg Cr(VI)) produced lung inflammation in rats. An LC_{50} value of 217 mg/m^3 (113 mg Cr(VI)/m^3) for chromium (VI) trioxide (presumably aerosol) has been reported for rats with a 4-hour exposure period. It is predicted that severe damage to tissues of the respiratory tract would occur at low concentrations due to the corrosive nature of this substance. In the case of all the Cr (VI) compounds under consideration, depending upon the pH of the Cr (VI) solution, corrosive effects can occur on contact.

Available oral LD_{50} values for chromium (VI) trioxide were 52-113 mg/kg (27-59 mg Cr(VI)/kg) in rats and 135-175 mg/kg (70-91 mg Cr(VI)/kg) in mice. Aqueous chromium (VI) trioxide produced bleeding and ulceration of the stomach due to its corrosive properties. LD_{50} values of 74 mg/kg (26 mg Cr(VI)/kg) (potassium dichromate), 59 mg/kg (23 mg Cr(VI)/kg) sodium dichromate), 55 mg/kg (23 mg Cr(VI)/kg) (ammonium dichromate) and 87 mg/kg (28 mgCr(VI)/kg) (sodium chromate) have been reported for male rats. Female rats were more sensitive with LD_{50} values of 48 mg/kg (17 mg Cr(VI)/kg), 46 mg/kg (16 mg Cr(VI)/kg), 48 mg/kg (20 mg Cr(VI)/kg) and 40 mg/kg (13 mg Cr(VI)/kg) for potassium dichromate, sodium dichromate, ammonium dichromate and sodium chromate respectively. Toxic effects reported at necropsy included pulmonary congestion and corrosion of mucosa in the gastrointestinal tract.

Highly water-soluble Cr (VI) compounds also expressed acute toxicity following skin application. In a standard dermal LD_{50} study in rabbit, the following values were determined: sodium dichromate 960 mg/kg (380 mg Cr(VI)/kg); potassium dichromate 1,150 mg/kg (410 mg Cr(VI)/kg); ammonium dichromate 1,860 mg/kg (770 mg Cr(VI)/kg) and sodium chromate 1,330 mg/kg (430 mg Cr(VI)/kg). In another study, percutaneous doses of 207 mg/kg sodium chromate (66 mg Cr(VI)/kg) and 170 mg/kg sodium dichromate (66 mg Cr(VI)/kg) produced death in guinea pigs. A dermal LD_{50} value of 57 mg/kg (30 mg Cr(VI)/kg) has been reported for chromium (VI) trioxide.

In relation to human data on acute toxicity, case reports show that inhalation by workers of aqueous solutions of Cr (VI) mists (sodium dichromate or chromium (VI) trioxide) have resulted in irritation and inflammation of the respiratory tract, with pain in the nose and chest, cough, dyspnoea and cyanosis; the associated airborne levels of Cr (VI) were not reported. Accidental or deliberate oral ingestion has resulted in pain, bleeding, vomiting, diarrhoea and in some cases a

burning sensation in mouth, throat and stomach. Some of these symptoms are indicative of corrosive damage. A large number of case reports have indicated that deaths in adults occurred at estimated oral doses of potassium dichromate of 10-230 mg/kg (2.5-80 mg Cr(VI)/kg); sodium dichromate 25-200 mg/kg (10-80 mg Cr(VI)/kg); ammonium dichromate 25-195 mg/kg (10-80 mg Cr(VI)/kg); chromium (VI) trioxide 20-155 mg/kg (10-80 mg Cr(VI)/kg). The validity of these fatal dose estimates is unclear because it is always difficult to determine the dose a person may have swallowed before being taken ill. In addition, treatment was usually given to decrease the amount of Cr (VI) in the body and some parts of some doses may have been vomited. However, the estimated levels are broadly consistent with the dose levels producing death in animal studies. In those individuals surviving beyond 24 hours, necrosis of hepatocytes and renal proximal tubule epithelial cells was evident with clinical manifestations of liver and kidney damage. There have also been cases of kidney damage and death following absorption of Cr (VI) through the skin. No estimations of exposure were available and in most of these cases the skin was damaged by acidity, or high temperature, facilitating Cr (VI) absorption.

4.1.2.2.1 Summary of acute toxicity

Case reports show that inhalation by workers of aqueous solutions of Cr (VI) mists have resulted in irritation and inflammation of the respiratory tract, with symptoms and signs including dyspnoea and cyanosis; associated airborne levels were not reported. Accidental or deliberate oral ingestion has resulted in signs and symptoms some of which are indicative of corrosive damage and deaths have been reported in numerous cases in adults. Among the survivors, clinical manifestations of liver and kidney damage were present. There have also been cases of kidney damage and death following dermal exposure to Cr (VI). In most of these cases the skin was broken or damaged by the acidity or high temperature of the solution, facilitating Cr (VI) absorption across the skin. The qualitative picture of acute toxicity seen in humans is supported by observations from studies in experimental animals. Aerosols were toxic when inhaled by rats. LC_{50} values of 99 mg/m^3 (35 mg Cr(VI)/m^3) (potassium dichromate), 200 mg/m^3 (70 mg Cr(VI)/m^3) (sodium and potassium dichromate), 200 mg/m^3 (ammonium dichromate) (83 mg Cr(VI)/m^3) and 104 mg/m^3 (sodium chromate) (33 mg Cr(VI)/m^3) have been reported for male rats with a 4-hour exposure period. Similarly, an LC_{50} value of 217 mg/m^3 (113 mg Cr(VI)/m^3) for chromium (VI) trioxide has been reported for rats with a 4-hour exposure period. It is predicted that severe damage to tissues of the respiratory tract would occur at low concentrations due to the corrosive nature of this substance.

Available oral LD_{50} values for chromium (VI) trioxide were 52-113 mg/kg (27-59 mg Cr(VI)/kg) in rats and 135-175 mg/kg (70-91 mg Cr(VI)/kg) in mice. Aqueous chromium (VI) trioxide produced bleeding and ulceration of the stomach due to its corrosive properties. Oral LD_{50} values of 74 mg/kg (26 mg Cr(VI)/kg) (potassium dichromate), 59 mg/kg (23 mg Cr(VI)/kg) sodium dichromate), 55 mg/kg (23 mg Cr(VI)/kg) (ammonium dichromate) and 87 mg/kg (28 mg Cr(VI)/kg) (sodium chromate) have been reported for male rats. Female rats were more sensitive with LD_{50} values of 48 mg/kg (17 mg Cr(VI)/kg), 46 mg/kg (16 mg Cr(VI)/kg), 48 mg/kg (20 mg Cr(VI)/kg) and 40 mg/kg (13 mg Cr(VI)/kg) for potassium dichromate, sodium dichromate, ammonium dichromate and sodium chromate respectively. Toxic effects reported at necropsy included pulmonary congestion and corrosion of mucosa in the gastrointestinal tract.

Highly water-soluble Cr (VI) compounds were also toxic following skin application. In a standard dermal LD_{50} study in rabbit, the following values were determined: sodium dichromate 960 mg/kg (380 mg Cr(VI)/kg); potassium dichromate 1,150 mg/kg (410 mg Cr(VI)/kg); ammonium dichromate 1,860 mg/kg (770 mg Cr(VI)/kg) and sodium chromate 1,330 mg/kg

(430 mg Cr(VI)/kg). In another study, percutaneous doses of 207 mg/kg sodium chromate (66 mg Cr(VI)/kg) and 170 mg/kg sodium dichromate (66 mg Cr(VI)/kg) produced death in guinea pigs. A dermal LD_{50} value of 57 mg/kg (30 mg Cr(VI)/kg) has been reported for chromium (VI) trioxide.

In conclusion, highly water-soluble Cr (VI) compounds are very toxic by inhalation and toxic by ingestion. The respiratory tract and the kidney are damaged by these compounds following inhalation and oral exposure respectively. Although acutely harmful or toxic by the dermal route, more severe responses may be observed due to greater uptake via the skin if there is any prior or simultaneous damage to the skin. Depending upon the pH of the Cr (VI) solution, corrosive effects can occur on contact.

4.1.2.3 Irritation

Data on irritation are covered in the sections of the HSE Review on pages 27-28 and 50-51 and the IOH Review on pages 129-131, 194-195 and 198-199. No relevant studies have become available over and above those covered by these previous reviews.

4.1.2.3.1 Skin irritation

Chromium (VI) trioxide is considered separately under corrosivity (see Section 4.1.2.4.). Single application of sodium chromate, sodium dichromate, potassium dichromate or ammonium dichromate to rabbit skin for 4 hours resulted in irritant responses of erythema and oedema of grade 3 or less when the compounds were in solution or moistened with saline. The reactions appeared to subside but irritation was still present at 6 days after application. In general, abrasion of the skin before treatment had no effect on the outcome. It was claimed in one study that single application of potassium dichromate solution to abraded skin in the guinea pig caused skin "sores". Repeated application animal studies are considered under corrosivity (see Section 4.1.2.4.).

In terms of human experience, direct accidental contact with very acidic or high temperature solutions of highly water-soluble Cr (VI) compounds has resulted in severe burns to human skin. It is not clear from the available reports whether intact skin is damaged by single contact with neutral solutions of such compounds. In one patch test study, some volunteers responded to 0.5% aqueous potassium dichromate with mild irritation especially around hair follicles. Repeated-exposure skin effects in exposed workers are considered under corrosivity (see Section 4.1.2.4.).

4.1.2.3.2 Summary of skin irritation

Single application of a low concentration of highly water-soluble Cr(VI) in solution to undamaged human skin resulted in only a mild irritant response around the hair follicles. Animal data indicate that irritation occurs following single application to the skin for 4 hours. It is not possible to determine a clear concentration-response relationship for human skin irritation from the single-exposure animal or occupational data available. Repeated-exposure skin responses are considered under corrosivity (see Section 4.1.2.4).

4.1.2.3.3 Eye irritation

A neutralised sodium chromate solution was not irritant to the rabbit eye. In contrast, repeated administration of potassium dichromate in powder form daily for 7 days caused severe irritation including necrosis of the conjunctivae and ulceration of the cornea.

Accidental splashing of highly water-soluble Cr(VI) compounds in solution into the eye has resulted in damage to the human eye. A number of case reports have detailed both inflammation of the cornea and conjunctivae and in more severe cases, corneal erosion and ulceration. The severity of response is increased by low pH or high temperature. Accidental eye contact with the corrosive aqueous chromium (VI) trioxide results in conjunctival congestion and necrosis and corneal oedema and opacity.

4.1.2.3.4 Summary of eye irritation

Significant damage to the eye can occur upon accidental exposure to highly water-soluble Cr (VI) compounds. Severe and persistent effects occur when there is contact with the low pH aqueous chromium (VI) trioxide or Cr (VI) solutions at high temperature. Repeated, but not single administration of highly water-soluble Cr (VI) caused severe irritation in the rabbit eye. This is probably explained by the use of a neutralised solution in the single application study. It is not possible to determine a clear concentration-response relationship from the data available.

4.1.2.3.5 Respiratory tract sensory irritation

Data on respiratory irritation are covered in the sections of the HSE Review on page 49 and the IOH Review on page 194.

In a very poorly-reported volunteer study, 10 subjects were apparently exposed to chromium (VI) trioxide at concentrations of 10-24 mg/m^3 (5-12 mg Cr(VI)/m^3) for “brief periods of time”. It was claimed that this exposure caused nasal irritation. According to the authors, exposure to lower but unspecified concentrations produced slight if any irritation of the upper respiratory tract. Given the poor reporting in this study the results cannot be considered to be reliable.

Symptoms of sensory irritation of the respiratory tract are known to occur among chrome plating workers exposed to a mist of aqueous chromium (VI) trioxide. Since this is corrosive, such symptoms are to be expected. No quantitative data on such irritation are available from studies of workers. No studies reporting symptoms of sensory irritation are available for the other Cr(VI) compounds. Overall, it is not possible to determine a reliable concentration-response relationship for respiratory tract irritation using the available data.

4.1.2.4 Corrosivity

Data on corrosivity are covered in the sections of the HSE Review on pages 27 and 50-51 and the IOH Review on pages 129-130 and 198-199. No relevant studies have become available over and above those covered by these previous reviews.

Aqueous chromium (VI) trioxide is a corrosive substance due to its low pH. Concentration-dependent erythema was observed in guinea pig when repeated applications were made daily for 4 days on unabraided skin using potassium dichromate solution. In another study in the guinea pig, daily repeated application up to 28 days resulted in a more severe response only when the

skin was traumatised by wax depilation or non-scarring abrasion prior to application. The severity of response was dependent on the concentration of potassium dichromate and the degree of trauma to the skin. Chrome ulcers with thick eschar and underlying tissue necrosis were observed.

In workers regularly exposed to highly water-soluble Cr (VI) in solution, chrome ulcers develop after some initial damage to the skin. This has been described for dye workers handling sodium or potassium dichromate solutions and frequently in exposed workers in the chromate production and chrome plating industries. The severity of the ulcer depends upon the frequency and duration of skin contamination. Small papules develop initially, progressing to an ulcer which penetrates gradually to deeper skin layers. Typically, chrome ulcers have a hard circular periphery and a cavity leading to a base covered with exudate or a crust.

4.1.2.4.1 Summary of corrosivity

Aqueous chromium (VI) trioxide is a corrosive substance due to its low pH. In addition, when high temperature solutions of Cr (VI) are splashed onto the skin, serious burns occur.

Highly water-soluble Cr (VI) compounds can cause very severe skin effects under certain conditions. In workers repeatedly exposed to highly water-soluble Cr (VI), where there is some slight initial damage to the skin, ulcers can develop which constitute a serious and persistent effect. Animal data are consistent with the observations made in humans. It is not possible to determine a clear concentration-response relationship for repeated-exposure human skin effects from the occupational data available and quantitative data could be misleading given the potential for severe effects resulting from repeated contamination of slightly damaged skin. Overall, highly water-soluble Cr (VI) compounds should be regarded as corrosive.

4.1.2.5 Sensitisation

4.1.2.5.1 Skin

Data on skin sensitisation are covered in the sections of the HSE Review on pages 28 and 51-52 and the IOH Review on pages 132- 33 and 200- 202. No relevant studies have become available over and above those covered by these previous reviews.

Highly water-soluble Cr (VI) compounds (sodium/potassium dichromate) have been tested in standard or modified guinea pig maximisation studies and found to produce a skin sensitisation response. Skin sensitisation potential was also demonstrated in a mouse ear swelling test with potassium dichromate. Cross reactivity has been observed in the guinea pig; animals sensitised to Cr (VI) responded positively to Cr (III) compounds and vice versa. This is consistent with current mechanistic understanding which indicates that Cr (III) is the ultimate hapten, following reduction of Cr (VI) in the skin.

Allergic contact dermatitis resulting from exposure to Cr (VI) is commonly encountered and has been demonstrated in patch testing studies of contact dermatitis patients with potassium dichromate solution and in investigations of different occupational groups. It has been reported that concentrations of 0.5% and below potassium dichromate elicited a response in patch testing studies. In one study a minimum (10% reacting) elicitation concentration of 0.09 μg Cr(VI)/cm^2 was calculated after 54 Cr(VI)-sensitive volunteers were exposed to potassium dichromate.

However, these data are limited in that the Cr (VI) compounds and the concentrations of these which induced the sensitisation are unknown and it is not known whether other Cr (VI) compounds covered in this review would share a similar response-relationship. Overall, therefore it is not possible to reliably determine a threshold for either induction or challenge in an exposed population using the available data.

4.1.2.5.2 Summary of skin sensitisation

Skin sensitisation resulting from contact with Cr (VI) is relatively common in humans working with the compounds. This has been demonstrated in patch testing of contact dermatitis patients and in investigations of various occupational groups. In addition, skin sensitisation potential has been clearly demonstrated in standard and modified guinea pig maximisation tests and in the mouse ear swelling test.

Current understanding of the mechanism involved in the sensitisation indicates that Cr (III) is the ultimate hapten. Skin contact with Cr (VI) leads to penetration of Cr (VI) into the skin where it is reduced to Cr (III). There is some evidence for cross-reactivity between Cr (III) and Cr (VI); Cr(VI)-sensitised subjects may also react to Cr (III). Overall, it is not possible to reliably determine a threshold for either induction or challenge in an exposed population using the available data.

4.1.2.5.3 Occupational asthma

Data on occupational asthma are covered in the sections of the HSE Review on page 53 and the IOH Review on pages 202-203. A judgement of the data against the revised EU criteria for classification as a respiratory sensitiser (a cause of asthma) and labelling with R42 is given in the compendium entry in "Asthmagen? Critical assessments of the evidence for agents implicated in occupational asthma", 1997. One relevant study (Bright et al, 1997) has become available over and above those covered by the HSE and IOH reviews but this study has been evaluated in the HSE compendium entry.

Asthma arising from exposure to Cr(VI) was first suggested in the 19th century. A number of case reports, mainly within the chrome plating industry, provide evidence that inhaled Cr (VI) can cause asthma, although the total number of reported cases is small in relation to the number of workers potentially exposed. Positive findings are available from several well-conducted bronchial challenge tests. No information is available on the dose-response relationships for induction of the hypersensitive state or elicitation of an asthmatic response in hypersensitive individuals.

4.1.2.5.4 Summary of occupational asthma

The available case reports and evidence from well-conducted bronchial challenge tests, show that inhalation of Cr (VI) compounds can cause occupational asthma. As with skin, Cr (VI)-sensitised subjects may react to Cr (III). It is not possible to determine a no-effect level or exposure-response relationship for induction or elicitation of occupational asthma.

4.1.2.6 Repeated dose toxicity

Data on repeated dose toxicity are covered in the sections of the HSE Review on pages 30-33 and 54-56 and the IOH Review on pages 134-140 and 205-210. Relevant studies have become available over and above those covered by these previous reviews and are summarised below. Only limited animal repeated dose toxicity testing was available. Inhalation of sodium chromate dust for 8 months caused reduction in bodyweight gain and deaths in mice exposed to 0.3-3.7 mg/m^3 (0.1-1.2 mg Cr(VI)/m^3). Rats appeared to be less sensitive (no deaths occurring at the same concentrations after 16 months). Concentrations down to 0.07 mg/m^3 sodium dichromate aerosol (0.025 mg Cr(VI)/m^3) produced increased alveolar macrophage and spleen lymphocyte activities following a 90-day exposure in the rat. Much of this enhancement was lost at 0.57 mg/m^3 sodium dichromate (0.2 mgCr(VI)/m^3); this dose inhibited alveolar macrophage phagocytosis. Repeated chromic acid mist (chromium (VI) trioxide) exposure produced irritant and corrosive effects in the respiratory tract at 3.5 mg/m^3 (1.8 mg Cr(VI)/m^3) and above in an 8-month study. Overall, it was not possible to determine with confidence any no effect level from repeated exposure inhalation studies. Repeated intratracheal instillation of sodium dichromate resulted in lung inflammation, fibrosis and emphysema.

In one repeated-dose oral study, no effect on weight gain, haematology or clinical chemistry was found in a 12-month drinking water study in the mouse with approximately 17 mg/kg/day potassium dichromate (6 mg Cr(VI)/kg/day).

In a study that was performed to specifically evaluate the effects of hexavalent chromium on the testicular spermatogenic and steroidogenic activities (Chowdhury and Mitra, 1995), groups of 10 sexually mature Charles Foster male rats were administered oral gavage doses of 0, 20, 40 or 60 mg/kg/day sodium dichromate (0, 7, 14, 21 mg Cr(VI)/kg/day) for 90 days. At sacrifice, blood levels of testosterone were measured and a range of macroscopic, microscopic, biochemical and histochemical investigations of the testes were made.

No deaths or treatment-related clinical signs of toxicity were observed. A dramatic reduction in body weight gain of 55% and 54% was seen in mid-dose and high-dose animals. A statistically significant decrease in absolute testis weight was also seen in these two groups. However, when comparing the relative weight, a minor decrease of 10% was observed only at the top dose. Other testicular parameters (proteins, DNA, RNA, seminiferous tubule diameter, Leydig cell population, spermatogenic cell count, succinic dehydrogenase and 3β-Δ-^{5}-hydroxy steroid dehydrogenase activity, serum testosterone) were all statistically significantly decreased at 40 and 60 mg/kg/day (14 and 21 mg Cr(VI)/kg/day) in accordance with the reduced organ weight seen at these two dose levels. However, in the absence of any investigations in other organs, it is difficult to deem whether or not these absolute decreases seen in the testes were specifically treatment-related or occurred as a non-specific accompaniment to the severe reduction in body weight gain. Histopathological investigations showed there was also partial degeneration in germinal cells at 40 mg/kg/day (14 mg Cr(VI)/kg/day), and cellular disorganisation, disruption of seminiferous tubules and marked depletion of germinal cells at 60 mg/kg/day (21 mg Cr(VI)/kg/day). It can be concluded that these degenerative effects seen at 40 and 60 mg/kg/day (14 and 21 mg Cr(VI)/kg/day) represent treatment-related effects on the testis at dose levels causing some general toxicity. There were no significant findings at 20 mg/kg/day (7 mg Cr(VI)/kg/day); the only effects noted were minor changes in testicular proteins, 3β-Δ-^{5}-hydroxy steroid dehydrogenase activity and serum testosterone levels. Therefore, a NOAEL for testicular atrophy of 20 mg/kg/day (7 mg Cr(VI)/kg/day) can be identified from this study.

In a study involving repeated oral exposure to potassium dichromate, special attention was given to the potential for testicular toxicity of this hexavalent chromium compound (NTP, 1996a).

Groups of 24 male and 48 female BALB/c mice were administered in the diet 0, 15, 50, 100 or 400 ppm of potassium dichromate (equivalent to doses of approximately 0, 3/5, 10/16, 21/34 and 92/137 mg/kg/day, 0, 1/2, 4/6, 7/12 and 32/45 mg Cr(VI)/kg/day, males/females) for 9 weeks. Six males and 12 females from each dose group were then terminated after 3, 6 or 9 full weeks of treatment and after a recovery period of 8 weeks. Investigations of body weight, food and water consumption, organ weights, microscopic evaluation of the liver, kidney and ovaries, haematology, histology of the testis and epididymis for Sertoli nuclei and preleptotene spermatocyte counts in stage X or XI tubules, and chromatin analysis were included.

No treatment-related deaths or clinical signs of toxicity were observed. A statistically significant decrease in body weight gain of 16% was seen only in the 400 ppm males during the dosing period. The body weight gain of the 400 ppm females was slightly decreased by 7%, but was not statistically significantly different from the controls. Food consumption was generally increased in the treated groups, especially in the top dose group, during the treatment period. During the recovery period, food consumption was comparable across groups. There were no treatment-related gross lesions or organ weight changes in any of the treated groups. During haematological investigations, a statistically significant decrease of 2-4% in mean corpuscular volume (MCV) was seen at weeks 3, 6 and 9 in the 400 ppm males and females and at week 6 in the 100 ppm females. MCV returned to normal after the recovery period in the female mice but increased by 2.8% in the 400 ppm males. The mean corpuscular haemoglobin (MCH) was also significantly decreased in the 400 ppm males at week 9 (by 3.7%), in the 400 ppm females at weeks 3 (by 3.6%) and 6 (by 2.3%) and in the 100 ppm females at week 3 (by 1.8%). After the recovery period, the MCH was again comparable across groups. The decreases in MCV and MCH noted at 100 ppm are regarded as being incidental findings, because they were seen only transiently at single sampling times during the course of the study. The decreases in MCV and MCH noted at 400 ppm are also considered to be of no toxicological significance since the decreases were small, were stated to be within historical control ranges, and since both the MCV and MCH are derived indices using the haematocrit, erythrocyte count, or haemoglobin concentration and no treatment-related differences were observed in these latter parameters. No treatment-related histopathological changes were observed in the ovaries. Minimal hepatocyte cytoplasmic vacuolisation indicative of lipid accumulation was noted at 0 (1/12 females), 50 (1/6 males and 3/12 females), 100 (2/5 males and 2/12 females) and 400 ppm (2/6 males and 4/12 females). Given that these findings were described as minimal, did not show a clear dose-response relationship and occurred also in controls, they are not considered to be toxicologically significant. Renal damage (1 male with minimal tubular degeneration, 1 male with minimal tubular regeneration, 1 male with minimal inflammation and 2 females with minimal tubular degeneration) was also seen at 400 ppm. These kidney changes are regarded as being incidental, as they were described as minimal and occurred as occasional observations. No alterations in structure or relative cell numbers were found in the testes.

Overall, the results of this study indicate that dietary administration of potassium dichromate for 9 weeks to mice did not produce any significant toxicity up to the highest dose level tested of 92 mg/kg/day (32 mg Cr(VI)/kg/day) and 137 mg/kg/day (45 mg Cr(VI)/kg/day) in males and females, respectively.

Using the same method, the study was repeated using Sprague-Dawley rats treated for up to 9 weeks (NTP, 1996b). The same concentrations of potassium dichromate in the diet of 0, 15, 50, 100 and 400 ppm were employed, which corresponded to mean dose levels of approximately 0, 1, 3, 6 and 24 mg/kg/day (0, 0.4, 1, 2 and 8 mg Cr(VI)/kg/day) in males, and 0, 1, 3, 7, and 28 mg/kg/day (0, 0.4, 1, 2 and 10 mg Cr(VI)/kg/day) in females, respectively.

No deaths or treatment-related clinical signs of toxicity were observed. No effects were seen on body weight, water and food consumption, organ weights and microscopic evaluation of the liver, kidneys and ovaries. During haematological investigations, a statistically significant decrease of 3% and 6% in mean corpuscular volume (MCV) was seen at week 3 in the 400 ppm females and at week 9 in the 400 ppm males, respectively. Although not statistically significant, the MCV values were also decreased by 3% in the 400 ppm females at week 9. This effect returned to normal in all animals after the recovery period. The mean corpuscular haemoglobin (MCH) was also significantly decreased at week 9 in the 400 ppm males (by 5%) and in the 400 ppm females (by 6%). After the recovery period, the MCH was again comparable across groups. Similarly to the mouse findings (see above), these decreases in the MCV and MCH are also considered to be of no toxicological significance since the decreases were small, were stated to be within historical control ranges, and since both the MCV and MCH are derived indices using the haematocrit, erythrocyte count, or haemoglobin concentration and no treatment-related differences were observed in these latter parameters. No alterations in structure or relative cell numbers were found in the testes.

Overall, the results of this study indicate that dietary administration of potassium dichromate for 9 weeks to rats did not produce any significant toxicity up to the highest dose level tested of 24 mg/kg/day (8 mg Cr(VI)/kg/day) and 28 mg/kg/day (10 mg Cr(VI)/kg/day) in males and females, respectively.

No repeated-dose dermal studies are available.

All the human information on the toxic effects arising from repeated exposure to highly water-soluble Cr (VI) relates to workers in the chromate production and chromium plating industries. These workers were exposed to sodium and potassium chromates and dichromates either in solid form (dusts) or in aqueous solution or to airborne mists of chromium (VI) trioxide in aqueous solution (chromic acid). Some of the principal toxic effects produced in these workers reflect the irritant and (at low pH) corrosive action of Cr (VI) ion toward mucous membranes. Nasal septum ulceration and perforation, inflammation of the respiratory tract along much if not all of its length, lung fibrosis, emphysema and chronic obstructive bronchopneumopathy and inflammation and ulceration of the gastrointestinal tract from the buccal cavity to the intestines have been observed. Many of these effects were particularly predominant among workers in these industries in the past when atmospheric Cr (VI) levels were probably relatively high. However it is not possible, from the available information, to relate many of these effects to reliable measures of Cr (VI) exposure. Although in principle a threshold dose should be identifiable, in practice the location of such a threshold is not possible from the data available. There is some evidence that atrophy of the nasal mucosa occurs in chromium plating workers exposed to very low average levels (below 0.004 mg/m^3 chromium (VI) trioxide, below 0.002 mg Cr(VI)/m^3) in the atmosphere. An important confounding factor in the development of nasal lesions is the possible transfer of Cr (VI) in solution from fingers to the nose due to poor personal hygiene.

Some evidence of kidney damage, such as proteinuria, has also been found among chromate production and chromium plating workers. It is noted that kidney damage was also reported following single exposure. Although in principle a threshold dose should be identifiable, in practice the location of such a threshold is not possible from the data available.

4.1.2.6.1 Summary of repeated dose toxicity

With respect to repeated exposure, a large number of studies are available relating to exposure of workers to highly water-soluble Cr (VI), specifically sodium or potassium chromate/dichromate and chromium (VI) trioxide. The main effects reported are irritant and corrosive responses in relation to inhalation and dermal exposure. These include inflammation in the lower respiratory tract, and nasal septum perforation in the upper respiratory tract. It is not possible to relate these effects to reliable measures of Cr (VI) exposure. Although in principle a threshold dose should be identifiable, in practice the location of such a threshold is not possible from the data available. Some evidence of kidney damage has also been found among chromate production and chromium plating workers. No exposure-response data or no-effect levels are available. However, it appears that the exposure levels at which kidney toxicity occurs overlaps with the atmospheric concentrations at which respiratory tract effects have been reported.

Only limited animal repeated dose toxicity testing is available. In general, the effects seen are consistent with those found in humans. Although in principle a threshold dose should be identifiable, in practice the location of such a threshold is not possible from the data available. Inhalation of sodium chromate dust for 8 months caused deaths in mice exposed to 0.3-3.7 mg/m^3 (0.1-1.2 mg Cr(VI)/m^3). Rats appeared to be less sensitive (no deaths occurring after 16 months). Cr (VI) concentrations down to 0.06 mg/m^3 (0.025 mg Cr(VI)/m^3) sodium dichromate (aerosol) produced increased alveolar macrophage and spleen lymphocyte activities following a 90-day exposure in the rat. Much of this enhancement was lost at 0.57 mg/m^3 sodium dichromate (0.2 mg Cr(VI)/m^3); this dose inhibited alveolar macrophage phagocytosis. Repeated chromic acid mist (chromium (VI) trioxide) exposure produced irritant and corrosive effects in the respiratory tract at 3.5 mg/m^3 (1.8 mg Cr(VI)/m^3) and above in an 8-month study. Overall, little useful dose-response information is available.

In the rat, testicular degeneration was observed at a dose level (40 mg/kg/day (14 mg Cr(VI)/kg/day)) which caused a large decrease in body weight gain following gavage administration of sodium dichromate for 90 days. A NOAEL of 20 mg/kg/day (7 mg Cr(VI)/kg/day) was determined for effects on the testis, the only organ examined. Other studies found no significant toxicity, including no effects on the testis, following administration of potassium dichromate by the dietary route for 9 weeks. The highest dose levels in these studies were 24 mg/kg/day (8 mg Cr(VI)/kg/day) in the rat and 92 mg/kg/day (32 mg Cr(VI)/kg/day) in the mouse.

No repeated dermal studies are available, although these substances are recognised as being corrosive on repeated dermal exposure.

4.1.2.7 Mutagenicity

Data on mutagenicity are covered in the sections of the HSE Review on pages 36-39 and the IOH Review on pages 164-181. No relevant studies have become available over and above those covered by these previous reviews.

4.1.2.7.1 Studies *in vitro*

There is a very large body of evidence indicating that the Cr (VI) ion in solution is directly mutagenic in *in vitro* systems. Extensive *in vitro* testing of highly water-soluble Cr(VI) compounds has produced positive results for point mutations and DNA damage in bacteria, point

mutations, mitotic crossing-over, gene conversion, disomy and diploid in yeasts, and gene mutation, DNA damage, chromosome aberrations, sister chromatid exchanges and unscheduled DNA synthesis in mammalian cells.

The *in vitro* genotoxicity of Cr (VI) was diminished considerably by the presence of reducing agents, in the form of tissue S9 or S12 fractions, gastric juice or reducing agents such as glutathione, ascorbate or sulphite. These all serve to reduce Cr (VI) to Cr (III) outside the cell therefore greatly reducing entry of chromium into the cell.

4.1.2.7.2 Studies in animals

The genotoxicity of Cr (VI) compounds *in vivo* has been less extensively studied. Parenteral administration of sodium or potassium dichromate or potassium chromate to rats or mice resulted in significant increases in chromosome aberrations and micronucleated cells in the bone marrow and DNA single-strand breaks, interstrand cross-links and DNA-protein cross-links in the liver, kidneys and lung. A mouse spot test involving intraperitoneal injection of potassium chromate gave positive results. Oral studies have been negative but these employed lower dose levels and absorption is known to be poor by the oral route. Overall, water soluble Cr (VI) compounds are *in vivo* somatic cell mutagens in animal studies.

A significant increase in post implantation deaths in a dominant lethal assay was reported in mice following intraperitoneal injection of potassium dichromate. Toxicokinetic data for water-soluble Cr(VI) compounds indicate that chromium will reach the germ cells following inhalation exposure (i.e. a relevant route of exposure for humans). Therefore taking these two observations together, it can be concluded that water-soluble Cr(VI) compounds have the potential to produce germ cell mutagenicity.

4.1.2.7.3 Studies in humans

A few studies have been conducted in which circulating lymphocytes have been isolated from chromium-exposed workers and examined for chromosome aberrations, micronuclei, SCE and changes in chromosome numbers. In general, the results from better-conducted and reported studies including chromium plating workers in Japan and SS-MMA welders in Scandinavia have been negative.

Evidence of genotoxicity has been reported in several other studies of chromate production workers in Eastern Europe and chromium plating workers in Italy. However the manner in which these were conducted and reported precludes full assessment of the significance of the findings.

4.1.2.7.4 Summary of mutagenicity

Few studies of genotoxic potential in humans are available. No evidence of genotoxic activity has been found in adequately-conducted studies in circulating lymphocytes from chromium-exposed workers. In contrast, there is a vast array of genotoxicity data *in vitro* and less extensive testing in animals available. The evidence clearly indicates that highly water-soluble Cr(VI) compounds can produce significant mutagenic activity *in vitro* and *in vivo*. The Cr (VI) compounds under consideration are therefore regarded as *in vivo* somatic cell mutagens. In addition, toxicokinetic and dominant lethal data suggest that water-soluble Cr (VI) has the potential to be an *in vivo* germ cell mutagen.

4.1.2.8 Carcinogenicity

Data on carcinogenicity are covered in the sections of the HSE Review on pages 57-71 and 42-46 and the IOH Review on pages 211-251 and 141-163.

A few animal carcinogenicity studies were available. Results indicated that sodium dichromate was clearly carcinogenic, producing lung tumours when administered to rats by continuous inhalation of aqueous aerosol or long-term repeated intratracheal instillation in saline. Also, there was a single incidence of a squamous cell carcinoma of the pharynx after inhalation of sodium dichromate aerosol in rats.

In rats and mice, inhalation studies using an aerosol or mist of chromium (VI) trioxide produced 1-2 test group animals with lung tumours where such were mainly absent among corresponding controls. These studies suffered from some deficiencies in design such as small group size or inadequate dosing regimes. In two intrabronchial implantation studies in the rat, 1-2 animals with carcinomas of the respiratory tract were found in chromium (VI) trioxide-treated groups. No respiratory tract tumours were observed in controls in these studies.

One or two studies show the formation of tumours at the site of injection following intramuscular or intrapleural administration in rats but these findings are of no relevance in assessing carcinogenic hazard via relevant routes of exposure.

Thus, in animal studies there is some evidence of respiratory tract carcinogenic activity for sodium dichromate and chromium (VI) trioxide. Data for the oral and dermal routes and carcinogenicity studies on the other compounds under consideration are not available.

A number of epidemiology studies were available when the HSE and IOH reviews were written. These investigated cancer risks among workers exposed to various forms of Cr (III) and Cr (VI). Unfortunately, detailed analysis of smoking habits is almost invariably absent. In chromate production, workers are exposed to Cr (III) during the production of Cr (VI) in water-soluble form e.g. sodium chromate. Although studies of chromate production have clearly established that there is an increase in lung cancer mortality, it is not clear precisely which Cr (VI) compound(s) produced the effect. An excess risk of lung cancer mortality has also been reported for workers in the chromate pigment production industry. However, this industry involves exposure to sparingly soluble or poorly soluble zinc or lead chromates as well as the more water-soluble Cr (VI) compounds covered here. Chromium plating workers are exposed to aqueous chromium (VI) trioxide. One study provides clear evidence of an association between chromium plating work and increased lung cancer risk. It is not possible to relate in any reliable manner, the excess lung cancer mortality seen to particular levels of Cr (VI) in the atmosphere. Overall, it was concluded previously that chromium (VI) trioxide in solution is a human carcinogen but only limited information is available for the other Cr (VI) compounds of interest.

The following studies have become available since the publication of the HSE and IOH reviews:

<u>Chromate production in the US</u>

Two recently published studies have significant methodological weaknesses but are included here because they extend earlier studies which are found in the IOH and HSE reviews.

An epidemiology study of mortality among chromate production workers was recently carried out (Rosenman and Stanbury, 1996). The mortality of these chromate production workers has been studied previously (Machle and Gregorius, 1948 and Public Health Service, 1953). The cohort was compiled in 1990-91 from Social Security Administration forms submitted by US

companies. The workers had been employed at some time at one or more of 4 plants A-D between 1937 and 1971. Vital status was identified using multiple sources of information. Proportionate (cancer) mortality ratios (PCMR) were calculated using the US general population death figures to obtain expected mortalities and PCMRs were adjusted by 5-year age and 5- year time period of death categories. The number of individuals identified was 3,408; 10.9% of all workers could not be traced and of 1,858 known to have died, death certificates were available on approximately 94%. There was a statistically significant increase in proportional mortality for death from all cancer (PCMR 1.37, 95% CI 1.23-1.51), digestive tract cancer (PCMR 1.33, CI 1.08-1.61), stomach cancer (PCMR 2.05, CI 1.38-2.92), nasal cancer (PCMR 5.18, CI 2.18-11.30) and lung cancer (PCMR 1.51, CI 1.29-1.75) in white men. The number of deaths from lung cancer among white men was 170; 6 deaths were caused by nasal cancer. For black men, a statistically significant increase in proportional mortality for death from all cancer, lung cancer, bladder cancer and diseases of the digestive system was found among a total of 394 deaths. In black men, the proportion of deaths from lung cancer was slightly increased (PCMR 1.34 CI 1.00-1.75) while the proportion of bladder cancer deaths was statistically significantly higher; PCMR 3.30 (CI 1.42-6.51). Proportional mortality for lung cancer increased with increasing time employed and with latency since first employed.

A follow-up study (Mancuso, 1997) looked at a cohort previously described in an epidemiology study in the IOH and HSE reviews (Mancuso, 1975). Lung cancer deaths had been found to account for 62% of cancer deaths which seemed to be a high proportion. Members of the cohort of 332 males worked at the plant between 1931 and 1937 and were followed through to 1993. The methods used were those employed in the earlier study. Comparison with control values was not made; the standard was the distribution of person-years by age group for the total chromate population. It was stated that 49 employees were not traced. Of 283 deaths identified, lung cancer deaths accounted for about 23% (66 deaths). Cumulative exposures to Cr (III) or Cr (VI) were calculated; age-adjusted mortality rates for lung cancer increased with increasing cumulative exposure. The authors claim that there is an association between Cr(III) and increased lung cancer mortality but the association is probably spurious, the indirect consequence of a correlation between Cr(III) and Cr(VI) exposures.

Chrome plating in the UK

A follow-on study, concentrating on lung cancer deaths, has been conducted extending the period of follow-up on chromium platers in the Midlands, UK, to 1995 (Sorahan et al., 1998). The earlier study is summarised in the HSE and IOH reviews - and had a follow-up period of 1946-1975. Reliable, statistically significant excess mortality from cancer of the lung was found in the earlier study. There was a positive association between increased incidence of lung cancer and duration of chrome bath work in male workers. Personal quantitative exposure data were not available. Static sampling values in the vicinity of chrome baths were mainly below 0.025 mgCrVI/m^3 (8-hour TWA) from 1973 onwards. Atmospheric concentrations before 1973 are likely to have been higher. In the 1998 study, mortality was investigated in a cohort of 1,762 (812 men, 950 women) chrome workers defined as before and followed up for the period 1946-1995 using essentially the same methods as before. Follow-up was 93.5% complete (114 of the 1762 subjects were untraced). Most job histories were obtained but no data were available on personal exposure levels or smoking histories. Workers were placed in different categories according to duration of work with chromium at chrome baths.

There were 752 deaths. The mortality in the cohort was compared with that which might be expected based on mortalities for the general population of England and Wales, taking into account age, sex and calendar year. For those workers with no exposure to chrome bath work, no

excess in lung cancer mortality was found (observed 9, SMR 66) whereas a higher SMR was calculated from the statistics for men exposed to chrome bath work (for any period) (observed 40, expected 25.4, SMR 157, 95% CI 113-214, $p<0.01$). A statistically significant increased lung cancer SMR was calculated for all male chrome workers 10-19 years after first working with Cr(VI) (observed 18, expected 8.85, SMR 203 95% CI 121-321, $p<0.01$) but other periods of follow-up did not show a statistically significant excess. Poisson regression was used to investigate risk of death from lung cancer relative to 4 categories of cumulative exposure of chrome bath work or other chrome work (none, < 1 year, 1-4 years, > or = 5 years). A significant positive statistical trend was observed for lung cancer mortality in men and cumulative duration of chrome bath work ($p<0.01$). In the case of men employed for 5 years or more in chrome bath work, the SMR for lung cancer mortality was 375 (10 observed, 2.7 expected, 95% CI 180-689, $p<0.001$). A raised SMR was also found for women workers with any chrome bath work (observed 15, expected 8.6, SMR 175, 95% CI 98-289, $p=0.06$). This study confirms the earlier findings that exposure to Cr (VI) in chrome plating work causes a significant increase in the risk of death from lung cancer. It remains impossible to establish a clear dose-response relationship for this excess risk of lung cancer.

4.1.2.8.1 Summary of carcinogenicity

Chrome plating workers exposed to chromium (VI) trioxide in aqueous solution have shown a clear excess in mortality from lung cancer. Therefore chromium (VI) trioxide should be regarded as a human carcinogen. The excess in lung cancer mortality cannot be related to particular atmospheric Cr (VI) levels in any reliable manner. These chrome plating workers were exposed specifically to a mist of Cr (VI) in aqueous acidic solution, emanating from the surface of the plating bath. The acidic nature of the entity might be a significant contributory factor in the type and onset of lesions and uptake of Cr (VI), precluding direct extrapolation of the human carcinogenic activity of the trioxide to the ammonium, sodium or potassium chromates or dichromates. With respect to the other Cr (VI) compounds under review, epidemiology data from chromate production, chromium pigment manufacture and other chromium-exposed groups showing clear increases in lung cancers cannot be specifically related to exposure to any of the Cr (VI) compounds under consideration here. However, it is highly probable that Cr (VI) ions in solution were the ultimate carcinogenic entity in these situations. Hence these epidemiological studies raise concerns for the carcinogenic potential of the other four Cr (VI) compounds covered in this review.

Animal carcinogenicity studies have been conducted on only two of the compounds covered in this review. In these studies, sodium dichromate was carcinogenic in rats, causing lung tumour production, when given by repeated long term inhalation or intratracheal instillation. In rats and mice, inhalation or intrabronchial implantation studies using chromium (VI) trioxide produced 1-2 test group animals with lung tumours where such were mainly absent among corresponding controls. Thus, in animal studies there is some evidence of respiratory tract carcinogenic activity for sodium dichromate and chromium (VI) trioxide. Similar studies in rats using other Cr (VI) compounds (not covered by this review), able to produce Cr (VI) in solution, produced carcinogenicity in the lung. Hence there is good reason from animal studies to be concerned about the carcinogenic potential of all five Cr (VI) compounds covered by this review, in terms of the inhalation route and the respiratory tract as a site of action. Data for the oral and dermal routes and carcinogenicity studies on the other compounds under consideration are not available. Chromium (VI) compounds might be expected to have potential to cause cancer on repeated oral or dermal exposure. In the case of the oral route, any systemic carcinogenic potential could be

limited by poor absorption from, and reduction to Cr (III) within the gastrointestinal tract although site of contact activity would remain an issue. Similar considerations apply to the skin.

Overall, therefore, all five Cr (VI) compounds covered by this review are considered to have proven or suspect carcinogenic potential. From the available information, and taking into account the genotoxic potential of these substances, it is not possible to identify any dose-response relationship or thresholds for this effect.

4.1.2.9 Toxicity to reproduction

Data on toxicity to reproduction are covered in the sections of the HSE Review on pages 47- 48 and 73 and the IOH Review on pages 186-190 and 252-254. Additional studies have become available on the effects of chromium (VI) on reproduction in animals when administered orally. Parenteral studies produced embryo/fetolethality and malformations but the parenteral route of exposure is not relevant for assessing potential human reproductive effects.

A poorly reported study of the course of pregnancy and childbirth in a group of women employed in a chromate production plant produced inconclusive results. Another study claimed that a group of women engaged in the production of "chromium compounds" showed a much greater incidence of pregnancy complications in comparison with a control group without occupational exposure to chromium. The type of exposure to chromium was not specified and the study is of poor quality. No conclusions can be drawn regarding any potential effects of chromium on reproduction in humans due to the poor quality of the investigations conducted.

4.1.2.10 Studies in animals

Fertility studies

The effects of potassium dichromate on male and female fertility were investigated in sexually mature (7 weeks old) Swiss mice administered this hexavalent chromium compound in drinking water (Elbetieha and Al-Hamood, 1997). Groups of 9-20 males were administered 0, 1,000, 2,000, 4,000 or 5,000 mg/l potassium dichromate equivalent to doses of approximately 0, 166, 333, 666, 833 mg/kg/day (0, 60, 120, 235, 290 mg Cr(VI)/kg/day) for 12 weeks and then mated for ten days, 1 male to 2 untreated females. The exposed males were then removed and 1 week later the females were terminated. Similarly, groups of 11-18 females were administered 0, 2,000 or 5,000 mg/l potassium dichromate equivalent to doses of approximately 0, 400, 1,000 mg/kg/day (0, 140, 350 mg Cr(VI)/kg/day) for 12 weeks and then mated for ten days, 3 females to 1 untreated male. One week after the removal of the males, the females were terminated. Number of pregnant females, total implantations, viable fetuses and resorptions were recorded. In addition, satellite groups of 10-13 males and 8-10 females administered 0, 2,000 (males only) or 5,000 mg/l potassium dichromate for 12 weeks were sacrificed at the end of the treatment. Body and reproductive organ weights were recorded in these animals. No explanation is provided in the study report concerning the variability in group size. Also, it is unclear how dose levels were selected.

At higher concentrations, the treated animals consumed less water per day compared to the control group (no more details provided). It is unclear whether or not the dose was adjusted for the reduced water consumption or if these animals received a lower dose. There were no deaths or clinical signs of toxicity in any group of male or female mice exposed. Compared to the control group, a statistically significant reduction in absolute body weight of 10% and 12% was

seen in satellite group males at 2,000 and 5,000 mg/l (the only two dose levels at which body weight was recorded), respectively. Body weight of satellite group females administered 5,000 mg/l potassium dichromate (the only dose at which body weight was recorded) was unaffected. Relative testes weights were statistically significantly increased at 2,000 (by 17.5%) and 5,000 mg/l (by 21.5%). Relative seminal vesicles and preputial gland weights were statistically significantly reduced at 5,000 mg/l only (by 27% and 34%, respectively). A statistically significant increase in relative ovarian weight (by 50%) was reported at 5,000 mg/l. It is noted that in the absence of information on the absolute organ weights, the increase seen in relative testis weight could be accounted for by the reduction in absolute body weight observed in males. It is also noted that, in the absence of histopathological examinations, it is difficult to interpret the toxicological significance of these organ weight changes.

Compared to the control groups, the percentage of pregnant unexposed females mated with treated males and of pregnant exposed females mated with untreated males was unaffected by the treatment. The mean number of implantation sites was statistically significantly reduced in females impregnated by males treated with 2,000 (6.33 versus 8.18 in the control group) and 4,000 mg/l potassium dichromate (6.86 versus 8.18), but not with the highest dose (7.84 versus 8.18). Given the absence of a dose-response relationship, the toxicological significance of this finding is uncertain. However, it is possible that at higher concentrations, the actual doses the animals received were lower than the nominal doses, due to the reduced water consumption. There were no resorptions and dead fetuses in the control group and in the females impregnated by males treated with 2,000 or 4,000 mg/l potassium dichromate. However, 3 resorptions were noted in the females impregnated by males treated with the lowest dose (1,000 mg/l). Given the absence of a clear dose-response relationship and that it is not clearly reported whether these findings occurred in one single litter or in different litters, the 3 resorptions seen at 1,000 mg/l are regarded as being incidental. A total number of 6 resorptions and of 6 dead fetuses was also observed in the females impregnated by males treated with the highest dose (5,000 mg/l). Although it is not reported whether these findings occurred in one single litter or in different litters, given the incidence, it is unlikely they occurred in one isolated litter. Hence, the fetolethality reported at this dose level (5,000 mg/l) is regarded as being treatment-related. The mean number of implantations and of viable fetuses was also statistically significantly reduced in females treated with 2,000 mg/l (7.35 versus 9.00 and 6.55 versus 8.76, respectively) and 5,000 mg/l potassium dichromate (7.44 versus 9.00 and 5.88 versus 8.76, respectively). There was also a statistically significant increase in the number of pregnant females with resorptions at 2,000 (53% versus 11%) and at 5,000 mg/l (63% versus 11%). Similarly, a total number of 37 and 14 resorptions (versus 4 in the control group) were observed at 2,000 and 5,000 mg/l, respectively.

Overall, the results of this study indicate that oral administration of potassium dichromate to mice for 12 weeks produced adverse effects on male and female fertility (reduced number of implantations) at 2,000 mg/l (333 mg/kg/day (120 mg Cr(VI)/kg/day) and 400 mg/kg/day (140 mg Cr(VI)/kg/day) in males and females, respectively) and above. These effects occurred, for the males, at dose levels at which a significant reduction in absolute body weight was noted. In the females, no effects on body weight were noted, but at the highest dose of 1,000 mg/kg/day (350 mg Cr(VI)/kg/day) there was a significant increase in relative ovarian weight. A NOAEL for these fertility effects of 1,000 mg/l (equivalent to 166 mg/kg/day potassium dichromate or 60 mg Cr(VI)/kg/day) was identified in males from this study. No NOAEL value was determined for the females as these fertility effects (reduced number of implantations) were reported even at the lowest dose tested of 2,000 mg/l (equivalent to 400 mg/kg/day potassium dichromate or 140 mg Cr(VI)/kg/day). A reduced number of viable fetuses and an increased number of resorptions were observed in females treated with 2,000 and 5,000 mg/l (400 and

1,000 mg/kg/day (140 and 350 mg Cr(VI)/kg/day)). In addition, an increased number of resorptions and dead fetuses were seen in untreated females impregnated by males given the highest dose of 5,000 mg/l (833 mg/kg/day (290 mg Cr(VI)/kg/day).

Wolfe, 1997 (NTP) has conducted a continuous breeding study to a rigorous protocol under GLP and QA conditions. Twenty/sex/group BALB/c mice were administered potassium dichromate in the diet, achieving dose levels of 0, 19.4, 38.6 and 85.7 mg/kg/day (0, 7, 14 and 30 mg Cr(VI)/kg/day). Dose levels had been chosen on the basis of a preliminary 9-week study. Exposure began 1 week before cohabitation and continued throughout the breeding phase and after separation until necropsy of the F0 animals. At initiation of treatment, animals were singly housed for 7 days. On study day 8, one male and one female from the same dose group were cohabited for 12 weeks i.e. the continuous breeding phase. Litters that were produced were counted, weighed and killed one day after birth (day 1). The total number of pups, number of live and dead, number of male and female, and total pup weight were obtained. At the end of the 12 weeks, pairs were separated and exposure continued. Any litters born after the continuous breeding phase (F1) were reared by the dam until weaning on day 21. Numbers of pups (live/dead) and weight of pups were determined at intervals from day 1 to 21. F0 animals were necropsied after the completion of weaning and terminal body weights, organ weights, sperm analysis and a range of tissues preserved. Randomly selected weanlings were kept in same sex groups until day 74. After weaning, the F1 animals received potassium dichromate in the diet at the same dose levels as given to F0 until necropsy. Dose levels achieved were 0, 22.4, 45.5, 104.9 mg/kg/day (0, 8, 16 and 37 mg Cr(VI)/kg/day). At sexual maturity (74 +/- 10 days old), twenty male and female offspring from each group were randomly assigned to breeding pairs (avoiding sibling mating) and then cohabited until copulatory plug found or day 7 whichever came first before being separated. All offspring produced were counted and weighed by sex on day 1 after birth. F1 animals were weighed at weeks 2 and 4 and food consumption measured. At necropsy of F1 animals, terminal body weights and organ weights and sperm analysis were obtained and a range of tissues retained.

There was no effect due to treatment on fertility in the F0 animals. The number of dams delivering/number cohabiting was comparable between the groups. There were no differences due to treatment in the mean number of litters/pair, number of live pups/litter, sex ratio, and absolute or adjusted live pup weight. Gestation length was not affected. No signs of toxicity were observed. However, a slight decrease (10% at week 14) in body weights occurred in F0 females at 85.7 mg/kg/day (30 mg Cr(VI)/kg/day). At necropsy, F0 liver weights were decreased by 17% (males) and 12% (females) at the highest dose level. No treatment-related gross or microscopic lesions occurred in F0 animals. The results of the sperm analyses were comparable between groups. At the highest dose level, mean pup weight was slightly less than control values (9-15%, not statistically significant) at days 14 and 21 after birth. By day 74, the difference remained at 9%. Mean average pup weights during lactation, proportion of pups born alive and survival of F1 pups was generally comparable throughout the groups. No treatment-related signs of toxicity were observed in F1 adults. There were no treatment-related effects on reproductive performance (mating index, pregnancy index, fertility index, number of live pups/litter, proportion of pups born alive, sex ratio, adjusted live pup weight and gestation length) in the F1 breeding phase. Vaginal smear results indicated that there were no effects on oestrus cyclicity. No treatment-related changes in organ weight or sperm analysis data and no treatment-related gross or microscopic lesions occurred in the F1 groups at necropsy. Live female pup weight was decreased by 11% at the highest dose level. There were no differences in F2 number of live and dead pups per litter, sex ratios or pup weights between exposed groups and controls. Overall, at the highest dose level tested at which significant toxicity was seen, 30 mg Cr(VI)/kg/day, no effects on fertility were observed in this study.

Information on effects on the testes is available from repeated oral dose studies. These studies are described in detail in Section 4.1.2.6. In the rat, testicular degeneration was observed at a dose level (40 mg/kg/day (14 mg Cr(VI)/kg/day) which caused a large decrease in body weight gain following gavage administration of sodium dichromate for 90 days. A NOAEL of 20 mg/kg/day (7 mg Cr(VI)/kg/day) was determined for effects on the testis. Other studies found no effects on the testis, following administration of potassium dichromate by the dietary route for 9 weeks. The highest dose levels in these studies were 24 mg/kg/day (8 mg Cr(VI)/kg/day) in the rat and 92 mg/kg/day (32 mg Cr(VI)/kg/day) in the mouse.

Developmental studies

In a developmental toxicity study (Trivedi et al., 1989), groups of 10, 13, 12 and 10 pregnant female ITRC-bred albino mice were administered daily 0, 250, 500 and 1,000 ppm of potassium dichromate (equivalent to doses of approximately 0, 60, 120 and 230 mg/kg/day (0, 20, 40 and 80 mg Cr(VI)/kg/day)) in drinking water during gestation from day 0 (vaginal plug identified) to day 19 when dams were sacrificed. At sacrifice, fetuses were subjected to routine external, visceral and skeletal examination, and levels of total chromium in the maternal blood, in the placenta and in the fetuses were measured.

No deaths or clinical signs of toxicity were observed in any of the treated dams. Compared to controls, a statistically significant reduction in maternal body weight gain of 21% was seen at 500 ppm, while at 1,000 ppm, a body weight loss of 4% was recorded. Body weight gain was also reduced by 18% at 250 ppm, although it did not attain statistical significance. No litters were produced at the top dose. Also, 3 females of the low-dose group and 2 females of the mid-dose group did not have any litters. A dose-related (statistically significant in the mid-and high-dose groups) increase in pre-implantation loss was seen across treated groups. There were no implantations (100% pre-implantation loss) in the dams treated with 1,000 ppm. Statistically significantly increased incidences of post-implantation losses and resorptions were observed at 250 and 500 ppm. There was also a dose-related (statistically significant in the mid-dose group) reduction in litter size at 250 and 500 ppm. Fetal weight and crown-rump length were statistically significantly reduced in the low- and mid-dose groups. No malformations or major skeletal abnormalities were observed. A statistically significant increased incidence of kinky tail and subdermal hemorrhagic patches and/or streaks on the snout, limbs, back, neck and tail was seen at 500 ppm. A statistically significantly reduced ossification in the phalangeal, sternebral, cranial, thoracic and caudal bones was observed in fetuses of dams treated with 500 ppm. Fetal cranial ossification was also significantly reduced at 250 ppm. No significant abnormalities were seen during soft tissue examinations in any of the treated groups. Total chromium levels were significantly increased above levels in the control group for the maternal blood at 500 and 1,000 ppm, for the placenta at 250 and 500 ppm and for the fetal tissues at 500 ppm.

The complete absence of implantations seen at 1,000 ppm was associated with marked maternal toxicity (body weight loss). A range of adverse effects on development was noted at 500 ppm. These effects occurred at a dose level at which there was a maternal body weight gain reduction of 21%. However, since this reduction in body weight gain can be explained by the reduced litter size and the reduced fetal weight reported at this dose level, these findings may represent a direct effect of potassium dichromate on development. At 250 ppm, adverse effects on development (increased incidence of post-implantation losses and resorptions, reduced fetal weight, decreased crown-rump length and delayed cranial ossification) were observed in the absence of significant maternal toxicity and in association with significant placental levels of total chromium. It can be concluded from the results of this study that oral administration of potassium dichromate through drinking water to pregnant mice caused fetotoxic effects even at dose levels (250 and possibly

500 ppm) at which no maternal toxicity was observed. Thus, a NOAEL value of 120 mg/kg/day (40 mg Cr(VI)/kg/day) for maternal toxicity can be identified from this study, but no NOAEL can be identified for developmental effects as adverse effects were reported even at the lowest dose tested of 60 mg/kg/day (20 mg Cr(VI)/kg/day).

Junaid et al. (1996a) exposed pregnant Swiss albino mice (10 per group) to 0, 250, 500 or 750 ppm potassium dichromate in drinking water during days 6-14 of gestation. Dams were subject to caesarean section on day 19 and fetuses examined. Based on average daily water intakes, Cr levels received were and 2.00, 3.75 and 5.47 mg/mouse/day. Based on a bodyweight of 30 g, the estimated intake of potassium dichromate was 190, 350 and 520 mg/kg/day (70, 125 and 180 mg Cr(VI)/kg/day). There were no maternal deaths or clinical signs of toxicity but weight gain was decreased at 350 and 520 mg/kg/day (125 and 180 mg Cr(VI)/kg/day) (reductions of 8.2 and 24% respectively). The number of fetuses per litter was statistically significantly decreased by 20 and 18%, fetal weight was decreased (by 13 and 20% respectively compared to controls) and the number of dead fetuses increased (3 in 2 litters, 12 in 7 litters respectively) at 350 and 520 mg/kg/day (125 and 180 mg Cr(VI)/kg/day). Post implantation loss increased to statistically significant levels of 22 and 34% at 350 and 520 mg/kg/day (125 and 180 mg Cr(VI)/kg/day). Reduced ossification, incidence of dropped wrist and subdermal haemorrhagic patches were increased at these dose levels. Overall, chromium (VI) caused fetotoxicity but not malformations at 350 mg/kg/day (125 mg Cr(VI)/kg/day), a dose level which did not produce overt signs of maternal toxicity but caused a small decrease in bodyweight gain. The NOAEL for fetal effects was 190 mg/kg/day (70 mg Cr(VI)/kg/day).

Other studies

In a study (Junaid et al., 1996b) specifically performed to assess the effect of pregestational exposure to chromium on development, groups of 15 female Swiss albino mice of proven fertility were administered daily 0, 250, 500 or 750 ppm potassium dichromate (equivalent to doses of approximately 0, 63, 119 and 174 mg/kg/day (0, 20, 40 and 60 mg Cr(VI)/kg/day) in drinking water for 20 days. The animals were then immediately mated for 24 hours with untreated males, and, subsequently, 10 pregnant females were randomly selected from each group and sacrificed on day 19 of gestation. Both ovaries were removed from the dams to determine the number of corpora lutea. Numbers of implantations and resorptions were recorded and the fetuses were subjected to routine external, visceral and skeletal examination. In addition, at sacrifice, levels of total chromium in the maternal blood, in the placenta and in the fetal tissues were measured.

No clinical signs of toxicity were observed in any of the treated females. Mortality (3/15) was noted at the top dose. Although autopsy of these animals could not establish the cause of death, given the number of deaths and the fact that they occurred at the highest dose, they are likely to be treatment-related. Body weight gain was unaffected during the treatment. However, during gestation, almost no body weight gain was seen in the top-dose dams, and a reduction in body weight gain of 14% was observed in the mid-dose dams. Compared to controls, a statistically significant reduction in the number of corpora lutea of 44% was noted at 750 ppm. Also, no implantations were seen in this group. The number of implantations was also statistically significantly reduced (by 29% of the control value) in the dams pregestationally treated with 500 ppm potassium dichromate. A dose-related (statistically significant in the mid-dose group) increase in pre-implantation loss was seen at 250 and 500 ppm. Statistically significantly increased incidences of post-implantation losses were observed at 250 and 500 ppm, and of resorptions at 500 ppm. Fetal weight and crown-rump length were statistically significantly reduced in the low- and mid-dose groups. There was also a dose-related (statistically significant

in the mid-dose group) reduction in litter size at 250 and 500 ppm. No malformations or major skeletal abnormalities were observed. A statistically significant increased incidence of kinky tail, short tail and subdermal hemorrhagic patches was seen at 500 ppm. A statistically significant reduced ossification in the parietal, interparietal and caudal bones was observed in fetuses of dams pregestationally treated with 500 ppm. Fetal caudal ossification was also significantly reduced at 250 ppm. No significant abnormalities were seen during soft tissue examinations in any of the treated groups. Total chromium levels were significantly increased above levels in the control group for the maternal blood in all the treated groups, for the placenta at 250 and 500 ppm and for the fetal tissues at 500 ppm.

Overall, the results of this study indicate that pregestational oral administration through drinking water of potassium dichromate for 20 days to female mice produced adverse effects on female fertility (reduced number of corpora lutea and/or increased pre-implantation loss) at 500 ppm (119 mg/kg/day (40 mg Cr(VI)/kg/day)) and above. Fetotoxic effects were also seen starting from the lowest dose level tested, 250 ppm (63 mg/kg/day (20 mg Cr(VI)/kg/day)). Significant maternal toxicity (mortality) was observed at 750 ppm. Body weight gain was also dramatically reduced at this dose level. However, it is noted that this reduction was mainly due to the complete absence of implantations. No significant maternal toxicity was seen at the low and mid-dose levels. Although there was a reduction in body weight gain of 14% at 500 ppm, this was accounted for by the reduced litter size and the reduced fetal weight. It is finally noted that significant levels of total chromium were found in all treated animals at sacrifice, i.e. at around 21 days after the end of the treatment. NOAEL values of 119 mg/kg/day (40 mg Cr(VI)/kg/day) and 63 mg/kg/day (20 mg Cr(VI)/kg/day) can be identified from this study for maternal toxicity and fertility effects respectively. No NOAEL can be identified for developmental effects. Developmental toxicity including increased post-implantation losses and resorptions, reduced litter size, fetal weight and crown-rump length, increased incidence of kinky tail, short tail and subdermal hemorrhagic patches, and delayed ossification of the parietal, interparietal and caudal bones, occurred even in the absence of maternal toxicity.

4.1.2.10.1 Summary of toxicity for reproduction

Human data relating to effects on reproduction are limited to poorly reported studies of female workers from which no conclusions can be drawn. There are three animal studies available which focus on fertility. Adverse effects were produced in mice receiving potassium dichromate for 12 weeks in drinking water at 333 mg/kg/day (120 mg Cr(VI)/kg/day) and 400 mg/kg/day (140 mg Cr(VI)/kg/day) and above in males and females respectively. A NOAEL of 166 mg/kg/day (60 mg Cr(VI)/kg/day) was identified in males but no NOAEL was found for females as 400 mg/kg/day was the lowest dose level tested. An increase in resorptions following treatment of males and a decrease in implantations in treated females were among the findings in this study. In another study, pregestational oral administration of potassium dichromate in drinking water to female mice produced adverse effects on fertility (reduced number of corpora lutea and increased pre-implantation loss) at 500 ppm (119 mg/kg/day (40 mg Cr(VI)/kg/day)) and above. NOAEL values of 119 mg/kg/day (40 mg Cr(VI)/kg/day) and 63 mg/kg/day (20 mg Cr(VI)/kg/day) can be identified from this study for maternal toxicity and fertility effects respectively. In a third study, also in the mouse, at 86 mg/kg/day (30 mg Cr(VI)/kg/day), the highest dose level tested, there were no effects of treatment on fertility parameters. Fetotoxicity, including post-implantation losses, has been observed in the mouse following administration of potassium dichromate in drinking water during gestation (days 0-19). Significant developmental effects occurred at the lowest dose level tested, 60 mg/kg/day (20 mg Cr(VI)/kg/day) in the absence of maternal toxicity. Therefore no developmental NOAEL was determined.

Qualitatively similar results were obtained in another study in which (350 mg/kg) potassium dichromate (125 mg Cr(VI)/kg) was administered for a shorter period, on days 6-14 of gestation. In a pregestational study in female mice, fetotoxic effects were seen starting from the lowest dose level tested, 250 ppm (63 mg/kg/day (22.1 mg Cr(VI)/kg/day)) potassium dichromate. Significant levels of total chromium were found in treated animals at sacrifice. No NOAEL could be identified for the developmental effects, which included post-implantation losses. These fetal effects may possibly be explained by the presence of chromium in the dams after the end of treatment.

Overall, highly water-soluble chromium (VI) compounds should be considered to be developmental toxicants in the mouse. These findings can be regarded as relevant to humans.

It is noted that some of the adverse effects on reproduction observed in animal studies may be related to the germ cell mutagenicity of these chromium (VI) compounds (see Mutagenicity section).

No reproductive toxicity studies are available using the inhalation or dermal routes of exposure.

4.1.3 RISK CHARACTERISATION

4.1.3.1 General aspects

This assessment deals with the manufacture of the five chromium (VI) compounds, as well as their use as source materials for other chromium (VI) and chromium (III) compounds, in wood preservatives, in metal treatments and in a number of minor uses.

The main uses of the five chromium (VI) compounds are listed in **Table 4.19**.

Table 4.19 Main uses of the five chromium (VI) compounds

Chromium (VI) compound	Use
sodium chromate	manufacture of other chromium compounds
sodium dichromate	manufacture of other chromium compounds, manufacture of wood preservation products, vitamin K manufacture, mordant in dyeing, wax manufacture and metal finishing
chromium trioxide	metal finishing, manufacture of wood preservation products, catalyst manufacture, chromium dioxide manufacture and pigment manufacture
potassium dichromate	pigment manufacture, manufacture of wood preservation products, dye manufacture, catalyst manufacture, chromium metal manufacture and colouring agent in ceramics
ammonium dichromate	magnetic tape manufacture, catalyst manufacture, mordant in dyeing and pigment manufacture

The scope of this assessment is the five chromium (VI) compounds so once the chromium (VI) has been converted to a chromium (III) substance then this is not considered further in the assessment.

The reasonable worst-case inhalation exposures are based on the 90th percentile of available measured data with professional judgement used where limited data are available.

The manufacturing process for the five chromates is largely enclosed with breaching for bagging of product and some maintenance activities. The measured exposure data indicate that inhalation exposures for operators are usually very low, with those for maintenance staff and packers slightly higher. Exposures during the manufacture of the five chromates range from none detected to 0.78 mg/m^3. A reasonable worst-case exposure is 0.02 mg/m^3.

In the manufacture of the five chromate compounds EASE predicted dermal exposures to be 0 to 0.1 mg/cm^2/day during packing operations. It was not possible to predict dermal exposures

during maintenance operations because of lack of information. PPE is worn during all manufacturing stages. PPE, properly selected and worn will significantly reduce exposure.

There are two types of chromium pigments: those that remain as chromium (VI) and those which are reduced to chromium (III). For both types, exposures usually occur during weighing and mixing of ingredients. Once they have been mixed and reacted then there is no further exposure to any of the five chromates involved in this assessment. The range of exposures is quite large, from none detected to 1.4 mg/m^3. It seems likely that the high exposures were obtained when LEV was not in use. A reasonable worst-case exposure is 0.5 mg/m^3.

Chrome tanning salts are made either by reacting sodium dichromate with sulphur gas in an enclosed process or by reacting sodium dichromate and sodium chromate with a reducing sugar. In both cases liquid chromates are used and exposures will be low as there is little potential for exposure except when liquid chromate is discharged from a road tanker into a storage vessel. The range of exposures is 0.00001 - 0.025 mg/m^3. A reasonable worst-case exposure is 0.007 mg/m^3.

Copper chrome arsenate wood preservation products are manufactured using chromium trioxide flake. Exposure can occur during weighing and mixing of reactants and during packing of the finished product. However, use is made of remote working and automatic filling lines to reduce exposures. The range of exposures reported by industry are 0.0002 to 0.06 mg/m^3. A reasonable worst-case exposure is 0.01 mg/m^3.

Potassium dichromate is used as an oxidising agent in the manufacture of chromium metal. Exposure to chromium (VI) is only likely at the start of the process, particularly during weighing, before it is converted to chromium (III). Exposures range from none detected to 0.02 mg/m^3. A reasonable worst-case exposure is 0.01 mg/m^3.

Both dry and liquid metal treatment formulations are produced, the exact contents of which tend to be kept secret. Essentially, this use of chromates is one of mixing without any reactions taking place. Exposures will occur during weighing and mixing of ingredients and during packing of the final product. The results range from none detected to 0.15 mg/m^3. The highest result was obtained when the LEV was not working. Other results at the same plant when the LEV was working indicate that in general exposures were much lower (less than 0.02 mg/m^3). A reasonable worst-case exposure would be 0.02 mg/m^3.

In the manufacture of other chromium-containing chemicals dermal exposures most often occur during weighing and charging of reactants to vessels. In the manufacture of dyestuffs dermal exposure is predicted to be 0.1-1 mg/cm^2/day. In chrome tan manufacture dermal exposures are predicted to be 0-0.1 mg/cm^2/day. When CCA is manufactured dermal exposures are predicted to be 0-0.1 mg/cm^2/day. Dermal exposures are predicted to be very low during manufacture of chromium metal. During formulation of metal treatment products dermal exposure is predicted to be either 0-0.1 mg/cm^2/day or 0.1-1 mg/cm^2/day, depending on the level of process activity. PPE is worn during the tasks involved in the manufacture of all chromium-containing compounds. PPE, properly selected and worn will significantly reduce exposure.

Inhalation exposures during use of CCA for the preservation of wood are likely to be highest when the treatment vessel's doors are opened at the end of the cycle and the treated wood is pulled out and removed to the drip area. HSE data for this process indicated that exposures are in the range of none detected to 0.009 mg/m^3. A reasonable worst-case exposure would be 0.006 mg/m^3.

Measured data for the amount of chromium (VI) on the skin were available for dermal exposures during CCA use. Dermal exposure can occur at a number of stages in the wood treatment process, particularly when the bogie containing the treated wood is unloaded, during maintenance of the treatment vessel and from contact with contaminated surfaces. Exposures ranged from 1.37 to 41.71 mg chromium (VI) on the skin. A reasonable worst-case exposure is 16.5 mg chromium (VI) on the skin. PPE is worn during all tasks involved in this process. PPE, properly selected and worn will significantly reduce exposure.

Occupational exposure to chromium (VI) during metal treatment can be from either electrolytic or passive processes. When electric current is used airborne chromium (VI) in the form of mist is generated. This mist is not generated with passive processes and so inhalation exposures during passive metal treatment will be very low. Exposure will also occur in both types of process when chromate solutions are made up and added to the treatment bath. Exposure for electrolytic metal treatment range from less than 0.001 to 0.05 mg/m^3. A reasonable worst-case exposure is 0.02 mg/m^3.

In metal treatment dermal exposures are likely to be similar for both electrolytic and passive processes. They can occur during making up of treatment solutions, adding the solution to the treatment bath, from drag out and splashing and when re-threading treated steel strips. EASE predicted dermal exposures to be 0 to 0.1 mg/cm^2/day during mixing of solutions and adding to the treatment bath, 0.1 to 1 mg/cm^2/day during re-threading of steel strips and 1 to 5 mg/cm^2/day from dragout. PPE may be worn for these tasks. PPE, properly selected and worn will significantly reduce exposure.

Chromium dioxide is used to make magnetic tapes and is made by reacting chromic acid with chromium (III) oxide. The operations likely to lead to exposure are charging of reagents and packing. Reported inhalation exposures range from 0 to 0.0084 mg/m^3. A reasonable worst-case exposure is 0.005 mg/m^3. Insufficient information was available to enable dermal exposure predictions to be made for the manufacture of magnetic tapes.

There is little information available on chromium (VI) inhalation exposures during the manufacture of montan wax and vitamin K. However, inhalation exposure during both of these processes is likely to be very low as they are mostly enclosed. Insufficient information was available to enable dermal exposure predictions to be made for the manufacture of montan wax. In the manufacture of vitamin K dermal exposure to liquid sodium dichromate is only likely to occur during road tanker unloading. The EASE prediction for this task is 0 to 0.1 mg/cm^2/day. PPE may be worn for this task. PPE, properly selected and worn will significantly reduce exposure.

Exposures to sodium dichromate during its use as a mordant in wool dyeing occur during weighing and mixing with water. Once it is in solution inhalation exposure will be negligible as sodium dichromate solution has no vapour pressure. Measured exposure data gives a range of exposures from 0.001 to 0.042 mg/m^3. A reasonable worst-case exposure is 0.52 mg/m^3.

When sodium dichromate is used as a mordant in wool dyeing dermal exposure can occur during weighing, making up of solutions and during addition of the solution to the dyeing vat. The prediction for all of these tasks is 0.1 to 1 mg/cm^2/day. PPE is worn for all of these tasks. PPE, properly selected and worn will significantly reduce exposure.

Exposures to chromium (VI) during catalyst manufacture occur when sodium dichromate solution is unloaded into storage tanks and during sampling of the reaction process. Data provided by one company show chromium (VI) exposures to be in the range 0.0001 to 0.009 mg/m^3. A reasonable worst-case exposure is 0.005 mg/m^3.

In catalyst manufacture dermal exposure to sodium dichromate solution occurs during unloading of the liquid to storage tanks and during sampling of the process. The prediction for unloading of sodium dichromate is 0 to 0.1 mg/cm^2/day. During sampling of the process dermal exposure is predicted to be very low with no direct handling and 0.1 to 1 mg/cm^2/day with direct handling. PPE may be worn for these tasks. PPE, properly selected and worn will significantly reduce exposure.

Effects assessment summary

The toxicological database for chromium (VI) (Cr(VI)) is generally extensive. Sodium chromate, dichromates of sodium, potassium and ammonium, and chromium (VI) trioxide, the substances covered in this review are all highly water-soluble hexavalent compounds.

Chromium (VI) trioxide in solution produces chromic acid, concentrated solutions that are highly acidic. Hence, of the five Cr(VI) compounds covered by the assessment, there are site-of-contact issues related to low pH that are a consideration for chromium (VI) trioxide but not for the other four.

Beyond this, the five Cr (VI) compounds will all readily dissolve in aqueous environments in the body, to release chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) ions. These two ions will co-exist, in equilibrium, regardless of the particular Cr (VI) compound involved. The chromate/dichromate ions produced from all five compounds will behave similarly in biological tissues and hence, other than the additional property of acidity and its potential influence on toxicity for chromium (VI) trioxide, the five can be treated as a common group. Furthermore, toxicological observations made with other chromium (VI) compounds that can similarly readily dissociate to produce chromate/dichromate ions in solution can be legitimately made use of in predicting the toxicity of these five compounds.

There is a reasonably good database available on the toxicokinetics of the chromium (VI) compounds under review, although there are relatively few human data. The available data indicate that generally the chromium (VI) compounds covered by this document are likely to behave in a similar manner in respect of toxicokinetics, and that the kinetic behaviour of these substances would be similar in those species studied, including humans.

Following inhalation exposure, animal studies have shown that 20-30% of the administered Cr (VI) is absorbed via the respiratory tract. Highly water-soluble Cr (VI) is poorly absorbed via the gastrointestinal tract (only 2-9% of the dose was absorbed in human studies) due to reduction to the relatively poorly absorbed Cr (III). Only limited dermal absorption takes place through intact skin, with 1-4% Cr (VI) from an aqueous solution crossing the skin in guinea pig studies.

According to results of animal testing, chromium derived from these compounds can remain in the lungs for several weeks after inhalation exposure and also becomes bound to haemoglobin in erythrocytes for the lifespan of the cells. Cr(VI) becomes reduced to Cr(III) after entering the body due to the influence of reducing agents, for example glutathione. Distribution is widespread even after a single dose and includes transfer of absorbed Cr (VI) across the placenta. Excretion occurs in urine and faeces. Repeated exposure leads to accumulation of chromium in several tissues, particularly the spleen because of uptake of senescent erythrocytes.

Case reports show that inhalation by workers of aqueous solutions of Cr (VI) mists have resulted in irritation and inflammation of the respiratory tract, with symptoms and signs including dyspnoea and cyanosis; associated airborne levels were not reported. Accidental or deliberate oral ingestion has resulted in signs and symptoms some of which are indicative of corrosive damage and deaths have been reported in numerous cases in adults. Among the survivors,

clinical manifestations of liver and kidney damage were present. There have also been cases of kidney damage and death following dermal exposure to Cr (VI). In most of these cases the skin was broken or damaged by the acidity or high temperature of the solution, facilitating Cr (VI) absorption across the skin.

The qualitative picture of acute toxicity seen in humans is supported by observations from studies in experimental animals.

Aerosols were toxic when inhaled by rats. LC_{50} values of 99 mg/m^3 (potassium dichromate) (35 mg Cr(VI)/m^3), 200 mg/m^3 (sodium and potassium dichromate) (70 mg Cr(VI)/m^3), 200 mg/m^3 (ammonium dichromate) (83 mg Cr(VI)/m^3) and 104 mg/m^3 (sodium chromate) (33 mg Cr(VI)/m^3) have been reported for male rats with a 4-hour exposure period. Similarly, an LC_{50} value of 217 mg/m^3 (113 mg Cr(VI)/m^3) for chromium (VI) trioxide has been reported for rats with a 4-hour exposure period. It is predicted that severe damage to tissues of the respiratory tract would occur at low concentrations due to the corrosive nature of this substance.

Available oral LD_{50} values for chromium (VI) trioxide were 52-113 mg/kg (27-59 mg Cr(VI)/kg) in rats and 135-175 mg/kg (70-91 mg Cr(VI)/kg) in mice. Aqueous chromium (VI) trioxide produced bleeding and ulceration of the stomach due to its corrosive properties. Oral LD_{50} values of 74 mg/kg (26 mg Cr(VI)/kg) (potassium dichromate), 59 mg/mg (23 mg Cr(VI)/kg) sodium dichromate), 55 mg/kg (23 mg Cr(VI)/kg) (ammonium dichromate) and 87 mg/kg (28 mg Cr(VI)/kg) (sodium chromate) have been reported for male rats. Female rats were more sensitive with LD_{50} values of 48 mg/kg (17 mg Cr(VI)/kg), 46 mg/kg (16 mg Cr(VI)/kg), 48 mg/kg (20 mg Cr(VI)/kg) and 40 mg/kg (13 mg Cr(VI)/kg) respectively. Toxic effects reported at necropsy included pulmonary congestion and corrosion of mucosa in the gastrointestinal tract.

Highly water-soluble Cr (VI) compounds were also toxic following skin application. In a standard dermal LD_{50} study in rabbit, the following values were determined: sodium dichromate 960 mg/kg (380 mg Cr(VI)/kg); potassium dichromate 1,150 mg/kg (410 mg Cr(VI)/kg); ammonium dichromate 1,860 mg/kg (770 mg Cr(VI)/kg) and sodium chromate 1,330 mg/kg (430 mg Cr(VI)/kg). In another study, percutaneous doses of 207 mg/kg sodium chromate (66 mg Cr(VI)/kg) and 170 mg/kg sodium dichromate (66 mg Cr(VI)/kg) produced death in guinea pigs. A dermal LD_{50} value of 57 mg/kg (30 mg Cr(VI)/kg) has been reported for chromium (VI) trioxide.

In conclusion, highly water-soluble Cr (VI) compounds are very toxic by inhalation and toxic by ingestion. The respiratory tract and the kidney are damaged by these compounds following inhalation and oral exposure respectively. Although acutely harmful or toxic by the dermal route, more severe responses may be observed due to greater uptake via the skin if there is any prior or simultaneous damage to the skin. Depending upon the pH of the Cr (VI) solution, corrosive effects can occur on contact.

Single application of highly water-soluble chromium (VI) in solution to undamaged human skin resulted in only a mild irritant response around the hair follicles. Aqueous chromium (VI) trioxide is a corrosive substance due to its low pH. In addition, when high temperature solutions of Cr (VI) are splashed onto the skin, serious burns occur. Animal data are consistent with the observations made in humans. It is not possible to determine a clear concentration-response relationship for human skin irritation from the single-exposure animal or occupational data available. Highly water-soluble chromium (VI) compounds can cause very severe skin effects under certain conditions. In workers repeatedly exposed to highly water-soluble chromium (VI), where there is some slight initial damage to the skin, ulcers can develop which constitute a

serious and persistent effect. Again, animal data are consistent with the observations made in humans. It is not possible to determine a clear concentration-response relationship for repeated-exposure human skin effects from the occupational data available and quantitative data could be misleading given the potential for severe effects resulting from repeated contamination of slightly damaged skin. Overall, highly water-soluble chromium (VI) compounds should be regarded as corrosive.

Significant damage to the eye can occur upon accidental exposure to highly water-soluble chromium (VI) compounds. Severe and persistent effects occur when there is contact with the low pH aqueous chromium (VI) trioxide or Cr (VI) solutions at high temperature. Repeated, but not single administration of highly water-soluble chromium (VI) caused severe irritation in the rabbit eye. It is not possible to determine a clear concentration-response relationship from the data available.

Symptoms of sensory irritation of the respiratory tract are known to occur among chrome plating workers exposed to a mist of aqueous chromium (VI) trioxide. Since this is corrosive, such symptoms are to be expected. No quantitative data on such irritation are available from studies of workers. No studies reporting symptoms of sensory irritation are available for the other chromium (VI) compounds. Overall, it is not possible to determine a reliable concentration-response relationship for respiratory tract irritation using the available data.

Skin sensitisation resulting from contact with Cr (VI) is relatively common in humans working with the compounds. This has been demonstrated in patch testing of contact dermatitis patients and in investigations of various occupational groups. In addition, skin sensitisation potential has been clearly demonstrated in standard and modified guinea pig maximisation tests and in the mouse ear swelling test.

Current understanding of the mechanism involved in the sensitisation indicates that Cr (III) is the ultimate hapten. Skin contact with Cr (VI) leads to penetration of Cr (VI) into the skin where it is reduced to Cr (III). There is some evidence for cross-reactivity between Cr (III) and Cr (VI); Cr (VI)-sensitised subjects may also react to Cr (III). Overall, it is not possible to reliably determine a threshold for either induction or challenge in an exposed population using the available data.

The available case reports and evidence from well-conducted bronchial challenge tests, show that inhalation of chromium (VI) compounds can cause occupational asthma. As with skin, Cr (VI)-sensitised subjects may react to Cr (III). It is not possible to determine a no-effect level or exposure-response relationship for induction or elicitation of occupational asthma.

With respect to repeated exposure, a large number of studies are available relating to exposure of workers to highly water-soluble chromium (VI), specifically sodium or potassium chromate/dichromate and chromium (VI) trioxide. The main effects reported are irritant and corrosive responses in relation to inhalation and dermal exposure. These include inflammation in the lower respiratory tract, and nasal septum perforation in the upper respiratory tract. It is not possible to relate these effects to reliable measures of Cr (VI) exposure. Although in principle a threshold dose should be identifiable, in practice the location of such a threshold is not possible from the data available. Some evidence of kidney damage has also been found among chromate production and chromium plating workers. No exposure-response data or no-effect levels are available. However, it appears that the exposure levels at which kidney toxicity occurs overlaps with the atmospheric concentrations at which respiratory tract effects have been reported.

Only limited animal repeated dose toxicity information is available. In general, the effects seen are consistent with those found in humans. Although in principle a threshold dose should be identifiable, in practice the location of such a threshold is not possible from the data available.

Inhalation of sodium chromate dust for 8 months caused deaths in mice exposed to 0.3-3.7 mg/m^3 (0.1-1.2 mg Cr(VI)/m^3). Rats appeared to be less sensitive (no deaths occurring after 16 months). Concentrations down to 0.07 mg/m^3 (0.025 mg Cr(VI)/m^3) sodium dichromate (aerosol) produced increased alveolar macrophage and spleen lymphocyte activities following a 90-day exposure in the rat. Much of this enhancement was lost at 0.57 mg/m^3 sodium dichromate (0.2 mg Cr(VI)/m^3); this dose inhibited alveolar macrophage phagocytosis. Repeated chromic acid mist (chromium (VI) trioxide) exposure produced irritant and corrosive effects in the respiratory tract at 3.5 mg/m^3 (1.8 mg Cr(VI)/m^3) and above in an 8-month study. Overall, little useful dose-response information is available.

In the rat, testicular degeneration was observed at a dose level (40 mg/kg/day (14 mg Cr(VI)/kg/day)) which caused a large decrease in body weight gain following gavage administration of sodium dichromate for 90 days. A NOAEL of 20 mg/kg/day (7 mg Cr(VI)/kg/day) was determined for effects on the testis, the only organ examined. Other studies found no significant toxicity following administration of potassium dichromate by the dietary route for 9 weeks. The highest dose levels in these studies were 24 mg/kg/day (8 mg Cr(VI)/kg/day) in the rat and 92 mg/kg/day (32 mg Cr(VI)/kg/day in the mouse.

No repeated dermal studies are available, although these substances are recognised as being corrosive on repeated dermal exposure.

Few studies of genotoxic potential in humans are available. No evidence of genotoxic activity has been found in adequately-conducted studies in circulating lymphocytes from chromium-exposed workers. In contrast, there is a vast array of genotoxicity data *in vitro* and less extensive testing in animals available. The evidence clearly indicates that highly water-soluble chromium (VI) compounds can produce significant mutagenic activity *in vitro* and *in vivo*. The chromium (VI) compounds under consideration are therefore regarded as *in vivo* somatic cell mutagens. In addition, toxicokinetic and dominant lethal data suggest that water-soluble chromium (VI) has the potential to be an *in vivo* germ cell mutagen.

Chrome plating workers exposed to chromium (VI) trioxide in aqueous solution have shown a clear excess in mortality from lung cancer. Therefore chromium (VI) trioxide should be regarded as a human carcinogen. The excess in lung cancer mortality cannot be related to particular atmospheric Cr (VI) levels in any reliable manner. These chrome plating workers were exposed specifically to a mist of Cr (VI) in aqueous acidic solution, emanating from the surface of the plating bath. The acidic nature of the entity might be a significant contributory factor in the type and onset of lesions and uptake of Cr (VI), precluding direct extrapolation of the human carcinogenic activity of the trioxide to the ammonium, sodium or potassium chromates or dichromates.

With respect to the other chromium (VI) compounds under review, epidemiology data from chromate production, chromium pigment manufacture and other chromium-exposed groups showing clear increases in lung cancers cannot be specifically related to exposure to any of the chromium (VI) compounds under consideration here. However, it is highly probable that Cr (VI) ions in solution were the ultimate carcinogenic entity in these situations. Hence these epidemiological studies raise concerns for the carcinogenic potential of the other four chromium (VI) compounds covered in this review.

Animal carcinogenicity studies have been conducted on only two of the compounds covered in this review. In these studies, sodium dichromate was carcinogenic in rats, causing lung tumour production, when given by repeated long-term inhalation or intratracheal instillation. In rats and mice, inhalation or intrabronchial implantation studies using chromium (VI) trioxide produced

1-2 test group animals with lung tumours where such were mainly absent among corresponding controls. Thus, in animal studies there is some evidence of respiratory tract carcinogenic activity for sodium dichromate and chromium (VI) trioxide. Similar studies in rats using other chromium (VI) compounds (not covered by this review), able to produce Cr(VI) in solution, produced carcinogenicity in the lung. Hence there is good reason from animal studies to be concerned about the carcinogenic potential of all five Cr (VI) compounds covered by this review, in terms of the inhalation route and the respiratory tract as a site of action. Data for the oral and dermal routes and carcinogenicity studies on the other compounds under consideration are not available. Chromium (VI) compounds might be expected to have potential to cause cancer on repeated oral or dermal exposure. In the case of the oral route, any systemic carcinogenic potential could be limited by poor absorption from, and reduction to Cr (III) within the gastrointestinal tract although site of contact activity would remain an issue. Similar considerations apply to the skin.

Overall, therefore, all five chromium (VI) compounds covered by this review are considered to have proven or suspect carcinogenic potential. From the available information, and taking into account the genotoxic potential of these substances, it is not possible to identify any dose-response relationship or thresholds for this effect.

Human data relating to effects on reproduction are limited to poorly reported studies of female workers from which no conclusions can be drawn.

There are two animal studies available which focus on fertility. Adverse effects were produced in mice receiving potassium dichromate for 12 weeks in drinking water at 333 mg/kg/day (120 mg Cr(VI)/kg/day) and 400 mg/kg/day (140 mg Cr(VI)/kg/day) and above in males and females respectively. A NOAEL of 166 mg/kg/day (60 mg Cr(VI)/kg/day) was identified in males but no NOAEL was found for females as 400 mg/kg/day was the lowest dose level tested. An increase in resorptions following treatment of males and a decrease in implantations in treated females were among the findings in this study. In another study, pregestational oral administration of potassium dichromate in drinking water to female mice produced adverse effects on fertility (reduced number of corpora lutea and increased pre-implantation loss) at 500 ppm (119 mg/kg/day (40 mg Cr(VI)/kg/day)) and above. NOAEL values of 119 mg/kg/day (40 mg Cr(VI)/kg/day) and 63 mg/kg/day (20 mg Cr(VI)/kg/day) can be identified from this study for maternal toxicity and fertility effects respectively. In a third study, also in the mouse, at 86 mg/kg/day (30 mg Cr(VI)/kg/day), the highest dose level tested, there were no effects of treatment on fertility parameters.

Fetotoxicity, including post-implantation losses, has been observed in the mouse following administration of potassium dichromate in drinking water during gestation (days 0-19). Significant developmental effects occurred at the lowest dose level tested, 60 mg/kg/day (20 mg Cr(VI)/kg/day) in the absence of maternal toxicity. Therefore no developmental NOAEL was determined. Qualitatively similar results were obtained in another study in which 350 mg/kg potassium dichromate (125 mg Cr(VI)/kg) was administered for a shorter period, on days 6-14 of gestation. In a pregestational study in female mice, fetotoxic effects were seen starting from the lowest dose level tested, 250 ppm (63 mg/kg/day (20 mg Cr(VI)/kg/day)) potassium dichromate. Significant levels of total chromium were found in treated animals at sacrifice. No NOAEL could be identified for the developmental effects which included post-implantation losses. These fetal effects may possibly be explained by the presence of chromium in the dams after the end of treatment.

Overall, highly water-soluble chromium (VI) compounds should be considered to be developmental toxicants in the mouse. These findings can be regarded as relevant to humans.

It is noted that some of the adverse effects on reproduction observed in animal studies may be related to the germ cell mutagenicity of these chromium (VI) compounds (see Mutagenicity section).

No reproductive toxicity studies are available using the inhalation or dermal routes of exposure.

4.1.3.2 Workers

The health effects of concern for the chromium (VI) compounds covered in this risk characterisation for workers are acute toxicity, skin, eye and respiratory irritation, skin sensitisation, occupational asthma, repeat dose toxicity to the respiratory tract, effects on the kidney, genotoxicity, carcinogenicity and reproductive toxicity.

A risk characterisation for each health effect of concern for chromium (VI) compounds under review is presented below.

The main route of occupational exposure is inhalation. Although dermal exposure can occur, given the corrosive nature of the chromium (VI) compounds, it is considered that measures taken to preclude substantial skin contact mean that under intended exposure conditions there would be no prospect of systemic effects arising via dermal exposure. Significant oral exposure is not expected to occur in the workplace.

Acute toxicity

The five Cr (VI) compounds under review can cause acute toxicity following single exposure by all relevant routes of exposure.

With respect to the workplace, inhalation is considered to be the most important route of exposure to these compounds as damage to the respiratory tract occurs at relatively low airborne concentrations. Animal studies have shown that inhalation of relatively high concentrations can be fatal.

With respect to inhalation, the highest reasonable worst-case 8-hour TWA occupational exposures of 0.5 mg Cr(VI)/m^3 are found in the manufacture of dyestuffs and during the use of sodium dichromate as a mordant in wool dyeing.

In the absence of data indicating a no-effect level or a lowest lethal concentration, the lowest LC_{50} value available of 35 mg Cr(VI)/m^3 (4-hour exposure) for potassium dichromate and sodium chromate in the rat has been taken as representative of these compounds.

Normally it would be appropriate to adjust the 4-hour LC_{50} value to allow a direct comparison with the 8-hour TWA workplace exposure estimate. However, given that the main health concern associated with single exposure to Cr(VI) compounds is local damage to the respiratory tract, an effect which is likely to be directly related to exposure concentration rather than dose (i.e. concentration *x* time), the 4-hour LC_{50} value will be compared directly with the 8-hour TWA exposure estimate without adjustment.

Table 4.20 Summary of the risk characterisation for acute toxicity (4 hour)

Exposure: 8-hour TWA	LC_{50} (8 hour exposure)	MOS	Conclusion
0.5 mg Cr(VI)/m^3	35 mg Cr(VI)/m^3	70	ii

This MOS, 70, is considered to be sufficiently large because:-

- The effects leading to lethality are direct and local in nature, namely damage to tissues or membranes of the respiratory tract and lungs which come into contact with Cr (VI) ions. It is considered that the relative simplicity of this process means that there is less scope for variation between humans and other species than, for example, if there was dependence on metabolism for the expression of toxicity.
- Variation in response within the human working population is not anticipated to be great, again due to the type of effect caused by these compounds.
- Considerable human experience in industry over a long historical period indicates that normal handling under occupational conditions does not lead to incidences of severe acute toxicity.

Since the MOS analysis represents a worst-case situation (lowest available LC_{50}, highest reasonable worst-case exposure), the same conclusion would apply across other occupational situations where exposure to any of the five compounds occurs. In addition to full shift exposure, there is the possibility of higher occupational exposure levels being reached over short periods of time. Tasks which involve weighing, manual tipping or transfer of solid could generate short-term peaks of airborne exposure. However, only very few exposure data are available. The higher of the two measurements available indicates that in a weighing operation exposure to 0.475 mg Cr(VI)/m^3 TWA occurred over 10 minutes. Taking into account that the reasonable worst-case 8 hour TWA exposure is 0.5 mg/m^3, a reasonable worst-case short-term exposure (3 times the 8 hour TWA value) would be 1.5 mg Cr(VI)/m^3.

Again, given the nature of the health effects, no adjustment for time is considered to be necessary and the short-term exposure estimate is compared directly with the 4-hour LC_{50} value. The resultant MOS is shown in **Table 4.21**.

Table 4.21 Summary of the risk characterisation for acute toxicity (short-term exposure period)

Exposure: 10 minute period	LC_{50}	MOS	Conclusion
1.5 mg Cr(VI)/m^3	35 mg Cr(VI)/m^3	23	iii

This MOS, 23, is considered to be insufficient, even taking into account the different exposure periods involved, given that any adverse local effects are likely to be related to exposure concentration rather than dose.

Overall, it is considered that there is no cause for concern with respect to acute toxicity in relation to full shift exposures - conclusion (ii). However, there may be concerns associated with short-term peak exposures and such exposures should be avoided – conclusion (iii).

Skin irritation, eye irritation and skin sensitisation

The five chromium (VI) compounds under review are considered to be corrosive. Severe and persistent eye and skin effects, including ulcers, have been observed in humans following single or repeated exposures. These effects have been reproduced in animals. Furthermore, there is clear evidence that the chromium (VI) compounds are skin sensitisers[4].

[4]Hexavalent chromium is present endogenously in cements and so cements are a potentially important source of exposure to Cr(VI). However, the source of Cr(VI) in cement is unclear, although there is no direct evidence that it derives from any of the five hexavalent chromium compounds covered by this assessment. Given this, no formal risk characterisation for exposure to Cr(VI) in cement has been conducted. However, owing to their soluble

Despite the amount of qualitative data available, no quantitative information of any reliability is available with respect to dose-response relationships for these endpoints. Therefore, it is not possible to calculate MOSs because of the lack of exposure-response data. However, given the type and severity of effects, uninhibited contact with these compounds is of concern. Personal protective equipment, properly selected and worn, will significantly reduce exposure.

Overall, conclusion (iii) applies to all workplace situations.

Respiratory tract sensory irritation

Respiratory tract sensory irritation has been reported in workers exposed to mists of aqueous chromium (VI) trioxide. Data on exposure-response relationships are not available. No sensory irritation data are available for the other chromium (VI) compounds under review. It is possible that they may produce similar effects, given their generally irritant properties, although the acidity of chromium (VI) trioxide might be an important contributory factor here.

Tasks which involve weighing, manual tipping or transfer of solid could generate short-term peaks of airborne exposure which could lead to respiratory tract irritation. This was considered to be a practical possibility in maintenance work, manufacture of pigments and dyes, formulation of metal treatment products and wool dyeing. The only single exposure data points available are for weighing and mixing. Although it is not possible to calculate an MOS because of the lack of dose-response relationship data, it is considered that uninhibited exposure to the compounds in these situations is of concern for respiratory tract sensory irritation. However, personal protective equipment, properly selected and worn, will significantly reduce exposure.

Conclusion (iii) therefore applies to all industrial uses, particularly the tasks of weighing, manual tipping or transfer of solid, in maintenance work, manufacture of pigments and dyes, formulation of metal treatment products and wool dyeing.

Occupational asthma

Inhalation of chromium (VI) compounds can cause occupational asthma, a serious condition. From the data available, it is not possible to determine a no-effect level or exposure-response relationship for either induction of the hypersensitive state or elicitation of an asthmatic response. Thus it is not possible to calculate a formal MOS. However, given the severe nature of this effect, and that once the hypersensitive state is induced in an individual then even low-levels of exposure might induce an asthmatic response, there is cause for concern across all industrial uses and thus conclusion (iii) applies.

Repeated exposure toxicity - local and systemic

Inflammation in the lower respiratory tract and nasal septum perforation can occur following repeated inhalation exposure to Cr(VI) in the workplace. In the case of nasal septum damage, an important confounding factor is the possible transfer of Cr (VI) in solution from fingers to the

chromate content, cements have been shown to cause skin sensitisation and allergic reactions in occupationally exposed workers. Therefore, although no formal risk characterisation has been conducted for this source of exposure, nevertheless it should be recognised that there are concerns for skin sensitisation in workers exposed to Cr(VI) in cement. A labelling requirement has been included in Annex VB of Directive 1999/45/EC to address this concern. The European Commission (EC) has also recently been exploring the need for restrictions on the use of Cr(VI) in cement. Although there is support from most Member States, at this stage it is unclear how soon the EC will bring forward formal proposals, but an agreement has been reached to ask the Commission to take all necessary effort for the rapid introduction of further measures within the framework of Directive 76/769/EEC.

nose due to poor personal hygiene. Kidney toxicity related to occupational exposure has also been reported. No reliable exposure-response data or no-effect levels are available for respiratory tract or kidney effects. The available animal data are also not suitable for use in such calculations.

Thus, it is not possible to formally calculate an MOS for the respiratory tract or kidney effects because no NOAELs have been identified. Hence it is not possible to assess risk under contemporary working conditions. To be able to do this, one would require further exposure-response information for respiratory tract and kidney effects. Hence conclusion (i) is appropriate.

By the oral route, adverse effects on the testes were observed following exposure to 14 mg Cr(VI)/kg/day (as sodium dichromate) in a repeated exposure oral gavage study in the rat in which the testis was the only tissue examined. As this effect has potential consequences for fertility, the risk characterisation for this endpoint is considered under the section 'Toxicity to reproduction'.

Mutagenicity

The five chromium (VI) compounds under review are considered to be *in vivo* mutagens with the potential to induce both somatic and germ cell mutations. Since it is not possible to identify a threshold level of exposure below which there would be no risk to human health, it is not possible to derive a toxicologically valid MOS. The consequences of mutagenicity can be serious and it is not possible to exclude the risk of such effects being expressed at occupational levels of exposure, and therefore there is cause for concern across all industrial uses, leading to conclusion (iii).

Carcinogenicity

Chromium (VI) trioxide is regarded as a human carcinogen. Evidence from epidemiological studies has shown an excess in lung cancer. However, this excess cannot be related to particular airborne Cr (VI) levels in any reliable manner. The evidence for the other four chromium (VI) compounds is less clear, but on balance, taking into account all the human and animal evidence, together with their genotoxicity profile, they are also likely to have carcinogenic potential, at least at the site of contact. In the workplace this is of concern particularly for inhalation exposure. From the available information and taking into account the mutagenic properties of these compounds, it is not possible to identify any dose-response relationship or thresholds for this effect. Thus it is not therefore possible to calculate a formal MOS. However, given the serious and irreversible nature of the effect and the fact that it is not possible to exclude the risk of this being expressed at occupational levels of exposure, there is cause for concern across all industrial uses, leading to conclusion (iii). The same conclusion is reached by applying a quantitative approach to the risk characterisation of this endpoint as shown in the Annex to this document.

Toxicity to reproduction

Effects on fertility

Adverse effects on fertility have been found in studies in mice following repeated oral exposure. In addition, adverse effects on the testes have been seen following repeated oral exposure in the rat.

In relation to the fertility studies in mice, in males the NOAEL was 60 mg Cr(VI)/kg/day from a drinking water study. Toxicokinetic data indicate that around 2-9% absorption occurs by the oral route. If it is assumed that 5% of the substance is absorbed from the gastrointestinal tract, then the oral dose of 60 mg Cr(VI)/kg/day would be equivalent to 3 mg Cr(VI)/kg/day as an internal body burden. With respect to inhalation, the highest reasonable worst-case 8-hour TWA occupational exposure of is 0.5 mg Cr(VI)/m^3. If it is assumed that a 70 kg person breathes in 10 m^3 of air during an 8-hour day, then this level of exposure would equate to a body burden of 0.07 mg Cr(VI)/kg/day, if all was absorbed. However, toxicokinetic data indicate that absorption of Cr (VI) from the respiratory tract for these compounds is around 20-30%. If it is assumed that 25% is absorbed, then this gives a body burden of 0.02 mg Cr(VI)/kg/day. Comparing this body burden with the adjusted internal dose of 3 mg Cr(VI)/kg/day, gives an MOS of approximately 150. Considering the LOAEL, adverse effects (reduced implantations) were seen at 120 mg Cr(VI)/kg/day. Allowing for 5% absorption by the oral route, this is equivalent to an internal dose of 6 mg Cr(VI)/kg/day, which is a factor of 300 below the estimated worker exposure.

These MOSs for male fertility are considered to be sufficient, even allowing for potential toxicokinetic and toxicodynamics differences between species. Thus, conclusion (ii) would appear to be appropriate. However, it should be noted that effects on the testes have been identified following repeated oral exposure in the rat. A NOAEL of 7 mg Cr(VI)/kg was identified, which is consistent with the findings of a more extensive study in the rat in which no effects were seen at the highest dose of 8 mg Cr(VI)/kg/day. Toxicokinetic data indicate that around 2-9% absorption occurs by the oral route. If it is assumed that 5% of the substance is absorbed from the gastrointestinal tract, then the oral dose of 7 mg Cr(VI)/kg/day would be equivalent to 0.35 mg Cr(VI)/kg/day as an internal body burden. With respect to inhalation the highest reasonable worst-case 8-hour TWA occupational exposure is 0.5 mg Cr(VI)/m^3. Using the same assumptions as previously, this equates to a body burden of 0.02 mg Cr(VI)/kg/day. Comparing this body burden with the internal rat NOAEL of 0.35 mg Cr(VI)/kg/day, gives an MOS of 17. Comparison with the LOAEL results in a margin of 34 below the dose level at which partial degeneration in germinal cells was seen.

This MOS is considered insufficient, for a number of reasons. In calculating the internal dose for the rat, an oral absorption of 5% has been assumed, based on the midpoint of the range of oral absorption, 2 - 9%. If the lower end of this range were assumed i.e. 2%, rather than the midpoint, then the MOS based on the internal rat NOAEL would be at least 2-fold lower than that calculated above. In addition, the underlying mechanism for the testes effects is unknown. There is no evidence to indicate that humans would be different from rodents in relation to expression of this hazardous property, nor is there any evidence to indicate the relative sensitivity of humans and rodents for such an effect. Therefore the results in the rat are assumed to be relevant to humans. In relation to the route of exposure, the NOAEL is based on an oral gavage study, resulting in the delivery of a bolus dose to the systemic circulation. There is no significant first-pass metabolism of Cr (VI), although reduction of Cr (VI) to Cr (III) is likely to occur to some extent in the liver. Although oral gavage dosing is likely to result in faster delivery to the systemic circulation than that resulting from workplace inhalation exposure, nevertheless the MOS does not provide a sufficient margin to address the remaining uncertainties.

Overall, an MOS of 17 is insufficient to provide reassurance that adverse effects would not be expressed in humans, taking into account potential differences in toxicokinetics and toxicodynamics between rodents and humans. Therefore, for testicular effects, conclusion (iii) is reached.

In relation to effects on female fertility, no effects were seen at the highest dose tested in a continuous breeding dietary study in the mouse, 30 mg Cr(VI)/kg/day. In another study in which female mice were exposed to Cr (VI) (as potassium dichromate) in the drinking water prior to mating, an adverse effect on fertility (reduction in implantations) was seen at a dose level of 40 mg Cr(VI)/kg/day; a NOAEL of 20 mg Cr(VI)/kg/day was identified from this study. Using the same reasoning and assumptions as above, the highest NOAEL of 30 mg Cr(VI)/kg/day represents an internal dose of about 1 mg Cr(VI)/kg/day. For a worst-case scenario, the inhalation exposure body burden for a worker is 0.02 mg Cr(VI)/kg/day, giving an MOS of 50 based on the NOAEL. Exposures are 100 fold lower than the dose level giving rise to adverse effects.

An MOS of 50 is not sufficient for this endpoint for a number of reasons. In calculating the internal dose for the rat, an oral absorption of 5% has been assumed, based on the midpoint of the range of oral absorption, 2 - 9%. If the lower end of this range were assumed i.e. 2%, rather than the midpoint, then the MOS based on the internal mouse NOAEL would be at least 2-fold lower than that calculated above. In addition, the underlying mechanism for the adverse effects of fertility is unknown. There is no evidence to indicate that humans would be different from rodents in relation to expression of this hazardous property, nor is there any evidence to indicate the relative sensitivity of humans and rodents for such an effect. Therefore the results in the rat are assumed to be relevant to humans. In addition, the findings are consistent with the germ cell mutagenicity of Cr (VI). Finally, these effects were seen in studies using dietary or drinking water administration. In terms of dose delivery, this route of exposure is comparable with workplace inhalation exposure and thus there is no reason to assume that the findings would be different following inhalation exposure.

Overall, an MOS of 50 is insufficient to provide reassurance that adverse effects on female fertility would not occur, taking into account toxicokinetic and toxicodynamic differences between species. Conclusion (iii) is reached.

Effects on development

Significant developmental effects were found following administration of chromium (VI) by the oral route. No NOAEL could be identified in these studies. The lowest LOAEL was 20 mg Cr(VI)/kg/day from a drinking water study in the mouse, equivalent to a body burden of 1 mg/kg/day, assuming absorption of 5% from the gastrointestinal tract. With respect to inhalation exposure of workers, the highest reasonable worst-case 8-hour TWA of 0.5 mg Cr(VI)/m^3 is equivalent to a body burden of 0.02 mg Cr(VI)/kg/day, based on the same assumptions as previously. This gives an MOS of 50.

This MOS is insufficient to provide reassurance that adverse effects on development would not occur, for the reasons given above in relation to effects on female fertility and additionally, as the MOS is calculated on the basis of a LOAEL rather than a NOAEL. Overall, conclusion (iii) is reached.

Table 4.12 lists the conclusions reached for the endpoints of concern from the risk characterisation for workers. The conclusions are reached for all workplaces.

Table 4.22 Conclusions of the risk characterisation for workers

Endpoint of concern	Conclusion
acute toxicity (full shift exposures)	ii
acute toxicity (short-term peak exposures)	iii
skin and eye irritation	iii
respiratory tract sensory irritation	iii
skin sensitisation	iii
occupational asthma	iii
repeated dose toxicity– local and systemic	
local effects on respiratory tract	i
systemic effects – kidney	i
mutagenicity	iii
carcinogenicity	iii
fertility	iii
developmental toxicity	iii

4.1.3.3 Consumers

Consumer exposure to Cr (VI) from the five chromates under review is considered to be relevant only in the case of copper chrome arsenate (CCA) treated wood. There are no other known products used by consumers where exposure to the five chromates will occur.

CCA treatment of wood involves solutions that contain either sodium dichromate or chromium trioxide as the Cr (VI) source. The exposure will be infrequent, maybe no more than once a year, although it might be of several days' duration. Full details of the assumptions made in the modelling can be found in the consumer exposure section (4.1.1.3). Estimates do not include any allowance for the wearing of protective equipment. However, it can be predicted that exposure will be reduced by the wearing of gloves which is likely due to the more physical hazards of handling wood.

Consideration was given in the consumer exposure assessment to the possibility of exposure to Cr (VI) from handling wood that was still wet following CCA treatment. As indicated in the exposure assessment, such a possibility should be prevented by legislative controls (in the UK, a condition of the approval of the use of the preservative under The Control of Pesticides Regulations, 1986 is that only dry treated wood may be sold to consumers). In view of this, no exposure assessment has been derived for this scenario and thus no risk characterisation will be performed. However, although no formal risk characterisation is appropriate, it should be recognised that if consumer exposure to Cr (VI) from wet treated wood did occur, there would be concerns for human health, for all relevant endpoints.

Toxicokinetic studies indicate that absorption varies for the different routes and this has been taken account of when calculating body burden values.

Acute toxicity

The risk characterisations for acutely toxic effects of Cr (VI) for the consumer exposure scenarios described in Section 4.1.1.3 are presented below.

No human toxicity data exist for acute effects for these 5 compounds. The available animal data is used for the risk characterisations, although data from any one particular animal species for all five chromates is not available. Therefore the lowest available toxicological values have been used assuming that the value will not be lower for the chromate to which the consumer is exposed. NOAELs are not available for acute exposure so LD_{50} values have been used to derive the margins of safety.

Handling of CCA treated wood (adults)

Consumers may buy CCA treated wood for use outdoors e.g. building fences. The exposure estimates and resultant MOSs for single exposure toxicity as a result of handling CCA treated wood during fence building are given in **Table 4.23**.

Table 4.23 MOS for acute toxicity during the handling of CCA treated wood

Exposure Cr(VI)		LD_{50}		Margin of Safety		Conclusion	
inhalation	dermal	inhalation**	dermal*	inhalation	dermal	inhalation	dermal
13 µg/m³	1.6 µg/kg	35 mg/m³	1.2 mg/kg	2,700	750	ii	ii

* LD_{50} (dermal) of 30 mg Cr(VI)/kg in the rabbit for sodium trioxide, adjusted for 4% absorption.
** LC_{50} (inhalation) of 35 mg Cr(VI)/m³ in the rat for sodium dichromate

When CCA treated wood is used to install a fence there are very high margins of safety for acute effects. The level of wood dust (5 mg/m^3, equivalent to 13 µg/m^3 Cr(VI)) assumed in the consumer exposure section is a very worst-case scenario. It is anticipated that even higher margins of safety would be achieved if measured data were available. Hence conclusion (ii) is reached.

Contact with CCA treated wood (children)

Wooden playing structures may be installed in children's outdoor play areas and may be treated with CCA products to prolong the lifetime of the wood. This exposure scenario looks at the potential transfer of chromium content from the surface of the wood onto the skin based on a 5-year old child playing on a wooden surface. The exposure estimates and resultant MOSs for single exposure toxicity as a result of contact with CCA treated wooden playing structures are given in **Table 4.24**.

Table 4.24 MOSs for acute toxicity as a result of contact with CCA treated wooden playing structures

Exposure Cr(VI)		LD_{50} (mg/kg)		Margin of Safety		Conclusion	
oral	dermal	oral*	dermal**	oral	dermal	oral	dermal
0.02 µg/kg	0.08 µg/kg	0.65	1.2	32,500	15,000	ii	ii

* LD_{50} (oral) of 13 mg Cr(VI)/kg in the rat for sodium chromate, adjusted for 5% absorption.
** LD_{50} (dermal) of 30 mg Cr(VI)/kg in the rabbit for sodium trioxide, adjusted for 4% absorption.

It can be seen that the MOSs for oral and dermal exposure are at least 4 orders of magnitude. It should also be noted that again the exposure estimates are worst-case scenario and that actual exposure levels of Cr (VI) would most likely be lower due to weathering of the wood and the Cr

(VI) being reduced to Cr (III). This would lead to even higher MOS values and therefore conclusion (ii) is reached.

Irritation

Cr (VI) compounds are severe skin, eye and respiratory irritants (see Section 4.1.3.1).

Skin and eye

Severe and persistent skin and eye effects have been reported in humans following single or repeated exposures to Cr (VI) compounds. However, there is no reliable information available on the concentration-response relationship for these endpoints. Given the nature of the potential exposure scenarios for consumers and the very low concentrations to which they are exposed on infrequent occasions, it is considered that there is no cause for concern for these endpoints. Therefore, conclusion (ii) is reached for all uses.

Respiratory system

There is no reliable data available on respiratory irritation and a concentration-response relationship cannot be determined. It is not possible to quantify what the effect would be to a consumer from exposure to wood dust from using CCA treated wood. Cr (VI) is known to cause respiratory irritation amongst plating workers exposed to a mist of aqueous chromium trioxide, although no quantitative data is available. However, the concentrations to which consumers would be exposed are very low. In addition, as outlined in the consumer exposure section (4.1.1.3) it is unlikely that available chromium in CCA treated wood that consumers use would be available as Cr (VI). It is more likely to be available as Cr (III) and there is evidence to support this (Nygren et al., 1992).

Due to the very low concentrations at which exposure occurs, conclusion (ii) is reached.

Sensitisation

Skin sensitisation resulting from contact with Cr (VI) is common in humans. It is not possible to determine a threshold for induction or challenge in an exposed population using the available data. It is, therefore, not possible to quantify the risk from consumer exposures. However, exposure during handling CCA treated wood is considered to be negligible. It will be to very low concentrations of chromates, in low volumes and by means which may not result in systemic exposure. Therefore the risk of sensitisation is also considered low and conclusion (ii) is reached.

Repeated dose toxicity

The available information on repeated dose toxicity is summarised in section 4.1.3.1. For humans there are reports of irritant and corrosive responses in relation to inhalation and dermal exposure in workers exposed to highly water-soluble chromium (VI), specifically sodium or potassium chromate/dichromate and chromium (VI) trioxide. Although in principle a threshold dose should be identifiable, in practice the location of such a threshold is not possible from the data available. Some evidence of kidney damage has also been found among chromate production and chromium plating workers. No exposure-response data or no-effect levels are available. However, it appears that the exposure levels at which kidney toxicity occurs overlaps with the atmospheric concentrations at which respiratory tract effects have been reported.

By the oral route, adverse effects on the testes were observed following exposure to 14 mg Cr(VI)/kg/day (as sodium dichromate) in a repeated exposure oral gavage study in the rat in which the testis was the only tissue examined. As this effect has potential consequences for fertility, the risk characterisation for this endpoint is considered under the section 'Toxicity to reproduction'.

The limited animal repeated dose toxicity information available is, in general, consistent with the effects reported in humans. Again, although in principle a threshold dose should be identifiable, in practice the location of such a threshold is not possible from the data available. Overall, little useful dose-response information is available and calculated risk characterisations are not possible for exposure via any route.

Using a qualitative approach, one can observe that the consumer use of CCA treated wood, during which residual exposure of an adult can occur is not likely to be repeated very often and each activity is not likely to last more than a couple of days. Exposure is low and a large proportion of the Cr (VI) is reduced to Cr (III). Given these circumstances, conclusion (ii) is proposed in regard to repeated dose toxicity for the handling of CCA treated wood.

For exposure of children playing on wooden structures, although the exposure may be repeated frequently, the estimated body burdens calculated for a worst-case scenario are very low. In addition, it is expected that as the wood is exposed to weathering, levels of Cr (VI) will continually decrease. Overall conclusion (ii) is reached.

Genotoxicity

There is no known threshold below which there is no risk from the genotoxic potential of these chromate compounds. Conclusion (iii) is therefore reached for all scenarios. However, modelling of consumer exposure indicates low daily intakes, and hence, the concern for human health for this endpoint is low.

Carcinogenicity

There is no known threshold below which there is no risk from the carcinogenic potential of these chromate compounds. Conclusion (iii) is therefore reached for all scenarios. However, modelling of consumer exposure indicates low daily intakes, and hence, the concern for human health for this endpoint is low.

Toxicity to reproduction

Effects on fertility

Adverse effects on fertility have been found in studies in mice following repeated oral exposure. In addition, adverse effects on the testes have been seen following repeated oral exposure in the rat.

In relation to the fertility studies in mice, in males the NOAEL was 60 mg Cr (VI)/kg/day from a drinking water study, equivalent to 3 mg Cr (VI)/kg/day as an internal body burden. The estimated body burden for a consumer installing a fence using CCA treated wood is 1.63 μg Cr(VI)/kg ($1.63 \cdot 10^{-3}$ mg/kg). Comparing this body burden with the adjusted internal dose of 3 mg Cr (VI)/kg/day, gives an MOS of approximately 1,900.

Effects on the testes have been identified following repeated oral exposure in the rat. A NOAEL of 7 mg Cr(VI)/kg was identified, which is consistent with the findings of a more extensive study

in the rat in which no effects were seen at the highest dose of 8 mg Cr(VI)/kg/day. The oral dose of 7 mg Cr (VI)/kg/day is equivalent to 0.35 mg Cr (VI)/kg/day as an internal body burden. Comparing this body burden with the estimated body burden of $1.63 \cdot 10^{-3}$ mg/kg for a consumer installing a fence from CCA treated wood gives an MOS of 220.

These MOSs are considered to be sufficient, even allowing for potential toxicokinetic and toxicodynamics differences between species and considering that consumer exposure is likely to be infrequent. Thus conclusion (ii) is appropriate.

In relation to effects on female fertility, no effects were seen at the highest dose tested in a continuous breeding dietary study in the mouse, 30 mg Cr(VI)/kg/day. In another study in which female mice were exposed to Cr(VI) (as potassium dichromate) in the drinking water prior to mating, an adverse effect on fertility (reduction in implantations) was seen at a dose level of 40 mg Cr(VI)/kg/day; a NOAEL of 20 mg Cr(VI)/kg/day was identified from this study. The highest NOAEL of 30 mg Cr(VI)/kg/day represents an internal dose of about 1 mg Cr(VI)/kg/day. Comparing this body burden with the estimated body burden of $1.63 \cdot 10^{-3}$ mg/kg for a consumer installing a fence (dry wood) gives an MOS of about 600. This is considered to be sufficient, even allowing for potential toxicokinetic and toxicodynamics differences between species and thus conclusion (ii) is reached.

In terms of children exposed via wooden play structures, consideration should be given to possible adverse effects on the testes. Comparing the body burden at the NOAEL (0.35 mg/kg) with the estimated body burden for a child playing on a CCA treated wooden structure (0.1 μg/kg), the resultant MOS is ~ 3,500. This is considered to be sufficient, given that the exposure estimate is based on worst-case assumptions, and that it is expected that as the wood ages and is exposed to weathering, levels of Cr (VI) will continually decrease. Therefore conclusion (ii) is reached.

Effects on development

Significant developmental effects were found following administration of chromium (VI) by the oral route. No NOAEL could be identified in these studies. The lowest LOAEL was 20 mg Cr(VI)/kg/day from a drinking water study in the mouse, equivalent to a body burden of 1 mg/kg/day, assuming absorption of 5% from the gastrointestinal tract. Comparing this body burden with the estimated body burden of $1.63 \cdot 10^{-3}$ mg/kg for a consumer installing a fence using CCA treated wood gives an MOS of about 600. This is considered to be sufficient, even allowing for potential toxicokinetic and toxicodynamics differences between species and thus conclusion (ii) is reached.

A risk characterisation for effects on the developing fetus as a result of maternal exposure is not relevant for children exposed via wooden play structures.

4.1.3.3.1 Summary of risk characterisation for consumers

Table 4.25 Summary of risk characterisation for handling CCA treated wood

Endpoint	MOS	Conclusion
Acute toxicity – inhalation - dermal	2,700 750	li ii
Irritation – Skin and eye Irritation – Respiratory system	n/a n/a	li ii
Sensitisation	n/a	ii
Repeated dose toxicity	n/a	ii
Mutagenicity	Not applicable	iii
Carcinogenicity	Not applicable	iii
Toxicity to reproduction		
Effects on fertility	220-1,900	ii
Effects on development	600	ii

n/a: not available

Table 4.26 Summary of risk characterisation for children

Endpoint	MOS	Conclusion
Acute toxicity – oral - dermal	32,500 15,000	li ii
Irritation – Skin and eye Irritation – Respiratory system	n/a	ii
Sensitisation	n/a	ii
Repeated dose toxicity	n/a	ii
Mutagenicity	Not applicable	iii
Carcinogenicity	Not applicable	iii
Toxicity to reproduction		
Effects on fertility	3,500	ii
Effects on development	Not applicable	ii

4.1.3.4 Indirect exposure via the environment

Although endpoints of concern for the relevant chromium (VI) compounds include acute toxicity, skin, eye and respiratory irritancy, skin sensitisation and occupational asthma, it is considered that these are not relevant for risk characterisation for exposure via the environment, which is mainly low-level, repeated exposures via the oral route. Where estimates of MOSs are possible, these have been calculated for the highest environmental exposure scenario, manufacture of chrome tanning salts, as described in section 4.1.1.4. Exposure is by the oral route. In calculating MOSs, no adjustment for absorption has been made; these exposure estimates are compared directly with the NOAELs and LOAELs derived from the relevant animal studies. Repeated dose toxicity (systemic)

The available information on repeated dose toxicity is summarised in section 4.1.3.1. There are no data available on effects following oral exposure to humans. By the oral route, adverse effects on the testes were observed following exposure to 14 mg Cr(VI)/kg/day (as sodium dichromate) in a repeated exposure oral gavage study in the rat in which the testis was the only tissue examined. As this effect has potential consequences for fertility, the risk characterisation for this endpoint is considered under the section 'Toxicity to reproduction'.

Genotoxicity

There is no known threshold below which there is no risk from the genotoxic potential of these chromate compounds. Conclusion (iii) is therefore reached for all scenarios. However, modelling of exposure via the environment indicates low daily intakes, and hence, the concern for human health for this endpoint is low.

Carcinogenicity

There is no known threshold below which there is no risk from the carcinogenic potential of these chromate compounds. Conclusion (iii) is therefore reached for all scenarios. However, modelling of exposure via the environment indicates low daily intakes, and hence, the concern for human health for this endpoint is low.

Fertility and developmental toxicity

Adverse effects on fertility have been found in studies in mice following repeated oral exposure. In addition, adverse effects on the testes have been seen following repeated oral exposure in the rat.

In relation to the fertility studies in mice, in males the NOAEL was 60 mg Cr(VI)/kg/day from a drinking water study. Comparing this with the highest estimated uptake of 11 μg/kg/day (0.011 mg/kg/day; arising from manufacture of chrome tanning salts) gives an MOS of approximately 5,400. This MOS is considered to be sufficient, even allowing for potential toxicokinetic and toxicodynamics differences between species.

However, it should also be noted that effects on the testes have been identified following repeated oral exposure in the rat. A NOAEL of 7 mg Cr(VI)/kg was identified, which is consistent with the findings of a more extensive study in the rat in which no effects were seen at the highest dose of 8 mg Cr(VI)/kg/day. Comparing this with the estimated environmental uptake of 11 μg/kg/day (0.011 mg/kg/day) gives an MOS of about 600. The LOAEL for effects on the testes is 14 mg Cr(VI)/kg/day, which are about 1,300 higher than the estimated uptake. These MOSs are considered to be sufficient to provide reassurance that adverse effects would not occur, even allowing for toxicokinetic and toxicodynamic differences between species. Conclusion (ii) is reached.

In relation to effects on female fertility, no effects were seen at the highest dose tested in a continuous breeding dietary study in the mouse, 30 mg Cr(VI)/kg/day. In another study in which female mice were exposed to Cr (VI) (as potassium dichromate) in the drinking water prior to mating, an adverse effect on fertility (reduction in implantations) was seen at a dose level of 40 mg Cr(VI)/kg/day; a NOAEL of 20 mg Cr(VI)/kg/day was identified from this study. Comparing the highest NOAEL of 30 mg Cr(VI)/kg/day with the highest estimated uptake of 0.011 mg/kg/day results in a MOS of about 2,700. This MOS is considered to be sufficient to provide reassurance that adverse effects would not occur, even allowing for toxicokinetic and toxicodynamic differences between species. Conclusion (ii) is reached.

Significant developmental effects were found following administration of chromium (VI) by the oral route. No NOAEL could be identified in these studies. The lowest LOAEL was 20 mg Cr(VI)/kg/day from a drinking water study in the mouse. This gives an MOS of about 1,800 when compared with the estimated uptake of 0.011 mg/kg/day. Although based on a LOAEL, nevertheless, this MOS is considered to be of sufficient magnitude to provide reassurance that adverse effects on development would not occur. This is because the estimated exposure is likely to over-estimate the actual exposure, as conversion of Cr (VI) to Cr (III) is expected to occur under the vast majority of environmental conditions. Overall, conclusion (ii) is reached.

Table 4.27 Risk characterisation of indirect exposure via the environment (for effects on fertility and developmental toxicity)

	Body burden	**Effects on fertility**		**Developmental toxicity**	
Toxicity	mg/kg bw/day	NOAEL = 7 mg Cr(VI)/kg/day		LOAEL = 20 mg Cr(VI)/kg/day	
		MOS	Conclusion	MOS	Conclusion
Scenario					
Chrome tanning salts	0.011	600	(ii)	1,800	(ii)

Large margins of safety for both effects on fertility and developmental toxicity are obtained for the scenario with the highest estimated uptake. Consequently conclusion (ii) is reached for both endpoints and all scenarios.

4.1.3.5 Combined exposure

For a combined exposure, consideration is given to a consumer who is also exposed indirectly via the environment. The worst-case scenario would be that of someone living in the vicinity of a plant producing chrome tanning salts (0.011 mg/kg), and who installs a fence using CCA treated wood (1.63 μg/kg). This would lead to a total exposure of 0.013 mg/kg.

For all endpoints of concern, the calculated MOSs are high and conclusion (ii) or, where appropriate, (iii) has been concluded for consumers and for humans exposed indirectly via the environment. The combination of consumer exposure with indirect exposure via the environment does not produce significantly higher total exposures and therefore conclusion (ii) or, where appropriate, (iii) also applies to combined exposure.

4.2 HUMAN HEALTH (PHYSICO-CHEMICAL PROPERTIES)

The physico-chemical properties of sodium, ammonium and potassium dichromate, chromium trioxide and sodium chromate are well known and there is a general consensus as to the values of the particular physico-chemical parameter relating to each substance.

Ammonium dichromate is flammable and can self ignite at about 180°C and above to give a self sustaining and very exothermic reaction. It does not meet the criteria for a class 1 explosive.

All of the compounds are corrosive, particularly chromium trioxide which can form chromic acid in the presence of moisture. However, given the level of control in manufacture and use the risks from physico-chemical properties are small.

Overall risk assessment for physico-chemical properties:

Conclusion (ii) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already.

5 RESULTS

5.1 INTRODUCTION

The production of the five hexavalent chromium compounds begins with the chromium ore, chromite, $MgFe^{II}(Fe^{III}CrAl)_2O_4$. Chromite ore is mined in Russia, the Philippines, southern Africa and Finland. The first step in the manufacture of the compounds is the extraction of the chromium as sodium chromate through the high temperature alkaline oxidation of ground ore using kilns. The vast majority of sodium chromate produced is converted into sodium dichromate, and the other compounds are produced either directly or indirectly from this.

Europe is a net exporter of chromium (III) and chromium (VI) products, but localised importing may occur from outside the EU. After taking into account these exports and imports, the amounts of the substances used in the EU are estimated to be 17,000 tonnes of chromium trioxide and 25,000 tonnes of dichromates (as sodium dichromate dihydrate).

The main uses of the chromium (VI) compounds covered by this assessment are: manufacture of other chromium compounds (sodium chromate, chromium trioxide and sodium dichromate are used in this way); manufacture of wood preservation products (sodium dichromate, chromium trioxide, potassium dichromate); vitamin K manufacture (sodium dichromate); as a mordant in dyeing (sodium dichromate, ammonium dichromate); wax manufacture (sodium dichromate); metal finishing (sodium dichromate, chromium trioxide); catalyst manufacture (chromium trioxide, potassium dichromate, ammonium dichromate); pigment and/or dye manufacture (chromium trioxide, potassium dichromate, ammonium dichromate); chromium metal manufacture (potassium dichromate); colouring agent in ceramics (potassium dichromate); magnetic tape manufacture (ammonium dichromate).

5.2 ENVIRONMENT

The environmental assessment addresses the life cycle of the chromium (VI) substances under the following areas:

- Production
- Pigment production
- Chromium oxide production
- Tanning salts
- Wood preservative formulation
- Wood preservative application
- Treated wood in use
- Metal treatment formulation
- Metal treatment - electroplating, passivating, anodising, brightening
- Mordant dyeing

In addition the following processes are not considered to have significant releases to the environment: chromium metal production; chromium dioxide production; and Montan wax production. Use of chromium (VI) compounds in the oxidation of sulphur dyes is also discussed, but not assessed as this no longer occurs in Europe.

Releases from the production of the substances and the use areas listed above are calculated, based on a combination of specific data and default assumptions. The assessment uses the added

risk approach, and considers only the impact of the added chromium released from these processes. In the environment, the main fate process for chromium (VI) is expected to be reduction to chromium (III) in most environments. The assessment is based on the concentrations of chromium (VI) immediately after release, with the exception of the terrestrial compartment where reduction to chromium (III) is expected to be rapid. Effect data for all chromium (VI) compounds have been combined, as the species present in the environment following releases are expected to be the same irrespective of the source compound.

The PNEC for chromium (VI) for the aquatic compartment is derived using the statistical extrapolation method, combined with an assessment factor to take account of the extent and quality of the available database. The PNEC for sediment is estimated using the partitioning method as there are only limited data for sediment organisms. For the terrestrial compartment a PNEC for chromium (III) is derived, also using the statistical extrapolation method together with an assessment factor.

5.2.1.1 Results

Conclusion (i) There is a need for further information and/or testing.

This conclusion applies to sediment for all areas except for mordant dyeing. The effect concentration used in the risk characterisation is derived from data for aquatic organisms, and could be refined with data for sediment dwelling organisms. Although there may be value in trying to establish the relative sensitivity of sediment and aquatic organisms, measures to reduce water concentrations as a result of the assessment will also lead to reduced sediment levels.

This conclusion also applies to indirect exposure of predators through the mussel-based food chain, for all areas except production, wood preservative application and use in mordant dyeing. Further work could be done to test whether the mussel-based food chain is of concern, for example through further investigation of the uptake of chromium into organisms other than fish, characterisation of the nature of the chromium in organisms and consideration of the toxicity of chromium in other forms to organisms consuming prey containing chromium. However it should be noted that reductions in the emissions of chromium (VI) to water will reduce the estimated levels in biota as well.

At present it is not proposed to carry out any further work, but to await the development of risk reduction measures.

Conclusion (ii) There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

For the aquatic compartment this conclusion applies to use in mordant dyeing, and to production (two sites only).

For sediment this conclusion applies to use in mordant dyeing.

For wastewater treatment plants, this conclusion applies to production, wood preservative application, anodising and use in mordant dyeing.

For the terrestrial compartment, this conclusion applies to production and to use in mordant dyeing.

This conclusion also applies to all areas for the air compartment and for indirect exposure of predators though the fish-based food chain.

Conclusion (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

This conclusion applies to all use areas for the aquatic and terrestrial compartments, with the exception of use in mordant dyeing (both compartments) and production (terrestrial only, although the conclusion only applies to one production site for the aquatic). It also applies to wastewater treatment plants for all use areas, with the exception of production, wood preservative application, anodising and use in mordant dyeing.

5.3 HUMAN HEALTH

5.3.1 Human health (toxicity)

The toxicological database for chromium (VI) (Cr(VI)) is generally extensive.

Following inhalation exposure, animal studies have shown that 20-30% of the administered Cr (VI) is absorbed via the respiratory tract. Highly water-soluble Cr (VI) is poorly absorbed via the gastrointestinal tract (only 2-9% of the dose was absorbed in human studies) due to reduction to the relatively poorly absorbed Cr (III). Only limited dermal absorption takes place through intact skin, with 1-4% Cr (VI) from an aqueous solution crossing the skin in guinea pig studies. According to results of animal testing, chromium derived from these compounds can remain in the lungs for several weeks after inhalation exposure and also becomes bound to haemoglobin in erythrocytes for the lifespan of the cells. Cr(VI) becomes reduced to Cr(III) after entering the body due to the influence of reducing agents, for example glutathione. Distribution is widespread even after a single dose and includes transfer of absorbed Cr (VI) across the placenta. Excretion occurs in urine and faeces. Repeated exposure leads to accumulation of chromium in several tissues, particularly the spleen because of uptake of senescent erythrocytes.

A range of health hazards is associated with exposure to these Cr (VI) compounds. There are concerns for acute toxicity by all routes of exposure, corrosivity, skin sensitisation, asthmagenicity, repeated exposure toxicity, genotoxicity, carcinogenicity and reproductive toxicity.

5.3.1.1 Workers

Conclusion (i) There is a need for further information and/or testing.

Conclusion (i) is reached for repeated dose toxicity to the respiratory tract and the kidney. It is not possible to formally calculate an MOS for these effects since no NOAELs have been identified. Hence it is not possible to assess risk under contemporary working conditions. Further exposure-response information for respiratory tract and kidney effects is required.

Conclusion (ii) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied.

Conclusion (ii) is reached for acute toxicity for full shift exposures since MOS values indicate there is no cause for concern.

Conclusion (iii) There is a need for limiting the risks: risk reduction measures which are already being applied shall be taken into account.

In view of the genotoxic and carcinogenic properties of these Cr (VI) compounds, there are concerns for all exposure scenarios. Conclusion (iii) is reached for these endpoints. In addition, there are concerns for acute toxicity as a result of short-term peak exposures, skin and eye irritation, respiratory tract sensory irritation, skin sensitisation, occupational asthma and reproductive toxicity (fertility and developmental toxicity). Conclusion (iii) is also reached for these endpoints.

5.3.1.2 Consumers

Conclusion (ii) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied.

Conclusion (ii) is reached for all endpoints other than mutagenicity and carcinogenicity for the handling of CCA treated wood, both for adults and for children exposed via wooden playing structures.

Conclusion (iii) There is a need for limiting the risks: risk reduction measures which are already being applied shall be taken into account.

Conclusion (iii) is reached for mutagenicity and carcinogenicity because no threshold below which there would be no risk to human health can be identified for these endpoints. However, modelling of consumer exposure indicates low daily intakes. Therefore, the concern for human health for this endpoint is low.

No formal risk characterisation has been conducted for consumer exposure to wet CCA treated wood. In the UK the supply of wood not fully dried following CCA treatment is prohibited as a condition of approval under the Control of Pesticides Regulations (1986). Similar controls may already exist in all other Member States. However, if specific controls are not available in each Member State, then there would be concerns for all relevant human health endpoints.

5.3.1.3 Humans exposed indirectly via the environment

Conclusions are presented for both local and regional scenarios together.

Conclusion (ii) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied.

Conclusion (ii) is reached for all endpoints other than mutagenicity and carcinogenicity.

Conclusion (iii) There is a need for limiting the risks: risk reduction measures which are already being applied shall be taken into account.

Conclusion (iii) is reached for mutagenicity and carcinogenicity because no threshold below which there would be no risk to human health can be identified for these endpoints. However, modelling of exposure via the environment indicates low daily intakes. Therefore, the concern for human health for this endpoint is low.

5.3.1.3.1 Combined exposure

The combination of consumer exposure with indirect exposure via the environment does not produce significantly higher total exposures than those calculated for the separate individual

contributions and therefore conclusion (ii) or, where appropriate, (iii) also applies to combined exposure.

5.3.2 Human health (risks from physico-chemical properties)

Conclusion (ii) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already.

Given the level of control in manufacture and use the risks from physico-chemical properties are small.

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ABBREVIATIONS

ADI	Acceptable Daily Intake
AF	Assessment Factor
ASTM	American Society for Testing and Materials
ATP	Adaptation to Technical Progress
AUC	Area Under The Curve
B	Bioaccumulation
BBA	Biologische Bundesanstalt für Land- und Forstwirtschaft
BCF	Bioconcentration Factor
BMC	Benchmark Concentration
BMD	Benchmark Dose
BMF	Biomagnification Factor
BOD	Biochemical Oxygen Demand
bw	body weight / *Bw*, *bw*
C	Corrosive (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
CA	Chromosome Aberration
CA	Competent Authority
CAS	Chemical Abstract Services
CEC	Commission of the European Communities
CEN	European Standards Organisation / European Committee for Normalisation
CEPE	European Committee for Paints and Inks
CMR	Carcinogenic, Mutagenic and toxic to Reproduction
CNS	Central Nervous System
COD	Chemical Oxygen Demand
CSTEE	Scientific Committee for Toxicity, Ecotoxicity and the Environment (DG SANCO)
CT_{50}	Clearance Time, elimination or depuration expressed as half-life
d.wt	dry weight / dw
dfi	daily food intake
DG	Directorate General
DIN	Deutsche Industrie Norm (German norm)
DNA	DeoxyriboNucleic Acid
DOC	Dissolved Organic Carbon
DT50	Degradation half-life or period required for 50 percent dissipation / degradation
DT90	Period required for 90 percent dissipation / degradation
E	Explosive (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
EASE	Estimation and Assessment of Substance Exposure Physico-chemical properties [Model]

EbC50	Effect Concentration measured as 50% reduction in biomass growth in algae tests
EC	European Communities
EC10	Effect Concentration measured as 10% effect
EC50	median Effect Concentration
ECB	European Chemicals Bureau
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECVAM	European Centre for the Validation of Alternative Methods
EDC	Endocrine Disrupting Chemical
EEC	European Economic Communities
EINECS	European Inventory of Existing Commercial Chemical Substances
ELINCS	European List of New Chemical Substances
EN	European Norm
EPA	Environmental Protection Agency (USA)
ErC50	Effect Concentration measured as 50% reduction in growth rate in algae tests
ESD	Emission Scenario Document
EU	European Union
EUSES	European Union System for the Evaluation of Substances [software tool in support of the Technical Guidance Document on risk assessment]
F(+)	(Highly) flammable (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
FAO	Food and Agriculture Organisation of the United Nations
FELS	Fish Early Life Stage
foc	Organic carbon factor (compartment depending)
GLP	Good Laboratory Practice
HEDSET	EC/OECD Harmonised Electronic Data Set (for data collection of existing substances)
HELCOM	Helsinki Commission -Baltic Marine Environment Protection Commission
HPLC	High Pressure Liquid Chromatography
HPVC	High Production Volume Chemical (> 1000 tonnes/annum)
IARC	International Agency for Research on Cancer
IC	Industrial Category
IC50	median Immobilisation Concentration or median Inhibitory Concentration
ILO	International Labour Organisation
IPCS	International Programme on Chemical Safety
ISO	International Organisation for Standardisation
IUCLID	International Uniform Chemical Information Database (existing substances)
IUPAC	International Union for Pure and Applied Chemistry
JEFCA	Joint FAO/WHO Expert Committee on Food Additives
JMPR	Joint FAO/WHO Meeting on Pesticide Residues

Koc	organic carbon normalised distribution coefficient
Kow	octanol/water partition coefficient
Kp	solids-water partition coefficient
L(E)C50	median Lethal (Effect) Concentration
LAEL	Lowest Adverse Effect Level
LC50	median Lethal Concentration
LD50	median Lethal Dose
LEV	Local Exhaust Ventilation
LLNA	Local Lymph Node Assay
LOAEL	Lowest Observed Adverse Effect Level
LOEC	Lowest Observed Effect Concentration
LOED	Lowest Observed Effect Dose
LOEL	Lowest Observed Effect Level
MAC	Maximum Allowable Concentration
MATC	Maximum Acceptable Toxic Concentration
MC	Main Category
MITI	Ministry of International Trade and Industry, Japan
MOE	Margin of Exposure
MOS	Margin of Safety
MW	Molecular Weight
N	Dangerous for the environment (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC
NAEL	No Adverse Effect Level
NOAEL	No Observed Adverse Effect Level
NOEL	No Observed Effect Level
NOEC	No Observed Effect Concentration
NTP	National Toxicology Program (USA)
O	Oxidising (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
OC	Organic Carbon content
OECD	Organisation for Economic Cooperation and Development
OEL	Occupational Exposure Limit
OJ	Official Journal
OSPAR	Oslo and Paris Convention for the protection of the marine environment of the Northeast Atlantic
P	Persistent
PBT	Persistent, Bioaccumulative and Toxic
PBPK	Physiologically Based PharmacoKinetic modelling

PBTK	Physiologically Based ToxicoKinetic modelling
PEC	Predicted Environmental Concentration
pH	logarithm (to the base 10) (of the hydrogen ion concentration $\{H^+\}$
pKa	logarithm (to the base 10) of the acid dissociation constant
pKb	logarithm (to the base 10) of the base dissociation constant
PNEC	Predicted No Effect Concentration
POP	Persistent Organic Pollutant
PPE	Personal Protective Equipment
QSAR	(Quantitative) Structure-Activity Relationship
R phrases	Risk phrases according to Annex III of Directive 67/548/EEC
RAR	Risk Assessment Report
RC	Risk Characterisation
RfC	Reference Concentration
RfD	Reference Dose
RNA	RiboNucleic Acid
RPE	Respiratory Protective Equipment
RWC	Reasonable Worst-Case
S phrases	Safety phrases according to Annex IV of Directive 67/548/EEC
SAR	Structure-Activity Relationships
SBR	Standardised birth ratio
SCE	Sister Chromatic Exchange
SDS	Safety Data Sheet
SETAC	Society of Environmental Toxicology And Chemistry
SNIF	Summary Notification Interchange Format (new substances)
SSD	Species Sensitivity Distribution
STP	Sewage Treatment Plant
T(+)	(Very) Toxic (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
TDI	Tolerable Daily Intake
TG	Test Guideline
TGD	Technical Guidance Document
TNsG	Technical Notes for Guidance (for Biocides)
TNO	The Netherlands Organisation for Applied Scientific Research
ThOD	Theoritical Oxygen Demand
UC	Use Category
UDS	Unscheduled DNA Synthesis
UN	United Nations
UNEP	United Nations Environment Programme

US EPA	Environmental Protection Agency, USA
UV	Ultraviolet Region of Spectrum
UVCB	Unknown or Variable composition, Complex reaction products of Biological material
vB	very Bioaccumulative
VOC	Volatile Organic Compound
vP	very Persistent
vPvB	very Persistent and very Bioaccumulative
v/v	volume per volume ratio
w/w	weight per weight ratio
WHO	World Health Organisation
WWTP	Waste Water Treatment Plant
Xn	Harmful (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)
Xi	Irritant (Symbols and indications of danger for dangerous substances and preparations according to Annex II of Directive 67/548/EEC)

Appendix A Summary of aquatic toxicity data for sodium chromate

This Appendix reports the available aquatic toxicity data for sodium chromate. However, there are several test results available for the related potassium chromate. Although potassium chromate is not covered by this risk assessment report, this toxicity data may also be useful for the analysis of the toxicity of sodium chromate in the risk assessment. For this reason, toxicity data for potassium chromate have also been reported in this Appendix. These data are identified in the comments field of the valuation. Unless otherwise stated in this comments field, the data refer to sodium chromate.

Values which have been used in the risk assessment report are highlighted with light grey shading. The following paragraphs provide some information about the selection process; these apply to the overall data set for chromium (VI) and not all comments apply to data in this appendix.

For short term test results, the values selected are the lowest for each species which come from tests with a validity marking of I or II. In some cases a number of valid results may have been produced by one study, using different experimental conditions (for example, hardness, salinity and temperature). For properties such as temperature and salinity the test conditions closest to the 'real' environment have been chosen (so avoiding high or low temperatures, and preferring tests at salinities similar to sea water); for hardness, the lowest test result is preferred as a range of hardness is found in natural waters. These 'rules' have been applied flexibly so as to allow interpretation of the individual studies.

For long term tests, all data from validity marking I and II have been selected, but some studies with marking IIIb have also been included. Multiple values have been taken from some studies, where a number of different endpoints were measured (for example, mortality, reproduction and growth). Where several measures of the same endpoint are reported in one study, values from longer exposure periods are generally preferred, with the exception of algal studies where the maintenance of exponential growth conditions is considered.

The further treatment of the long term data to derive the PNEC is described in the main risk assessment report. In some cases, notes on data not used in the PNEC derivation have also been included in the comments on the tests in the appendix

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Table A.1 Summary of ecotoxicity data for sodium (and potassium) chromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp. (°C)	Val.[h]	Test details	Reference
FISH - freshwater - short-term studies													
Gambusia affinis	mosquito fish	adult females	24h-TLm[e]	241[f]	n	static	7.7- 8.6		<100	20-22	IV	No. of organisms: 10 fish/concentration in 15 litres of solution. Test concentrations: 10, 18. 32, 56, 100, 180, 320, 560 and 1,000 mg/l as N, plus control. The substance was weighed directly into the test tanks. Dilution water: Used pond water with a high turbidity (260-280 ppm). Aeration was used to maintain the dissolved oxygen level and the disperse the turbidity-producing soil. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Tail-rot disease was seen in the holding tank. The fish were treated with medication prior to use.	Wallen et al, 1957
			48-h TLm[e]	161[f]	n	static	7.7-8.6		<100	20-22	IV		
			96-h TLm[e]	135[f]	n	static	7.7-8.6		<100	20-22	IV		
Lepomis macrochirus	bluegill	5 cm	96h-LC_{50}	132.9	m	flow	7.1-8.3	20-44	30-550	22.5	II	No. of organisms: 10 per concentration in 6.7 litres of solution. The test was carried out twice. Test concentrations: Test 1 used 37.6, 62.8, 119.8, 181.0 and 289.0 mg Cr/l, plus control. Test 2 used 66.8, 109.6, 119.8, 331.2 and 525.2 mg Cr/l, plus control. Dilution water: Tap water. The dissolved oxygen level was >6.6 mg/l throughout the test. The concentration of total Cr in the dilution water was reported to be 0.1 mg Cr/l. Control response: 80% survival in test 1 and 100% survival in test 2. Comments: Substance tested was potassium chromate.	Cairns Jr. et al, 1981
Lepomis macrochirus	bluegill	20-35 g	24h-TLm[e]	298[f]	n	static	8.1	75-150	60-120	22.5	IV	No. of organisms: Number of fish/replicate was 6. 2 replicates were run, each of 12 litres. Test concentrations: Number of concentrations not given. A control was run. Dilution water: Reconstituted fresh water. The water was continuously aerated to maintain the dissolved oxygen level. The Cr concentration in the dilution water was not given. Control response: Not given. There appear to have been some problems with the initial survival of the fish in the holding tanks. Comments:	Abegg, 1950

Table A.1 continued overleaf

Table A.1 continued Summary of ecotoxicity data for sodium (and potassium) chromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Lepomis macrochirus	bluegill	0.96 g	96h-LC50	120	n	static		44		20	II	No. of organisms: 10 fish/replication, 2 replicates/ concentrations. Loading was 10 fish per 5 gallon jar (large fish limited to 5 per tank). Test concentrations: Not given. Dilution water: Synthetic soft water. Continuously aerated. Dissolved oxygen was 5-9 mg/l throughout the test. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Substance tested was potassium chromate. Similar results for potassium dichromate chromate (LC50 = 113 mg/l for all three sizes of fish). Test carried out with small (3.9 cm), medium (6.1 cm) and large (14.2 cm) fish: LC50 was similar with all fish. A similar or the same LC50 for potassium chromate of 168 mg/l was reported by Patrick et al (1968).	Cairns Jr. and Scheier, 1959
		2.8 g	96h-LC50	168	n	static		44		20	II		
		54.3 g	96h-LC50	147	n	static		44		20	II		
Lepomis macrochirus	bluegill		96h-LC50	182	m		8.0-8.2	75-105	50-60		II	No. of organisms: 10 animals/replicate, 2 replicates/ concentration. Loading was 10 organisms in 10 litres of solution. Test concentrations: 55, 100, 125, 150, 200, 250, 300 mg/l plus a control. Dilution water: Moderately hard reconstituted water. Dissolved oxygen was 7.0-9.0 mg/l. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Substance tested was potassium chromate. Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. The pH of the test solution decreased with increasing Cr concentration. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. A similar 96h-LC50 of 154 mg/l was obtained with potassium dichromate.	Jop et al, 1987
Lepomis macrochirus	bluegill	12-14 day old	96h- LC_{50}	183	m	static		72-80			II	No. of organisms: 10 organisms/replicate, 2 replicates/concentration. Test concentrations: 5 concentrations plus control. Dilution water: Reconstituted water. Dissolved oxygen levels and Cr concentrations in the dilution water are not given. Control response: No mortality in controls. Comments: Substance tested was potassium chromate. Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013 and 1978, EPA/600/4/78/012]. Concentrations analysed by atomic absorption spectrometry (total Cr) and Cr(VI) using diphenylcarbazide-colourimetric procedure (Cr(VI) persisted throughout tests with little conversion of Cr(VI) to Cr(III)). Result is mean of 3 tests. The range of 96h-LC_{50}s was 148-201 mg Cr/l.	Dorn et al, 1987

Table A.1 continued overleaf

Table A.1 continued Summary of ecotoxicity data for sodium (and potassium) chromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Lepomis macrochirus	bluegill	1-9 g	96h- TLm[e]	170		static	7.5-8.8	45	37	20	II	No. of organisms: 10 fish/replicate, 2 replicates/ concentration. The loading was 10 fish in 20.4 litres of solution. Test concentrations: 86, 113, 131, 150, 174, 210 and 233 mg/l plus controls. Dilution water: Reconstituted dilution water. Water was continuously aerated throughout the test and the dissolved oxygen was >60% of saturation. Concentration of Cr in dilution water not reported Control response: No deaths occurred. Comments: Substance tested was potassium chromate. A 96h-TLm of 113 mg/l was obtained with potassium dichromate at pH 6.0-6.8.	Trama and Benoit, 1960
Morone saxatilis	striped bass	63 day old	96h-LC_{50}	28	n	static	8.1	40	30	20	II	No. of organisms: 10 fish/concentration in 15 litres of solution. Test concentrations: Used a logarithmic series of concentrations, plus control. Dilution water: Natural soft and hard waters. Brackish test media prepared by addition of Instant Ocean sea salt to well water. The dissolved oxygen level and the concentration of Cr in the dilution water is not given. Control response: Mortality did not exceed 10%. Comments: Tests conducted according to a standard ASTM method "The annual book of ASTM standards; standard practice for conducting acute toxicity tests with fishes, macroinvertebrates and amphibians. American Society for Testing and Materials, ASTM E729-80, 1980".	Palawski et al, 1985
			96-h LC_{50}	38	n	static	7.9	285	262	20	II		
			96h-LC_{50}	58	n	static	7.9	455 and 1‰	270	20	IIIb		
Oncorhynchus mykiss	rainbow trout	0.1-0.3 g	*96h-LC50*	0.57	n		6.9	1.55 meq/l		12	IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given Control response: Not given. Comments: Few experimental details are available. 50 to 200 fold increase in toxicity was observed when pH decreased from 7.9 to 6.9.	Hogendoorn-Roozemond et al, 1978

Table A.1 continued overleaf

Table A.1 continued Summary of ecotoxicity data for sodium (and potassium) chromate to fish.

Species	Common name	Lifestage	*Endpoint*	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Oncorhynchus mykiss	rainbow trout	0.1-0.3 g	*96h-LC50*	0.57	n		6.9	1.55 meq/l		12	IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given Control response: Not given. Comments: Few experimental details are available. 50 to 200 fold increase in toxicity was observed when pH decreased from 7.9 to 6.9.	Hogendoorn-Roozemond et al, 1978
Oncorhynchus mykiss	rainbow trout	0.2 g (4 month old)	*96h-LC50*	3.4	m	flow	6.5	80	92	12	II	No. of organisms: 12 fish/concentration. Small fish were tested in 20 litres of solution. Fish exceeding 6.0 g were tested in 60 litres of solution. Test concentrations: One control and five treatment levels. Dilution water: Tap water. The dissolved oxygen level was always >90% of saturation. The Cr concentration of the dilution water were not given. Control response: Not given. Comments: The Cr(VI) concentration in the test solutions was checked daily by the diphenylcarbazide colourimetirc method. Increased sensitivity to Cr(VI) in younger fish at all pHs. The toxicity increased with decreasing pH. At pH 7.8 morphological changes associated with acute Cr(VI) toxicity were found in gills, kidney, stomach. These changes were restricted to gills at pH 6.5.	Van Der Putte et al. 1981b
			96h-LC50	7.6	m	flow	7.0	80	92	12	II		
			96h-LC50	12.2	m	flow	7.8	80	92	12	II		
		1.9 g (7 month old)	*96h-LC50*	7.5	m	flow	6.5	80	92	12	II		
			96h-LC50	12.8	m	flow	7.0	80	92	12	II		
			96h-LC50	27.3	m	flow	7.8	80	92	12	II		
		6.0 g (7 month old)	*96h-LC50*	15.6	m	flow	6.5	80	92	12	II		
			96h-LC50	29.5	m	flow	7.0	80	92	12	II		
			96h-LC50	53.2	m	flow	7.8	80	92	12	II		
		13.1 g (8 month old)	*96h-LC50*	13.0	m	flow	6.5	80	92	12	II		
			96h-LC50	25.9	m	flow	7.0	80	92	12	II		
			96h-LC50	46.8	m	flow	7.8	80	92	12	II		
		25.0 g (9 month old)	*96h-LC50*	20.2	m	flow	6.5	80	92	12	II		
			96h-LC50	45.0	m	flow	7.0	80	92	12	II		
			96h-LC50	65.5	m	flow	7.8	80	92	12	II		
Pimephales promelas	fathead minnow	1-2g	*48h-TLm*	60.4	n	static	7.5	20	18	25	II	No. of organisms: 5 fish/replicate, 2 replicates/ concentration. The fish loading was 5 fish in 10 litres of solution. Test concentrations: 5 concentrations plus control. A logarithmic series was used. Dilution water: Soft water was a mixture of 5 parts natural limestone spring water with 95 parts distilled, demineralised water. Dissolved oxygen was >4 mg/l throughout the test. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Substance tested was potassium chromate. Used test protocol recommended by APHA[9] (1960 version). During the test the pH of the solution often fell with time. The pH was always within the range tolerated by the species.	Pickering and Henderson, 1966
			96h-TLm	45.6	n	static	7.5	20	18	25	II		

Table A.1 continued overleaf

Table A.1 continued Summary of ecotoxicity data for sodium (and potassium) chromate to fish.

Species	Common name	Lifestage	*Endpoint*	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Pimephales promelas	fathead minnow		*96h- LC50*	46	m		7.7-7.9	75-105	50-60	20±2	II	No. of organisms: 10 animals/replicate, 2 replicates/ concentration. Loading was 10 organisms in 2 litres of solution. Test concentrations: 10, 20, 30, 35, 45, 50 mg/l plus control. Dilution water: Moderately hard reconstituted water. Dissolved oxygen was 7.0-9.0 mg/l. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Substance tested was potassium chromate. Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. The LC_{50} value reported is the mean of three determinations. A similar 96h-LC_{50} of 34 mg/l was obtained with potassium dichromate.	Jop et al, 1987
FISH - saltwater - short-term studies													
Cyprinodon variegatus	sheepshead minnow		96h- LC_{50}	21.4	m	static		20‰			II	No. of organisms: 10 organisms/replicate, 2 replicates/concentration. Test concentrations: 5 concentrations plus control. Dilution water: Reconstituted water. Dissolved oxygen levels and Cr concentrations in the dilution water are not given. Control response: 0-5% mortality in controls. Comments: Substance tested was potassium chromate. Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013 and 1978, EPA/600/4/78/012]. Concentrations analysed by atomic absorption spectrometry (total Cr) and Cr(VI) using diphenylcarbazide-colourimetric procedure (Cr(VI) persisted throughout tests with little conversion of Cr(VI) to Cr(III)). Result is mean of 4 tests. The range of 96h-LC_{50}s was 16.3-26.8 mg Cr/l.	Dorn et al, 1987

Table A.1 continued overleaf

Table A.1 continued Summary of ecotoxicity data for sodium (and potassium) chromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Cyprinodon variegates	sheepshead minnow		96h- LC50	25	m		8.4	20‰	300-400		II	No. of organisms: 10 animals/replicate, 2 replicates/ concentration. Loading was 10 organisms in 2 litres of solution. Test concentrations: 10, 20, 25, 30, 45, 50 mg/l plus control. Dilution water: Reconstituted sea water. Dissolved oxygen was 7.0-9.0 mg/l. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Substance tested was potassium chromate. Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. The LC50 value reported is the mean of two determinations. A similar 96h-LC50 of 25 mg/l was obtained with potassium dichromate.	Jop et al, 1987
Gasterosteus aculeatus	stickleback		96h- LC50	35	m		8.0-8.1	5‰	350-380		II	No. of organisms: 10 animals/replicate, 2 replicates/ concentration. Loading was 10 organisms in 10 litres of solution. Test concentrations: 20, 35, 60, 75 and 100 mg/l plus control. Dilution water: Reconstituted sea water, diluted to give a salinity of 5‰. Dissolved oxygen was 7.0-9.0. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Substance tested was potassium dichromate. Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. A similar 96h-LC50 of 33 mg/l was obtained with potassium dichromate.	Jop et al, 1987

Table A.1 continued overleaf

Table A.1 continued Summary of ecotoxicity data for sodium (and potassium) chromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
FISH - freshwater - long-term studies													
Oncorhynchus mykiss	rainbow trout	embryo to juvenile	LOEC (%hatch; <20% effect)	2.0	m	flow	6.5	80	92	12	II	No. of organisms: Loading rate was 2-3 litres/g fish. Various developmental stages were used. For the embryo to juvenile test, 100 eyed-embryo/concentration were used. After hatch, the alevins were reduced to 50/conc. For the alevin to juvenile test, 50 alevins/concentration were used. For the tests using yearling trout, 25 fish/concentration were used. Test concentrations: 0.02, 0.2 and 2.0 mg Cr/l, plus control. Dilution water: Tap water. The water was gently aerated to maintain the dissolved oxygen level. The Cr concentration in the dilution water was not given. Control response: In the embryo to juvenile test, % hatch was 98-100% and survival was 82%. In the alevin to juvenile study, the survival was 78-79%. In the test using yearling trout survival was 100% Endpoint: Survival and % hatch. Comments: Only three, widely-spaced concentrations used. This means that the actual concentration causing no effects is not well defined. Measured test concentrations of Cr(VI) did no vary by more than 5% from nominal values using the diphenylcarbazide colourimetric method. In the embryo to juvenile test, the % hatch was unaffected at pH 7.8 at any concentration, but was slightly reduced (84%) at 2.0 mg Cr/l at pH 6.5. At both pHs, survival was reduced compared with controls at 2.0 mg Cr/l (32% survival at pH 7.8 and 0% survival at pH 6.5). Survival was also reduced at 0.2 mg Cr/l at pH 6.5 (survival was 40%). No effects on survival were seen at 0.2 mg Cr/l at pH 7.8 and 0.02 mg Cr/l at pH 6.5. Growth was unaffected at any Cr treatment at any pH. In the alevins to juvenile test no effects on growth was seen at any concentration at any pH. At pH 7.8, survival was similar to controls at 0.02 and 0.2 mg Cr/l, but was 44% at 2 mg Cr/l. At pH 6.5, survival was again similar to controls at 0.02 and 0.2 mg Cr/l, but was 0% at 2.0 mg Cr/l. In the experiments using yearling rainbow trout, mortality (30%) occurred at 2 mg Cr/l at pH 6.5. No significant mortality occurred at any other concentration or at pH 7.8. The statistical significance of the results is not always clear.	Van Der Putte et al. 1982a
			NOEC (hatch)	>2.0	m	flow	7.8	80	92	12	II		
			32 week NOEC (survival)	0.02	m	flow	6.5	80	92	12	IIIb		
			32 week NOEC (survival)	0.2	m	flow	7.8	80	92	12	IIIb		
			32 week NOEC (growth)	>2	m	flow	6.5	80	92	12	II		
			32 week NOEC (growth)	>2	m	flow	6.5	80	92	12	II		
		alevins to juvenile	32 week NOEC (survival)	0.2	m	flow	6.5	80	92	12	IIIb		
			32 week NOEC (survival)	0.2	m	flow	7.8	80	92	12	IIIb		
			32 week NOEC (growth)	>2	m	flow	6.5	80	92	12	II		
			32 week NOEC (growth)	>2	m	flow	7.8	80	92	12	II		
		yearling	12 week NOEC (survival)	0.2	m	flow	6.5	80	92	12	IIIb		
			12 week LOEC (survival; 30% effect)	2.0	m	flow	6.5	80	92	12	II		
			12 week NOEC (survival)	>2.0	m	flow	7.8	80	92	12	II		

Table A.1 continued overleaf

Table A.1 continued Summary of ecotoxicity data for sodium (and potassium) chromate to fish.

Species	Common name	Lifestage	*Endpoint*	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Oncorhynchus mykiss	rainbow trout	1-2 yr, 195±65 g	*Sublethal effects (over 4 days)*	1-10	m	flow	6.5	80	92	13	IV	No. of organisms: 1 fish/replicate, 5 replicates/concentration. Test concentrations: Tested two series plus controls. The first series was 5, 10, 25 and 50 mg Cr/l. The second series was 1, 2, 5 and 10 mg Cr/l. Dilution water: Tap water. The dissolved oxygen level and the Cr concentration in the dilution water were not given. Control response: Assumed to exhibit normal behaviour. Endpoint: Sublethal effects on respiratory activity and osmoregulatory function. Comments: The results are based on the nominal concentrations added to the test solution. Daily analysis for Cr(VI) by the diphenylcarbazide colourimetric method indicated that the actual concentrations were within 10% of the nominal values. Sublethal concentrations of Cr(VI) affected the respiratory activity and osmoregulatory function of trout at pH 7.8 and 6.5. The dosage required to induce comparable effects on plasma osmolality, ventilation frequency and coughing rate were 2-5 times greater at pH 7.8 than 6.5. The significance of the sublethal effects is uncertain.	Van Der Putte et al. 1982b
			Sublethal effects (over 4 days)	5-50	m	flow	7.8	80	92	13	IV		

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) TLm = median threshold or tolerance limit - equivalent to LC50
f) concentration converted from salt to chromium ion concentration
g) American Public Health Association. Standard Methods for the examination of water and wastewater
h) Val. = test validation marking (see text)

Table A.2 Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp. (°C)	Val.[g]	Test details	Reference
INVERTEBRATES - freshwater - short-term studies													
Crangonyx pseudogracilis	freshwater shrimp	adult 4mm	48h-LC_{50}	2.7	n	24h renew.	6.75	50	40-60	13	II	No. of organisms: 20-30 animals/replicate, 2 replicates/concentration. The loading rate was 20-30 animals in 200 ml solution. Test concentrations: A minimum of 8 concentrations plus control. The concentrations to be tested were determined by a range finding study/ Dilution water: A 1:3 mixture of tap water and deionised water. Dissolved oxygen concentration was adequately maintained by the 24 hour renewal method used. The concentration of Cr in the dilution water was not given. Control response: Not given Endpoints: Mortality Comments: Substance tested was potassium chromate. The 48h- and 96h-LC_{50} obtained with potassium dichromate were 2.2 mg Cr/l and 0.42 mg Cr/l respectively.	Martin and Holdich, 1986
			96h-LC_{50}	0.81	n	24 renew.	6.75	50	40-60	13	II		
Cyclops abyssorum prealpinus	copepod	0.62 mm	48h-LC_{50}	10	n	static	7.2		0.58 meq/l	10	IIIb	No. of organisms: Single animals exposed in 20 ml of solution. 5-20 individuals used per concentration. Test concentrations: Based on results of a range finding test. Dilution water: Filtered (5 µm) lake water. Dissolved oxygen level and Cr concentration in dilution water not given. Control response: <1% mortality. Endpoints: Mortality. Comments: Substance tested was potassium chromate. Tests were carried out at a relatively low temperature.	Baudouin and Scoppa, 1974
Daphnia hyalina	water flea	1.27 mm	48h-EC_{50}	0.022	n	static	7.2		0.58 meq/l	10	IIIb	No. of organisms: 15-20 animals/concentration in 300 ml solution. Test concentrations: Based on results of a range finding test. Dilution water: Filtered (5 µm) lake water. Dissolved oxygen level and Cr concentration in dilution water not given. Control response: 11.2% mortality was seen in 5 days. The mortality rate over 48 hours was not given. Endpoints: Mortality Comments: Substance tested was potassium chromate. Tests were carried out at a relatively low temperature.	Baudouin and Scoppa, 1974

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Daphnia magna	water flea	juv-<12 h	100h- LC_{50}	0.13[f]	n	static	7.8	100		23	II	No of organisms: 10 animals/concentration. The test was carried out 3 times. Test concentrations: Geometric series of 9 concentrations with a geometrical progression of 1.33, plus control. A preliminary range finding test was carried out to determine the concentration to be tested. Dilution water: Standard reference water. The dissolved oxygen level and Cr concentration of the dilution water are not given. Control response: Not given. Endpoints: Immobilisation/mortality. Comments:	Freeman and Fowler, 1953
Daphnia magna	water flea	adult	48h-LC_{50}	0.12[f]	n	static					IIIb	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Centrifuged lake water. Dissolved oxygen level and Cr concentration in dilution water is not given. Control response: 80-100% survival in 48 hours. Endpoints: Immobilisation Comments: Value estimated from 50% immobilisation-time curves.	Anderson, 1946
Daphnia magna	water flea		96h-EC_{50}	0.0178				50			IIIa	No of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Results as published in USEPA (1985).	Call et al, 1981
Daphnia magna	water flea	adults and <24h	96h-LC_{50}	0.05	m	static	8-8.5			21	II	No of organisms: 20 animals/concentration. Test concentrations: 0.01, 0.05, 0.1 and 1.0 mg/l, plus control. Dilution water: Spring water. The dissolved oxygen concentration was not given. The dissolved Cr concentration in the dilution water was 0.42 µg/l. Control response: Not given. Endpoints: Immobilisation/mortality. Comments:Test carried out with both adults (>7 day old) and juveniles (<24h old). The LC_{50} was the same for both groups.	Trabalka and Gehrs, 1977
Daphnia magna	water flea		acute LC_{50}	0.164	m	static	8.2-8.6	185			IIIa	No of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Results as published in USEPA (1985).	Call et al, 1981
			acute LC_{50}	0.0758	m	static	7.5-7.6	215			IIIa		
			acute LC_{50}	0.0206	m	static	7.5	50			IIIa		

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Daphnia pulex	water flea		48h-LC_{50}	0.18	m		7.5-7.9	75-105	50-60		II	No. of organisms: 10 animals/replicate, 5 replicates/ concentration. Loading was 10 organisms in 200 ml solution. Test concentrations: 5 concentrations and a control. Dilution water: Reconstituted moderately hard water. Dissolved oxygen was 7.0-9.0 mg/l. Concentration of Cr in dilution water not reported. Control response: Not given. Endpoints: Immobilisation/mortality. Comments: Substance tested was potassium chromate. Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. The LC_{50} value reported is the mean of two determinations. A similar 48h-LC_{50} of 0.18 mg/l was obtained with potassium dichromate.	Jop et al, 1987
Eudiaptomus padanus padanus	copepod	0.43 mm	48h-LC_{50}	10.1	n	static	7.2		0.58 meq/l	10	IIIb	No. of organisms: Single animals exposed in 20 ml of solution. 5-20 individuals used per concentration. Test concentrations: Based on results of a range finding test. Dilution water: Filtered (5 µm) lake water. Dissolved oxygen level and Cr concentration in dilution water not given. Control response: 9.8% mortality seen in 10 days. The mortality rate after 48 hours was not given. Endpoints: Mortality Comments: Substance tested was potassium chromate. Tests were carried out at a relatively low temperature.	Baudouin and Scoppa, 1974
Gammarus pseudolimnaous	scud		acute EC_{50}	0.10	m			48			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Substance tested was potassium chromate. Summary of results only reported in EPA (1985).	Call et al, 1981

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Philodina roseola	rotifer		48h-TLm[e]	31	m	static				5	IIIb	No of organisms: 40 animals/replicate, 3 replicates/concentration. Loading was 40 animals in 40 ml solution. Test concentrations: 5, 10, 20 and 40 mg Cr/l, plus control. Dilution water: Distilled water infused with lettuce (boiled 1.5 g of lettuce in 1 litre water), filtered and calcium carbonate added. The dissolved oxygen level and Cr concentration was not given. Control response: Not given. Endpoints: Mortality. Comments: Total Cr concentrations determined by atomic absorption spectrometry(AAS). Greater toxicity observed at higher temperatures. The 96h-TLM at 30°C is questionable as the test period is within the confidence limits of the mediam life span of the organisms at this temperature.	Schaefer and Pipes, 1973
			48h-TLm[e]	22	m	static				15	II		
			48h-TLm[e]	18	m	static				20	II		
			48h-TLm[e]	14	m	static				25	II		
			48h-TLm[e]	11	m	static				30	IIIb		
			48h-TLm[e]	9.1	m	static				35	IIIb		
			96h-TLm[e]	12	m	static				5	IIIb		
			96h-TLm[e]	8.9	m	static				15	II		
			96h-TLm[e]	7.4	m	static				20	II		
			96h-TLm[e]	5.5	m	static				25	II		
			96h-TLm[e]	4.4	m	static				30	IV		
Physa heterostropha	snail		96h-LC_{50}	16.8	n	static		soft		20	IIIa	No. of organisms: Not given. Probably 10 animals per replicate/concentration in 1 litre of solution. Test concentrations: Not given. Dilution water: Soft synthetic dilution water. Dissolved oxygen was 5-9 mg/l. The dissolved oxygen concentration. The concentration of Cr in dilution water is not given. Control response: Not given Endpoints: Mortality. Comments: Substance tested was potassium chromate.	Patrick et al, 1968
Procambarus clarkia	crayfish	adults (10-15 g)	96h-LC_{40}	500	n	static	7-7.5	180-300	3.8- 4.4 mmol/l	20	IIIb	No of organisms: 10 animals/concentration in 15 litres solution. Test concentrations: Not given. A preliminary range-finding test was carried out. Dilution water: Tap water. Dissolved oxygen level was 80% of saturation. The Cr concentration of dilution water not given. Control response: Not given. Endpoints: Mortality. Comments: LC_{50} not determined since the highest concentration of Cr tested (500 mg/l) caused only 40% mortality.	Del Ramo et al, 1987

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
INVERTEBRATES - saltwater - short-term studies													
Artemia salina	brine shrimp	3 d old nauplii	48h-LC_{50}	7.9	n	static				24	II	No of organisms: 1 organism/replicate, 20 replicates/concentration. Each organism was placed individually in 50 ml of solution. Test concentrations: 1, 2, 5, 6, 7, 10, 20, 40, 50, 100 and 200 mg Cr/l, plus control. Dilution water: Seawater from unpolluted source used as test medium. The water was filtered, autoclaved and aerated before use. The dissolved oxygen level was not given. The Cr concentration in the dilution water was not measured but was thought to be very low. Control response: Not given. Endpoints: Mortality. Comments:	Kissa et al, 1984
Artemia salina	brine shrimp	adults (25 d old)	48h-LC_{50}	12.8	n	static		38‰		22	II	No of organisms: Animals placed individually in 200 ml solution. The number of animals/concentration is not given. Test concentrations: Tested concentrations in the range 7-20 mg Cr/l, plus control. Dilution water: Synthetic seawater. The dissolved oxygen level and the Cr concentration of the dilution water are not given. Control response: Not given. Endpoints: Mortality. Comments:Synthetic sea water media; Cr toxicity additive with oil and with Finasol; less than additive with Cu; Cr toxicity less than additive in mixtures of 3 and 4 chemicals; order of toxicity Cu>Finasol>Cr>oil. Respiration rate (µl/ind/h) in *Artemia* increased at exposure to 48h LC_{50}, rate = 0.002964 compared with control rate = 0.001675;	Verriopoulos et al, 1987; Verriopoulos et al, 1988

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Mysidopsis bahia	mysid shrimp		48h-LC_{50}	6.0	m		8.0-8.4	20‰	300-400		II	No. of organisms: 10 animals/replicate, 5 replicates/ concentration. Loading was 10 organisms in 1 litre of solution. Test concentrations: 5 concentrations plus control. Dilution water: Reconstituted sea water. Dissolved oxygen was 7.0-9.0 mg/l. Concentration of Cr in dilution water not reported. Control response: Not given Endpoints: Mortality. Comments: Substance tested was potassium chromate. Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. The LC_{50} value reported is the mean of two determinations. A similar 96h-LC_{50} of 6.3 mg/l was obtained with potassium dichromate.	Jop et al, 1987
Palaemonetes pugio	grass shrimp	adults (intermoult stages D_2-D_4)	96h-LC_{50}	4.86		24h renew.	8.1	10‰		20	II	No of organisms: 20 animals/concentration Test concentrations: Used 5 concentrations, plus control. Dilution water: Natural seawater, diluted with distilled water. The solutions were aerated to maintain the dissolved oxygen level. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Mortality. Comments: The paper appears to investigate the toxicity mainly Cr present in drilling mud but does appear to report the results of a toxicity test with sodium chromate.	Conklin et al, 1983; Rao and Doughtie, 1984
Tisbe holothuriae	benthic copepod	adult females	48h-LC_{50}	14.1	n	static		38‰		22	II	No of organisms: 20 animals/concentration, each placed individually in 100 ml solution. The experiment was replicated 3 times. Test concentrations: Used 6 concentrations covering the range 10-16 mg Cr/l, plus control. Dilution water: Synthetic seawater. The dissolved oxygen level and the Cr concentration of the dilution water were not given. Control response: Not given. Endpoints: Mortality. Comments:	Verriopoulos and Dimas, 1988

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Tisbe holothuriae	benthic copepod	adult females	48h-LC_{50}	17.4	n					14	II	No of organisms: 20 animals/concentration, each placed individually in 50 ml solution. Test concentrations: 10.0, 12.0, 14.0, 14.5, 15, 15.5, 16 and 20 mg Cr/l, plus control. Dilution water: The source of seawater was not clear. The dissolved oxygen level and Cr concentration are not given. Control response: Not given. Endpoints: Mortality. Comments: The temperatures used correspond to the three thermic periods characteristic of the Aegean Sea.	Verriopoulos, 1980
			48h-LC_{50}	15.8	n					18	II		
			24-h LC_{50}	16.1	n					24	II		
Tisbe holothuriae	benthic copepod	adults females	48h-LC_{50}	8.1	n	static				24	II	No of organisms: 30 animals/concentration in 50 ml solution. Test concentrations: 8 concentrations covering the range ~6.5 to 9 mg Cr/l, plus control. Dilution water: Filtered (0.8 µm) natural seawater. The dissolved oxygen level and Cr concentration are not given. Control response: Given graphically, clearly <10% mortality. Endpoints: Mortality. Comments:	Moraitou-Apostolopoulou and Verriopoulos, 1982
INVERTEBRATES - freshwater - long-term studies													
Daphnia magna	water flea	juvenile	16d-NOEC (mortality)	0.052	n	24h renew.	8.4	880[b] and 3.3‰		20	IIIb	No of organisms: 15 organisms/concentration in 500 ml solution. Test concentrations: Concentrations from 10^{-6} to 10^{-4} mole/l, plus control. Dilution water: Synthetic seawater made by dissolving sea and bioelements in distilled water to give a salinity of 33‰. The 10% seawater (salinity 3.3‰) used in this test was obtained by dilution of the seawater with distilled water. Various salts (100 mg/l $NaHCO_3$, 20 mg/l $KHCO_3$, 200 mg/l $CaCl_2.H_2O$ and 180 mg/l $MgSO_4$) were then added. The dissolved oxygen level and Cr concentration of the dilution water was not given. Control response: Mortality was 2% on day 10 and 7% on day 26. Endpoints: Mortality. Comments: Tested in very hard, brackish water. The MEC is the minimum effective concentration and is the lowest concentration determined statistically that causes a significant increase in mortality over controls and can be considered as a LOEC.	van der Meer et al, 1988
			30d-MEC/LOEC (mortality)	0.312	n	24h renew.	8.4	880[b] and 3.3‰		20	IIIb		

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Daphnia magna	water flea	<24 h juveniles	28-day NOEC	<0.010	m	7 d renew.	8-8.5			21	IV	No of organisms: 20 animals/concentration. Test concentrations: 0.01, 0.05, 0.1, 1.0, plus control. Dilution water: Spring water. The dissolved oxygen concentration was not given. The dissolved Cr concentration in the dilution water was 0.42 µg/l. Control response: Mean survival time was 27.7 days for the experiments with juveniles and 23.6 days for the experiments with adults. The total number of young produced was 1,470 in experiments with juveniles and 1,234 in the experiments with adults. Endpoints: Mean survival time and number of young poduced. Comments: Both adult survival time and reproduction rate were affected by the lowest concentration tested (0.01 mg Cr/l) in both the juveniles (mean survival time was 14.8 days and the total number of young produced was 501) and adults (mean survival time was 7.4 days and the total number of young produced was 235). Most of the decrease in young production could be accounted for by life-span shortening of the parents. The mean survival times for the controls implies that considerable control mortality was seen in this study.	Trabalka and Gehrs, 1977
		adults	28-day NOEC	<0.010	m	7 d renew.	8-8.5			21	IV		
Neomysis integer	crustacean	adult	14d-NOEC (mortality)	0.156	n	24h renew.	8.4	880[b] and 3.3‰		20	IIIb	No of organisms: Appears to have used 5 adults/replicate in 500 ml solution. The average group size/concentration was given as 13. Test concentrations: Used 10^{-6} to 3.5×10^{-5} mole/l, plus control. Dilution water: Synthetic seawater made by dissolving sea and bioelements in distilled water to give a salinity of 33‰. The 70% seawater (salinty 23‰) and 10% seawater (salinity 3.3‰) used in this test was obtained by dilution of the seawater with distilled water. Various salts (100 mg/l $NaHCO_3$, 20 mg/l $KHCO_3$, 200 mg/l $CaCl_2.H_2O$ and 180 mg/l $MgSO_4$) were then added to the 10% seawater. The dissolved oxygen level and Cr concentration of the dilution water was not given. Control response: Mortality in controls started at day 14. Mortality was 20% at 15 days, 50% at 19 days and 80% at 24 days. The experiment was restricted to 14 days duration. Endpoints: Mortality. Comments: Mortality seen in controls after 15 days. The MEC is the minimum effective concentration and is the lowest concentration determined statistically that causes a significant increase in mortality over controls and can be considered as a LOEC.	van der Meer et al, 1988
			14d-MEC/LOEC (mortality)	0.312	n	24h renew.	8.4	880[b] and 3.3‰		20	IIIb		

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Philodina roseola	rotifer	hatched eggs	life-span TLm[e]	3.5	m	static				15	IV	No of organisms: 40 eggs/replicate, 3 replicates/concentration. Loading was 40 eggs in 40 ml solution. Chromium exposure was only started once the eggs had hatched (within 1 day). Test concentrations: 5 concentrations plus control. Dilution water: Distilled water infused with lettuce (boiled 1.5 g of lettuce in 1 litre water), filtered and calcium carbonate added. The dissolved oxygen level and Cr concentration was not given. Control response: Preliminary tests were carried out to check that the animals could survive and reproduce at the temperatures used. The hatching success was about 50%. The hatched animals at 5°C failed to reproduce, but the mean doubling time of the population was 5.1 days at 15°C, 4.2 days at 20°C, 3.1 days at 25°C and 2.0 days at 35°C. The mean life span was >60 days at 5°C, 28 days at 15°C, 10.2 days at 20°C, 5.9 days at 25°C, 3.7 days at 30°C and 3.0 days at 35°C. Endpoints: Survival time of parent population. Comments: Total Cr concentrations determined by atomic absorption spectrometry(AAS). Greater toxicity observed at higher temperatures. The mean life span of controls at the higher temperatures was quite short. The data are difficult to interpret meaningfully.	Schaefer and Pipes, 1973
			life-span TLm[e]	4.6	m	static				20	IV		
			life-span TLm[e]	4.5	m	static				25	IV		
			life-span TLm[e]	3.8	m	static				30	IV		
			life-span TLme	3.7	m	static				35	IV		
INVERTEBRATES - saltwater - long-term studies													
Artemia salina	brine shrimp	cysts	NOEL (hatching)	7.11	n	static				24	IIIb	No of organisms: ~30 eggs/concentration in 80 ml solution. Test concentrations: 0.5, 1, 2, 3, 4, 6, 8, 10, 15, 20, 30, 40, 60, 80 and 100 mg Cr/l, plus control. Dilution water: Seawater from unpolluted source used as test medium. The water was filtered, autoclaved and aerated before use. The dissolved oxygen level was not given. The Cr concentration in the dilution water was not measured but was thought to be very low. Control response: Hatching rate in controls was only 24.3%. Endpoints: Hatching rate. Comments: The low control hatching rate and the fact that different numbers of eggs were used at different concentrations means that the significance of the results are uncertain. The highest hatching rate was reported at 40 mg Cr/l (55.6% hatch), but the hatching rate was clearly reduced at higher concentrations, and the hatching as a fraction of control appeared to decrease in a dose responsive manner.	Kissa et al, 1984
			48h-EC_{50} (hatching)	10.3	n	static				24	IIIb		

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Callinectes sapidus	blue crab	larvae-adults	EC50 (survival - hatch to megalopa)	0.93[f]	n	24h renew.		30‰		25	IIIb	No of organisms: 50 larvae/replicate, 3 replicates/concentration. Test concentrations: 0.35, 0.77, 1.51 and 2.3 mg Cr/l[f], plus control Dilution water: Filtered seawater. The dissolved oxygen level and Cr concentration of the dilution water was not given. Control response: Percentage survival to megalopa = 61.3%, survival to first crab = 38.0 %. Mean duration of development was 33.5 days for zoea and 7.6 days for magalopa. The total duration of hatch to fist crab was 39.6 days. Endpoints: Survival and development time. Comments: A dose-related increase in the development time of both megalopa and time to first crab was seen, but the statistical significance of this increase was uncertain. The control suvival was relatively poor, with better survival being seen in some the Cr treatments. This makes the derived EC_{50} values uncertain.	Bookhout et al, 1984
			EC_{50} (survival - megalopa to first crabs)	0.32[f]	n	24h renew.		30‰		25	IIIb		
Carcinus maenas	shore crab	adult	12d NOEC (mortality)	40		static				14-17	II	No of organisms: 11-12 animals/concentration in 16 litres of solution. Test concentrations: Not clear, but tested at least 20, 40, and 60 mg Cr/l, plus control. Dilution water: Natural seawater. The dissolved oxygen level was not given. The report indicates that the background levels of total Cr in seawater are usually in the range 0.1-0.2 µg/l, with a maximum value of 0.7 µg/l. It is not clear if this refers to the seawater used in the study. Control response: 10 animals survived. Endpoints: Mortality Comments: Generally few experimental details are given. Approximated 50% of the organisms died at 60 mg Cr/l over 12 days.	Raymont and Shields, 1963
Leander squilla	prawn	juvenile	7d NOEC (toxic threshold)	5							IIIb	No of organisms: Not given. Test concentrations: Not given. Dilution water: Natural seawater. The dissolved oxygen level was not given. The report indicates that the background levels of total Cr in seawater are usually in the range 0.1-0.2 µg/l, with a maximum value of 0.7 µg/l. It is not clear if this refers to the seawater used in the study. Control response: No mortality in first week, a few specimens died over the subsequent 2 days. Endpoints: Mortality. Comments:No experimental details are given. Larger prawns appeared to be more resistant.	Raymont and Shields, 1963

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Nereis vivens	polychaete worm		21-d NOEC (mortality)	1		static				14-20	IIIb	No of organisms: Not clear. Probably 10 animals/concentration in 2 litres of solution. Test concentrations: Not clear. Probably 0.06-10 mg Cr/l, plus control. Dilution water: Natural seawater. The dissolved oxygen level was not given. The report indicates that the background levels of total Cr in seawater are usually in the range 0.1-0.2 µg/l, with a maximum value of 0.7 µg/l. It is not clear if this refers to the seawater used in the study. Control response: Not given. Endpoints: Mortality. Comments: Initial tests suggested a toxicity threshold of around 1 mg Cr/l. No mortality was seen over 3 weeks exposure to 0.5 or 1.0 mg Cr/l, but some mortalities occurred at 1.5 mg Cr/l. More accurate, longer-term (5 week) tests confirmed a threshold concentration of just under 1 mg Cr/l. Further tests, with even longer periods of exposure suggested that the threshold fell to around 0.6-0.7 mg Cr/l. Generally few details of the test are given.	Raymont and Shields, 1963
			>5 week NOEC (mortality)	0.6-0.7		static				14-20	IIIb		
Palaemon elegans	decapod (prawn)	larvae	38d-NOEC (mortality)	1.56	n	24h renewal	8.4	33‰		17-20	II	No of organisms: 15 larvae/concentration in 500 ml solution. Test concentrations: Used 10-5 to 3□10-4 mol/l, plus control. Dilution water: Synthetic seawater made by dissolving sea and bioelements in distilled water to give a salinity of 33‰. The dissolved oxygen level and Cr concentration of the dilution water was not given. Control response: No mortality in controls. Endpoints: Mortality and larval development (number of larvae reaching the first post-larval stage). Comments: The MEC is the minimum effective concentration and is the lowest concentration determined statistically that causes a significant increase in mortality over controls and can be considered as a LOEC.	van der Meer et al. 1988
			36d-NOEC (larval develop.)	0.52	n	24h renewal	8.4	33‰		17-20	II		
			23d-MEC/LOEC (mortality)	5.2	n	24h renewal	8.4	33‰		17-20	II		
			38d-MEC/LOEC (larval develop.)	1.56	n	24h renewal	8.4	33‰		17-20	II		

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Palaemonetes varians	prawn	larvae	30d-NOEC (mortality)	5.2	n	24h renew.	8.4	33‰		20	II	No of organisms: Average number of animals/concentration was 29 for lareve and 13 for adults. Used groups of either 5 adults or 15 larvae in 500 ml solution. Test concentrations: Used concentrations of 10^{-4}-2×10^{-3} mole/l, plus control, for adults and concentrations of 10^{-5}-2×10^{-3} mole/l, plus control, for the larvae. Dilution water: Synthetic seawater made by dissolving sea and bioelements in distilled water to give a salinity of 33‰. The 70% seawater (salinity 23‰) and 10% seawater (salinity 3.3‰) used in this test was obtained by dilution of the seawater with distilled water. Various salts (100 mg/l $NaHCO_3$, 20 mg/l $KHCO_3$, 200 mg/l $CaCl_2.H_2O$ and 180 mg/l $MgSO_4$) were then added to the 10% seawater The dissolved oxygen level and Cr concentration of the dilution water was not given. Control response: No mortality. Endpoints: Mortality and larval development (number of larvae reaching the first post-larval stage). Comments: The MEC is the minimum effective concentration and is the lowest concentration determined statistically that causes a significant increase in mortality over controls and can be considered as a LOEC. No difference in toxicity (NOEC, LOEC) from 33 to 23‰ salinity.	van der Meer et al, 1988
			30d-MEC/LOEC (mortality)	10.4	n	24h renew.	8.4	33‰		20	II		
			23d-NOEC (mortality)	5.2	n	24h renew.	8.4	23‰		20	II		
			19d-MEC/LOEC (mortality)	10.4	n	24h renew.	8.4	23‰		20	II		
			30d-MEC/LOEC (mortality)	0.312	n	24h renew.	8.4	3.3‰		20	II		
			14d-MEC/LOEC (larval develop.)	5.2	n	24h renew.	8.4	33‰		20	II		
			13d-LOEC (larval develop.)	5.2	n	24h renew.	8.4	23‰		20	II		
			32d-LOEC (larval develop.)	0.312	n	24h renew.	8.4	3.3‰		20	II		
		young adults (~2 cm)	26d MEC/LOEC (mortality)	10.4	n	24h renew.	8.4	33‰		20	II		
			28d NOEC (mortality)	5.2	n	24h renew.	8.4	23‰		20	II		
			28d MEC/LOEC (mortality)	10.4	n	24h renew.	8.4	23‰		20	II		
			40d MEC/LOEC (mortality)	3.12	n	24h renew.	8.4	3.3‰		20	II		

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Praunus flexuosus	crustacean (mysid)	adult	6d-NOEC (mortality)	2.6	n	24 h renewal	8.4	33‰		20	II	No of organisms: Used 6 organisms/concentration in 500 ml solution. Test concentrations: Used concentrations of 2×10^{-5}-6×10^{-4} mol/l, plus control. Dilution water: Synthetic seawater made by dissolving sea and bioelements in distilled water to give a salinity of 33‰. The 70% seawater (salinity 23‰) used in this test was obtained by dilution of the seawater with distilled water. The dissolved oxygen level and Cr concentration of the dilution water was not given. Control response: Control mortality was reported to be low. Endpoints: Mortality. Comments: The MEC is the minimum effective concentration and is the lowest concentration determined statistically that causes a significant increase in mortality over controls and can be considered as a LOEC. No difference in toxicity (NOEC, LOEC) from 33 to 23‰ salinity. The number of organisms/concentration used in this study was small.	van der Meer et al, 1988
			6d-MEC/LOEC (mortality)	5.2	n	24 h renew.	8.4	33‰		20	II		
			23d-NOEC (mortality)	1.0	n	24 h renew.	8.4	23‰		20	II		
			23d-MEC/LOEC (mortality)	3.12	n	24 h renew.l	8.4	23‰		20	II		
Rhithropanopeus harrisii	mud crab	larvae-adults	19d NOEC (survival - hatch to first crab)	0.36[f]	n	24 h renew.		20‰		25	II	No of organisms: 50 larvae/replicate, 6 replicates/concentration. The larvae were <24 hour old. Test concentrations: 0.36, 2.3, 4.7 and 9.3 mg Cr/l[f], plus control. Dilution water: Filtered seawater. The dissolved oxygen level and Cr concentration of the dilution water was not given. Control response: Percentage survival to megalopa = 95.0%, survival to first crab = 93.7 %. Mean duration of development was 11.9 days for zoea and 6.7 days for magalopa. The total duration of hatch to fist crab was 19 days. Endpoints: Survival and development time. Comments: A dose-related increase in the development time of both megalopa and time to first crab was seen, but the statistical significance of this increase was uncertain.	Bookhout et al, 1984
			12d LC_{50} (survival - hatch to megalopa)	5.7[f]	n	24 h renew.		20‰		25	II		
			7d LC_{50} (survival - megalopa to first crab)	4.4[f]	n	24 h renew.		20‰		25	II		

Table A.2 continued overleaf

Table A.2 continued Summary of ecotoxicity data for sodium chromate to aquatic invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.g	Test details	Reference
Tisbe holothuriae	benthic copepod	multigen. study using F_2 females	NOEC (longevity F_2 gen.)	0.5	n	static				14	IIIb	No of organisms: Experimental F_2 females were obtained from a common mother (F_1). After appearance of the first ovigerous sack, each female was placed in 50 ml test solution, with replicates/concentration. As soon as the nauplii hatched and a new sac was produced the females were transferred to fresh solution. Test concentrations: 0.5, 1.0 and 2.0 mg/l, plus control Dilution water: Filtered natural seawater. The dissolved oxygen level and Cr concentration of the dilution water was not given.	Verriopoulos and Moraitou-Apostolopoulou, 1981
			NOEC (longevity F_3 gen.)	<0.5	n	static				14	IIIb	Control response: Survival of the F_2 generation was 22.5 days, number of egg sacs/female was 5.86, interval between successive egg sacs was 4.03 days, the percentage aborted egg sacs was 36.9%, the number of F_3 offspring was 110, the survival of the F_3 generation was 34.5 days and the period of development (egg to adult) was 12 days. Endpoints: Longevity of the F_2 (parent) and F_3 (offspring) generation, numbers of egg sacs produced by F_2 females, interval between egg sacs, % egg sac abortion, numbers of F_3 offspring.	
			LOEC (decreased no. egg sacs and number of F_3 offspring)	<0.5	n	static				14	II	Comments:. All chromium concentrations affected the longevity of both the F_2 and F_3 generations, the latter being more sensitive. The reduced longevity of the F_2 generation was only statistically significant at concentrations of 1 mg Cr/l and above. For the F_3 generation, the lowest concentration tested significantly reduced the longevity (12.95 days compared to 34.5 days in controls). No inhibition on the number of egg sacs produced was seen at any concentration. In contrast the development of egg sacs was strongly influenced by Cr exposure and a dose related increase in the % egg sac abortion was seen. This decrease was statistically significant ($p=0.05$) at all concentrations tested. The number of egg sacs/female in the 0.5 mg/l group was 3.46 compared with 5.86 in the controls. The number of aborted egg sacs was significantly increased over controls at concentrations of 1.0 mg Cr/l and above. The numbers of F_3 offspring reduced with in a dose-responsive manner at all Cr concentrations. The number of F_3 offspring/female in the 0.5 mg Cr/l treatment was 52.8 compared with 110.2 in the controls. The statistical significance of this is not clear from the paper.	
			NOEC % aborted egg sacs	0.5	n	static				14	II		

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) TLm = median threshold or tolerance limit - equivalent to LC_{50}
f) concentration converted from salt to chromium ion concentration
g) Val. = validity marking of the test (see main text)

Table A.3 Summary of ecotoxicity data for sodium chromate to algae.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp. (°C)	Val.[e]	Test details	Reference
ALGAE													
Chlorella vulgaris	green algae		3-4 month NOEC	31[f]	n	static	~7.0				IV	No. of organisms: Used 50 ml solution. The inoculum concentration was not given but it was small so that no green tinge to the solution could be seen. Test concentrations: Range of concentrations tested. Dilution between steps was around 1/5-2. Dilution water: Basal mineral medium made up from a mixture of 80% distilled water and 20% activated carbon-treated tap or well water, and mineral salts. The concentration of Cr in dilution water is not given. Control response: Not given. The growth rate was reported to be rather low. Endpoints: Total cell counts at end of test (total biomass produced). Comments: The tests were carried out at room temperature on a north facing window. The growth rate was low and the first observations could only be made after several weeks after inoculation, and the test was carried on until the cultures were 3-4 months old. The highest concentration tolerated (NOEC) and the lowest inhibiting concentration (LOEC) were determined as 0.0006 moles/l and 0.0015 moles/l respectively.	Den Dooren De Jong, 1965
			3-4 month	78[f]	n	static	~7.0				IV		
Nitschia linearis	diatom		120h-EC_{50} (biomass)	7.8	n	static		soft			IIIa	No. of organisms: Organism inoculated into 150 ml flask. Initial concentration not given. Test concentrations: Not given. Several controls were run. Dilution water: Synthetic soft dilution water. Dissolved oxygen was 5-9 mg/l throughout the test. The concentration of Cr in dilution water is not given. Control response: Not given. Endpoints: Total cell counts at end of test (total biomass produced). Comments: Test substance was potassium chromate. A lower 120h-EC_{50} of 0.208 mg/l was obtained using potassium dichromate.	Patrick et al, 1968.
Selenastrum capricornutum	green algae		NOEC (growth inhibition)	0.045							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Results as reported in USEPA (1985).	Garton, 1972

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) Val. = validity marking of test (see main text)
f) concentration converted from salt to chromium ion concentration

Table A.4 Summary of ecotoxicity data for sodium chromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp. (°C)	Val.[e]	Test details	Reference
AQUATIC PLANTS													
Lemna gibba	duckweed		8d NOEC (biomass)	0.1		static	6.9- 7.7			17	IIIb	No. of organisms: 3 g (wet wt.) plant per 2 litres solution. 5 replicates/concentration. Test concentrations: 0.1-, 1.0, 10, and 20 mg/l, plus controls. Dilution water: Used filtered nutrient solution made from 10-20 g of fresh cow manure in 1 litre of water. Distilled and deionised water was added as necessary to replace evaporative losses. Dissolved oxygen level remained above 5 mg/l throughout the test. The concentration of total Cr in the nutrient water was <0.83 µg/l). Endpoints: Plant growth by dry weight biomass determination. Results expressed as % of control growth. Comments: The study was a semi-field study carried out in protected outdoor tanks. The air temperature ranged from -2 to 27°C with a mean of 17.1°C. Negative effects on growth were seen at or above 1.0 mg/l. The growth at 0.1 mg/l was 98% of control, whereas at 1.0 mg/l it was 63% of control. The statistical significance of the growth reductions is not given.	Staves and Knaus, 1985
Spirodela polyrhiza	duckweed		8d NOEC (effect on growth)	0.1-1.0		static	6.9-7.7			17	IIIb	No. of organisms: 3 g (wet wt.) plant per 2 litres solution. 5 replicates/concentration. Test concentrations: 0.1-, 1.0, 10, and 20 mg/l, plus controls. Dilution water: Used filtered nutrient solution made from 10-20 g of fresh cow manure in 1 litre of water. Distilled and deionised water was added as necessary to replace evaporative losses. Dissolved oxygen level remained above 5 mg/l throughout the test. The concentration of total Cr in the nutrient water was <0.83 µg/l). Endpoints: Plant growth by dry weight biomass determination. Results expressed as % of control growth. Comments: The study was a semi-field study carried out in protected outdoor tanks. The air temperature ranged from -2 to 27°C with a mean of 17.1°C. Negative effects on growth were seen at or above 1.0 mg/l. The growth at 0.1 mg/l was 123% of control, whereas at 1.0 mg/l it was 70% of control. The statistical significance of the growth reductions is not given.	Staves and Knaus, 1985

Table A.4 continued overleaf.

Table A.4 continued Summary of ecotoxicity data for sodium chromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.e	Test details	Reference
Spirodela punctata	duckweed		8d NOEC (effect on growth)	0.1-1.0		static	6.9-7.7			17	IIIb	No. of organisms: 3 g (wet wt.) plant per 2 litres solution. 5 replicates/concentration. Test concentrations: 0.1-, 1.0, 10, and 20 mg/l, plus controls. Dilution water: Used filtered nutrient solution made from 10-20 g of fresh cow manure in 1 litre of water. Distilled and deionised water was added as necessary to replace evaporative losses. Dissolved oxygen level remained above 5 mg/l throughout the test. The concentration of total Cr in the nutrient water was <0.83 µg/l). Endpoints: Plant growth by dry weight biomass determination. Results expressed as % of control growth. Comments: The study was a semi-field study carried out in protected outdoor tanks. The air temperature ranged from -2 to 27°C with a mean of 17.1°C. Negative effects on growth were seen at or above 1.0 mg/l. The growth at 0.1 mg/l was 100% of control, whereas at 1.0 mg/l it was 86% of control. The statistical significance of the growth reductions is not given.	Staves and Knaus, 1985
MICROORGANISMS													
Azobacter vinelandii	soil bacterium		LOEC (growth over 4 days)	<0.26	n	static				28-30	IIIb	No of organisms: Inoculum was 0.1 ml culture in 100 ml solution. Test concentrations: Tested 5, 25 and 125 µM solutions (0.26, 1.3 and 6.5 mg Cr/l), plus control. Dilution water: Artificial growth medium. Control response: Given graphically. Endpoints: Growth (biomass), determined by optical density measurements. Comments: Growth inhibition seen at all concentrations. The results are displayed graphically and so the statistical significance of the effects seen are uncertain. Chromium(III) chloride was less inhibitory at similar concentrations.	Ueda et al, 1988a
Escherichia coli	bacteria		24h-LC_{50}	0.42[e]	n					37°C	II	No. of organisms: Inoculum was 4×10^9 colony forming units/ml. All concentrations were run in duplicate. Test concentrations: 10, 20, 30, 40, 50, 60 and 100 mg Cr/l, plus control. Dilution water: Peptone water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Total biomass produced was 0.26-0.27 mg/ml. Endpoints: Growth (biomass). Comments: Substance tested was potassium chromate. Potassium chromate more toxic than dichromate (24h-LC_{50} was 3.5[e] mg/l).	Gaur and Bhattacherjee, 1991

Table A.4 continued overleaf.

Table A.4 continued Summary of ecotoxicity data for sodium chromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.e	Test details	Reference
Fusarium oxysporum	soil fungus		NOEC/ LOEC (growth over 27 hours)	0.26	n	static				28-30	IIIb	No of organisms: Inoculum was 0.1 ml culture in 100 ml solution. Test concentrations: Tested 5, 25 and 125 µM solutions (0.26, 1.3 and 6.5 mg Cr/l), plus control. Dilution water: Artificial growth medium. Control response: Given graphically. Endpoints: Growth (biomass), determined by optical density measurements. Comments: Little or no growth inhibition at 0.26 mg Cr/l, and almost complete growth inhibition at 6.5 mg Cr/l. The results are displayed graphically and so the statistical significance of the effects seen are uncertain. Little or no effect seen with chromium(III) chloride at concentrations up to 6.5 mg Cr/l.	Ueda et al, 1988a
Mixed populations	activated sludge		inhibition of oxygen	458							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Cell multiplication. Comments: The test was reported to be an OECD 209 test. No experimental details are given.	Bayer, 1988

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) Val. - validation marking of test (see main text)

References

The references for this appendix appear in the full reference list (Section 6) of the main report.

Appendix B Summary of aquatice toxicity data for sodium dichromate

This appendix reviews the aquatic toxicity data for sodium dichromate. Values which have been used in the risk assessment report are highlighted with light grey shading. The following paragraphs provide some information about the selection process; these apply to the overall data set for chromium (VI) and not all comments may apply to data in this particular appendix.

For short term test results, the values selected are the lowest for each species which come from tests with a validity marking of I or II. In some cases a number of valid results may have been produced by one study, using different experimental conditions (for example, hardness, salinity and temperature). For properties such as temperature and salinity the test conditions closest to the 'real' environment have been chosen (so avoiding high or low temperatures, and preferring tests at salinities similar to sea water); for hardness, the lowest test result is preferred as a range of hardness is found in natural waters. These 'rules' have been applied flexibly so as to allow interpretation of the individual studies.

For long term tests, all data from validity marking I and II have been selected, but some studies with marking IIIb have also been included. Multiple values have been taken from some studies, where a number of different endpoints were measured (for example, mortality, reproduction and growth). Where several measures of the same endpoint are reported in one study, values from longer exposure periods are generally preferred, with the exception of algal studies where the maintenance of exponential growth conditions is considered.

The further treatment of the long term data to derive the PNEC is described in the main risk assessment report. In some cases, notes on data not used in the PNEC derivation have also been included in the comments on the tests in the appendix

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Table B.1 Summary of the ecotoxicological data for sodium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp. (°C)	Val.[h]	Test details	Reference
FISH - freshwater - short-term tests													
Gambusia affinis	mosquitofish	adult	24h-TLm[e]	183[f]	n	static	6-7.9		<100	24-27	IV	No. of organisms: 10 fish/concentration in 15 litres of solution. Test concentrations: 10, 18. 32, 56, 100, 180, 320, 560 and 1,000 mg/l as N, plus control. The substance was weighed directly into the test tanks. Dilution water: Used pond water with a high turbidty (100-650 ppm). Aeration was used to maintain the dissolved oxygen level and the disperse the turbidity-producing soil. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Tail-rot disease was seen in the holding tank. The fish were treated with medication prior to use.	Wallen et al, 1957
			48h-TLm[e]	167[f]	n	static	6-7.9		<100	24-27	IV		
			96h-TLm[e]	105[f]	n	static	6-7.9		<100	24-27	IV		
			6d-TLm[e]	58[f]	n	static	6-7.9		<100	24-27	IV		
Lepomis macrochirus	bluegill		24h-TLm[e]	728	n	static	5.9	75-150	60-120	22.5	IV	No. of organisms: Number of fish/replicate was 6. 2 replicates were run, each of 12 litres. Test concentrations: Number of concentrations not given. A control was run. Dilution water: Reconstituted fresh water. The water was continuously aerated to maintain the dissolved oxygen level. The Cr concentration in the dilution water was not given. Control response: Not given. Comments: There appear to have been some problems with the initial survival of the fish in the holding tanks.	Abegg, 1950
Lepomis macrochirus	bluegill	5 g	24h-TLm[e]	260[f]	n	static	6.9-7.5	84-63	33-81	20	II	No. of organisms: 10 fish/concentration in 15 litres of solution. Test concentrations: Not given. Dilution water: Tap water. The water was aerated during the test to maintain the dissolved oxygen level at >5 mg/l. The Cr concentration in the dilution water was not given. Control response: Not given. Comments: Results originally expressed as CrO_3 and it is not clear if Cr(VI) added as sodium dichromate or as chromic acid.	Turnbull et al, 1954
			48h-TLm[e]	213[f]	n	static	6.9-7/5	84-63	33-81	20	II		
Leuciscus idus melanotus	Golden ide		48h-LC_{50}	88.9[f]							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Results from 2 laboratories. Few details of the method are given.	Juhnke and Ludemann,
			48h-LC_{50}	153[f]							IIIa		
Oncorhynchus mykiss	rainbow trout	adult (14 month old)	96h-LC_{50}	69	m	flow	7-8	45	42	12	II	No. of organisms: 10 fish/concentration. Test concentrations: Not given. Dilution water: Lake water. Dissolved oxygen was in the range 5-13 mg/l. The concentration of total Cr in the dilution water was <0.01 mg/l Control response: Not given. Comments: Test carried out according to APHA[g] (1965 version)	Benoit, 1976

Table B.1 continued overleaf

Table B.1 continued Summary of the ecotoxicological data for sodium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Pimephales promelas	fathead minnow	juvenile (0.079g)	96h-LC_{50}	33.2	m	flow	7.8	220	235	25	II	No. of organisms: 20 fish/concentration in 35 litres of solution. Test concentrations: A geometric series of 4 concentrations, plus control. Dilution water: Well water. Inflow-water was aerated to maintain the dissolved oxygen concentration at around 80% of saturation. The Cr concentration of the dilution water was not given. Control response: Not given. Comments: The concentration of CrVI in the test solutions was measured by the diphenylcarbazide method.	Broderius and Smith Jr., 1979
Salvelinus fontinalis	brook trout	juvenile	96h-LC_{50}	59	m	flow	7-8	45	42	12	II	No. of organisms: 10 fish/concentration. Test concentrations: Not given. Dilution water: Lake water. Dissolved oxygen was in the range 5-13 mg/l. The concentration of total Cr in the dilution water was <0.01 mg/l Control response: Not given. Comments: Test carried out according to APHA[g] (1965 version)	Benoit, 1976
FISH - freshwater - long-term studies													
Catostomus commersoni	white sucker	egg-fry (<24 hours old)	NOEC (hatching)	>1.975	m	flow	6.9-7.2	38.8	34.6	17	II	No. of organisms: 200 eggs/replicate, 2 replicates/concentration. The volume of water used was 21 litres/replicate with each replicate being divided into 2 groups of 100 eggs in each tank. Surviving fry were randomly reduced to 2 groups of 50 eggs/replicate (i.e. a total of 200 fry/concentration). Test concentrations: Used 5 concentrations (0.123, 0.290, 0.538, 0.963 and 1.975 mg Cr/l), plus a control. Dilution water: Well water. The mean dissolved oxygen concentration was 8.9 mg/l throughout the test. The concentration of Cr in the dilution water was not given. Control response: The percentage hatch was 88-97%. The survival was 42-74% over days 1-30 and 42-48% over days 31-60. Endpoints: Hatchability of eggs, survival and growth (total length at 30 and 60 days and wet weight of fish at 60 days). Comments: Test carried out according to "Proposed Recommended Bioassay Procedure of Egg and Fry Stages of Freshwater Fish. USEPA, 1972". Exposure started with <1 day old eggs and continued for 60 days posthatch. Eggs hatched on days 10-13. No effects were seen on % hatch or survival. At 30 days, the length of fish in the 1.975 mg Cr/treatment were reduced compared with controls. By day 60, gowth of the fish exposed to 0.538 mg Cr/l and above was reduced compared with controls. The control survival was a little low.	Sauter et al, 1976
			30d NOEC (survival)	>1.975	m	flow	6.9-7.2	38.8	34.6	17	IIIb		
			30d NOEC (growth)	0.963	m	flow	6.9-7.2	38.8	34.6	17	II		
			60d NOEC (survival)	>1.975	m	flow	6.9-7.2	38.8	34.6	17	IIIb		
			60d NOEC (growth)	0.29	m	flow	6.9-7.2	38.8	34.6	17	II		

Table B.1 continued overleaf

Table B.1 continued Summary of the ecotoxicological data for sodium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Esox lucius	northern pike	egg-fry (eyed)	NOEC (hatching)	>1.975	m	flow	6.7-7.0	37.8	35.6	17	II	No. of organisms: 200 eggs/replicate, 2 replicates/concentration. The volume of water used was 21 litres/replicate with each replicate being divided into 2 groups of 100 eggs in each tank. Surviving fry were randomly reduced to 2 groups of 50 eggs/replicate (i.e. a total of 200 fry/concentration). Test concentrations: Used 5 concentrations (0.123, 0.290, 0.538, 0.963 and 1.975 mg Cr/l), plus a control. Dilution water: Well water. The mean dissolved oxygen concentration was 9.0 mg/l throughout the test. The concentration of Cr in the dilution water was not given. Control response: The percentage hatch was 73-83%. The survival was 48% over days 1-20. Endpoints: Hatchability of eggs, survival and growth (total length at 30 and 60 days and wet weight of fish at 60 days). Comments: Test carried out according to "Proposed Recommended Bioassay Procedure of Egg and Fry Stages of Freshwater Fish. USEPA, 1972". Exposure started with 5 day old eggs and continued for 20 days posthatch. Eggs hatched after 4 days. Cannibalism in fish became significant after 20 days posthatch. No effects were seen on % hatch. A significant reduction in survival was seen at 20 days at concentrations of 0.963 mg Cr/l. The data on survival and growth at longer time periods are not reliable due to cannibalism. The control survival was a little low.	Sauter et al, 1976
			20d NOEC (survival)	0.538	m	flow	6.7-7.0	37.8	35.6	17	IIIb		
Ictalurus punctatus	channel catfish	egg-fry	NOEC (% hatch)	>1.29	m	flow	7.0-7.4	36.2	33.7	22	IIIb	No. of organisms: 200 eggs/replicate, 2 replicates/concentration. The volume of water used was 21 litres/replicate with each replicate being divided into 2 groups of 100 eggs in each tank. Surviving fry were randomly reduced to 2 groups of 50 eggs/replicate (i.e. a total of 200 fry/concentration). Test concentrations: Used 6 concentrations (0.039, 0.073, 0.150, 0.305, 0.570 and 1.290 mg Cr/l), plus a control. Dilution water: Well water. The mean dissolved oxygen concentration was 8.1 mg/l throughout the test. The concentration of Cr in the dilution water was not given. Control response: The percentage hatch was 31-37%. The survival was 42-62% over days 1-30 and 85-86% over days 31-60. Endpoints: Hatchability of eggs, survival and growth (total length at 30 and 60 days and wet weight of fish at 60 days). Comments: Test carried out according to "Proposed Recommended Bioassay Procedure of Egg and Fry Stages of Freshwater Fish. USEPA, 1972". Exposure started with 2-3 day old eggs and continued for 60 days posthatch. Eggs hatched on days 6-8. No effects were seen on % hatch compared with controls. At 30 days, the length of fish and percentage survival of the fish in the 0.305, 0.570 and 1.29 mg Cr/l treatment was significantly reduced compared with controls. During days 31-60 of the test, the survival of the remaining fish in the 0.305 mg/l and below was similar to that of controls. The growth of fish was significantly reduced at concentrations of 0.57 mg Cr/l and above. From these results it appears that the fish surviving the first 30 days of the exposure were or became more resistant to Cr. The control hatch rate and survival was a little low, probably due to a fungus infection. The current OECD Test Guidelines indicates that overall hatch and survival of these species should be >65% over 32 days.	Sauter et al, 1976
			30d NOEC (survival)	0.150	m	flow	7.0-7.4	36.2	33.7	22	IIIb		
			30d NOEC (growth)	0.150	m	flow	7.0-7.4	36.2	33.7	22	II		
			30-60d NOEC (survival)	0.305	m	flow	7.0-7.4	36.2	33.7	22	IIIb		
			30-60d NOEC (growth)	0.305	m	flow	7.0-7.4	36.2	33.7	22	II		

Table B.1 continued overleaf

Table B.1 continued Summary of the ecotoxicological data for sodium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Oncorhynchus mykiss	rainbow trout	egg-fry	NOEC (hatch)	3.2	m	flow	6.7-7.0	33.4	30.1	10	II	No. of organisms: 200 eggs/replicate, 2 replicates/concentration. The volume of water used was 21 litres/replicate with each replicate being divided into 2 groups of 100 eggs in each tank. Surviving fry were randomly reduced to 2 groups of 50 eggs/replicate (i.e. a total of 200 fry/concentration). Test concentrations: The first study used concentrations of 1.6, 3.2, 6.1, 12.2, 26.7 and 49.7 mg Cr/l, plus a control. A second study used 0.051, 0.105, 0.194, 0.384 and 0.822 mg Cr/l, plus a control. Dilution water: Well water. The mean dissolved oxygen concentration was 9.1 mg/l throughout the test. The concentration of Cr in the dilution water was not given. Control response: First study: percentage hatch was 76-77%; survival was 96-99% over days 1-30 and 88-96% over days 31-60. Second study: percentage hatch was 69-76%; survival was 91-98% over days 1-30 and 88-92% over days 31-60. Endpoints: Hatchability of eggs, survival and growth (total length at 30 and 60 days and wet weight of fish at 60 days). Comments: Test carried out according to "Proposed Recommended Bioassay Procedure of Egg and Fry Stages of Freshwater Fish. USEPA, 1972". Exposure started with <1 day old eggs and continued for 60 days posthatch. Eggs hatched on days 35-37. In the first study, the percentage hatch was significantly reduced compared with controls at concentrations of 6.1 mg Cr/l and above (no eggs hatched at 26.7 and 49.7 mg Cr/l). Survival of fry was significantly reduced by day 30 at concentrations of 3.2 mg Cr/l and above, and the growth of trout was significantly reduced at all exposure concentrations. During days 31-60, the survival and growth of trout was significantly lower than controls at all exposure concentrations. A second study was undertaken using lower test concentrations in order to better define some of the growth and survival endpoints. No effects were seen on % hatch or survival at 30 days at any concentration. At 30 days, the length of fish in the 0.822 mg Cr/l treatment was reduced compared with controls. Over 60 days, survival at 0.822 mg Cr/l was significantly reduced and the growth of fish (weight) was significantly reduced at concentrations of 0.105 mg Cr/l and above.	Sauter et al, 1976
			30d NOEC (growth)	0.384	m	flow	6.7-7.0	33.4	30.1	10	II		
			30d NOEC (survival)	1.6	m	flow	6.7-7.0	33.4	30.1	10	II		
			60d NOEC (growth)	0.051	m	flow	6.7-7.0	33.4	30.1	10	II		
			60d NOEC (survival)	0.384	m	flow	6.7-7.0	33.4	30.1	10	II		

Table B.1 continued overleaf

Table B.1 continued Summary of the ecotoxicological data for sodium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Lepomis macrochirus	bluegill	egg-fry	NOEC (% hatch)	>1.12	m	flow	6.7-7.1	38.3	33	25	II	No. of organisms: 200 eggs/replicate, 2 replicates/concentration. The volume of water used was 21 litres/replicate with each replicate being divided into 2 groups of 100 eggs in each tank. Surviving fry were randomly reduced to 2 groups of 50 eggs/replicate (i.e. a total of 200 fry/concentration). Test concentrations: Used 6 concentrations (0.057, 0.070, 0.140, 0.265, 0.522 and 1.122 mg Cr/l), plus a control. Dilution water: Well water. The mean dissolved oxygen concentration was 6.6 mg/l throughout the test. The concentration of Cr in the dilution water was not given. Control response: The percentage hatch was 85-90%. The survival was 18-30% over days 1-30 and 83-100% over days 31-60. Endpoints: Hatchability of eggs, survival and growth (total length at 30 and 60 days and wet weight of fish at 60 days). Comments: Test carried out according to "Proposed Recommended Bioassay Procedure of Egg and Fry Stages of Freshwater Fish. USEPA, 1972". Exposure started with <12 hour old eggs and continued for 60 days posthatch. Eggs hatched on day 2. No effects were seen on % hatch. The survival of bluegill fry to 30 days in both the treatment and control groups was highly variable due to feeding difficulties and so no reliable NOEC could be derived for this endpoint. The growth of fish at 0.265 mg Cr/l and above appeared to be reduced compared with controls, however, the variability in the data precluded ascribing a statistical significance to these. During days 31-60, the survival of the remaining fish in all groups was good and indicated no significant effects at any Cr concentration. The growth of fish over the period was significantly lower than controls at the highest concentration tested. The feeding difficulties encountered over the first 30 days means that the survival and growth results are unreliable.	Sauter et al, 1976
			30 d NOEC (growth)	~0.14	m	flow	6.7-7.1	38.3	33	25	IV		
			60d NOEC (growth)	0.522	m	flow	6.7-7.1	38.3	33	25	IV		
			60d NOEC (survival)	>1.12	m	flow	6.7-7.1	38.3	33	25	IV		
Oncorynchus mykiss	rainbow trout	alevin to juvenile	8 month NOEC/ LOEC (growth)	0.1	m	flow	7-8	42	45	7-15	II	No. of organisms: 40 alevin (1 week old)/concentration. 2 replicates/concentration. Fish were transferred to larger tanks after 2 months. Test concentrations: 0.1, 0.2, 0.34, 0.71 and 1.50 mg Cr/l, plus control. Dilution water: Dechlorinated tap water from a lake source. The dissolved oxygen was maintained at 5-13 mg/l throughout the test. The total concentration of Cr in the dilution water was <0.01 mg Cr/l. Control response: Control mortality was around 15%. Endpoints: Survival and growth (weight). Comments: All trout exposed to 0.34 mg Cr/l or higher died during the first 3 months of the test. The mortality at the next lowest concentration of 0.2 mg Cr/l was 20%. Growth was reduced relative to controls at all exposure concentrations (at 0.2 mg Cr/l, the fish weighed 30% less than controls). The Statistical significance of these findings is not given in the paper.	Benoit, 1976.
			8 month NOEC/ LOEC (mortality)	0.2	m	flow	7-8	42	45	7-15	II		

Table B.1 continued overleaf

Table B.1 continued Summary of the ecotoxicological data for sodium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Pimephales promelas	fathead minnow	juvenile (0.079g)	10d-LC_{50} (mortality)	12.4	m	flow	7.8	220	235	25	II	No. of organisms: 20 fish/concentration in 35 litres of solution for the lethality studies. For the growth studies, 50 1-day old larvae were used/replicate with 3 replicates/concentration. Test concentrations: A geometric series of 4 concentrations, plus control were used for the lethality studies. For the growth studies, 7 concentrations, in the range 0.05-3.06 mg/l, plus a control were used. Dilution water: Well water. Inflow-water was aerated to maintain the dissolved oxygen concentration at around 80% of saturation. The Cr concentration of the dilution water was not given. Control response: Not given for the mortality study. For the growth study, larval survival was around 60%. Endpoints: Mortality and growth (dry weight of fish). Comments: The concentration of CrVI in the test solutions was measured by the diphenylcarbazide method. In the growth study, survival was not affected by the Cr concentrations tested. A concentration of 3.06 mg Cr/l caused a 79% reduction in mean dry weight of the fish. Growth appeared to be reduced at concentrations of 0.1 mg Cr/l upwards, but not at 0.05 mg Cr/l. The data on growth reduction is presented graphically in the paper and the statistical significance of the growth reductions seen are not given.	Broderius and Smith Jr., 1979.
			20d-LC_{50} (mortality)	5.99	m	flow	7.8	220	235	25	II		
			30d-LC_{50} (mortality)	4.36	m	flow	7.8	220	235	25	II		
		larvae (1 day old)	30d-NOEC (mortality)	>3.06	m	flow	7.8	220	235	25	II		
			30d-NOEC (growth)	0.05	m	flow	7.8	220	235	25	II		

Table B.1 continued overleaf

Table B.1 continued Summary of the ecotoxicological data for sodium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Salvelinus fontinalis	brook trout	embryo to juvenile	8-month LOEC/ NOEC (mortality)	0.2	m	flow	7-8	45	42	7-15	II	No. of organisms: For the 8-month study, 500 eyed-embryos/concentration were used. After hatch, the alevins were randomly thinned to 100/concentration. The fish were removed to larger tanks 2 months after hatch. The 22-month study used 80 alevin (1 week old)/concentration. The fish were removed to larger tanks 2 months after hatch. Six months after the test started, the control fish were randomly thinned to 20 to avoid overcrowding. At 19 months the sex of each fish was determined and they were randomly thinned to 2 males and 4 females per exposure concentration and allowed to spawn. The embryos were incubated and the offspring were exposed to Cr for a further 3 months. Test concentrations: 0.01, 0.02, 0.04, 0.1 and 0.2 mg Cr/l, plus control for the 8-month study and 0.35, 0.76, 1.56, 3.10 and 6.37 mg Cr/l for the 22-month study. Dilution water: Dechlorinated tap water from a lake source (8-month study) or lake water itself (22-month study). The dissolved oxygen was maintained at 5-13 mg/l throughout the test. The concentration of Cr in the dilution water was <0.01 mg/l. Control response: Control mortality was around 20% in the 8-month study and 30% in the 22-month study. In the reproduction phase of the 22-month study, the mean spawning per female was 2.2, the mean number of eggs spawned/female was 338, the hatchability of embryos was 96% and the alevin-juvenile survival was 80%. Endpoints: Survival, growth (weight) and reproduction (hatch) Comments: In the study, all alevins exposed to 0.76 mg Cr/l or higher died during the first 3-months of the test and 72% of fish exposed at 0.35 mg Cr/l died during the first 3 months). This meant that fish were effectively exposed to only one concentration (0.35 mg Cr/l) in the spawning-phase of the 22-month study. Growth was found to be retarded at all concentrations in the 8-month study (at 0.2 mg Cr/l, the fish weighed 20% less than controls). However, the 22-month study showed that, although fish exposed to 0.35 mg Cr/l weighed 25% less than controls at 6 months, these effects were only temporary because by 12-22 months the weights of the exposed fish varied only slightly (10-12%) from controls. A serious bacterial disease occurred during the spawning phase of the 22-month study. This killed all but one female and one male in the 0.35 mg Cr treatment. These fish were able to spawn successfully before dying and the reproductive capacity was similar to that of controls. Around 99% of all spawned embryos hatched successfully at 0.35 mg Cr/l. However, after 3 months the survival of offspring was 22% less than control at this concentration and the offspring were statistically significantly smaller (p=0.05) than controls. The statistical significance of these findings is generally not given in the paper.	Benoit, 1976
			8-month NOEC/ LOEC (growth)	0.01	m	flow	7-8	45	42	7-15	II		
		alevin to adult	22-month LOEC (mortality)	<0.35	m	flow	7-8	45	42	7-15	IIIb		
			22-month LOEC (growth)	<0.35	m	flow	7-8	45	42	7-15	IIIb		
			22-month NOEC (repro.)	>0.35	m	flow	7-8	45	42	7-15	IIIb		

Table B.1 continued overleaf

Table B.1 continued Summary of the ecotoxicological data for sodium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Salvelinus namaycush	lake trout	egg-fry	NOEC (% hatch)	11.6	m	flow	6.8-7.1	34	31.5	10	IIIb	No. of organisms: 200 eggs/replicate, 2 replicates/concentration. The volume of water used was 21 litres/replicate with each replicate being divided into 2 groups of 100 eggs in each tank. Surviving fry were randomly reduced to 2 groups of 50 eggs/replicate (i.e. a total of 200 fry/concentration). Test concentrations: The first study used concentrations of 1.4, 2.9, 6.0, 11.6, 24.4 and 50.7 mg Cr/l, plus a control. A second study used 0.051, 0.105, 0.194, 0.384 and 0.822 mg Cr/l, plus a control. Dilution water: Well water. The mean dissolved oxygen concentration was 9.5 mg/l throughout the test. The concentration of Cr in the dilution water was not given. Control response: First study: percentage hatch was 38-40%; survival was 63-72% over days 1-30 and 84-94% over days 31-60. Second study: percentage hatch was 20%; survival was 76% over days 1-30 and 88% over days 31-60. Endpoints: Hatchability of eggs, survival and growth (total length at 30 and 60 days and wet weight of fish at 60 days). Comments: Test carried out according to "Proposed Recommended Bioassay Procedure of Egg and Fry Stages of Freshwater Fish. USEPA, 1972". Exposure started with <1 day old eggs and continued for 60 days posthatch. Eggs hatched on days 51-55. In the first study, the percentage hatch was significantly reduced compared with controls at concentrations of 24.4 mg Cr/l and above (no eggs hatched at 50.7 mg Cr/l). Survival of fry was significantly reduced by day 30 at concentrations of 6.0 mg Cr/l and above, and the growth of trout was significantly reduced at all exposure concentrations. During days 31-60, the survival and growth of trout was significantly lower than controls at all exposure concentrations. A second study was undertaken using lower test concentrations in order to better define some of the growth and survival endpoints. No significant effects were seen on % hatch, survival or growth at 30 days at any concentration. By day 60, survival of the fish was similar to controls at all concentrations tested. The growth of the fish exposed to 0.194 mg Cr/l and above was reduced compared with controls. The hatching rate in the controls was relatively low.	Sauter et al, 1976
			30d NOEC (survival)	2.9	m	flow	6.8-7.1	34	31.5	10	II		
			30d NOEC (growth)	>0.822 but <1.4	m	flow	6.8-7.1	34	31.5	10	II		
			60d NOEC (survival)	>0.822 but <1.4	m	flow	6.8-7.1	34	31.5	10	II		
			60d NOEC (growth)	0.105	m	flow	6.8-7.1	34	31.5	10	II		

Table B.1 continued overleaf

Table B.1 continued Summary of the ecotoxicological data for sodium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Stizostedion vitreum	walleye (pickerel)	egg-fry	NOEC (% hatch)	>2.167	m	flow	6.8-7.2	38.5	33.8	15	II	No. of organisms: 200 eggs/replicate, 2 replicates/concentration. The volume of water used was 21 litres/replicate with each replicate being divided into 2 groups of 100 eggs in each tank. Surviving fry were randomly reduced to 2 groups of 50 eggs/replicate (i.e. a total of 200 fry/concentration). Test concentrations: Used 6 concentrations (0.080, 0.133, 0.288, 0.558, 1.125 and 2.167 mg Cr/l), plus a control. Dilution water: Well water. The mean dissolved oxygen concentration was 9.5 mg/l throughout the test. The concentration of Cr in the dilution water was not given.	Sauter et al, 1976
			30d NOEC (growth)	>2.167	m	flow	6.8-7.2	38.5	33.8	15	IV	Control response: The percentage hatch was 62-69%. The survival was 10-14% over days 1-30. Endpoints: Hatchability of eggs, survival and growth (total length at 30 and 60 days and wet weight of fish at 60 days). Comments: Test carried out according to "Proposed Recommended Bioassay Procedure of Egg and Fry Stages of Freshwater Fish. USEPA, 1972". Exposure started with 2 day old eggs and continued for 60 days posthatch. Eggs hatched on days 9-12. The exposure was stopped after 30 days posthatch due to poor feeding success of fry of this species. No effects were seen on % hatch. The survival of fry to 30 days in both the treatment and control groups was poor due to feeding difficulties and so no reliable NOEC could be derived for this endpoint. The growth of fish were comparable with controls at all concentrations. The feeding difficulties encountered over the first 30 days means that the survival and growth results are unreliable.	
			30d NOEC (survival)	>2.167	m	flow	6.8-7.2	38.5	33.8	15	IV		

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) TLm = median threshold or tolerance limit - equivalent to LC_{50}
f) concentration converted from salt to chromium ion concentration
g) American Public Health Association. Standard Methods for the examination of water and wastewater
h) Val. = validity marking of test (see main text)

Table B.2 Summary of the ecotoxicological data for sodium dichromate to invertebrates

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp (°C)	Val.[h]	Test details	Reference
INVERTEBRATES - freshwater - short-term studies													
Ceriodaphnia reticulata	water flea		acute LC_{50}	0.0452	m	flow					IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985).	Mount, 1982
Ceriodaphnia reticulata	water flea	<24 h	48h-EC_{50}	0.195	n	static	8.0	240	230	23	II	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading rate was 10 animals in 200 ml solution. Test concentrations: Minimum of 5 concentrations, plus control. Dilution water: Unchlorinated, carbon-filtered well water. Dissolved oxygen level and Cr concentration of dilution water is not given but the heavy metal concentrations less than 0.01 µg/l in control test water. Control response: Not given. Endpoints: Immobilisation/mortality. Comments:	Elnabarawy et al, 1986
Daphnia magna	water flea		48h-LC_{50}	0.12[f]	n	static					IIIb	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Centrifuged lake water. Dissolved oxygen level and Cr concentration in dilution water is not given. Control response: 80-100% survival in 48 hours. Endpoints: Immobilisation Comments: Value estimated from 50% immobilisation-time curves.	Anderson, 1946
Daphnia magna	water flea		24h-TLm[e]	8.7[f]						21-25	IIIa	No. of organisms: Not given. Test concentrations: Not given Dilution water: Lake water. The dissolved oxygen level and Cr concentration is not given. Control response: Not given. Endpoints: Not given. Comments: Tests appear to have been carried out at room temperature.	Dowden and Bennett, 1965
			48h-TLm[e]	4.0[f]						21-25	IIIa		
Daphnia magna	water flea	<24h	24h-EC_{50}	0.67[f]	n	static	7.6-7.7	16[o]		20	II	No. of organisms: 10 organisms/replicate, 3 replicates/concentration. Loading was 10 animals in 20 ml solution. Test concentrations: Used a 1:2 dilution series defined by a rangefinding test. Additional dilutions of 1:1.3-1:1.1 were used in some cases to better define the toxicity value. Dilution water: Chlorine-free tap water. The dissolved oxygen level and Cr concentration in the dilution water is not given. Control response: Not given. Endpoints: Immobilisation/mortality. Comments: The paper indicates that the EC_{50} =1.4 mg/l, based on the effective ion concentration. This is taken to mean the concentration of $Cr_2O_7^{2-}$. The value given in the table has therefore been converted to mg Cr//.	Bringmann and Kühn, 1977b

Table B.2 continued overleaf

Table B.2 continued Summary of the ecotoxicological data for sodium dichromate to invertebrates

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp (oC)	Val.h	Test details	Reference
Daphnia magna	water flea	<24h	24h-EC_{50}	0.42[f]	n	static	8.0			20	IIIb	No. of organisms: 10 organisms/replicate, 2 replicates/concentration. Loading was 10 animals in 20 ml solution. Test concentrations: Used a 1:2 dilution series defined by a rangefinding test. Additional dilutions of 1:1.4-1:1.1 were used in some cases to better define the toxicity value. Dilution water: Artificial fresh water. The dissolved oxygen level was reported to never fall below 2 mg/l. The Cr concentration of the dilution water is not given. Control response: Not given. Endpoints: Immobilisation/mortality. Comments: It is possible that the dissolved oxygen level in some test solutions could have been relatively low. The paper indicates that the EC_{50}=0.89 mg/l, based on the effective ion concentration. This is taken to mean the concentration of $Cr_2O_7^{2-}$. The value given in the table has therefore been converted to mg Cr//.	Bringmann and Kühn, 1982
Daphnia magna	water flea	<24 h	48h-EC_{50}	0.112	n	static	8.0	240	230	23	II	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading rate was 10 animals in 200 ml solution. Test concentrations: Minimum of 5 concentrations, plus control. Dilution water: Unchlorinated, carbon-filtered well water. Dissolved oxygen level and Cr concentration of dilution water is not given but the heavy metal concentrations less than 0.01 µg/l in control test water. Control response: Not given. Endpoints: Immobilisation/mortality. Comments:	Elnabarawy et al, 1986
Daphnia magna	water flea		48h-EC_{50}	0.0199				50			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985).	Call et al, 1981
			96h-EC_{50}	0.0245				50			IIIa		
Daphnia magna	water flea		acute EC_{50}	0.0242	m	flow		45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985).	Mount, 1982
Daphnia magna	water flea		acute EC_{50}	0.131	m	static	8.2-8.4	185			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985).	Call et al, 1981
			acute EC_{50}	0.0736	m	static	7.5-7.6	196			IIIa		
			acute EC_{50}	0.0213	m	static	7.5	50			IIIa		

Table B.2 continued overleaf

Table B.2 continued Summary of the ecotoxicological data for sodium dichromate to invertebrates

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp (oC)	Val.h	Test details	Reference
Daphnia pulex	water flea		acute EC_{50}	0.0363	m	flow		45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985).	Mount, 1982
Daphnia pulex	water flea	<24 h	48h-EC_{50}	0.122	n	static	8.0	240	230	23	II	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading rate was 10 animals in 200 ml solution. Test concentrations: Minimum of 5 concentrations, plus control. Dilution water: Unchlorinated, carbon-filtered well water. Dissolved oxygen level and Cr concentration of dilution water is not given but the heavy metal concentrations less than 0.01 µg/l in control test water. Control response: Not given. Endpoints: Immobilisation/mortality. Comments:	Elnabarawy et al, 1986
Simocephalus serrulatus	water flea		acute LC_{50}	0.0409	m	flow		45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985).	Mount, 1982
Simocephalus vetulus	water flea		acute LC_{50}	0.0323	m	flow		45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985).	Mount, 1982

Table B.2 continued overleaf

Table B.2 continued Summary of the ecotoxicological data for sodium dichromate to invertebrates

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp (oC)	Val.h	Test details	Reference
INVERTEBRATES - freshwater - long-term studies													
Ceriodaphnia reticulate	water flea	<24 h	7d-EC_{50} (repro.)	>0.018	n	48h renew.	8.0	240	230	23	IIIb	No. of organisms: 1 animals/replicate, 10 replicates/concentration. Loading rate was 1 animal in 15 ml solution. Test concentrations: 0.0005, 0.0015, 0.005, 0.015 and 0.050 mg Cr/l, plus control. Dilution water: Unchlorinated, carbon-filtered well water. Dissolved oxygen level was >5 mg/l throughout. The Cr concentration of dilution water is not given but the heavy metal concentrations less than 0.01 µg/l in control test water. Control response: Adult survival was 100%. The cumulative number of young/adult was 23. Three broods were released by day 7 and no ephippia were observed. Endpoints: Reproductive impairment and mortality. Reproductive impairment was defined as the decrease in the average cumulative number of young/adult. Comments: No parent mortality was seen at any concentration. The number of young/adult was statistically significantly reduced (p=0.05) at all concentrations (the number of young/adult were 16, 16, 16, 14, and 14 and concentrations of 0.5, 1.5, 5, 15 and 50 µg Cr/l. A 7-day LC_{50} of 17.4 µg/l is quoted in the paper but it is not clear how this was derived as 100% of the adults survived at all concentrations. The range of concentrations tested does not appear to be appropriate.	Elnabarawy et al, 1986
			7d-EC_{50} (mortality)	0.017	n	48h renew.	8.0	240	230	23	IV		
Ceriodaphnia reticulate	water flea		life-cycle NOEC	0.025				45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985). LOEC 0.064 µg/l.	Mount, 1982
Daphnia magna	water flea	<24h	14d NOEC (repro.)	0.0005	n	static	8.0	240	230	23	II	No. of organisms: 1 animals/replicate, 10 replicates/concentration. Loading rate was 1 animal in 50 ml solution. Test concentrations: 0.0005, 0.0015, 0.005, 0.015 and 0.050 mg Cr/l, plus control. Dilution water: Unchlorinated, carbon-filtered well water. Dissolved oxygen level was >5 mg/l throughout. The Cr concentration of dilution water is not given but the heavy metal concentrations less than 0.01 µg/l in control test water. Control response: Adult survival was 100%. The cumulative number of young/adult was 85. Three broods were released by day 14 and no ephippia were observed. Endpoints: Reproductive impairment and mortality. Reproductive impairment was defined as the decrease in the average cumulative number of young/adult. Comments: The adult survival at 0.015 mg Cr/l was 60%. This was not statistically significantly different from controls. The next highest concentration caused 100% mortality. A 14d-LC_{50} of 0.0056 mg/l was derived in the paper but this appears to conflict with the survival rates given in the paper.	Elnabarawy et al. 1986
			14d-LOEC/ EC_{16} (repro.)	0.0017	n	static	8.0	240	230	23	II		
			14d- NOEC (mortality)	0.015	n	static	8.0	240	230	23	IIIb		

Table B.2 continued overleaf

Table B.2 continued Summary of the ecotoxicological data for sodium dichromate to invertebrates

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp (oC)	Val.h	Test details	Reference
Daphnia magna	water flea		lifecycle NOEC	0.0025				45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985).	Mount, 1982
Daphnia pulex	water flea		lifecycle NOEC	0.0047				45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985). LOEC = 0.008 mg/l.	Mount, 1982
Daphnia pulex	water flea	<24h	14d NOEC (repro.)	>0.05	n	static	8.0	240	230	23	IIIb	No. of organisms: 1 animals/replicate, 10 replicates/concentration. Loading rate was 1 animal in 50 ml solution. Test concentrations: 0.0005, 0.0015, 0.005, 0.015 and 0.050 mg Cr/l, plus control. Dilution water: Unchlorinated, carbon-filtered well water. Dissolved oxygen level was >5 mg/l throughout. The Cr concentration of dilution water is not given but the heavy metal concentrations less than 0.01 µg/l in control test water. Control response: Adult survival was 100%. The cumulative number of young/adult was 53. Three broods were released by day 14 and no ephippia were observed. Endpoints: Reproductive impairment and mortality. Reproductive impairment was defined as the decrease in the average cumulative number of young/adult. Comments: No statistically significant effects were seen on reproduction or mortality. The adult mortality at the highest concentration tested was 50% of controls, but this was not considered statistically significant. The paper gives a 14d- MATC and EC_{50} for reproduction of 0.0094 and >0.0175 mg Cr/l respectively. A 14d-LC_{50} for survival is given as 0.0174 mg Cr/l. It is not clear how these are derived from the reported data. The range of concentrations tested do not appear to have been appropriate for the substance.	Elnabarawy et al. 1986
			14d-EC_{50} (repro.)	>0.018	n	n	8.0	240	230	23	IIIb		
			14d-NOEC (survival)	~0.05	n	static	8.0	240	230	23	IIIb		
Simocephalus serrulatus	water flea		lifecycle NOEC	0.0139				45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985).	Mount, 1982

Table B.2 continued overleaf

Table B.2 continued Summary of the ecotoxicological data for sodium dichromate to invertebrates

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp (oC)	Val.h	Test details	Reference
Simocephalus vetulus	water flea		lifecycle NOEC	0.0047				45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in USEPA (1985).	Mount, 1982

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) TLm = median threshold or tolerance limit - equivalent to LC_{50}
f) concentration converted from salt to chromium ion concentration
g) Val. = validity of test (see main text)

Table B.3 Summary of the ecotoxicological data for sodium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d] ‰	Alk.[c]	Temp (°C)	Val.[f]	Test details	Reference
ALGAE - freshwater													
Microcystis aeruginosa	blue-green algae		8d NOEC (biomass)	0.002[e]	n	static	7.0				IIIb	No. of organisms: Not clear. Appears to use 5 ml algal suspension in 50 ml. 3 replicates/concentration appear to be used. Test concentrations: Not clear. Appears to use a 1:2 dilution series. Dilution water: Growth media. The Cr concentration in the dilution water was not given. Control response: Not given. Endpoints: Growth inhibition (biomass), determined by turbidity measurements. Comments: Result was expressed as a toxicity threshold, defined as a ~3% inhibitory effect compared to growth in non-toxic test cultures.	Bringmann and Kühn, 1976, 1978
Scenedesmus quadricauda	green algae		7-8d NOEC (biomass)	0.58[e]	n	static	7			27	IIIb	No. of organisms: Not clear. Appears to use 5 ml algal suspension in 50 ml. 3 replicates/concentration appear to be used. Test concentrations: Appears to use a 1:2 dilution series. Dilution water: Growth media. The Cr concentration in the dilution water was not given. Control response: Not given. Endpoints: Growth inhibition (biomass), determined by turbidity measurements. Comments: Result was expressed as a toxicity threshold, defined as a ~3% inhibitory effect compared to growth in non-toxic test cultures.	Bringmann and Kühn, 1977a; 1978; 1979; 1980a
Selenastrum capricornutum	green algae		96h-EC_{50}	0.185		static		53			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Unpublished results by J R Richter.	USEPA, 1985

Table B.3 continued overleaf

Table B.3 continued Summary of the ecotoxicological data for sodium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d] ‰	Alk.[c]	Temp (°C)	Val.[f]	Test details	Reference
ALGAE - saltwater													
Thalassiosira pseudonana	diatom		15d-EC (biomass)	0.01	n	static		0.03‰			IIIb	No. of organisms: Not clear. Test concentrations: 0.01 and 0.10 mg Cr/l, plus control in the first series of experiment and 0.02 and 0.20 mg Cr/l, plus control in the second series of experiments. Dilution water: Natural seawater from the freshwater end (0.03‰) and saltwater end (32.5‰) of an estuary. The water was filtered (0.45 µm) and autoclaved before used. Major nutrients (nitrate, phosphate and silicate) were added. A range of salinities were obtained by mixing the low and high salinity water. The Cr concentration of the dilution water is not given. Control response: Given graphically. Endpoints: Growth, determined by *in vivo* fluorescence. Comments: Investigated effects of salinity on toxicity. The first series investigated salinities in the range 0.03‰ -32.5‰. The second series investigated a narrower range of 0.03‰-2.11‰. Only two concentrations tested in each series and so the dose-response is not well defined. Experiments were carried out to show that Cr(VI) was stable in the seawater system used for at least 2 months (no reduction to Cr(III) was seen). At low salinity (0.03‰), a concentration of 0.01 mg Cr/l was slightly inhibiting to growth and a concentration of 0.1 mg Cr/l was severely inhibiting to growth. At higher salinities (4.0-32.5‰) there was not effect on growth at either concentration. The results are shown graphically and so the significance of the inhibition seen is unclear.	Frey et al, 1983
			15d-NOEC (biomass)	0.10	n	static		4-32.5‰			IIIb		

Table B.3 continued overleaf

Table B.3 continued Summary of the ecotoxicological data for sodium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d ‰	Alk.c	Temp (oC)	Val.f	Test details	Reference
Natural populations			39-59d EC	0.01	n	static		0.03‰			IIIb	No. of organisms: Used 10 ml of unfiltered seawater from the same location as where the dilution water was collected. The total volume of the growth chamber was 10 litres and so the algal concentration ~1,000 times less than the natural population. There were three replicates for each treatment. Test concentrations: 0.010 and 0.1 mg Cr/l, plus control. Dilution water: Natural seawater from various locations in an estuary. The water was filtered (0.45 µm) before use. Major nutrients (N, P and Si), trace metals (Fe, Cu, Zn, Co, Mn and Mo) and vitamins were added. The Cr concentration of the dilution water is not given. Control response: Given graphically. Endpoints: Growth, determined by *in vivo* fluorescence and extracted chlorophyll a., and species composition. Comments: Used the natural algal population present in estuary. The test was carried out at a temperature within 1°C of the water temperature when the sample was collected. Experiments were carried out to show that Cr(VI) was stable in the seawater system used for at least 2 months (no reduction to Cr(III) was seen). In total 4 tests were carried out at high salinity (32‰), 2 tests at low salinity (0.03-0.04‰) and one at intermediate salinity (20.4‰). Growth was generally not measurable until a number of cell divisions had taken place (generally 10-30 days) and was generally monitored for a further 18-20 days.	Frey et al, 1983
			39-59d NOEC	0.1	n	static		20.4-32.5‰			IIIb	No effects were generally seen in the high or intermediate salinity experiments (Cr caused a slight enhancement in growth was seen in some tests, possibly due to micro-nutrient deficiencies in the test media.). In contrast, in the low salinity experiments, the 0.1 mg Cr/l concentration either completely eliminated growth of greatly reduced growth and the 0.01 mg Cr/l concentration caused an apparent lag in growth relative to controls. Most sensitive species were *Surirella ovata*, *Cyclotella* sp., *Detonula confervacea* and *Skeletonema costatum*. The results are shown graphically and so the significance of the inhibition seen is unclear. Only two concentrations appear to have been tested and so the dose-response is not well defined.	

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) concentration converted from salt to chromium ion concentration
f) Val. = validity marking of test (see main text)

Table B.4 Summary of the ecotoxicological data for sodium dichromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp (°C)	Val.	Test details	Reference
MICROORGANISMS													
Mixed population	activated sludge bacteria		3h-IC_{50}	30[e]	n		7.4-8.0			21	II	No. of organisms: Activated sludge from a municipal waste water treatment plant. Inoculum was 200 ml of sludge (~800 mg of suspended solids) in 500 ml water. Test concentrations: Not given Dilution water: Synthetic sewage. Control response: Mean oxygen consumption rate was 0.96 mg O_2/l-min. Endpoints: Rate of oxygen consumption. Comments: OECD activated sludge, respiration inhibition test.	Klecka and Landi, 1985
Chilomonas paramaecium	protozoa		NOEC	5×10^{-5}[e]	n	static					IIIb	No. of organisms: Not clear. Test concentrations: Not clear. May use a 1:2 dilution series. Dilution water: Growth media. The Cr concentration in the dilution water was not given. Control response: Not given. Endpoints: Growth inhibition. Comments: Analogous to the cell multiplication inhibition test. Result was expressed as a toxicity threshold, defined as a ~5%inhibitory effect compared to growth in non-toxic test cultures. Duration of test is unclear but, by analogy with other work by these authors, was probably around 72 hours.	Bringmann and Kühn, 1981
Entosiphon sulcatum	protozoa		72h-NOEC	9.6[e]	n	static				25	IIIb	No. of organisms: Use 2 replicates/concentration. Inocculum was 2 ml of cell culture in 20 ml test solution (~15,000 cells/ml). Test concentrations: Appears to use a 1:2 dilution series. Dilution water: Growth media. The Cr concentration in the dilution water was not given. Control response: Not given. Endpoints: Growth inhibition (biomass), by cell counts. Comments: Analogous to the cell multiplication inhibition test. Result was expressed as a toxicity threshold, defined as a ~5%inhibitory effect compared to growth in non-toxic test cultures.	Bringmann and Kühn, 1979; 1980a; 1981
Pseudomonas fluorescens	bacteria		24h NOEC (glucose assimil.)	0.38	n	static	7.0			25	IIIb	No. of organisms: Not clear. Test concentrations: Not clear. Probably 1:2 dilutions. Dilution water: Growth media. The Cr concentration in the dilution water was not given. Control response: Not given. Endpoints: Inhibition of glucose assimilation. Comments: Result was expressed as a toxicity threshold, defined as a ~3% inhibitory effect compared with non-toxic test cultures.	Bringmann, 1973

Table B.4 continued overleaf

Table B.4 continued Summary of the ecotoxicological data for sodium dichromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp (oC)	Val.	Test details	Reference
Pseudomonas putida	bacteria		16h- NOEC	0.38[e]	n	static	7.0			25	IIIb	No. of organisms: Used 10 ml of bacterial suspension in 100 ml solution. 3 replicates/concentration. Test concentrations: A 1:2 dilution series was used. Dilution water: Growth media. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Growth (biomass), as determined turbidimetrically. Comments: Result was expressed as a toxicity threshold, defined as a ~3% inhibitory effect compared with non-toxic test cultures.	Bringmann and Kühn, 1976; 1977a; 1979; 1980a
Uronema parduczi	protozoa		20h-NOEC	1.0[e]	n	static	6.9			25	IIIb	No. of organisms: Not clear. Test concentrations: Not clear. A 1:2 dilution series was probably used. Dilution water: Growth media. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Growth (biomass) Comments: Result was expressed as a toxicity threshold, defined as a ~5% inhibitory effect compared with non-toxic test cultures.	Bringmann and Kühn; 1980b; 1981
AMPHIBIANS													
Rana cyanophlyctis	Indian skipper frog	adults (~30 g)	96h- LC_{50}	85[e]	n	24h renew.	7.2	65		26	II	No. of organisms: 10 animals/concentration, in 2 litres solution. Test concentrations: Not given. A control was run. Dilution water: Tap water. The dissolved oxygen concentration was 7.0 mg/l. The Cr concentration of the dilution water was not given. Control response: Not given. Endpoints: Mortality. Comments: 96h-LC_{50} for chromic acid and potassium dichromate were 43 and 81 mg/l, respectively.	Joshi and Patil, 1991

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) concentration converted from salt to chromium ion concentration
f) Val. = validity marking (see main text)

References

The references for this appendix appear in the full reference list (Section 6) of the main report.

Appendix C Summary of aquatice toxicity data for potassium dichromate

This appendix reviews the aquatic toxicity data for potassium dichromate. Values which have been used in the risk assessment report are highlighted with light grey shading. The following paragraphs provide some information about the selection process; these apply to the overall data set for chromium (VI) and not all comments may apply to data in this particular appendix.

For short term test results, the values selected are the lowest for each species which come from tests with a validity marking of I or II. In some cases a number of valid results may have been produced by one study, using different experimental conditions (for example, hardness, salinity and temperature). For properties such as temperature and salinity the test conditions closest to the 'real' environment have been chosen (so avoiding high or low temperatures, and preferring tests at salinities similar to sea water); for hardness, the lowest test result is preferred as a range of hardness is found in natural waters. These 'rules' have been applied flexibly so as to allow interpretation of the individual studies.

For long term tests, all data from validity marking I and II have been selected, but some studies with marking IIIb have also been included. Multiple values have been taken from some studies, where a number of different endpoints were measured (for example, mortality, reproduction and growth). Where several measures of the same endpoint are reported in one study, values from longer exposure periods are generally preferred, with the exception of algal studies where the maintenance of exponential growth conditions is considered.

The further treatment of the long term data to derive the PNEC is described in the main risk assessment report. In some cases, notes on data not used in the PNEC derivation have also been included in the comments on the tests in the appendix.

Table C.1 Summary of the ecotoxicological data for potassium dichromate to fish

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp. (°C)	Val.[h]	Test details	Reference
FISH - freshwater - short-term studies													
Brachydanio rerio	zebra fish	3.5±0.5 cm	48h-LC_{50}	67.0	n	static	7.8	100		20	II	No. of organisms: 10/replicate, 3 replicates/concentration. Test concentrations: 7 concentrations plus control. Determined by rangefinding test to cover 0% and 100% mortality. Dilution water: Artificial test water prepared from distilled water. Dissolved oxygen was >90% of saturation throughout the test. Concentration of Cr in dilution water not reported. Control response: Not given. Comments:	Bellavere and Gorbi, 1981
			96h-LC_{50}	58.5	n	static	7.8	100		20	II		
Campostoma anomalum	central stoneroller		acute LC_{50}	51.3	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White.	USEPA, 1985
Carassius auratus	goldfish	1-2 g	48h-TLm[c]	58.8	n	static	7.5	20	18	25	II	No. of organisms: 5 fish/replicate, 2 replicates/concentration. The fish loading was 5 fish in 10 litres of solution. Test concentrations: 5 concentrations plus control. A logarithmic series used. Dilution water: Mixture of 5 parts natural limestone spring water with 95 parts distilled, demineralised water. Dissolved oxygen was >4 mg/l throughout the test. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Used test protocol recommended by APHA[g] (1960 version). During the test the pH of the solution often fell, but was always within the range tolerated by the species.	Pickering and Henderson, 1966
			96h-TLm[e]	37.5	n	static	7.5	20	18	25	II		
Carassius auratus	goldfish		Acute- LC_{50}	90-135	m	flow		220			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985). Mean LC_{50} value 121 mg/l - used as part of test method development. 11d-LC_{50} was 30.4 mg/l.	Adelman and Smith Jr., 1976.
Carassius auratus	goldfish	4-7 g	96h- LC_{50}	110	n	static	4-6	770		22	IV	No. of organisms: 8 fish/concentration. The loading was 8 fish in 20 litres of solution (loading 0.5 g fish/l). Test concentrations: 110, 130, 150 and 170 mg/l plus control. Dilution water: Chlorine-free water. Dissolved oxygen levels maintained by continuous aeration. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Cr levels in gills of control fish = 55 µg/g dry wt. The pH was not controlled, and dropped from pH 6 to pH 4 with increasing Cr concentrations from 110-200 ppm. The toxic effect seen may be due to this drop in pH. Other experiments were carried out with the pH adjusted to 7.3±0.2 at each concentration. Toxicity was seen to increase with the Cr exposure concentration but no LC_{50} was reported.	Riva et al, 1981

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Carassius carassius	goldfish		24h- TLm[e]	249[f]							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Standard reference water (a lab-prepared medium, free from organics, containing all the major ions in concentrations and proportions of an average surface water in the US. Dissolved oxygen and concentration of Cr in dilution water not reported. Control response: Not given. Comments:	Dowden and Bennett, 1965
Carassius carassius	goldfish	1.93 g	24h-LC50	354	m	static	4.6-7.5	36		5	IIIb	No. of organisms: 10 fish/replicate, 2 replicates/concentration. The loading was 10 fish in 40 litres of solution. Test concentrations: 4 concentrations plus control. Concentrations were determined from a rangefinding study. Dilution water: Dechlorinated tap water. Dissolved oxygen was 9.0-12.5 mg/l, 6.2-9.9 mg/l and 4.2-7.9 mg/l in tests carried out at 5oC, 15oC and 30oC respectively. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Mean pH in all tests was 5.8. Toxicity increased with increasing temperature. The Cr concentration was found to decline by 8.8%, 19.1% and 7.1% in tests carried out at 5oC, 15oC and 30oC respectively.	Cairns Jr. et al, 1978
			24h-LC50	213	m	static	4.6-7.5	36		15	II		
			24h-LC50	109	m	static	4.6-7.5	36		30	IIIb		
Channa punctatus	not known	10-15 cm	48h-LC50	70.8	n	static	8.1	65	57		II	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Unchlorinated water. Dissolved oxygen was 6.5 mg/l. Concentration of Cr in dilution water not reported. Control response: No mortality. Comments:	Saxena and Parashari, 1983
			96h-LC50	45.2	n	static	8.1	65	57		II		
Ericymba buccata	silverjaw minnow		acute LC50	49.6	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White.	USEPA, 1985
Etheostoma nigrum	Johnny darter		acute LC50	46.0	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White.	USEPA, 1985

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Gambusia affinis	mosquitofish	adult females	24h-TLme	131f	n	static	5.4-6.7		<100	21-23	IV	No. of organisms: 10 fish/concentration. Loading rate was 10 fish in 15 litres. Test concentrations: 10, 18, 32, 56, 100 and/or 100, 180, 320, 560, 1000 plus control. Dilution water: Turbid water from farm ponds. The turbidity of the test solutions was 55-1,500 ppm. The tests were aerated to maintain the dissolved oxygen levels. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: The use of turbid water without analytical determination of the exposure concentrations means that the actual exposure during the test is uncertain. Tail rot was seen in fish in the holding tank - this was treated before the fish were used.	Wallen et al, 1957
			48h-TLme	113f	n	static	5.4-6.7		<100	21-23	IV		
			96h-TLme	99.0f	n	static	5.4-6.7		<100	21-23	IV		
			6d-TLme	49.5f	n	static	5.4-6.7		<100	21-23	IV		
Ictalurus punctatus	channel catfish	8.81 g	24h-LC50	50	m	static	4.6-7.5	36		5	IIIb	No. of organisms: 10 fish/replicate, 2 replicates/concentration. The loading was 10 fish in 40 litres of solution. Test concentrations: 4 concentrations plus control. Concentrations were determined from a range finding study. Dilution water: Dechlorinated tap water. Dissolved oxygen was 9.0-12.5 mg/l, 6.2-9.9 mg/l and 4.2-7.9 mg/l in tests carried out at 5oC, 15oC and 30oC respectively. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: The mean pH in all tests was 5.8. Toxicity increased with decreasing temperature. The Cr concentration was found to decline by 8.8%, 19.1% and 7.1% in tests carried out at 5oC, 15oC and 30oC respectively.	Cairns Jr. et al, 1978
			24h-LC50	58	m	static	4.6-7.5	36		15	II		
			24h-LC50	72	m	static	4.6-7.5	36		30	IIIb		
Lebistes reticulates	guppy	0.1-0.2 g	48h- TLm[e]	61.7	n	static	7.5	20	18	25	II	No. of organisms: 5 fish/replicate, 2 replicates/concentration. The fish loading was 5 fish in 2 litres of solution. Test concentrations: 5 concentrations plus control. A logarithmic series was used. Dilution water: Mixture of 5 parts natural limestone spring water with 95 parts distilled, demineralised water. Dissolved oxygen was >4 mg/l throughout the test. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Used test protocol recommended by APHA[g] (1960 version). During the test the pH of the solution often fell, but was always within the range tolerated by the species.	Pickering and Henderson, 1966
			96h- TLm[e]	30	n	static	7.5	20	18	25	II		
Lepomis cyanekius	green sunfish		acute LC_{50}	89.2-147.6	m	flow		400			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985). Mean LC_{50} = 114.7 mg/l.	Waheda, 1977

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Lepomis macrochirus	bluegill	1-2 g	48h-TLm[e]	171	n	static	7.5	20	18	25	II	No. of organisms: 5 fish/replicate, 2 replicates/concentration. The fish loading was 5 fish in 10 litres of solution. Test concentrations: 5 concentrations plus control. A logarithmic series was used. Dilution water: Hard water was natural limestone spring water. Soft water was a mixture of 5 parts natural limestone spring water with 95 parts distilled, demineralised water. Dissolved oxygen was >4 mg/l throughout the test. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Used test protocol recommended by APHA[g] (1960 version). During the test the pH of the solution in soft water often fell, and that in hard water increased with time. The pH was always within the range tolerated by the species.	Pickering and Henderson, 1966
			96h-TLm[e]	118	n	static	7.5	20	18	25	II		
			48h-TLm[e]	180	n	static	8.2	360	300	25	II		
			96h-TLm[e]	133	n	static	8.2	360	300	25	II		
Lepomis macrochirus	bluegill	0.96 g	96h-LC_{50}	113	n	static		44		20	II	No. of organisms: 10 fish/replication, 2 replicates/concentrations. Loading was 10 fish per 5 gallon jar (large fish limited to 5 per tank). Test concentrations: Not given. Dilution water: Synthetic soft water. Continuously aerated. Dissolved oxygen was 5-9 mg/l throughout the test. Concentration of Cr in dilution water not reported. Control response: No mortalities. Comments: Similar results for potassium chromate (LC_{50} = 120-168 mg/l). Test carried out with small (3.9 cm), medium (6.1 cm) and large (14.2 cm) fish: LC_{50} was similar with all fish.	Cairns Jr. and Scheier, 1958; 1959; 1968
		2.8 g	96h-LC_{50}	113	n	static		44		18-20	II		
		54.3 g	96h-LC_{50}	113	n	static		44		20	II		
Lepomis macrochirus	bluegill		96h-LC_{50}	113	n	static				18	IIIa	No. of organisms: Not given but was probably 10 fish per replication/concentration in 18 litres of solution. Test concentrations: Not given. Dilution water: Synthetic soft water. Dissolved oxygen was 5-9 mg/l throughout the test. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Probably the same results are Cairns Jr. and Scheier, 1958 reported above. A 96h LC_{50} of 168 m/l was reported using potassium chromate.	Patrick et al, 1968
Lepomis macrochirus	bluegill		acute LC_{50}	130.4-135	n	static		171			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985).	A.N.S., 1960
Lepomis macrochirus	bluegill		acute LC_{50}	144.5	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White	USEPA, 1985

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Lepomis macrochirus	bluegill		96h-LC_{50}	154	m		6.0-7.3	75-105	50-60		II	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading was 10 organisms in 10 litres of solution. Test concentrations: 55, 100, 125, 150, 200, 250, 300 mg/l plus a control. Dilution water: Moderately hard reconstituted water. Dissolved oxygen was 7.0-9.0 mg/l. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. The pH of the test solution decreased with increasing Cr concentration within the range 7.3 to 6.0. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. A similar 96h-LC_{50} of 182 mg/l was obtained with potassium chromate.	Jop et al, 1987
Lepomis macrochirus	bluegill	1-9 g	96h- TLm[e]	110		static	6.0-6.8	45	37	20	II	No. of organisms: 10 fish/replicate, 2 replicates/concentration. The loading was 10 fish in 20.4 litres of solution. Test concentrations: 55, 74, 99, 113, 148 and 173 mg/l plus controls. Dilution water: Reconstituted dilution water. Water was continuously aerated throughout the test and the dissolved oxygen was >60% of saturation. Concentration of Cr in dilution water not reported Control response: No deaths occurred. Comments: A 96h-TLm of 170 mg/l was obtained with potassium chromate at pH 7.5-8.8.	Trama and Benoit, 1960
Lepomis macrochirus	bluegill	0.64g	24h-LC_{50}	228	m	static	4.6-7.5	36		5	IIIb	No. of organisms: 10 fish/replicate, 2 replicates/concentration. The loading was 10 fish in 40 litres of solution. Test concentrations: 4 concentrations plus control. Concentrations were determined from a range finding study. Dilution water: Dechlorinated tap water. Dissolved oxygen was 9.0-12.5 mg/l, 6.2-9.9 mg/l and 4.2-7.9 mg/l in tests carried out at 5°C, 15°C and 30°C respectively. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: The mean pH in all tests was 5.8. The Cr concentration was found to decline by 8.8%, 19.1% and 7.1% in tests carried out at 5°C, 15°C and 30°C respectively.	Cairns Jr. et al, 1978
			24h-LC_{50}	280	m	static	4.6-7.5	36		15	II		
			24h-LC_{50}	214	m	static	4.6-7.5	36		30	IIIb		
Lepomis macrochirus	bluegill		48h-LC_{50}	155.5				43			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985).	Cairns Jr. et al, 1965

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Lepomis macrochirus	bluegill		24h-TLm[e]	261[f]							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Standard reference water (a lab-prepared medium, free from organics, containing all the major ions in concentrations and proportions of an average surface water in the US. Dissolved oxygen and concentration of Cr in dilution water not reported. Control response: Not given. Comments:	Dowden and Bennett 1965
Morone saxatilis	striped bass		acute LC_{50}	26.5-35	n	static		35			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985). Mean LC_{50}=30.5 mg/l.	Hughes, 1973
Notemigonus crysoleucas	golden shiner		96h- LC_{50}	55	n	Static	7.5	72.2	42.5		II	No. of organisms: Not given. Static tests conducted in 4 litre aquaria. Test concentrations: Not given. Dilution water: Dechlorinated tap water. Dissolved oxygen concentration not reported. Concentration of total Cr in dilution water was 0.5 µg/l. Control response: Not given. Comments: A flow-through avoidance test was also carried out using measured Cr concentrations. Here avoidance observed at 0.073 mg/l when the fish were observed over a 10 minute period.	Hartwell et al, 1989
Notemigonus crysoleucas	golden shiner	2.56 g	24h-LC_{50}	151	m	static	4.6-7.5	36		5	IIIb	No. of organisms: 10 fish/replicate, 2 replicates/concentration. The loading was 10 fish in 40 litres of solution. Test concentrations: 4 concentrations plus control. Concentrations were determined from a rangefinding study. Dilution water: Dechlorinated tap water. Dissolved oxygen was 9.0-12.5 mg/l, 6.2-9.9 mg/l and 4.2-7.9 mg/l in tests carried out at 5°C, 15°C and 30°C respectively. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Mean pH in all tests was 5.8. Toxicity increased with increasing temperature. The Cr concentration was found to decline by 8.8%, 19.1% and 7.1% in tests carried out at 5°C, 15°C and 30°C respectively.	Cairns Jr. et al, 1978
			24h-LC_{50}	109	m	static	4.6-7.5	36		15	II		
			24h-LC_{50}	104	m	static	4.6-7.5	36		30	IIIb		
Notropis atherinoides	emerald shiner		acute LC_{50}	48.4	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White.	USEPA, 1985

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Notropis chrysocephalus	striped shiner		acute LC_{50}	85.6	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White.	USEPA, 1985
Notropis stramineus	sand shiner		acute LC_{50}	74.6	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White.	USEPA, 1985
Oncorhynchus mykiss	rainbow trout	4.42 g	24h-LC_{50}	58.9	m	static	4.6-7.5	36		5	IIIb	No. of organisms: 10 fish/replicate, 2 replicates/concentration. The loading was 10 fish in 40 litres of solution. Test concentrations: 4 concentrations plus control. Concentrations were determined from a rangefinding study. Dilution water: Dechlorinated tap water. Dissolved oxygen was 9.0-12.5 mg/l, 6.2-9.9 mg/l and 4.2-7.9 mg/l in tests carried out at 5°C, 15°C and 30°C respectively. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Mean pH in all tests was 5.8. Toxicity increased with increasing temperature. The Cr concentration was found to decline by 8.8%, 19.1% and 7.1% in tests carried out at 5°C, 15°C and 30°C respectively.	Cairns Jr. et al, 1978
			24h-LC_{50}	141	m	static	4.6-7.5	36		15	II		
			24h-LC_{50}	95.5	m	static	4.6-7.5	36		30	IIIb		
Oncorhynchus mykiss	rainbow trout	5.21 g	96h-LC_{50}	66.4	m	static	5.8-7.9	73-76		15	I	No. of organisms: 10 fish/concentration. Loading in static test was 10 fish in 50 litres solution (1 g fish/litre). The semi-static test was carried out at two loadings: a) 10 fish in 50 litres solution (1 g fish/litre); b) 10 fish in 10 litres solution (5.2 g fish/l). Test concentrations: 19.8, 35.4, 63.6 and 113.1 mg Cr/l, plus control. Dilution water: Town supply. Dissolved oxygen was 8.2-10.2 mg/l. Concentration of Cr in dilution water was not given. Control response: No mortality. Comments: Test carried out according to OECD 203. GLP Study. Concentrations were found to be 97-107% of the nominal values throughout the study. No significant difference was found between the exposure methods used.	Brown et al, 1985
			96h-LC_{50}	63.6 and 69.6	m	semi static (24h renewal)	5.8-7.9	73-76			I		
Perca flavescens	yellow perch		acute LC_{50}	36.5	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White.	USEPA, 1985

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Pimephales notatus	bluntnose minnow		acute LC_{50}	54.2	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White.	USEPA, 1985
Pimephales promelas	fathead minnow	1-2 g	48h- TLm[e]	19.7	n	static	7.5	20	18	25	II	No. of organisms: 5 fish/replicate, 2 replicates/concentration. The fish loading was 5 fish in 10 litres of solution. Test concentrations: 5 concentrations plus control. A logarithmic series was used. Dilution water: Hard water was natural limestone spring water. Soft water was a mixture of 5 parts natural limestone spring water with 95 parts distilled, demineralised water. Dissolved oxygen was >4 mg/l throughout the test. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Used test protocol recommended by APHA[g] (1960 version). During the test the pH of the solution in soft water often fell, and that in hard water increased with time. The pH was always within the range tolerated by the species.	Pickering and Henderson, 1966
			96h- TLm[e]	17.6	n	static	7.5	20	18	25	II		
			48h- TLm[e]	35.4	n	static	8.2	360	300	25	II		
			96h- TLm[e]	27.3	n	static	8.2	360	300	25	II		
Pimephales promelas	fathead minnow	adult (42-56 day old)	96h- LC_{50}	26.1	m	static		40			II	No. of organisms: 10 organisms/replicate, 2 replicates/concentration. Test concentrations: 5 concentrations plus control. Dilution water: Reconstituted water. Dissolved oxygen levels and Cr concentrations in the dilution water are not given. Control response: No mortality in controls. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013 and 1978, EPA/600/4/78/012]. Concentrations analysed by atomic absorption spectrometry (total Cr) and Cr(VI) using diphenylcarbazide-colourimetric procedure (Cr(VI) persisted throughout tests with little conversion of Cr(VI) to Cr(III)).	Dorn et al, 1987
Pimephales promelas	fathead minnow	adult (42-56 day old)	96h- LC_{50}	26.1	m	static		40			II	No. of organisms: 10 organisms/replicate, 2 replicates/concentration. Test concentrations: 5 concentrations plus control. Dilution water: Reconstituted water. Dissolved oxygen levels and Cr concentrations in the dilution water are not given. Control response: No mortality in controls. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013 and 1978, EPA/600/4/78/012]. Concentrations analysed by atomic absorption spectrometry (total Cr) and Cr(VI) using diphenylcarbazide-colourimetric procedure (Cr(VI) persisted throughout tests with little conversion of Cr(VI) to Cr(III)).	Dorn et al, 1987

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Pimephales promelas	fathead minnow		96h- LC_{50}	34	m		7.1-7.6	75-105	50-60	20±2	II	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading was 10 organisms in 2 litres of solution. Test concentrations: 10, 20, 30, 35, 45, 50 mg/l plus control. Dilution water: Moderately hard reconstituted water. Dissolved oxygen was 7.0-9.0 mg/l. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. The pH of the test solution decreased with increasing Cr concentration within the range 7.6 to 7.1. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. The LC_{50} value reported is the mean of three determinations. A similar 96h-LC_{50} of 46 mg/l was obtained with potassium chromate.	Jop et al, 1987
Pimephales promelas	fathead minnow		acute LC_{50}	58	m	static	120-160				IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White.	USEPA, 1985
Pimephales promelas	fathead minnow		acute LC_{50}	26-60	m	flow	220				IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985) Mean LC_{50} = 46.4 mg/l - part of a study to develop test methodology. 11d-LC_{50} = 17.3 mg/l	Adelman and Smith Jr, 1976
Pimephales promelas	fathead minnow		acute LC_{50}	22.6-24.1	m	flow	400				IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985).	Waheda, 1977

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Pimephales promelas	fathead minnow	1 g juvenile	96h- LC_{50}	36.2	n	static	7.5-8.2	209±5	159± 20	25	II	No. of organisms: The static test used 5 fish/replicate, 2 replicates/concentration with a loading rate of 5 fish in 10 litres. The flow-through test used 10 fish/concentration with a loading rate of 10 fish in 10 litres. A later flow-through test was carried out with 10 fish/replicate, 2 replicates/concentration. Test concentrations: A dilution factor of 0.56 was used between concentrations in the static test and a dilution factor of 0.5 was used between concentrations in the flow-through test. Controls were also run. Dilution water: A mixture of pond water originating from a spring and carbon-filtered, demineralized tap water. Dissolved oxygen was 7.5±1.5 mg/l throughout the experiment. Chromium was not detected in the dilution water. Control response: Not given. Comments: Static and flow-through studies were conducted twice. Tests carried out according to APHA[g] (1965 version). The 96h-LC_{50}s reported are mean values. The values obtained in the two static test were 32.7 and 39.7 mg Cr/l. The values obtained in the three flow-through tests were 35.9, 37.0 and 37.7 mg Cr/l.	Pickering, 1980
			96h- LC_{50}	36.9	m	flow	7.5-8.2	209±5	159± 20	25	II		
Pimephales promelas	fathead minnow	0.2-0.5 g	96h- LC_{50}	>35.4[f]	n	static	6.5-8.5	130	93	20	IIIb	No. of organisms: Measured toxicity to seven species simultaneously. Used 10 organisms of each species per concentration. The biological loading was maintained below 0.5 g/l. Test concentrations: 100, 10, 1 and 0.1 mg $K_2Cr_2O_7$/l (equivalent to 35.4, 3.54, 0.354 and 0.0354 mg Cr/l) plus control. Dilution water: Lake water. Dissolved oxygen was maintained at >40% saturation with aeration if necessary. Level of total Cr in dilution water was <0.02 mg/l. Control response: Not given. Comments: The test method simultaneously exposed 7 species from 5 phyla. If the pH of the test solution fell out of the range 6.5-8.5, the pH was adjusted to 7.0. Widely space concentrations tested.	Ewell et al, 1986
Poecilia reticulate	guppy	4 week	4d-LC_{50}	56[f]							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Test carried out in accordance with OECD guidelines and "Degradability, ecotoxicity, and bio-accumulation. The determination of the possible effects of chemicals and wastes on the aquatic environment. Government Publishing Office, the Hague, 1980". Only a summary of the results is reported.	Adema et al, 1983
Ponoxis annularis	white crapple		acute LC_{50}	72.6	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by A. M. White.	USEPA, 1985

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Puntius conchonius	rosy barb - aquarium fish	adult	96h- LC_{50}	117.8[f]				400			IIIb	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given Comments: Acute (12 and 24 hours at 118 mg Cr/l) and chronic (30 and 60 days at 1.95 and 2.93 mg Cr(VI)/l) exposure caused hyperglycaemia, glycogenolysis in brain and liver, increment of myocardium glycogen. Test conditions not given.	Pant and Gill, 1984
FISH - saltwater - short-term studies													
Alburnus alburnus	bleak (cyprinide)	8 cm	96h- LC_{50}	84.8[f]	n	static	7.8	7‰		10		No. of organisms: 10 fish/concentration in 60l of solution. Test concentrations: A rangefinding test was used to determine the concentrations to be tested. At least 6 concentrations were tested plus control. Dilution water: Natural brackish seawater. The water was filtered (300 µm) before use. Dissolved oxygen concentrations were >5 mg/l at end of the test. The Cr concentrations in dilution water not given. Control response: Not given. Comments:	Lindén et al, 1979
Chelon labrosus	grey mullet	0.87g	48h-LC_{50}	90.0	m	flow	7.7± 0.8	34.5± 0.2‰		12	I	No. of organisms: 20 fish/concentration in 20 l of solution. Test concentrations: 5 concentrations (logarithmically-related) plus control. The concentration range tested was based on a 24 hour rangefinding test. Dilution water: Natural seawater, filtered (50 µm) before use. Dissolved oxygen was 7.9±0.6 mg/l over the test period. Concentration of Cr in dilution water not given. Control response: Not given Comments: Carried out according to OECD GLP guidelines. Used wild fish populations from uncontaminated areas. The levels of total Cr were measured in the test solutions. No significant differences were found in the concentrations before and after 0.45 µm filtering, implying that the Cr was present entirely in a soluble form.	Taylor et al, 1985
			96h- LC_{50}	47.2	m	flow	7.7± 0.8	34.5± 0.2‰		12	I		
Citlerichthys stigmaeus	speckled sanddab	1.5-17g	96h-LC_{50}	30	m	static		33.5‰		12.0-12.3	II	No. of organisms: Not given. Test concentrations: Range tested was 15.6-1,000 mg $K_2Cr_2O_7$/l (equivalent to 5.5-354 mg Cr/l) plus control. Dilution water: Natural seawater. The total Cr concentration in the dilution water was 0.5-1.0 µg/l. Water was aerated during the test to maintain the dissolved oxygen level. Control response: Not given. Comments: The pH of the test solutions was not adjusted and fell below pH 6.0 in the highest two concentrations tested.	Mearns et al, 1976.
Citlerichthys stigmaeus	speckled sanddab		acute LC_{50}	31		static					IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985). Possibly same results as Mearns et al (1976).	Sherwood, 1975

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Citlerichthys stigmaeus	speckled sanddab		acute LC_{50}	31		static					IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985). Possibly same results as Mearns et al (1976).	Sherwood, 1975
Cyprinodon variegates	sheepshead minnow		96h- LC_{50}	25	m		8.1-8.3	20‰	300-400		II	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading was 10 organisms in 2 litres of solution. Test concentrations: 10, 20, 25, 30, 45, 50 mg/l plus control. Dilution water: Reconstituted sea water. Dissolved oxygen was 7.0-9.0 mg/l. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. The LC_{50} value reported is the mean of two determinations. A similar 96h-LC_{50} of 25 mg/l was obtained with potassium chromate.	Jop et al, 1987
Gasterosteus aculeatus	stickleback		96h- LC_{50}	33	m		8.0-7.2	5‰	350-380		II	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading was 10 organisms in 10 litres of solution. Test concentrations: 20, 35, 60, 75 and 100 mg/l plus control. Dilution water: Reconstituted sea water, diluted to give a salinity of 5‰. Dissolved oxygen was 7.0-9.0. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. The pH of the test solution decreased with increasing Cr concentration but was always in the range 7.2-8.0. A similar 96h-LC_{50} of 35 mg/l was obtained with potassium chromate.	Jop et al, 1987
Leiastomus xanthurus	spot		acute LC_{50}	27	n	static					IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by D. J. Hansen.	USEPA, 1985

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Limanda limanda	dab	16.9 g	48h-LC_{50}	95.6	m	flow	7.7± 0.8	34.5 ± 0.2		12	I	No. of organisms: 10 fish/concentration in 10 l of solution. Test concentrations: 5 concentrations (logarithmically-related) plus control. The concentration range tested was based on a 24 hour rangefinding test. Dilution water: Natural seawater, filtered (50 µm) before use. Dissolved oxygen was 7.9±0.6 mg/l over the test period. Concentration of Cr in dilution water not given. Control response: Not given. Comments: Carried out according to OECD GLP guidelines. Used wild fish populations from uncontaminated areas. The levels of total Cr were measured in the test solutions. No significant differences were found in the concentrations before and after 0.45 µm filtering, implying that the Cr was present entirely in a soluble form.	Taylor et al, 1985
			96h- LC_{50}	47.0	m	flow	7.7± 0.8	34.5 ± 0.2		12	I		
Menidia menidia	atlantic silverside	larvae	acute LC_{50}	12.4-14.3	n	static					IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by J. A. Cardin.	USEPA, 1985
		juv.	acute LC_{50}	20.1	n	static					IIIa		
Menidia peninsulae	tidewater silverside		acute LC_{50}	22	n	static					IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Comments: Unpublished results by D. J. Hansen.	USEPA, 1985
FISH – fresh water - long-term studies													
Brachydanio rerio	zebrafish	embryo-larval	16d NOEC (mortality)	14.7-16.2[f]		24h renew.	7.1-8.0	100		26	IIIb	No. of organisms: 20 eggs/concentration in 50 ml solution. Test concentrations: 0.66, 1.33, 2.65, 5.30, 10.6, 21.2, 42.4, 84.8, plus two controls. Dilution water: Reconstituted dilution water. Dissolved oxygen was 80-104% of saturation throughout the test. The Cr concentration in the dilution water was not given. Control response: The Median Effective Time (MET) for hatch and survival was 2.7 days and 13.5 days. The validity criteria for the protocol is that the MET for hatch and survival should be between 2-4 and 12-15 days respectively. Endpoints: Looked at effects of exposure on the MET for hatch and survival (i.e. the time to 50% hatch and 50% survival of larvae). Comments: A ring-test of an ISO method for embryo-larval test. The test was carried out 9 times at 5 labs. No food is provided for the larvae and the test is terminated when at least 90% of the larvae in all concentrations and control have died (usually within 16 days). No significant effects were seen on the MET for hatch at any concentration. The NOEC for effects on the MET for mortality was in the range 2.65-21.2 mg Cr/l in the 9 determinations. The LOEC for the same endpoint was in the range 5.30-42.4 mg Cr/l. The mean value for the NOEC and LOEC was 14.7-16.2 mg Cr/l and 29.2-29.4 mg Cr/l respectively.	Dave et al, 1987
			16d LOEC (mortality)	29.1-29.4[f]		24h renew.	7.1-8.0	100		26	IIIb		
			16d NOEC (hatch)	84.8[f]		24h renew.	7.1-8.0	100		26	IIIb		

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Jordanella floridae	American flagfish	4 week	6 week-NOEC (overall)	1.13[f]							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: egg-larval development, mortality, growth, swimming behaviour, colour Comments: Test carried out in accordance with OECD guidelines and "Degradability, ecotoxicity, and bio-accumulation. The determination of the possible effects of chemicals and wastes on the aquatic environment. Government Publishing Office, the Hague, 1980". Only a summary of the results is reported.	Adema et al, 1983
Oryzias latipes	medaka	embryo-larval	40d NOEC (mortality; behaviour)	3.5[f]	n	semi-static				23	II	No. of organisms: 35/concentration in 1 litre solution. Test concentrations: Range of concentrations with a dilution factor of √10 between concentrations, plus control. Dilution water: Reconstituted dilution water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Not given. Endpoints: Mortality, growth, behaviour and hatching. Comments:	Slooff and Canton, 1983; Van Leeuwen,
			40d NOEC (hatching + growth)	35[f]	n	semi-static				23	II		
Pimephales promelas	fathead minnow	larval	7d NOEC (growth)	1.1[f]							II	No. of organisms: 10 animals/replicate, two replicates/concentration Test concentrations: 5 concentrations plus control. Dilution water: Not given. Control response: Any test with >20% mortality in the control was rejected. Overall survival in controls was 94%. Endpoints: Mortality and growth. Comments: Intra- and Inter-laboratory ring test of the USEPA "7-day Fathead Minnow Survival and Growth Test". The study involved 10 laboratories in two test periods over a total of 9 months. All laboratories tested the same concentrations. The mean 7day LC_{50} was 6.7 mg Cr/l from 8 experiments in the first test period and was 7.1 mg Cr/l from 8 experiments in the second test period. The NOECs for survival in the first test period were 2.1-4.2 mg Cr/l and in the second test period they were 2.1-8.5 mg Cr/l. The median NOEC for survival was 4.2 mg Cr/l. The NOECs for growth in the first test period was 1.1-4.2 mg Cr/l, and in the second test period they were 1.1-8.5 mg Cr/l. The median NOEC for growth was 1.1 mg Cr/l.	DeGraeve et al, 1991
			7d NOEC (survival)	4.2[f]							II		
			7d-LC_{50} (survival)	6.7-7.1[f]							II		

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Pimephales promelas	fathead minnow	larval	7d NOEC (growth)	1.1[f]							II	No. of organisms: 10 animals/replicate, two replicates/concentration Test concentrations: 5 concentrations plus control. Dilution water: Not given. Control response: Any test with >20% mortality in the control was rejected. Overall survival in controls was 94%. Endpoints: Mortality and growth. Comments: Intra- and Inter-laboratory ring test of the USEPA "7-day Fathead Minnow Survival and Growth Test". The study involved 10 laboratories in two test periods over a total of 9 months. All laboratories tested the same concentrations. The mean 7day LC_{50} was 6.7 mg Cr/l from 8 experiments in the first test period and was 7.1 mg Cr/l from 8 experiments in the second test period. The NOECs for survival in the first test period were 2.1-4.2 mg Cr/l and in the second test period they were 2.1-8.5 mg Cr/l. The median NOEC for survival was 4.2 mg Cr/l. The NOECs for growth in the first test period was 1.1-4.2 mg Cr/l, and in the second test period they were 1.1-8.5 mg Cr/l. The median NOEC for growth was 1.1 mg Cr/l.	DeGraeve et al, 1991
			7d NOEC (survival)	4.2[f]							II		
			7d-LC_{50} (survival)	6.7-7.1[f]							II		
Pimephales promelas	fathead minnow	4 week	412-day NOEC (1st gen. survival)	1	m	flow	7.5-8.2	209±5	159± 20	13-27	II	No. of organisms: Multigeneration study started in November with 35 juvenile fish/concentration. After 9 weeks these were reduced to 20/concentration (except at the highest concentration where only 13 fish survived). Excess males were removed during the spawning season (June). After spawning, 100 eggs/concentration were used for the second generation studies. After hatch (~7 days), 50 larvae/concentration were used to determine mortality after 30 and 60 days. Test concentrations: Mean measured concentrations were	Pickering, 1980
			9-week LOEC (1st gen. growth)	<0.018	m	flow	7.5-8.2	209±5	159± 20	13-27	II		
			412-day NOEC/ LOEC (1st gen. growth)	3.95	m	flow	7.5-8.2	209±5	159± 20	13-27	II		
			NOEC (repro.)	3.95	m	flow	7.5-8.2	209±5	159±20	13-27	II	0.018, 0.066, 0.26, 1.0 and 3.95 mg Cr/l. A control was also run. Dilution water: A mixture of pond water originating from a spring and carbon-filtered, demineralized tap water. Dissolved oxygen was 7.5±1.5 mg/l throughout the experiment. Chromium was not detected in the dilution water. Control response: Survival during first 9 weeks was 100%. Survival of second generation was 74% after 30 days and 72% after 60 days (survival of second generation was between 84% and 98% in the 4 lowest Cr treatments and 38% at the 3.95 mg Cr/l treatment)	
		eggs-larvae	60d- NOEC (2nd gen. survival)	1	m	flow	7.5-8.2	209±5	159± 20	13-27	II		

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Pimephales promelas			60d-NOEC (2nd gen growth)	1	m	flow	7.5-8.2	209±5	159± 20	13-27	II	Endpoints: Survival, growth and reproduction. Comments: The test was carried out at ambient temperature. The weekly mean temperature was around 16°C during the Autumn/Winter months and then slowly increased to 24°C until the end of the experiment. Mortality occurred at the highest concentration tested in the first generation. After 9 weeks, survival at this concentration was 37% and only 13% survived to the end of the experiment (412 days). Survival of the second generation fish was also greatly reduced at the highest concentration tested (38% after 30 days and 12% after 60 days). Survival of both the first and second generation were similar to controls at 1.0 mg/Cr/l. Survival of eggs that were spawned and incubated was not affected by any test treatment. Growth was found to be significantly reduced compared with controls ($p<0.05$) in all exposed first generation fish after 9 weeks exposure but the effect was temporary. At the end of the 412 day exposure, the length and weight of the fish was similar to controls. The one possible exception to this was the male fish in the 3.95 mg Cr/l treatment group, which appeared to be slightly smaller than control fish. The statistical significance of this apparent effect is unclear as a small excess of males were removed from the other treatments (but not the 3.95 mg Cr/l treatment) to reduce territorial conflict. Growth of the second generation fish was found to be reduced compared with controls at 3.95 mg Cr/l but not at lower concentrations. Reproduction was not affected at any exposure concentration.	
Poecilia reticulate	guppy	3-4 week	28d NOEC (mortality; behaviour)	3.5[f]	n	semi-static				23	II	No. of organisms: 25/concentration in 2 litres solution. Test concentrations: Range of concentrations with a dilution factor of √10 between concentrations, plus control. Dilution water: Reconstituted dilution water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Not given. Endpoints: Mortality, growth and behaviour. Comments:	Slooff and Canton, 1983; van Leeuwen, 1990
			28d NOEC (growth)	3.5[f]	n	semi-static				23	II		
Poecilia reticulata	guppy	4 week	4 week-NOEC (overall)	3.5[f]							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: egg-larval development, mortality, growth, swimming behaviour, colour. Comments: Test carried out in accordance with OECD guidelines and "Degradability, ecotoxicity, and bio-accumulation. The determination of the possible effects of chemicals and wastes on the aquatic environment. Government Publishing Office, the Hague, 1980". Only a summary of the results is reported.	Adema et al, 1983

Table C.1 continued overleaf

Table C.1 continued Summary of the ecotoxicological data for potassium dichromate to fish.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
FISH - saltwater - long-term studies													
Citharichthys stigmaeus	speckled sanddab		21d-LC_{50}	5.4							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985). Possibly the same results as Mearns et al, 1976.	Sherwood, 1975
Citharichthys stigmaeus	speckled sanddab	5 g	21d-LC_{50}	5	m	flow	~7.86-8.39	33.5‰		12.0-12.3	II	No. of organisms: 10 fish/concentration in 20 gallons of test solution. Test concentrations: Range tested was 0.08-10.0 mg Cr/l plus control. Dilution water: Natural seawater. The dissolved oxygen concentration was maintained at acceptable levels throughout the test. The total Cr concentration in the dilution water was 0.5-1.0 µg/l. Control response: Not given. Endpoints: Mortality. Effects such as signs of disease and percentage of population responding to food were monitored during the test. Comments:	Mearns et al, 1976

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity (‰)
e) TLm = median threshold or tolerance limit - equivalent to LC_{50}
f) concentration converted from salt to chromium ion concentration
g) American Public Health Association. Standard Methods for the examination of water and wastewater
h) Val. = validity marking of the test (see main text).

Table C.2 Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp. (°C)	Val.[h]	Test details	Reference
INVERTEBRATES - freshwater - short-term studies													
Aedes aegypt	mosquito	pupae	48h-EC_{10} (hatching)	0.5			6.1	4.0	4.0		IIIb	No. of organisms: 30/concentration in 400 ml of water. Test concentrations: 0.5 and 5.0 mg Cr/l plus a control. Dilution water: Not given. Control response: No mortality. Endpoints: Mortality, abnormal responses in swimming and flying, and incompleteness of the metamorphosis. Comments: Only two concentrations tested. The percentage mortality of unhatched pupae at 72 hours was 10% at 0.5 mg Cr/l and 30% at 5.0 mg Cr/l. All hatched control mosquitoes flew away from the test solution normally, whereas the chromium-exposed mosquitoes were considered to be abnormal (they either could not come out of the test solution or fell down soon after their first flight).	Abbasi et al, 1985
Aeolosoma headleyi	segmented worm		48h-LC_{50}	12.1	m	static	7.5	45	42	5	IIIb	No. of organisms: 10 organisms/replicate, 3 replicates/concentration. Loading was 10 organisms in 4 ml of solution. Test concentrations: Not given. A control was run. Dilution water: Charcoal-dechlorinated tap water. Tests were carried out without aeration. The dissolved oxygen concentration and concentration of Cr in dilution water are not reported. Control response: <10% mortality. Endpoints: Mortality Comments: Toxicity increased with increasing temperature. The test method was based on APHA[g] (1974 version). All animals were acclimated to the test conditions for 4 days.	Cairns Jr. et al, 1978
			48h-LC_{50}	10.0	m	static	7.5	45	42	10	IIIb		
			48h-LC_{50}	8.6	m	static	7.5	45	42	15	II		
			48h-LC_{50}	7.0	m	static	7.5	45	42	20	II		
			48h-LC_{50}	4.8	m	static	7.5	45	42	25	IIIb		
Asellus intermedius	pillbug	0.012 g	96h-LC_{50}	5.3[f]	n	static	6.5-8.5	130	93	20	IIIb	No. of organisms: Measured toxicity to seven species simultaneously. Used 10 organisms of each species per concentration. The biological loading was maintained below 0.5 g/l. Test concentrations: 100, 10, 1 and 0.1 mg $K_2Cr_2O_7$/l (equivalent to 35.4, 3.54, 0.354 and 0.0354 mg Cr/l) plus control. Dilution water: Lake water. Dissolved oxygen was maintained at >40% saturation with aeration if necessary. Level of total Cr in dilution water was <0.02 mg/l. Control response: Not given. Comments: The test method simultaneously exposed 7 species from 5 phyla. If the pH of the test solution fell out of the range 6.5-8.5, the pH was adjusted to 7.0. Widely space concentrations tested.	Ewell et al, 1986
Biomphalaria glabrata	freshwater snail	100 d juvenile	48h-LC_{50}	66.2	n	static	7.8	100		20	II	No. of organisms: 10/replicate, 3 replicates/concentration. Test concentrations: seven concentrations plus control. Determined by rangefinding test to cover 0% and 100% mortality. Dilution water: Artificial test water prepared from distilled water. Dissolved oxygen was >90% of saturation throughout the test. Concentration of Cr in dilution water not reported. Control response: Not given. Endpoints: Mortality. Comments:	Bellavere and Gorbi, 1981
			96h-LC_{50}	37.3	n	static	7.8	100			II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Biomphalaria glabrata	freshwater snail	100 d juvenile	48h-LC_{50}	66.2	n	static	7.8	100		20	II	No. of organisms: 10/replicate, 3 replicates/concentration. Test concentrations: seven concentrations plus control. Determined by rangefinding test to cover 0% and 100% mortality. Dilution water: Artificial test water prepared from distilled water. Dissolved oxygen was >90% of saturation throughout the test. Concentration of Cr in dilution water not reported.	Bellavere and Gorbi, 1981
			96h-LC_{50}	37.3	n	static	7.8	100			II	Control response: Not given. Endpoints: Mortality. Comments:	
Ceriodaphnia sp.	water flea		48h-EC_{50}	0.03	m	static		40-48			II	No. of organisms: 10 organisms/replicate, 5 replicates/concentration. Test concentrations: 5 concentrations plus control. Dilution water: Reconstituted water. Dissolved oxygen levels and Cr concentrations in the dilution water are not given. Control response: No mortality/immobilisation in control. Endpoints: Immobilisation/mortality. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013 and 1978, EPA/600/4/78/012]. Concentrations analysed by atomic absorption spectrometry (total Cr) and Cr(VI) using diphenylcarbazide-colourimetric procedure (Cr(VI) persisted throughout tests with little conversion of Cr(VI) to Cr(III)).	Dorn et al, 1987
Ceriodaphnia dubia	water flea	<24h	24h-EC_{50}	0.053	n	static	7.9	250		20	II	No. of organisms: 10 individuals/replicate, 2 replicates/concentration. Loading was 10 animals in 15 ml solution. Test concentrations: Duplicate controls and at least 5 test concentrations. The dilution factor between concentrations was 0.5. The range tested was determined from a range-finding test. Dilution water: Standard dilution water prepared from ultrapure water (British Standard, 1983: BS6068: Part 5, Section 5.1: Determination of the Inhibition of Mobility of Daphnia magna Straus (Cladocera, Crustacea). British Standards Institution). Dissolved oxygen level and Cr concentration in dilution water not given. Control response: Not given. Endpoints: Mortality/immobilisation Comments:	Hickey, 1989

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Ceriodaphnia dubia	water flea		48h-LC_{50}	~0.46[f]	n	24h renew.	8.4	102	81	26.4	II	No. of organisms: Used 10 organisms/concentration and 20 organisms for the control. The loading was 1 organism in 100 ml solution. Test concentrations: Used a declining series of concentration with a dilution factor of 0.6 between concentrations plus control. Dilution water: Reconstituted water. The water was autoclaved and supplemented with 2 µg Se/l and 2 µg B_{12}/l as C. daphnia requires these for successful reproduction. Dissolved oxygen was in the range 8.1-9.6 mg/l throughout the test. Control response: Not given. Endpoints: Mortality/immobilisation. Comments: The results are given in graphical form. The LC_{50} was estimated from the graph in the paper.	Cowgill and Milazzo, 1991
Ceriodaphnia pulchella	water flea	<24h	24h-EC_{50}	0.196	n	static	7.9	250		20	II	No. of organisms: 10 individuals/replicate, 2 replicates/concentration. Loading was 10 animals in 40 ml solution. Test concentrations: Duplicate controls and at least 5 test concentrations. The dilution factor between concentrations was 0.5. The range tested was determined from a range-finding test. Dilution water: Standard dilution water prepared from ultrapure water (British Standard, 1983: BS6068: Part 5, Section 5.1: Determination of the Inhibition of Mobility of Daphnia magna Straus (Cladocera, Crustacea). British Standards Institution). Dissolved oxygen level and Cr concentration in dilution water not given. Control response: Not given. Endpoints: Mortality/immobilisation. Comments:	Hickey, 1989
Chironomus tentans	midge	3rd instar larvae	24h-LC_{50}	22.0	n	static	6.3	25	25	14	II	No. of organisms: 10 larvae/replicate, 2 replicates/concentration. Loading was 10 larvae in 200 ml solution. Test concentrations: Not given. Dilution water: Natural water. Dissolved oxygen concentration was 5.5-8.0 mg/l. The Cr concentration in the dilution water was not given. Control response: No immobilisation. Endpoints: Immobilisation/mortality.	Khangarot and Ray, 1989a
			48h-LC_{50}	11.8	n	static	6.3	25	25	14	II	Comments: The bioassay was carried out according to the method recommended by APHA[g] (1981 version). The pH was found to be decreased in some of the higher test concentrations, but this was never by more than 0.5 pH unit.	
Chironomus tentans	midge	4th instar	48h- LC_{50}	61	m	static	7.5	101	248	21	II	No. of organisms: 10 larvae/replicate, 2 replicates/concentration. Test concentrations: 1.0, 1.8, 3.2, 5.6, 10, 18, 32, 56, 100 mg/l plus control. Dilution water: Carbon-filtered tap water. Dissolved oxygen level and Cr concentration in dilution water not given. Control response: 15% mortality. Endpoints: Mortality. Comments: First indications of altered behaviour occurred at 0.01-0.1 mg Cr/l over 90 minutes. The control-corrected mortality was used to determine the LC_{50}.	Batac-Catalan and White, 1983

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Crangonyx pseudogracilis	freshwater shrimp	adult 4mm	48h-LC_{50}	2.2	n	24h renew.	6.75	50	40-60	13	II	No. of organisms: 20-30 animals/replicate, 2 replicates/concentration. The loading rate was 20-30 animals in 200 ml solution. Test concentrations: A minimum of 8 concentrations plus control. The concentrations to be tested were determined by a range finding study/ Dilution water: A 1:3 mixture of tap water and deionised water. Dissolved oxygen concentration was adequately maintained by the 24 hour renewal method used. The concentration of Cr in the dilution water was not given. Control response: Not given Endpoints: Mortality Comments: The 48h- and 96h-LC_{50} obtained with potassium chromate were 2.7 mg Cr/l and 0.81 mg Cr/l respectively.	Martin and Holdich, 1986
			96h-LC_{50}	0.42	n	24 renew.	6.75	50	40-60	13	II		
Daphnia carinata	water flea	<24h	24h-EC_{50}	0.423	n	static	7.9	250		20	II	No. of organisms: 10 individuals/replicate, 2 replicates/concentration. Loading was 10 animals in 40 ml solution. Test concentrations: Duplicate controls and at least 5 test concentrations. The dilution factor between concentrations was 0.5. The range tested was determined from a range-finding test. Dilution water: Standard dilution water prepared from ultrapure water (British Standard, 1983: BS6068: Part 5, Section 5.1: Determination of the Inhibition of Mobility of Daphnia magna Straus (Cladocera, Crustacea). British Standards Institution). Dissolved oxygen level and Cr concentration in dilution water not given. Control response: Not given. Endpoints: Mortality/immobilisation. Comments:	Hickey, 1989
Daphnia magna	water flea	<24h	24h-EC_{50}	0.17[f]-0.22[f]	n	static	8.3	240		17	II	No. of organisms: 10 animals/concentration in 100 ml of solution. Test concentrations: Logarithmic series of test concentrations plus control. Dilution water: Filtered (8 µm) and dechlorinated mains water. The dissolved oxygen level was >70 saturation. The concentration of Cr in the dilution water is not given. Control response: Not given. Endpoints: Mortality/immobilisation. Comments: The test was based on "EPA Environmental Effects Testing Guidelines, EG-2 and ES-1. Chemical Regulation Reporter Supplement N-52. Bureau of National Affairs Inc., 1982" and OECD Guideline 202. Each test at the three temperatures was carried out three times using daphnia cultured on three different food sources. The results indicated that neither the temperature or food source used in culturing influenced the results significantly. The values given are the range of the mean values obtained from 3 studies for each temperature and food source combination.	Stephenson and Watts, 1984
			24h-EC_{50}	0.090[f]-0.16[f]	n	static	8.3	240		20	II		
			24h-EC_{50}	0.090[0]-0.19[f]	n	static	8.3	240		23	II		
			48h-EC_{50}	0.088[f]-0.12[f]	n	static	8.3	240		17	II		
			48h-EC_{50}	0.035[f]-0.11[f]	n	static	8.3	240		20	II		
			48h-EC_{50}	0.084[f]-0.11[f]	n	static	8.3	240		23	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia magna	water flea	<24h	24h-EC_{50}	0.16[f]	n	static		80		7	IIIb	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Standard synthetic dilution water. The hardness was varied by increasing or decreasing the concentrations of the 4 salts added to keep the Ca/Mg and Na/K ratios constant. The dissolved oxygen level and Cr concentration in the dilution water was not given. Control response: The test conditions used were reported not to induce mortality. An "internal" control was performed in each series of tests using $K_2Cr_2O_7$ under "standard" test conditions. If the EC_{50} from this test fell outside a certain range, the results for the entire series was considered invalid and the experiment was repeated. Endpoints: Immobilisation/mortality Comments: Test was carried out according to the EEC C.2 method (1984). The study was designed to look at the effect of the test conditions on the toxicity. The tolerance limits to temperature and hardness were determined in preliminary experiments. A prerequisite of the test conditions was that they should not induce mortality or any visible signs of stress. A reference test was also carried out using the conditions recommended in the test guidelines (20°C and 250 mg/l hardness as $CaCO_3$). Both temperature and hardness were found to have a significant effect on the toxicity of Cr over 24 hours.	Persoone et al, 1989
			24h-EC_{50}	0.11[f]	n	static		80		14	IIIb		
			24h-EC_{50}	0.028[f]	n	static		80		21	II		
			24h-EC_{50}	0.013[f]	n	static		80		28	IIIb		
			24h-EC_{50}	0.36[f]	n	static		250		20	II		
			24h-EC_{50}	0.91[f]	n	static		320		7	IIIb		
			24h-EC_{50}	0.71[f]	n	static		320		14	IIIb		
			24h-EC_{50}	0.37[f]	n	static		320		21	II		
			24h-EC_{50}	0.27[f]	n	static		320		28	IIIb		
			24h-EC_{50}	1.66[f]	n	static		560		7	IIIb		
			24h-EC_{50}	1.45[f]	n	static		560		14	IIIb		
			24h-EC_{50}	0.77[f]	n	static		560		21	II		
			24h-EC_{50}	0.28[f]	n	static		560		28	IIIb		
			24h-EC_{50}	2.79[f]	n	static		800		7	IIIb		
			24h-EC_{50}	1.77[f]	n	static		800		14	IIIb		
			24h-EC_{50}	0.85[f]	n	static		800		21	II		
			24h-EC_{50}	0.28[f]	n	static		800		28	IIIb		
Daphnia magna	water flea		100h-TLm[e]	0.14[f]							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Standard reference water (a lab-prepared medium, free from organics, containing all the major ions in concentrations and proportions of an average surface water in the US. Dissolved oxygen and concentration of Cr in dilution water not reported. Control response: Not given. Endpoints: Immobilisation. Comments:	Dowden and Bennett, 1965

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia magna	water flea	<24h old	24h-LC_{50}	0.16[f]	n	static		80	80		IV	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Reconstituted dilution water, made up from deionised water and varying amounts of Ca, K, Mg and Na salts to give waters of differing total hardness, alkalinity and Ca:Mg ratios. The water was aerated for 10 minutes to reach saturation and then left for 48 hours before use to stabilise. The dissolved oxygen concentration during the test or the Cr concentration of the dilution water are not given. Control response: Control mortality in some of the tests were around 50%. These occurred when Mg alone was used as the sole source of hardness in the dilution water. The control response in other dilution waters is not given. Endpoints: Immobilisation/mortality. Comments: Testing was based on the draft ISO guideline "Determination of the Inhibition of the Mobility of Daphnia magna Straus (Cladocera, Crustacea). International Organisation for Standardisation", but using <24 hour juveniles in the test. The results are only reported graphically (each point represents the mean of 2 values). The EC_{50} values were read from the graph and so are uncertain. The results reported in the Table are for tests investigating the effects of hardness and alkalinity on the toxicity. The dilution water used had a Ca:Mg ratio of 4:1 and a Na:K ratio of 10:1. The toxicity appears to decrease with increasing alkalinity and increasing hardness. The control response in some of the dilution waters used is uncertain.	Muller, 1980
			24h-LC_{50}	0.23[f]	n	static		160	80		IV		
			24h-LC_{50}	0.35[f]	n	static		240	80		IV		
			24h-LC_{50}	0.14[f]	n	static	7.4	250	30		IV		
			24h-LC_{50}	0.27[f]	n	static	7.8	250	60		IV		
			24h-LC_{50}	0.34[f]	n	static	8.0	250	75		IV		
			24h-LC_{50}	0.35[f]	n	static	8.0	250	90		IV		
			24h-LC_{50}	0.51[f]	n	static	8.0	250	120		IV		
			24h-LC_{50}	0.78[f]	n	static	8.0	250	150		IV		
			24h-LC_{50}	0.85[f]	n	static	8.1	250	180		IV		
			24h-LC_{50}	0.81[f]	n	static	8.2	250	210		IV		
			24h-LC_{50}	0.71[f]	n	static	8.3	250	240		IV		
			24h-LC_{50}	0.85[f]	n	static	8.2	250	270		IV		
Daphnia magna	water flea		48h NOEC	0.2[f]							IIIb	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Immobilisation.	Adema et al, 1983
			48h-EC_{50}	0.46[f]							IIIb	Comments: Test carried out in accordance with OECD guidelines and "Degradability, ecotoxicity, and bio-accumulation. The determination of the possible effects of chemicals and wastes on the aquatic environment. Government Publishing Office, the Hague, 1980". Only a summary of the results is reported.	

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia magna	water flea	1st and 2nd instar	96h-LC_{50}	0.074	n	static	6.5-8.5	130	93	20	IIIb	No. of organisms: Measured toxicity to seven species simultaneously. Used 10 organisms of each species per concentration. The biological loading was maintained below 0.5 g/l. Test concentrations: 100, 10, 1 and 0.1 mg $K_2Cr_2O_7$/l (equivalent to 35.4, 3.54, 0.354 and 0.0354 mg Cr/l) plus control. Dilution water: Lake water. Dissolved oxygen was maintained at >40% saturation with aeration if necessary. Level of total Cr in dilution water was <0.02 mg/l. Control response: Not given. Comments: The test method simultaneously exposed 7 species from 5 phyla. If the pH of the test solution fell out of the range 6.5-8.5, the pH was adjusted to 7.0. Widely space concentrations tested.	Ewell et al, 1986
Daphnia magna	water flea	<24h	24h-EC_{50}	0.60[f]	n	static	7.8-8.2	250		20.5	II	No. of organisms: 20 animals/concentration in 200 ml solution. Test concentrations: Concentrations were selected by logarithmic bisectioning. Dilution water: Hard reconstituted water. Dissolved oxygen was 92-100% of saturation throughout the test. Control response: Not given. Endpoints: Immobilisation/mortality. Comments: Method based on "The Committee on Methods for Toxicity Tests with Aquatic Organisms (1975). Methods for Acute Toxicity Tests with Fish, Macroinvertebrates and Amphibians. Ecological Research Series EPA-600/3-75-009, USEPA".	Berglind and Dave, 1984
			48h-EC_{50}	0.32[f]	n	static	7.8-8.2	250		20.5	II	Investigated differences in toxicity to Daphnia cultured in either hard or soft water. No information is given on the control survival. This may be important for the test using Daphnia cultured in soft water and so the results for the Daphnia cultured in hard water only are given in the table. However, the 24h- and 48h-EC_{50}s for both the Daphnia cultured in soft water were similar (24h-EC_{50}=0.64 and 96h-EC_{50}=0.27 mg Cr/l).	
Daphnia magna	water flea	<24h	48h-EC_{50}	0.39[f]	n	static		100		19	II	No. of organisms: 25/replicate in 1 litre solution. All experiments were carried out in duplicate. Test concentrations: The ratio between the adjacent concentrations tested was 3.2. Dilution water: Dutch Standard water. Dissolved oxygen level and Cr concentration in dilution water not given. Control response: Not given. Endpoints: Immobilisation/mortality. Comments: Tests carried out according to methods by the Dutch Standard Organization "Concept NEN6501 (1980). Determination of the Acute Toxicity with Daphnia magna. Concept NEN6502 (1980). Determination of the Chronic Toxicity with Daphnia magna. Dutch Standard Organization, Delft".	Hermens et al, 1984

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia magna	water flea	<24h	24h-EC_{50}	0.33	m	renew.	8.0	16°		25	II	No. of organisms: 5 animals/replicate, 4 replicates/concentration. Loading was 5 animals in 200 ml solution. Test concentrations: Dilution steps of 1:2 or 1:√10 were used. Dilution water: Synthetic fresh water. Dissolved oxygen level and Cr concentration of dilution water not given. Control response: Not given. Endpoints: Immobilisation/mortality. Comments: Test conducted according to "Provisional Procedure: Extending Toxicology Test with Daphnia magna, as of 1 January 1984. Recommendation of the Federal Environmental Agency on the Performance of Testing According to Section 5, para 1 No 3 of the Regulation on Application Documents and Evidence under the Chemicals Act. Federal Environment Agency."	Kuhn et al, 1989
Daphnia magna	water flea	<24h	24h-EC_{50}	0.224	n	static	7.9	250		20	II	No. of organisms: 10 individuals/replicate, 2 replicates/concentration. Loading was 10 animals in 40 ml solution. Test concentrations: Duplicate controls and at least 5 test concentrations. The dilution factor between concentrations was 0.5. The range tested was determined from a range-finding test. Dilution water: Standard dilution water prepared from ultrapure water (British Standard, 1983: BS6068: Part 5, Section 5.1: Determination of the Inhibition of Mobility of Daphnia magna Straus (Cladocera, Crustacea). British Standards Institution). Dissolved oxygen level and Cr concentration in dilution water not given. Control response: Not given. Endpoints: Mortality/immobilisation. Comments:	Hickey, 1989
Daphnia magna	water flea	adult	24h-EC_{50}	0.435		static				18	II	No. of organisms: 20 per concentration Test concentrations: 0.3, 0.5, 0.7, 0.9 mg/l Cr Dilution water: 3/2 mix of Volvic water/Lefevre-Czarda medium Control response: not presented Endpoints: mortality Comments: test method AFNOR T90301, 1974	Jouany et al, 1982
Daphnia magna	water flea	adult (~1 mm)	24h-IC_{50}	0.83	n	static	7.8	100		20	II	No. of organisms: 10/replicate, 3 replicates/concentration. Test concentrations: seven concentrations plus control. Determined by rangefinding test to cover 0% and 100% immobilisation. Dilution water: Artificial test water (hardness 100 mg/l as $CaCO_3$) and dechlorinated tap water (hardness 200 mg/l as $CaCO_3$). Dissolved oxygen was >90% of saturation throughout the test. Concentration of Cr in dilution water not reported. Control response: Not given. Endpoints: Immobilisation Comments: Toxicity decreased with increased water hardness.	Bellavere and Gorbi, 1981
			24h-IC_{50}	1.57	n	static	7.8	200		20	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia magna	water flea		acute EC_{50}	0.212	m	static	8.2	213			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985).	Call et al, 1981
			acute EC_{50}	0.0857	m	static	7.5	196					
			acute EC_{50}	0.0199	m	static	7.5	50					
Daphnia magna	water flea		acute EC_{50}	0.90	m	static		45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985).	Cairns Jr. et al, 1981
Daphnia magna	water flea	adults	24h-EC_{50}	2.2	n	static	7.6	240	400	13	IIIb	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading rate was 10 animals in 100 ml solution. Test concentrations: A range finding test was used to determine the range of concentrations to be tested. A logarithmic scale was used in the test. Dilution water: Well water. Dissolved concentration was in the range 5.2-6.4 mg/l during the test. The Cr concentration in the dilution water was not given. Control response: 5-10% mortality seen in 48 hours. Normal behaviour was observed.	Khangarot and Ray, 1987b and 1989b; Khangarot et al, 1987
			48h-EC_{50}	1.79	n	static	7.6	240	400	13	IIIb	Endpoints: Immobilisation/mortality. Comments: The test was carried out according to APHA[9] (1976 version). The test was carried out a low temperature. The pH decreased at some higher Cr concentrations, but the decrease was always <0.5 pH unit.	
Daphnia magna	water flea		acute EC_{50}	0.175	m	static		100			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985).	White, 1979
			acute EC_{50}	0.157	m	static		92					
Daphnia magna	water flea		72-EC_{50}	0.031-0.044				86			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985). May have been tested as a mixture with other metals.	Debelak, 1975
			72h-EC_{50}	0.064-0.081				163			IIIa		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia magna	water flea	adults >1 mm	48h-EC_{50}	7.6	m	static	7.5	45	42	5	IIIb	No. of organisms: 10 organisms/replicate, 3 replicates/concentration. Loading was 10 organisms in 300 ml of solution. Test concentrations: Not given. A control was run. Dilution water: Charcoal-dechlorinated tap water. Tests were carried out without aeration. The dissolved oxygen concentration and concentration of Cr in dilution water are not reported. Control response: <10% mortality/immobilisation. Endpoints: Immobilisation. Comments: Toxicity increased with increasing temperature. The test method was based on APHA[9] (1974 version). All animals were acclimated to the test conditions for 2-4 days.	Cairns Jr. et al, 1978
			48h-EC_{50}	5.6	m	static	7.5	45	42	10	IIIb		
			48h-EC_{50}	4.3	m	static	7.5	45	42	15	IIIb		
			24h-EC_{50}	1.0	m	static	7.5	45	42	20	II		
			48h-EC_{50}	0.9	m	static	7.5	45	42	20	II		
			48h-EC_{50}	0.56	m	static	7.5	45	42	25	IIIb		
Daphnia magna	water flea		48h-EC_{50}	0.0216				50			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985). Similar results with potassium chromate (48h-EC_{50} = 0.019 mg/l).	Call et al, 1981
			96h-EC_{50}	0.0169				50					
Daphnia obtuse	water flea	<24h	48h-LC_{50}	0.061	n	static				20	II	No. of organisms: 10 animals/replicate, 3 replicates/concentration. Test concentrations: 0.020, 0.040, 0.060, 0.080, 0.10, 0.12, and 0.14 mg Cr/l plus control. Dilution water: Natural lake water. The water was filtered (0.45 µm) and UV sterilized before use. Control response: No mortality Endpoints: Immobilisation/mortality. Comments: The animals were exposed to Cr for 48 hours and then the surviving animals were transferred to clean water until the death of the last individual. The resulting lifetables were then used to assess if the exposure had effects on mortality and reproductive endpoints. These tests showed that exposure to sub-lethal concentrations of Cr reduces the lifespan, delays the time to first reproduction, shortens the reproductive period and decreases the brood size.	Coniglio and Baudo, 1989

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia pulex	water flea		48h-EC_{50}	0.063	m	static		40-48 (Lab 2)			II	No. of organisms: 10 organisms/replicate, 5 replicates/concentration. Test concentrations: 5 concentrations plus control. Dilution water: Tests carried out at two laboratories. Lab 1 used moderately hard, reconstituted water and Lab 2 used soft reconstituted water. Dissolved oxygen levels and Cr concentration in the dilution water are not given. Control response: Survival in the control was 80%-92% (mean 86%) in the experiments at Lab 1 and 87-90% (mean 89%) in the experiments at Lab 2. Endpoints: Immobilisation/mortality. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013 and 1978, EPA/600/4/78/012]. Concentrations analysed by atomic absorption spectrometry (total Cr) and Cr(VI) using diphenylcarbazide-colourimetric procedure (Cr(VI) persisted throughout tests with little conversion of Cr(VI) to Cr(III)). The results given in the table are the mean values obtained from 6 test carried out at Lab 1 and 3 tests carried out at Lab 2. The range of values obtained was 0.08-0.17 mg Cr/l at Lab 1and 0.02-0.13 mg Cr/l at Lab 2. The survival in mortality in controls was greater than the currently recommended value of 10% in some of the experiments, particularly at Lab 1.	Dorn et al, 1987
			48h-EC_{50}	0.096	m	static		72-80 (Lab 1)			IV		
Daphnia pulex	water flea	<24h	96h-LC_{50}	0.265	n		7.65	53.5	68.1		II	No. of organisms: 20 animals/concentration in 200 ml solution. Test concentrations: At least 5 concentrations plus control. Dilution water: Aged, dechlorinated tap water which was filtered through activated charcoal and a 0.45 µm membrane. The dissolved oxygen level and the Cr concentration in the dilution water is not given. Control response: Not given. Endpoints: Immobilisation/mortality. Comments: Further experiments were carried out to investigate the effect of humic acid on the toxicity. These showed that humic acid concentrations of 0.5, 5.0 and 50 mg/l caused a small apparent decrease in Cr toxicity over 48 hours (the 48h EC_{50} was 0.434 mg Cr/l at the highest humic acid concentration), but there was little or no effect on the toxicity of Cr over 96 hours.	Stackhouse and Benson, 1988
			72h-LC_{50}	0.320	n		7.65	53.5	68.1		II		
			48h-LC_{50}	0.363	n		7.65	53.5	68.1		II		
			24h-LC_{50}	0.455	n		7.65	53.5	68.1		II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia pulex	water flea	adult >1 mm	48h-EC_{50}	4.8	m	static	7.5	45	42	5	IIIb	No. of organisms: 10 organisms/replicate, 3 replicates/concentration. Loading was 10 organisms in 300 ml of solution. Test concentrations: Not given. A control was run. Dilution water: Charcoal-dechlorinated tap water. Tests were carried out without aeration. The dissolved oxygen concentration and concentration of Cr in dilution water are not reported. Control response: <10% mortality/immobilisation. Endpoints: Immobilisation. Comments: Toxicity increased with increasing temperature. The test method was based on APHA[9] (1974 version). All animals were acclimated to the test conditions for 2-4 days.	Cairns Jr. et al, 1978
			48h-EC_{50}	3.2	m	static	7.5	45	42	10	IIIb		
			48h-EC_{50}	0.9	m	static	7.5	45	42	15	IIIb		
			24h-EC_{50}	0.8	m	static	7.5	45	42	20	II		
			48h-EC_{50}	0.76	m	static	7.5	45	42	20	II		
			48h-EC_{50}	0.4	m	static	7.5	45	42	25	IIIb		
Daphnia pulex	water flea		48h-LC_{50}	0.18	m		7.5-7.9	75-105	50-60		II	No. of organisms: 10 animals/replicate, 5 replicates/concentration. Loading was 10 organisms in 200 ml solution. Test concentrations: 5 concentrations and a control. Dilution water: Reconstituted moderately hard water. Dissolved oxygen was 7.0-9.0 mg/l. Concentration of Cr in dilution water not reported. Control response: Not given. Endpoints: Immobilisation/mortality. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. The LC_{50} value reported is the mean of two determinations. A similar 48h-LC_{50} of 0.18 mg/l was obtained with potassium chromate.	Jop et al, 1987

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia similes	water flea	24±4h old	48h-EC_{50}	0.070-0.35	n	static	8.0	100		22	IIIb	No. of organisms: 5 animals/replicate, 5 replicates/concentration. The loading was 5 animals in 20 ml solution. Test concentrations: 6 concentrations plus a control. The dilution factor was 1.25. Dilution water: Reconstituted dilution water prepared from deionized and distilled water with 1.0 mM $NaHCO_3$ and variable amounts of $CaCl_2$, $MgCl_2$ and Na_2SO_4. The test waters were aerated for 10 minutes and then left for 48 hours before use to stabilise. The dissolved oxygen concentration during the test and the Cr concentration in the dilution water was not given. Control response: Not given. Endpoints: Immobilisation/mortality. Comments: Investigated the effects of sulphate, Ca and Mg on toxicity of Cr. The EC_{50} values are displayed graphically in the paper. The values reported here are taken from the graphs and so are uncertain. No information was given on the control survival in the various test media. Toxicity was found to decrease with increasing sulphate concentration (i.e. EC_{50} = 0.070 mg Cr/l at 0.1 mM $NaSO_4$; EC_{50} = 0.26 mg/l at 0.5 mM $NaSO_4$; EC_{50} = 0.35 mg/l at 1 mM $NaSO_4$). Similar effect seen with increasing $CaCl_2$ but no effect with increasing Mg^{2+}.	Hosokawa et al, 1991
Dugesia tigrina	flatworm	0.006 g	96h-LC_{50}	14.1[f]	n	static	6.5-8.5	130	93	20	IIIb	No. of organisms: Measured toxicity to seven species simultaneously. Used 10 organisms of each species per concentration. The biological loading was maintained below 0.5 g/l. Test concentrations: 100, 10, 1 and 0.1 mg $K_2Cr_2O_7$/l (equivalent to 35.4, 3.54, 0.354 and 0.0354 mg Cr/l) plus control. Dilution water: Lake water. Dissolved oxygen was maintained at >40% saturation with aeration if necessary. Level of total Cr in dilution water was <0.02 mg/l. Control response: Not given. Comments: The test method simultaneously exposed 7 species from 5 phyla. If the pH of the test solution fell out of the range 6.5-8.5, the pH was adjusted to 7.0. Widely space concentrations tested.	Ewell et al, 1986
Enallagma aspersum	damsel fly		acute LC_{50}	140	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Mortality. Comments: Unpublished results by A. M. White.	USEPA, 1985

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Enchytraeus albidus	segmented worm	adults	96h-LC_{50}	0.67[f]	n	static	5.9-7.8			12	II	No. of organisms: 10 animals/replicate, 3 replicates/concentration. Loading was 10 animals in 50 ml solution, Test concentrations: Dilution water: Reconstituted water. Dissolved oxygen level and concentration of Cr in dilution water not given. Control response: Not given. Endpoints: Mortality, but also behavioural and pathological symptoms were monitored. Comments: Test conditions analogous to OECD 202 Daphnia Immobilization test. The pH was checked at the end of each test and did not fall below pH 5.9. The pH of the dilution water was 7.8. E. albidus is a terrestrial worm, typical inhabitant of decaying organic matter. The 28-day EC_{50} for this organism exposed through soil was 417 mg/kg dry wt. soil. The results of another test with E. buchholzi is reported. Few details of the test method are given, but presumably a similar method was used. Here the 96h-LC_{50} is given as 0.83[f] mg Cr/l for juveniles (~2 mm) and 1.56[f] mg Cr/l for adults (~8 mm).	Roembke and Knacker, 1989
Gammarus fasciatus	sideswimmer	0.007 g	96h-LC_{50}	0.11[f]	n	static	6.5-8.5	130	93	20	IIIb	No. of organisms: Measured toxicity to seven species simultaneously. Used 10 organisms of each species per concentration. The biological loading was maintained below 0.5 g/l. Test concentrations: 100, 10, 1 and 0.1 mg $K_2Cr_2O_7$/l (equivalent to 35.4, 3.54, 0.354 and 0.0354 mg Cr/l) plus control. Dilution water: Lake water. Dissolved oxygen was maintained at >40% saturation with aeration if necessary. Level of total Cr in dilution water was <0.02 mg/l. Control response: Not given. Comments: The test method simultaneously exposed 7 species from 5 phyla. If the pH of the test solution fell out of the range 6.5-8.5, the pH was adjusted to 7.0. Widely space concentrations tested.	Ewell et al, 1986
Gammarus italicus	scud	juveniles (1-7d)	24h-LC_{50}	15.9[f]	n	flow	7.8	140	130	8	IIIb	No. of organisms: Either 20 males/concentration, 30 females/concentration or 40 juveniles/concentration Test concentrations: A range finding test was carried out to determine the concentrations to be tested. Dilution water: Reconstituted dilution water. Dissolved oxygen level was found to be adequate without the need for aeration. The level of Cr in the dilution water was not given. Control response: Not given. Endpoints: Mortality. Comments: The test was carried out at low temperature. A series of LT_{50} experiments (time to 50% death) were also carried out at various temperatures (8°C and 18°C) and water harness (35, 70, 140, 280 and 560 mg $CaCO_3$/l. Low hardness and high temperature generally produced the highest mortality. However, in these tests the control mortality at 18°C was also higher than at 8°C.	Pantani et al, 1989
		adult males	24h-LC_{50}	52.3[f]	n	flow	7.8	140	130	8	IIIb		
		adult females	24h-LC_{50}		n	flow	7.8	140	139	8	IIIb		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Gammarus pseudolimnaous	scud		acute EC_{50}	0.0941	m	static		48			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985). Similar result (EC_{50} = 0.10 mg/l) for potassium chromate.	Call et al, 1981
			acute EC_{50}	0.067	m	flow		48					
Goniobasis livescens	snail		24h-LC_{50}	10	n	static	8.0-8.6	137-171		23.5	II	No. of organisms: 10 animals/concentration in 2 litres test water. Test concentrations: Preliminary time-to-death studies were used to estimate the range of concentrations to be tested in the definitive study. The concentrations were chosen so that the LC_{50} was bracketed by concentrations causing <50% mortality and concentrations causing >50% mortality. Dilution water: Filtered lake water. Dissolved oxygen level was in the range 6 to 9 mg/l over the course of the experiment. The concentration of Cr in the dilution water was not given. Control response: Control mortality was <10%. Endpoints: Mortality. Comments: The initial pH was 8.0-8.6 and this generally dropped by 0.3-1.0 pH units during the test.	Cairns Jr. et al, 1976
			48h-LC_{50}	2.4	n	static	8.0-8.6	137-171		23.5	II		
Helisoma trivolvis	snail	0.180 g	96h-LC_{50}	11.3[f]	n	static	6.5-8.5	130	93	20	IIIb	No. of organisms: Measured toxicity to seven species simultaneously. Used 10 organisms of each species per concentration. The biological loading was maintained below 0.5 g/l. Test concentrations: 100, 10, 1 and 0.1 mg $K_2Cr_2O_7$/l (equivalent to 35.4, 3.54, 0.354 and 0.0354 mg Cr/l) plus control. Dilution water: Lake water. Dissolved oxygen was maintained at >40% saturation with aeration if necessary. Level of total Cr in dilution water was <0.02 mg/l. Control response: Not given. Comments: The test method simultaneously exposed 7 species from 5 phyla. If the pH of the test solution fell out of the range 6.5-8.5, the pH was adjusted to 7.0. Widely space concentrations tested.	Ewell et al, 1986
Hydra vulgaris	hydra	budless	10 h toxic conc.	10.4							IIIb	No. of organisms: Probably 10/concentration. Test concentrations: 10.4 and 104 mg Cr/l plus control. Dilution water: Not clear (report says aquarium water). Control response: Not given. Endpoints: Mortality and regeneration. Comments: Budless hydra were cut in the region of gastral cavity and exposed to either 10.4 mg Cr/l for 10 hours or 104 mg Cr/l for 1 hour and the regeneration process was monitored for 7 days. No effects on regeneration of amputated parts was seen, but both concentrations were found to be toxic to hydra.	Kalafatic, 1987

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Lumbriculus variegates	segmented worm	0.006 g	96h-LC_{50}	11.3[f]	n	static	6.5-8.5	130	93	20	IIIb	No. of organisms: Measured toxicity to seven species simultaneously. Used 10 organisms of each species per concentration. The biological loading was maintained below 0.5 g/l. Test concentrations: 100, 10, 1 and 0.1 mg $K_2Cr_2O_7$/l (equivalent to 35.4, 3.54, 0.354 and 0.0354 mg Cr/l) plus control. Dilution water: Lake water. Dissolved oxygen was maintained at >40% saturation with aeration if necessary. Level of total Cr in dilution water was <0.02 mg/l. Control response: Not given. Comments: The test method simultaneously exposed 7 species from 5 phyla. If the pH of the test solution fell out of the range 6.5-8.5, the pH was adjusted to 7.0. Widely space concentrations tested.	Ewell et al, 1986
Lymnaea acuminata	snail	adult (0.48 g)	48h-LC_{50}	9.69	n	24h renew.	7.5	375	280	27.5	I	No. of organisms: 10 snails/replicate, 2 replicates/concentration. Loading was 10 snails in 10 litres of solution. Test concentrations: 3.2, 5.6, 6.4, 7.5, 10, 15 and 20 mg Cr/l plus control. Dilution water: The source was unclear but the dilution water was well characterised. The dissolved oxygen concentration was 6.5-8.2 mg/l throughout the test. The Cr concentration in the dilution water was not given. Control response: All snails survived. Endpoints: Mortality. Comments: Test carried out according to methods prescribed by APHA[g] (1978 version).	Khangarot et al, 1982
			96h-LC_{50}	5.97	n	24h renew.	7.5	375	280	27.5	I		
Lymnaea emarginata	snail		24h-LC_{50}	52.0	n	static	8.0-8.6	137-171		23.5	II	No. of organisms: 10 animals/concentration in 2 litres test water. Test concentrations: Preliminary time-to-death studies were used to estimate the range of concentrations to be tested in the definitive study. The concentrations were chosen so that the LC_{50} was bracketed by concentrations causing <50% mortality and concentrations causing >50% mortality. Dilution water: Filtered lake water. Dissolved oxygen level was in the range 6 to 9 mg/l over the course of the experiment. The concentration of Cr in the dilution water was not given. Control response: If control mortality was >10% then the experiment was repeated. Endpoints: Mortality. Comments: The initial pH was 8.0-8.6 and this generally dropped by 0.3-1.0 pH units during the test.	Cairns Jr. et al, 1976
			48h-LC_{50}	34.8	n	static	8.0-8.6	137-171		23.5	II		
Lymnaea luteola	pond snail	adult	48h-LC_{50}	5.85	n	24h renew.	7.4	195	160	32	IIIb	No. of organisms: 10 snails/replicate, 2 replicates/concentration. Test concentrations: 7-10 concentrations used. Dilution water: Source not given. The dissolved oxygen concentration was in the range 5.2-6.5 mg/l. The Cr concentration in the dilution water was not given. Control response: Not given. Endpoints: Mortality Comments: Test carried out according to methods prescribed by APHA[g] (1978 version). The test was carried out under ambient summer temperature of 32°C.	Khangarot and Ray, 1988
			96h-LC_{50}	3.88	n	24h renew.	7.4	195	160	32	IIIb		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Macrobrachium lamarrei	prawn	adult (1.5 g)	24h-LC_{50}	1.92[f]	n	24h renew.	7.4	110.8		25	II	No. of organisms: 10 animals/replicate in 10 litres solution. The experiment was replicated 3 times. Test concentrations: 6 concentrations plus control. The concentrations used were determined from a range finding study. Dilution water: Dechlorinated tap water. Dissolved oxygen concentration was 7.5±0.5 mg/l and was maintained by continuous aeration. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Mortality. Comments: The test was carried out according to methods recommended by APHA[g] (1971 version).	Murti et al, 1983
			48h-LC_{50}	1.30[f]	n	24h renew.	7.4	110.8		25	II		
			96h-LC_{50}	0.65[f]	n	24h renew.	7.4	110.8		25	II		
Nitrocris sp.	snail	adults	48h-LC_{50}	9.1	m	static	7.5	45	42	5	IIIb	No. of organisms: 10 organisms/replicate, 3 replicates/concentration. Loading was 10 organisms in 500 ml of solution. Test concentrations: Not given. A control was run. Dilution water: Charcoal-dechlorinated tap water. Tests were carried out without aeration. The dissolved oxygen concentration and concentration of Cr in dilution water are not reported. Control response: <10% mortality. Endpoints: Mortality. Comments: Toxicity increased with increasing temperature. The test method was based on APHA[g] (1974 version). All animals were acclimated to the test conditions for at least 7 days.	Cairns Jr. et al, 1978
			48h-LC_{50}	7.8	m	static	7.5	45	42	10	IIIb		
			48h-LC_{50}	3.7	m	static	7.5	45	42	15	IIIb		
			48h-LC_{50}	1.2	m	static	7.5	45	42	20	II		
			48h-LC_{50}	0.8	m	static	7.5	45	42	25	II		
Neophasganophora caoitata	stonefly		acute LC_{50}	1870	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Mortality. Comments: Unpublished results by A. M. White.	USEPA, 1985
Orconectes rusticus	crayfish		acute LC_{50}	176	m	static		120-160			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Mortality. Comments: Unpublished results by A. M. White.	USEPA, 1985

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Philodina acuticumis	rotifer		48h-LC_{50}	54.0	m	static	7.5	45	42	5	IIIb	No. of organisms: Approximately 90 organisms/replicate, 3 replicates per concentration. Loading was ~90 organisms in 5 ml of solution. Test concentrations: Not given. A control was run. Dilution water: Charcoal-dechlorinated tap water. Tests were carried out without aeration. The dissolved oxygen concentration and concentration of Cr in dilution water are not reported. Control response: <10% mortality. Endpoints: Mortality. Comments: Toxicity increased with increasing temperature. Toxicity increased with increasing temperature. The test method was based on APHA[9] (1974 version). All animals were acclimated to the test conditions for at 2-4 days.	Cairns Jr. et al, 1978
			48h-LC_{50}	50.6	m	static	7.5	45	42	10	IIIb		
			48h-LC_{50}	39.2	m	static	7.5	45	42	15	IIIb		
			48h-LC_{50}	31.0	m	static	7.5	45	42	20	II		
			48h-LC_{50}	29.0	m	static	7.5	45	42	25	II		
Physa heterostropha	snail		96h-LC_{50}	17.3	n	static		soft		20	IIIa	No. of organisms: Not given. Probably 10 animals per replicate/concentration in 1 litre of solution. Test concentrations: Not given. Dilution water: Soft synthetic dilution water. Dissolved oxygen was 5-9 mg/l. The concentration of Cr in dilution water is not given. Control response: Not given Endpoints: Mortality. Comments: A similar 96h-LC_{50} of 16.8 mg/l was reported for potassium chromate.	Patrick et al, 1968
Physa integra	snail		24h-LC_{50}	3.8	n	static	8.0-8.6	137-171		23.5	II	No. of organisms: 10 animals/concentration in 2 litres test water. Test concentrations: Preliminary time-to-death studies were used to estimate the range of concentrations to be tested in the definitive study. The concentrations were chosen so that the LC_{50} was bracketed by concentrations causing <50% mortality and concentrations causing >50% mortality. Dilution water: Filtered lake water. Dissolved oxygen level was in the range 6 to 9 mg/l over the course of the experiment. The concentration of Cr in the dilution water was not given.	Cairns Jr. et al, 1976
			48h-LC_{50}	0.66	n	static	8.0-8.6	137-171		23.5	II	Control response: If control mortality was >10% then the experiment was repeated. Endpoints: Mortality. Comments: The initial pH was 8.0-8.6 and this generally dropped by 0.3-1.0 pH units during the test.	

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Simocephalus vetulus	water flea	<24h	24h-EC_{50}	0.154	n	static	7.9	250		20	II	No. of organisms: 10 individuals/replicate, 2 replicates/concentration. Loading was 10 animals in 40 ml solution. Test concentrations: Duplicate controls and at least 5 test concentrations. The dilution factor between concentrations was 0.5. The range tested was determined from a range-finding test. Dilution water: Standard dilution water prepared from ultrapure water (British Standard, 1983: BS6068: Part 5, Section 5.1: Determination of the Inhibition of Mobility of Daphnia magna Straus (Cladocera, Crustacea). British Standards Institution). Dissolved oxygen level and Cr concentration in dilution water not given. Control response: Not given. Endpoints: Mortality/immobilisation Comments:	Hickey, 1989
Tanytanus dissimilis	midge		acute LC_{50}	57.3	m	flow		47			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985).	Call et al, 1983
INVERTEBRATES - saltwater - short-term studies													
Acartia clausi	oar-footed crustacean		acute LC_{50}	6.6	n	static					IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Mortality. Comments: Unpublished results by S. M. Gentile.	USEPA, 1985
Allorchestes compressa	amphipod	adult (3.5 mg)	96h-LC_{50}	5.56	m	flow	8.0	33‰		19.7	II	No. of organisms: 25 animals/replicate, 2 replicates/concentration. Loading was 25 animals in 8 litres of solution. Test concentrations: Mean measured concentrations of 2.0, 4.5, 5.5, 9.8 and 18.2 mg Cr/l, plus control Dilution water: The average dissolve oxygen concentration during the test was 104% of saturation. The concentration of Cr in the dilution water was not given. Control response: All control animals survived. Endpoints: Mortality. Comments: Animals from two stock cultures tested. Similar results were obtained in both experiments.	Ahsanullah, 1982
		adult (2.2 mg)	96h-LC_{50}	6.34	m	flow	8.0	33‰		19.7	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Artemia sp.	brine shrimp	nauplii (mixed instar II-III)	24h-LC_{50}	13.7[f]	n	static	8	35‰		25	I	No. of organisms: 10 animals/replicate, 3 replicates/concentration. Loading was 10 animals in 10 ml of solution. Test concentrations: At least 5 concentrations plus control. The concentrations were on a logarithmic scale, with at least two concentrations causing mortality in the 5-95% range. Dilution water: Reconstituted seawater. Around 34% of the laboratories provided information on the dissolved oxygen concentration at the end of the test. The mean dissolved oxygen concentration was >90% of saturation. The concentration of Cr in the dilution water is not given. Control response: The mean control mortality was 2.7%. In most cases no control mortality was observed. Endpoints: Mortality. Comments: Mean results for 59 labs participating a ring test of the ARC-test developed by the Artemia Reference Centre. Full details of the test protocol are given. The mean 24h-LC_{50} was 13.7 mg Cr/l based on the 146 valid results obtained.	Vanhaecke and Persoone, 1981
Artemia salina	brine shrimp	nauplii (mixed instar II-III)	24h-LC_{50}	64.5[f]	n	static	7.9-8.1	5‰		10	IIIb	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Artificial seawater. Different salinities were obtained by dilution with deionized water. The dissolved oxygen level was >90% of saturation at the start of the test. The Cr concentration in the dilution water was not given. Control response: The test conditions used were reported not to induce mortality. An "internal" control was performed in each series of tests using $K_2Cr_2O_7$ under "standard" test conditions. If the EC_{50} from this test fell outside a certain range, the results for the entire series was considered invalid and the experiment was repeated. Endpoints: Mortality Comments: Test was carried out according to the standard ARC procedure (Artemia Reference Centre test). The study was designed to look at the effect of the test conditions on the toxicity. The tolerance limits to temperature and salinity were determined in preliminary experiments. A prerequisite of the test conditions was that they should not induce mortality or any visible signs of stress. A reference test was also carried out using the conditions recommended in the test guidelines (25°C and 35‰ salinity). The effect of temperature on the toxicity was found to be more pronounced than that of salinity, although both variables had a significant effect on the toxicity.	Persoone et al, 1989
			24h-LC_{50}	55.1[f]	n	static	7.9-8.1	5‰		15	IIIb		
			24h-LC_{50}	45.2[f]	n	static	7.9-8.1	5‰		20	II		
			24h-LC_{50}	10.9[f]	n	static	7.9-8.1	5‰		25	II		
			24h-LC_{50}	5.0[f]	n	static	7.9-8.1	5‰		30	IIIb		
			24h-LC_{50}	59.4[f]	n	static	7.9-8.1	20‰		10	IIIb		
			24h-LC_{50}	56.6[f]	n	static	7.9-8.1	20‰		15	IIIb		
			24h-LC_{50}	40.1[f]	n	static	7.9-8.1	20‰		20	II		
			24h-LC_{50}	9.7[f]	n	static	7.9-8.1	20‰		25	II		
			24h-LC_{50}	3.1[f]	n	static	7.9-8.1	20‰		30	IIIb		
			24h-LC_{50}	93.1[f]	n	static	7.9-8.1	35‰		10	IIIb		
			24h-LC_{50}	67.6[f]	n	static	7.9-8.1	35‰		15	IIIb		
			24h-LC_{50}	17.1[f]	n	static	7.9-8.1	35‰		20	II		
			24h-LC_{50}	7.8[f]	n	static	7.9-8.1	35‰		25	II		
			24h-LC_{50}	5.0[f]	n	static	7.9-8.1	35‰		30	IIIb		
			24h-LC_{50}	103.0[f]	n	static	7.9-8.1	50‰		10	IIIb		
			24h-LC_{50}	73.0[f]	n	static	7.9-8.1	50‰		15	IIIb		
			24h-LC_{50}	18.5[f]	n	static	7.9-8.1	50‰		20	IIIb		
			24h-LC_{50}	11.0[f]	n	static	7.9-8.1	50‰		25	IIIb		
			24h-LC_{50}	7.3[f]	n	static	7.9-8.1	50‰		30	IIIb		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Branchionus plicatilis	rotifer	adult females	24h-LC_{50}	80.2[f]	n	static	7.9-8.1	5‰		10	IIIb	No. of organisms: 5 animals/replicate, 4 replicates/concentration. Loading rate was 5 animals in 5 ml of solution. Test concentrations: Not given. Dilution water: Artificial seawater. Different salinities were obtained by dilution with deionized water. The dissolved oxygen level was >90% of saturation at the start of the test. The Cr concentration in the dilution water was not given. Control response: The test conditions used were reported not to induce mortality. An "internal" control was performed in each series of tests using $K_2Cr_2O_7$ under "standard" test conditions. If the EC_{50} from this test fell outside a certain range, the results for the entire series was considered invalid and the experiment was repeated. Endpoints: Mortality Comments: The study was designed to look at the effect of the test conditions on the toxicity. The tolerance limits to temperature and salinity were determined in preliminary experiments. A prerequisite of the test conditions was that they should not induce mortality or any visible signs of stress. A reference test was also carried out using "standard" conditions (25°C and 35‰ salinity). Both salinity and temperature were found to have a major effect on the toxicity of chromium.	Persoone et al, 1989
			24h-LC_{50}	60.8[f]	n	static	7.9-8.1	5‰		17	II		
			24h-LC_{50}	51.6[f]	n	static	7.9-8.1	5‰		24	II		
			24h-LC_{50}	46.0[f]	n	static	7.9-8.1	5‰		31	IIIb		
			24h-LC_{50}	134[f]	n	static	7.9-8.1	25‰		10	IIIb		
			24h-LC_{50}	122[f]	n	static	7.9-8.1	25‰		17	II		
			24h-LC_{50}	126[f]	n	static	7.9-8.1	25‰		24	II		
			24h-LC_{50}	84.1[f]	n	static	7.9-8.1	25‰		31	IIIb		
			24h-LC_{50}	123[f]	n	static	7.9-8.1	35‰		25	II		
			24h-LC_{50}	177[f]	n	static	7.9-8.1	45‰		10	IIIb		
			24h-LC_{50}	244[f]	n	static	7.9-8.1	45‰		17	IIIb		
			24h-LC_{50}	228[f]	n	static	7.9-8.1	45‰		24	IIIb		
			24h-LC_{50}	212[f]	n	static	7.9-8.1	45‰		31	IIIb		
			24h-LC_{50}	183[f]	n	static	7.9-8.1	65‰		10	IIIb		
			24h-LC_{50}	162[f]	n	static	7.9-8.1	65‰		17	IIIb		
			24h-LC_{50}	143[f]	n	static	7.9-8.1	65‰		24	IIIb		
			24h-LC_{50}	122[f]	n	static	7.9-8.1	65‰		31	IIIb		
Callinectes sapidus	blue crab	juvenile (1.5 cm)	48h-LC_{50}	39	n	static	6.5-7.9	1‰		20-22	II	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading was 10 animals in 3 litres of solution. The animals were placed in individual compartment within the tanks to prevent cannibalism. Test concentrations: A range finding test was used to determine the concentrations to be tested. Dilution water: Artificial seawater. The seawater was prepared at 70‰ salinity and diluted to the desired salinity with aged tap water. Control response: Not given. Endpoints: Mortality. Comments: The study investigated the effects of salinity on toxicity. The toxicity increased with decreasing salinity.	Frank and Robertson, 1979
			48h-LC_{50}	126	n	static	6.5-7.9	15‰		20-22	II		
			48h-LC_{50}	130	n	static	6.5-7.9	35‰		20-22	II		
			96h-LC_{50}	34	n	static	6.5-7.9	1‰		20-22	II		
			96h-LC_{50}	89	n	static	6.5-7.9	15‰		20-22	II		
			96h-LC_{50}	98	n	static	6.5-7.9	35‰		20-22	II		
Cancer magister	Dungeness crab	first-stage zoeae	96h-LC_{50}	3.44	n		8.1	33.8 ‰		15	II	No. of organisms: 5 organisms/replicate, 4 replicates/concentration. Loading rate was 5 organisms in 200 ml solution. Test concentrations: Serial dilutions of a stock solution with seawater. The concentration of Cr in the stock solution was verified by analysis. Dilution water: Natural seawater. The seawater was filtered (1 µm) and U.V. sterilised before use. The dissolved oxygen level was in the range 6.5 to 8.0 mg/l throughout the test. The concentration of Cr in the dilution water was below the limit of detection of the analytical method used (atomic absorption). Control response: <5% mortality Endpoints: Mortality. Comments: The organisms were fed at start of the test and at 48 hours.	Martin et al, 1981

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Corophium valuator	amphipod		96h-LC_{50}	5	m	24h renew.		5‰		5	IIIb	No. of organisms: 10 animals/concentration. Test concentrations: 2, 4, 8, 16, 32, 64 and 128 mg Cr/l, plus control. Dilution water: Filtered natural seawater was used. Salinities of 5-30‰ were prepared by dilution of natural seawater with deionised water. Salinities of 35-40‰ were prepared by addition of sea salt to natural seawater. The dissolved oxygen concentration was monitored regularly during the test (values not given). The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Mortality. 48 hour LC_{50}'s were also generated. Comments: The study investigated the effects of temperature and salinity on the toxicity to estuarine species. The protocol used in the test was the SCA protocol "Working Group 7.4. Acute Toxicity Tests in Seawater. TTP31 (Revise IV), 33pp. SCA Biological Methods (1980). Sterile sand was provided in all test vessels The organisms were obtained from an estuary where the natural temperature and low-tide salinity ranges were 3-16°C and 11-32‰. All animals were fully acclimated to each temperature/salinity test combination before use. The Cr(VI) concentrations in the test were checked by the S-diphenylcarbazide method. The measured concentrations were found to be close to nominal values, and there was no appreciable loss of metal from solution during the experiment. The LC_{50} appeared to decrease with decreasing salinity, particularly at low temperatures. This effect was less pronounced at 15°C.	Bryant et al, 1984
			96h-LC_{50}	8	m	24h renew.		10‰		5	IIIb		
			96h-LC_{50}	15	m	24h renew.		15‰		5	IIIb		
			96h-LC_{50}	7	m	24h renew.		20‰		5	IIIb		
			96h-LC_{50}	36	m	24h renew.		25‰		5	IIIb		
			96h-LC_{50}	38	m	24h renew.		30‰		5	IIIb		
			96h-LC_{50}	40	m	24h renew.		35‰		5	IIIb		
			96h-LC_{50}	36	m	24h renew.		40‰		5	IIIb		
			96h-LC_{50}	2.3	m	24h renew.		5‰		10	IIIb		
			96h-LC_{50}	5.8	m	24h renew.		10‰		10	II		
			96h-LC_{50}	20	m	24h renew.		15‰		10	II		
			96h-LC_{50}	20	m	24h renew.		20‰		10	II		
			96h-LC_{50}	25	m	24h renew.		25‰		10	II		
			96h-LC_{50}	25	m	24h renew.		30‰		10	II		
			96h-LC_{50}	36	m	24h renew.		35‰		10	II		
			96h-LC_{50}	38	m	24h renew.		40‰		10	IIIb		
			96h-LC_{50}	4.4	m	24h renew.		15‰		15	II		
			96h-LC_{50}	6	m	24h renew.		20‰		15	II		
			96h-LC_{50}	4.7	m	24h renew.		25‰		15	II		
			96h-LC_{50}	9.5	m	24h renew.		30‰		15	II		
			96h-LC50	5.8	m	24h renew.		35‰		15	II		
			96h-LC50	2.2	m	24h renew.		40‰		15	IIIb		
Crassostrea gigas	giant oyster	larvae	48h-EC50 (abnormal shell)	4.54	n		8.1	33.8 ‰		20	IIIb	No. of organisms: 3 replicates/concentration with approximately 100 larvae used per concentration. Test concentrations: Serial dilutions of a stock solution with seawater. The concentration of Cr in the stock solution was verified by analysis. Dilution water: Natural seawater. The seawater was filtered (1 µm) and U.V. sterilised before use. The dissolved oxygen level was in the range 6.5 to 8.0 mg/l throughout the test. The concentration of Cr in the dilution water was below the limit of detection of the analytical method used (atomic absorption). Control response: <5% mortality. The abnormal development rate in controls was not given. Endpoints: Abnormal development rate. Larvae which failed to transform to the shelled, hinged 'D' shaped veliger were considered abnormal. Comments: The abnormal development rate in controls was not given.	Martin et al, 1981

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Macoma balthica	mollusc		96h-LC_{50}	190	m	24h renew.		15‰		5	IIIb	No. of organisms: 20 animals/concentration. Test concentrations: 2, 4, 8, 16, 32, 64, 128, 256 and 512 mg Cr/l, plus control. Dilution water: Filtered natural seawater was used. Salinities of 5-30‰ were prepared by dilution of natural seawater with deinoised water. Salinities of 35-40‰ were prepared by addition of sea salt to natural seawater. The dissolved oxygen concentration was monitored regularly during the test (values not given). The concentration of Cr in the dilution water was not given. Control response: Not given. The organism was tested only under conditions in which it could survive in the laboratory. Endpoints: Mortality. 196 hour LC_{50}'s were also generated but these may be less reliable as the control response was not available for this extended time period. Comments: The study investigated the effects of temperature and salinity on the toxicity to estuarine species. The protocol used in the test was the SCA protocol "Working Group 7.4. Acute Toxicity Tests in Seawater. TTP31 (Revise IV), 33pp. SCA Biological Methods (1980). Sterile sand was provided in all test vessels. The organisms were obtained from an estuary where the natural temperature and low-tide salinity ranges were 3-16°C and 11-32‰. All animals were fully acclimated to each temperature/salinity test combination before use. The Cr(VI) concentrations in the test were checked by the S-diphenylcarbazide method. The measured concentrations were found to be close to nominal values, and there was no appreciable loss of metal from solution during the experiment. Some of the 96h-LC_{50} values are above the highest concentration tested and hence are extrapolated values. The 192h-LC_{50}s were in the range 16-340 mg Cr/l. Toxicity generally increased with increased temperature and decreasing salinity.	Bryant et al, 1984
			96h-LC_{50}	220	m	24h renew.		20‰		5	IIIb		
			96h-LC_{50}	>512	m	24h renew.		25‰		5	IIIb		
			96h-LC_{50}	>512	m	24h renew.		30‰		5	IIIb		
			96h-LC_{50}	>512	m	24h renew.		35‰		5	IIIb		
			96h-LC_{50}	>512	m	24h renew.		40‰		5	IIIb		
			96h-LC_{50}	70	m	24h renew.		15‰		10	II		
			96h-LC_{50}	120	m	24h renew.		20‰		10	II		
			96h-LC_{50}	160	m	24h renew.		25‰		10	II		
			96h-LC_{50}	320	m	24h renew.		30‰		10	II		
			96h-LC_{50}	29	m	24h renew.		15%		15	II		
			96h-LC_{50}	46	m	24h renew.		20‰		15	II		
			96h-LC_{50}	64	m	24h renew.		25‰		15	II		
			96h-LC_{50}	98	m	24h renew.		30‰		15	II		
			96h-LC_{50}	110	m	24h renew.		35‰		15	II		
Mysidopsis almyra	shrimp	24-96h	48h-EC_{50}	5.13	m	static		20‰			II	No. of organisms: 10 organisms/replicate, 5 replicates/concentration. Test concentrations: 5 concentrations plus control. Dilution water: Reconstituted seawater. Dissolved oxygen levels and Cr concentrations in the dilution water are not given. Control response: 93% survival. Endpoints: Mortality. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013 and 1978, EPA/600/4/78/012]. Concentrations analysed by atomic absorption spectrometry (total Cr) and Cr(VI) using diphenylcarbazide-colourimetric procedure (Cr(VI) persisted throughout tests with little conversion of Cr(VI) to Cr(III)).	Dorn et al, 1987

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Mysidopsis bahia	mysid shrimp	24h juvenile	96h-LC_{50}	2.03	m	flow		30‰		20-25	I	No. of organisms: 5 animals/replicate, 6 replicates/concentration. Total loading was 30 animals in 76 litres. Test concentrations: Four concentrations plus control. Dilution water: Filtered (15 µm) natural seawater. Dissolved oxygen level not given although the flow through system used should have maintained an adequate level. The concentration of total Cr in the dilution water was <1 µg/l. Control response: 100% survival. Endpoints: Immobilisation/mortality Comments: The test was conducted according the ASTM Standard Methods "Standard Practice for Conducting Acute Toxicity Tests with Fishes, Macroinvertebrates, and Amphibians. ASTM Designation E 729-80. American Society for Testing and Materials, 1980". The exact temperature of the test is unclear. The study used a temperature in the range 20-25°C, but the temperature within the test was controlled to ±1°C.	Lussier et al, 1985
Mysidopsis bahia	mysid shrimp	24h	48h-EC_{50}	5.44 (Lab 1)	m	static		20‰			II	No. of organisms: 10 organisms/replicate, 5 replicates/concentration. Test concentrations: 5 concentrations plus control. Dilution water: Reconstituted seawater. Dissolved oxygen levels and Cr concentration in the dilution water are not given. Control response: Survival in the control was 82%-94% (mean 88%) in the experiments at Lab 1 and 97-100% (mean 99%) in the experiments at Lab 2. Endpoints: Mortality. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013 and 1978, EPA/600/4/78/012]. Concentrations analysed by atomic absorption spectrometry (total Cr) and Cr(VI) using diphenylcarbazide-colourimetric procedure (Cr(VI) persisted throughout tests with little conversion of Cr(VI) to Cr(III)). The results given in the table are the mean values obtained from 5 test carried out at Lab 1 and 3 tests carried out at Lab 2. The range of values obtained was 4.21-7.14 mg Cr/l at Lab 1and 6.72-7.23 mg Cr/l at Lab 2. The mortality in mortality in controls in some experiments at Lab 1 was high.	Dorn et al, 1987
		24-96h	48h-EC_{50}	7.03 (Lab 2)	m	static		20‰			II		
Mysidopsis bahia	mysid shrimp		48h-LC_{50}	6.3	m		8.0-8.4	20‰	300-400		II	No. of organisms: 10 animals/replicate, 5 replicates/concentration. Loading was 10 organisms in 1 litre of solution. Test concentrations: 5 concentrations plus control. Dilution water: Reconstituted sea water. Dissolved oxygen was 7.0-9.0 mg/l. Concentration of Cr in dilution water not reported. Control response: Not given Endpoints: Mortality. Comments: Test carried out by standard USEPA methodology [Methods for measuring the acute toxicity of effluents to freshwater and marine organisms, 3rd Edition, 1985, EPA/600/4/85/013]. Mean measured total Cr concentration was within 95% of nominal; selected analysis confirmed that it was essentially all present in the hexavalent state. The LC_{50} value reported is the mean of two determinations. A similar 96h-LC_{50} of 6.0 mg/l was obtained with potassium chromate.	Jop et al, 1987

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Mysidopsis bigelowi	shrimp		acute LC_{50}	4.4	m	static					IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Mortality. Comments: Unpublished results by S. M. Gentile.	USEPA, 1985
Mytilus edulis	mussel	embryo	48h-EC_{50} (abnormal shell)	4.47	n		8.1	33.8 ‰		17	IIIb	No. of organisms: 3 replicates/concentration with approximately 100 larvae used per concentration. Test concentrations: Serial dilutions of a stock solution with seawater. The concentration of Cr in the stock solution was verified by analysis. Dilution water: Natural seawater. The seawater was filtered (1 µm) and U.V. sterilised before use. The dissolved oxygen level was in the range 6.5 to 8.0 mg/l throughout the test. The concentration of Cr in the dilution water was below the limit of detection of the analytical method used (atomic absorption). Control response: <5% mortality. The abnormal development rate in controls was not given. Endpoints: Abnormal development rate. Larvae which failed to transform to the shelled, hinged 'D' shaped veliger were considered abnormal. Comments:	Martin et al, 1981
Neanthes arenaceoden tata	ragworm	juvenile (1 cm, 30-40 segment stage)	96h-LC_{50}	2.2-4.3	m	static	7.6-7.8	33.6 ‰		20	II	No. of organisms: 1 organism/replicate, 20 replicates/concentration. Test concentrations: Not given Dilution water: Filtered (0.45 µm) natural seawater. Mean dissolved oxygen concentration was 7.0 mg/l throughout the test. The total Cr concentration in the dilution water was not given. Control response: Not given. Endpoints: Mortality. Comments: The 96h-LC_{50} was found to be in the range 2.2 to 4.3 mg Cr/l for laboratory reared populations. The study also investigated the 7-days toxicity to a range of organisms, including wild populations and populations cultured in elevated levels of Cr (0.0125-0.05 mg/l) during lifecycle experiments. The 7-day LC_{50} ranged between 1.46 and 1.78 mg Cr/l. Previous exposure to elevated levels of Cr did not significantly alter the LC_{50} obtained. The mean 7-day LC_{50} from 9 populations was 1.66 mg Cr/l.	Oshida et al, 1981
			7d-LC_{50}	1.66	m	static	7.6-7.8	33.6 %		20	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Neanthes arenaceodentata	ragworm	juvenile (10 mg 30-40 segment stage)	96h-LC_{50}	3.1	m	static	7.8-8.0	33.5 ‰		20	II	No. of organisms: 1 organisms/replicate, 20 replicates/concentration. Each organism was placed in 100 ml test solution. Test concentrations: Generally in the range 0.3-5.0 mg Cr/l, plus control. Dilution water: Natural seawater. The dissolved oxygen concentration was maintained at >75% of saturation. The total Cr concentration in the dilution water was 0.5-1.0 µg/l. Control response: Not given. Endpoints: Mortality. Also observed ability to build and live in mucoid tubes and effects on normal movement. Comments: A range of organisms were tested including juveniles cultured in elevated levels of Cr (0.0125-0.05 mg/l) during lifecycle experiments, laboratory cultured and wild populations. The 7-day LC_{50} ranged between 1.15 and 1.89 mg Cr/l and the 96-hour LC_{50} range between 2.22 and 3.63 mg Cr/l. Previous exposure to elevated levels of Cr did not significantly alter the LC_{50} obtained. The values given in the Table are mean values from 7 different populations (7 day values) or 4 different populations (96 hour values).	Mearns et al, 1976
			7d-LC_{50}	1.63	m	static	7.8-8.0	33.5 ‰		20	II		
Nereis diversicolor	sandworm		96h-LC_{50}	56	m	24h renew.		5‰		5	IIIb	No. of organisms: 10 animals/concentration. Test concentrations: 0.5, 1, 2, 4, 8, 16, 32 and 64 mg/l, plus control. Dilution water: Filtered natural seawater was used. Salinities of 5-30‰ were prepared by dilution of natural seawater with deionised water. Salinities of 35-40‰ were prepared by addition of sea salt to natural seawater. The dissolved oxygen concentration was monitored regularly during the test (values not given). The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Mortality. 196 hour LC_{50}'s were also generated but these may be less reliable as the control response was not available for this extended time period. Comments: The study investigated the effects of temperature and salinity on the toxicity to estuarine species. The protocol used in the test was the SCA protocol "Working Group 7.4. Acute Toxicity Tests in Seawater. TTP31 (Revise IV), 33pp. SCA Biological Methods (1980). Sterile sand was provided in all test vessels. The organisms were obtained from an estuary where the natural temperature and low-tide salinity ranges were 3-16°C and 0.2-20.6‰. All animals were fully acclimated to each temperature/salinity test combination before use. The Cr(VI) concentrations in the test were checked by the S-diphenylcarbazide method. The measured concentrations were found to be close to nominal values, and there was no appreciable loss of metal from solution during the experiment. Some of the 96h-LC_{50} values are above the highest concentration tested and hence are extrapolated values. The 192h-LC_{50}s were in the range 1-27 mg Cr/l. Toxicity generally increased with increasing temperature and decreasing salinity.	Bryant et al, 1984
			96h-LC_{50}	80	m	24h renew.		10‰		5	IIIb		
			96h-LC_{50}	>64	m	24h renew.		15‰		5	IIIb		
			96h-LC_{50}	>64	m	24h renew.		20‰		5	IIIb		
			96h-LC_{50}	>64	m	24h renew.		25‰		5	IIIb		
			96h-LC_{50}	>64	m	24h renew.		30‰		5	IIIb		
			96h-LC_{50}	>64	m	24h renew.		35‰		5	IIIb		
			96h-LC_{50}	>64	m	24h renew.		40‰		5	IIIb		
			96h-LC_{50}	19	m	24h renew.		5‰		10	II		
			96h-LC_{50}	22	m	24h renew.		10‰		10	II		
			96h-LC_{50}	27	m	24h renew.		15‰		10	II		
			96h-LC_{50}	65	m	24h renew.		20‰		10	II		
			96h-LC_{50}	55	m	24h renew.		25‰		10	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Nereis diversicolor	sandworm		96h-LC_{50}	34	m	24h renew.		30‰		10	II		
			96h-LC_{50}	52	m	24h renew.		35‰		10	IIIb		
			96h-LC_{50}	40	m	24h renew.		40‰		10	IIIb		
			96h-LC_{50}	7.5	m	24h renew.		5‰		15	II		
			96h-LC_{50}	9.5	m	24h renew.		10‰		15	II		
			96h-LC_{50}	8.5	m	24h renew.		15‰		15	II		
			96h-LC_{50}	12	m	24h renew.		20‰		15	II		
			96h-LC_{50}	12	m	24h renew.		25‰		15	II		
			96h-LC_{50}	7.5	m	24h renew.		30‰		15	II		
			96h-LC_{50}	22	m	24h renew.		35‰		15	IIIb		
			96h-LC_{50}	16	m	24h renew.		40‰		15	IIIb		
Nitocra spinipes	shrimp	adult (3-6 week old)	96h-LC_{50}	5.7[f]	n	static	7.8	7‰		21	II	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading rate was 10 animals in 10 ml of solution. Test concentrations: A rangefinding test was used to determine the concentrations to be tested. At least 6 concentrations were tested plus control. Dilution water: Natural brackish seawater. The water was filtered (filter paper) before use. Dissolved oxygen concentrations and he Cr concentrations in dilution water not given. Control response: Not given Endpoints: Mortality Comments:	Lindén et al, 1979

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Ophryotrocha diadema	polychaete		48h-LC_{50}	1-3.3	n	static		32‰		21	IV	No. of organisms: 10 animals/replicate, 2 replicates/concentration. Loading rate was 10 animals in 50 ml solution. Test concentrations: A half-logarithmic series of concentrations used, plus control. Dilution water: Sterile filtered seawater. The dissolved oxygen level and concentration of Cr in dilution water not given. Control response: No deaths occurred in controls. Endpoints: Mortality. The mortality was recorded both during the 48 hour exposure period and during the following week where exposed organisms were transferred to clean seawater. Comments: The range within which the 48h-LC_{50} lies was given as 1-3.3 mg Cr/l. This may have been determined based on the combined mortality seen in the 48 hour exposure period and the 7 day observation period in clean seawater. Chromium (III) was much less toxic (48h-LC_{50} = 100 mg/l).	Parker, 1984
Paracentrotus lividus	sea urchin	eggs	60h LOEC (embryo toxicity)	2.6	n	static					IIIb	No. of organisms: 500 ml solutions of eggs at a density of 400 cells/ml. Test concentrations: 0.0026, 0.026, 0.26 and 2.6 mg Cr/l. Dilution water: Natural seawater. The tests were carried out in sealed containers. Dissolved oxygen level and Cr concentration of dilution water not given. Control response: Little information given other than winter embryos developed earlier than spring embryos. The tests with Cr were carried out with spring embryos. Endpoints: Morphological observations (in vitro development of the blastula to the mature pluteus) used to investigate embryotoxicity. Comments: Chromium added 20 minutes after fertilisation. A Cr(VI) concentration of 2.6 mg/l blocked egg development after the blastula phase (22 hours) and killed all embryos within 60 hours. The response at lower exposure concentrations is not given.	Congiu et al, 1984

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Praunus flexuosus	crustacean (mysid)		96h-LC_{50}	4	n	24h renew.		4.5‰		5	IV	No. of organisms: 20 animals/concentration. Test concentrations: 8, 16 and 32 mg/l plus control Dilution water: Natural seawater (27‰). This was diluted with tap water of low mineral content to given the desired salinity. Control response: The LT_{50} for controls was given as >300 days. Endpoints: Mortality. Comments: Study to investigate the effects of temperature and salinity on toxicity. Increased temperature (5 to 15°C) resulted in increased toxicity Increased salinity (4.5 to 22.5‰) generally resulted in decreased toxicity but there was evidence that the toxicity increased again at 27‰. This indicated that that the maximal survival of animals occurred at around 22.5‰, which is close to the iso-osmotic point for the species. The toxicity of Cr was thought to be related to a decrease in the ability of the animals to osmoregulate. As only three concentrations were tested many of the actual LC_{50}s reported are outside this range (8-32 mg/l) and so are more uncertain. The study also determined LT_{50} values (time to 50% mortality) at the various concentrations tested and these showed the same variation in toxicity with salinity and temperature as the LC_{50} values.	McLusky and Hagerman, 1987
			96h-LC_{50}	2.5	n	24h renew.		4.5‰		15	IV		
			96h-LC_{50}	8	n	24h renew.		9‰		5	IV		
			96h-LC_{50}	8	n	24h renew.		9‰		15	IV		
			96h-LC_{50}	22	n	24h renew.		13.5‰		5	IIIb		
			96h-LC_{50}	11	n	24h renew.		13.5‰		15	II		
			96h-LC_{50}	22	n	24h renew.		18‰		5	IIIb		
			96h-LC_{50}	13	n	24h renew.		18‰		15	II		
			96h-LC_{50}	22	n	24h renew.		22.5‰		5	IIIb		
			96h-LC_{50}	13	n	24h renew.		22.5‰		15	II		
			96h-LC_{50}	18	n	24h renew.		27‰		5	IIIb		
			96h-LC_{50}	10	n	24h renew.		27‰		15	II		
Pseudodiaptomus coronatus	copepod		acute LC_{50}	3.65	n	static					IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Mortality. Comments: Unpublished results by S. M. Gentile.	USEPA, 1985
Rangia cuneata	brackish water clam	adults	48h-TLm[e]	0.96	n	static		<1‰		24	II	No. of organisms: 15 clams/replicate, 2 replicates/concentration. The loading rate was 15 clams in 6 litres of solution. Test concentrations: A rangefinding study was used to determine the concentrations to be tested. Usually 5 concentrations plus a control were tested, but further concentrations were added if necessary to establish the LC_{50}. A factor of 0.5 was used between concentrations. Dilution water: Reconstituted seawater. The dissolved oxygen level was not monitored during the test but it was thought that the test design would have maintained it at close to saturation. The level of Cr in the dilution water is not given. Control response: Not given. Endpoints: Mortality. Comments: The LC_{50} was determined by the standard methods recommended by APHA[9] (1965 version). Investigated the toxicity over a range of salinities (<1‰-22‰) that represent the approximate limit of the normal salinity range for R. cuneata. The test solutions were normally not changed during the test but in some cases fungi invaded the test vessels and these were renewed after 48 hours.	Olson and Harrel, 1973
			96h-TLm[e]	0.21	n	static		<1‰		24	II		
			48h-TLm[e]	66.0	n	static		5.5‰		24	II		
			96h-TLm[e]	14.0	n	static		5.5‰		24	II		
			48h-TLm[e]	86.0	n	static		22‰		24	II		
			96h-TLm[e]	35.0	n	static		22‰		24	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
INVERTEBRATES -freshwater - long-term studies													
Ceriodaphnia dubia	water flea	<24h	14d LOEC (repro.)	0.010	n	48h renew	7.9	250		20	II	No. of organisms: 10 individuals/replicate, 2 replicates/concentration. Loading was 10 animals in 15 ml solution. Test concentrations: Duplicate controls and at least 5 test concentrations. The dilution factor between concentrations was 0.5. The range tested was determined from a range-finding test. Dilution water: Standard dilution water prepared from ultrapure water (British Standard, 1983: BS6068: Part 5, Section 5.1: Determination of the Inhibition of Mobility of Daphnia magna Straus (Cladocera, Crustacea). British Standards Institution). Dissolved oxygen level and Cr concentration in dilution water not given. Control response: Not given. Endpoints: Total number of young per adult female (reproduction). Comments: Effects appear to have been seen at the lowest concentration tested.	Hickey, 1989
			14d NOEC (repro.)	<0.010	n	48h renew.	7.9	250		20	II		
Ceriodaphnia dubia	water flea		7d NOEC (survival)	<0.0057[f]-0.028	m						II	No. of organisms: Not given. Test concentrations: Each test was carried out using the same test concentrations. The lowest concentration tested was 0.0057 mg Cr/l in the first series of tests and 0.0018 mg/l in the second series of tests, and a factor of 2 was used between subsequent concentrations. Dilution water: Reconstituted water. The dissolved oxygen concentration was monitored but the value was not given. The Cr concentration in the dilution water was not given. Control response: The test was considered valid if survival was ≥80% and ≥9 young per female were produced over the 7 day period. Endpoints: Survival and reproduction. Reproduction was based on total reproductive output for each female and so is a combination of the reproductive output of females that survived the exposure period and also those that died during the exposure period. Comments: The study was an intra- and inter-laboratory study of the USEPA 7-day Ceriodaphnia dubia survival and reproduction test "Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. 2nd Ed. EPA 600/4-89-001, United States Environmental Protection Agency. The concentrations were analysed during the test and it was found that the actual concentrations were very close to the nominal values. In all the results from 18 valid studies were obtained from 11 laboratories in two series (carried out at two different times). For survival in the first series of experiments, 3 NOECs were <0.0057[f] mg Cr/l, 3 NOECs were 0.0057[f] mg Cr/l, 1 NOEC was 0.0113[f] mg Cr/l and 1 NOEC was 0.0226[f] mg Cr/l. For survival i n the second series of experiments, 4 NOECs were 0.0071[f] mg Cr/l, 5 NOECs were 0.014[f] mg Cr/l and 1 NOEC was 0.028[f] mg C/l/ For reproduction, in the first series of experiments 5 NOECs were <0.0057[f] mg Cr/l and 3 NOECs were 0.0057[f] mg Cr/l. In the second series of experiments 1 NOEC was <0.0018[f] mg Cr/l, 1 NOEC was 0.0035[f] mg Cr/l, 7 NOECs were 0.0071[f] mg Cr/l and 1 NOEC was 0.014[f] mg Cr/l. The mean L(E)C_{50}'s for survival and reproduction 0.0105[f] and 0.0127[f] respectively for the first series of experiments and 0.0175[f] and 0.0162[f] mg Cr/l respectively for the second series of experiments.	DeGraeve et al, 1992
			7d NOEC (repro.)	<0.0018[f]-0.014[f]	m						II		
			7d LC_{50} (survival)	0.0105[f] & 0.0175[f]	m						II		
			7d EC_{50} (repro.)	0.0127[f] & 0.0162[f]	m						II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Ceriodaphnia dubia	water flea		7d NOEC (survival)	<0.0057[f]-0.028	m						II	No. of organisms: Not given. Test concentrations: Each test was carried out using the same test concentrations. The lowest concentration tested was 0.0057 mg Cr/l in the first series of tests and 0.0018 mg/l in the second series of tests, and a factor of 2 was used between subsequent concentrations. Dilution water: Reconstituted water. The dissolved oxygen concentration was monitored but the value was not given. The Cr concentration in the dilution water was not given. Control response: The test was considered valid if survival was ≥80% and ≥9 young per female were produced over the 7 day period. Endpoints: Survival and reproduction. Reproduction was based on total reproductive output for each female and so is a combination of the reproductive output of females that survived the exposure period and also those that died during the exposure period. Comments: The study was an intra- and inter-laboratory study of the USEPA 7-day Ceriodaphnia dubia survival and reproduction test "Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. 2nd Ed. EPA 600/4-89-001, United States Environmental Protection Agency. The concentrations were analysed during the test and it was found that the actual concentrations were very close to the nominal values. In all the results from 18 valid studies were obtained from 11 laboratories in two series (carried out at two different times). For survival in the first series of experiments, 3 NOECs were <0.0057[f] mg Cr/l, 3 NOECs were 0.0057[f] mg Cr/l, 1 NOEC was 0.0113[f] mg Cr/l and 1 NOEC was 0.0226[f] mg Cr/l. For survival i n the second series of experiments, 4 NOECs were 0.0071[f] mg Cr/l, 5 NOECs were 0.014[f] mg Cr/l and 1 NOEC was 0.028[f] mg C/l/ For reproduction, in the first series of experiments 5 NOECs were <0.0057[f] mg Cr/l and 3 NOECs were 0.0057[f] mg Cr/l. In the second series of experiments 1 NOEC was <0.0018[f] mg Cr/l, 1 NOEC was 0.0035[f] mg Cr/l, 7 NOECs were 0.0071[f] mg Cr/l and 1 NOEC was 0.014[f] mg Cr/l. The mean L(E)C_{50}'s for survival and reproduction 0.0105[f] and 0.0127[f] respectively for the first series of experiments and 0.0175[f] and 0.0162[f] mg Cr/l respectively for the second series of experiments.	DeGraeve et al, 1992
			7d NOEC (repro.)	<0.0018[f]-0.014[f]	m						II		
			7d LC_{50} (survival)	0.0105[f] & 0.0175[f]	m						II		
			7d EC_{50} (repro.)	0.0127[f] & 0.0162[f]	m						II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Ceriodaphnia dubia	water flea		~7d 3-brood NOEC (survival)	0.07[f]	n	24h renew.	8.4	102	81	26.4	IIIb	No. of organisms: Used 10 organisms/concentration and 20 organisms for the control. The loading was 1 organism in 100 ml solution. Test concentrations: Used a declining series of concentration with a dilution factor of 0.6 between concentrations plus control. Dilution water: Reconstituted water. The water was autoclaved and supplemented with 2 µg Se/l and 2 µg B_{12}/l as C. daphnia requires these for successful reproduction. Dissolved oxygen was in the range 8.1-9.6 mg/l throughout the test. Control response: Mean values from 15 controls were: total young produced = 468; total young produced in 3 broods = 369; total young/female=24; total young/female in 3 broods=19; brood size=7.1; time to first brood 67 hours; time to 3 broods=182 hours. The validation criteria of the test required that at least 15 young were produced by 80% of the controls. Endpoints: Survival and reproduction (number of offspring). Comments: The results are given in graphical form. The effect concentrations were estimated from the graph in the paper.	Cowgill and Milazzo, 1991
			~7d 3-brood LC_{50} (survival)	~0.28[f]	n	24h renew.	8.4	102	81	26.4	IIIb		
			~7d 3-brood EC_{50} (repro.)	0.07[f]	n	24h renew.	8.4	102	81	26.4	IIIb		
Culex pipiens	mosquito fly	1st instar	25d NOEC (mortality)	1.1[f]	n	semi-static				27	II	No. of organisms: 30/replicate, 2 replicates/concentration. Loading was 30 organisms in 50 ml solution. Test concentrations: Range of concentrations with a dilution factor of √10 between concentrations, plus control. Dilution water: Reconstituted dilution water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Not given. Endpoints: mortality and development Comments:	Slooff and Canton, 1983; Van Leeuwen, 1990
			25d NOEC (devel.)	1.1[f]	n	semi-static				27	II		
Daphnia carinata	water flea	<24h	14d LOEC (repro.)	0.10	n	48h renew.	7.9	250		20	II	No. of organisms: 10 individuals/replicate, 2 replicates/concentration. Loading was 10 animals in 40 ml solution. Test concentrations: Duplicate controls and at least 5 test concentrations. The dilution factor between concentrations was 0.5. The range tested was determined from a range-finding test. Dilution water: Standard dilution water prepared from ultrapure water (British Standard, 1983: BS6068: Part 5, Section 5.1: Determination of the Inhibition of Mobility of Daphnia magna Straus (Cladocera, Crustacea). British Standards Institution). Dissolved oxygen level and Cr concentration in dilution water not given. Control response: Not given. Endpoints: Total number of young per adult female (reproduction). Comments:	Hickey, 1989
			14d NOEC (repro.)	0.050	n	48h renew.	7.9	250		20	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia magna	water flea	<24h	21d NOEC (mortality)	0.018	m	~48h renew.	8.0	16[o]		25	I	No. of organisms: 5 animals/replicate, 4 replicates/concentration. Loading was 5 animals in 200 ml solution. Test concentrations: Dilution steps of 1:2. The concentration range tested was 0.0046-0.142 mg Cr/l and was determined from a range finding test. Dilution water: Synthetic fresh water. Dissolved oxygen level was >69% of saturation throughout the study. The Cr concentration of dilution water was not given Control response: Overall in the study 64 controls were run. The mean number of offspring/animal produced after 21 days was 88.8. The mean parent animal mortality after 21 days was 7.1%. First offspring appeared on 7th day. Endpoints: Reproduction, mortality and appearance of offspring Comments: Test conducted according to "Provisional Procedure: Extending Toxicology Test with Daphnia magna, as of 1 January 1984. Recommendation of the Federal Environmental Agency on the Performance of Testing According to Section 5, para 1 No 3 of the Regulation on Application Documents and Evidence under the Chemicals Act. Federal Environment Agency." The pH of the test solutions was around 8.0 at the start of the test and never fell below pH 7.0 during the test. All measured exposure concentrations were >80% of nominal values.	Kuhn et al, 1989
			21d NOEC (repro.)	0.018	m	~48h renew	8.0	16[o]		25	I		
Daphnia magna	water flea	24h	21d NOEC (mortality)	0.035[f]	n	semi-static				19	II	No. of organisms: 25/replicate, 2 replicates/concentration. Loading was 25 organisms in 1 litre solution. Test concentrations: Range of concentrations with a dilution factor of √10 between concentrations, plus control. Dilution water: Reconstituted dilution water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Not given. Endpoints: Mortality and reproduction Comments:	Slooff and Canton, 1983; Van Leeuwen, 1990
			21d NOEC (repro.)	0.035[f]	n	semi-static				19	II		
Daphnia magna	water flea	<24h	survival 21d-LC_{50} 21d NOEC	 0.5 0.20	m	semi-static	8.1	225			II	No. of organisms: 10 per concentration in survival/growth experiment; 20 per concentration in yield experiment. Test concentrations: 0.06-1.13 mg/l as Cr, in series increasing by 1.8x. Dilution water: Lake Ijssel water, filtered and sterilised. Control response: included. Endpoints: mortality and carapace length (growth) in one series; intrinsic rate of net increase of numbers (yield) in the second series. Comments: For the yield experiments, an expanding population of mixed ages was used and the total number of daphnids present was monitored. Results from this are comparable to the results from standard test.	Van Leeuwen et al , 1987.
			growth 21d LOEC 21d NOEC	 0.11 0.06	m	semi-static	8.1	225			II		
		mixed	yield 21d-EC_{50} 21d NOEC	 0.64 0.35	m	semi-static	8.1	225			II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia magna	water flea		14-21d NOEC (overall)	0.035[f]							IIIb	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Mortality and reproduction. Effects on growth also determined qualitatively. Comments: Test carried out in accordance with OECD guidelines and "Degradability, ecotoxicity, and bio-accumulation. The determination of the possible effects of chemicals and wastes on the aquatic environment. Government Publishing Office, the Hague, 1980". Only a summary of the results is reported.	Adema et al, 1983
Daphnia magna	water flea		16d EC_{50} (3 brood) (repro.)	0.095[f]	n	~48 renew.		100		19	II	No. of organisms: 15/replicate in 1 litre solution. All experiments were carried out in duplicate. Test concentrations: The ratio between the adjacent concentrations tested was 3.2. Dilution water: Dutch Standard water. Dissolved oxygen level and Cr concentration in dilution water not given. Control response: 3-4 broods produced over 16 days. Endpoints: Inhibition of reproduction. Comments: Tests carried out according to methods by the Dutch Standard Organization "Concept NEN6501 (1980). Determination of the Acute Toxicity with Daphnia magna. Concept NEN6502 (1980). Determination of the Chronic Toxicity with Daphnia magna. Dutch Standard Organization, Delft".	Hermens et al, 1984
Daphnia magna	water flea	<24h	14d LOEC (repro.)	0.100	n	48h renew.	7.9	250		20	II	No. of organisms: 10 individuals/replicate, 2 replicates/concentration. Loading was 10 animals in 40 ml solution. Test concentrations: Duplicate controls and at least 5 test concentrations. The dilution factor between concentrations was 0.5. The range tested was determined from a range-finding test. Dilution water: Standard dilution water prepared from ultrapure water (British Standard, 1983: BS6068: Part 5, Section 5.1: Determination of the Inhibition of Mobility of Daphnia magna Straus (Cladocera, Crustacea). British Standards Institution). Dissolved oxygen level and Cr concentration in dilution water not given. Control response: Not given. Endpoints: Total number of young per adult female (reproduction). Comments:	Hickey, 1989
			14d NOEC (repro.)	0.025	n	48h renew.	7.9	250		20	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Daphnia magna	water flea	<24 hour	21d NOEC (survival)	~0.175[f]		flow					IV	No. of organisms: 10 animals/concentration were used in 18 litres of solution.. Test concentrations: The substances was added to the effluent of a treatment plant simulation model at a concentration of 0.176[f] and 0.35[f] mg Cr/l. Dilution water: Effluent from a OECD Confirmatory Test Unit (treatment plant simulation model) diluted 1:6 with synthetic fresh water. The dissolved oxygen level and Cr concentration of the dilution water are not given. Control response: 100 % survival over 28 days. The reproduction rate was 61 young/adult over 21 days. Endpoints: Reproduction rate of parents. Comments: The test coupled the OECD confirmatory test with D. magna reproduction test. It is not clear if the concentrations given in the paper take into account the 1:6 dilution of the effluent. The actual exposure concentrations in the toxicity test vessel could be 6 times lower than reported.	Scholz, 1991
			21d NOEC (repro.)	~0.175[f]		flow					IV		
Hydra littoralis	hydra		11d threshold conc. (repro.)	0.035[f]		semi-static	8.15				II	No. of organisms: 10 per replicate, 4 replicates per concentration Test concentrations: no information Dilution water: distilled water with inorganic salts (specified for Hydra culture). Control response: not included Endpoints: reduction in growth rate, based on number of organisms (Hydra reproduces by budding) Comments: Daily water changes. Hardness = 3.5 degrees (German)	Dannenberg, 1984
Hydra oligactis	hydra	budless	21d NOEC (growth rate)	1.1[f]	n	semi-static				18	II	No. of organisms: 2/replicate, 5 replicates/concentration. Loading was 2 organisms in 50 ml solution. Test concentrations: Range of concentrations with a dilution factor of √10 between concentrations, plus control. Dilution water: Reconstituted dilution water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Not given. Endpoints: Specific growth rate. Comments:	Slooff and Canton, 1983; Van Leeuwen, 1990
Lymnaea stagnalis	great pond snail	adults (5 month old)	40d NOEC (repro.)	0.11[f]	n	semi-static				20	II	No. of organisms: 20 adults/concentration in 20 litre of solution or 5 egg capsules/concentration in 50 ml of solution. Test concentrations: Range of concentrations with a dilution factor of √10 between concentrations, plus control. Dilution water: Reconstituted dilution water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Not given. Endpoints: Mortality, reproduction and hatching. Comments:	Slooff and Canton, 1983; Van Leeuwen, 1990
			40d NOEC (mortality)	3.5[f]	n	semi-static				20	II		
		Eggs	7d NOEC (hatching)	0.35[f]	n	semi-static				20	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Simocephalus vetulus	water flea	<24h juvenile	14d LOEC (repro.)	>0.100	n	48h renew.	7.9	250		20	IV	No. of organisms: 10 individuals/replicate, 2 replicates/concentration. Loading was 10 animals in 40 ml solution. Test concentrations: Duplicate controls and at least 5 test concentrations. The dilution factor between concentrations was 0.5. The range tested was determined from a range-finding test. Dilution water: Standard dilution water prepared from ultrapure water (British Standard, 1983: BS6068: Part 5, Section 5.1: Determination of the Inhibition of Mobility of Daphnia magna Straus (Cladocera, Crustacea). British Standards Institution). Dissolved oxygen level and Cr concentration in dilution water not given. Control response: Not given. Endpoints: Total number of young per adult female (reproduction). Comments: The variability in the number of neonates born in the control populations was high, indicating that the test conditions used may not have been suitable for this species. This introduces uncertainty into the LOEC value.	Hickey, 1989
INVERTEBRATES - saltwater - long-term studies													
Barentsia matsushimana	entoproct	buds	49d EC_0 (colony growth)	0.013	n	72h/96h renew. or flow		30‰		15	IIIb	No. of organisms: Up to 7 resting buds were attached to a plastic slide and incubated in a dish containing the test substance. A total of 5 replicates were used for each concentration. Test concentrations: 0.010, 0.10 and 1.0 mg Cr/l plus control. Dilution water: Not given. Control response: Growth was lower in the flow-through experiments than the semi-static experiments and may be related to the colonies being overfed. To eliminate this discrepancy, all growth in the exposed colonies was expressed as a % of control growth. Endpoints: Colony growth (number of newly established calyces per colony and per day) over a total of 49 days. Comments: The resting buds were germinated incubating at 5°C for 4 days and then incubating at 15°C for two weeks. For further development and growth, the newly hatch colonies (1-3 calyces) were either transferred to a semi-static system or suspended in a flow through system and fed algal suspensions. An EC_{50} and a EC_m was calculated from the data. The EC_m is the minimal effect level or the concentration above which a statistically significant effect may occur and so is similar to an EC_o. The reliability of these values is uncertain as only 3, widely space concentrations were tested.	Scholz, 1987
			49d EC_{50}	0.139	n	72h/96h renew. or flow		30‰		15	IIIb		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Capitella capitata	polychaete worm	larvae	5-month NOEC (mortality)	0.05	n	static		35‰		19.5	II	No. of organisms: 25 trochophore larvae/replicate, 4 replicates/concentration. The loading rate was 25 larvae in 2.5 litres solution. Test concentrations: 0.025, 0.05, 0.1, 0.2 and 0.4 mg Cr/l, plus control. Dilution water: Natural seawater. The test solutions were aerated to maintain the dissolved oxygen level. The Cr concentration in the dilution water was not given. Control response: Endpoints: Survival and reproduction (number of females which reproduced, average number of offspring produced, occurrence of abnormal larvae). Comments: Survival was 86%. The number of females that reproduced was 33. The average number of offspring was 243. The % occurrence of abnormal larvae was 0%. Static system was used has it had been shown that the chromium concentration did not decrease with time. The number of survivors was markedly reduced at 0.1 mg Cr/l over that at the lower concentrations and controls. The statistical significance of this decrease is not given but the number of survivors at 0.1 mg/l was 58% compared with 86% in the controls. Also, this concentration and above a downward trend was seen in the numbers of females reproducing and the average number of offspring. The decrease in the average numbers of offspring was statistically significant ($p<0.05$) when compered with controls. The percentage of abnormal larvae also appeared to increase with increasing concentration at all concentrations (0% in controls, 0.44% at 0.025 mg Cr/l, 0.88% at 0.050 mg Cr/l, 1.3% at 0.1 mg Cr/l, 1.2% at 0.2 mg Cr/l and 1.7% at 0.4 mg Cr/l), although the statistical significance of this increase is unclear.	Reish, 1977
			5-month NOEC (repro.)	0.05	n	static		35‰		19.5	II		
			5 month NOEC (abnormal larvae)	<0.025	n	static		35‰		19.5	IIIb		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Cancer anthonyi	crab	embryos	7d LOEC (mortality)	0.01	m	48h renew.	7.8	34‰		20	II	No. of organisms: 50-100 embryos/replicate, 5 replicates/concentration. Loading was 50-100 embryos in 5 ml solution. Test concentrations: 0.01, 0.1, 1.0, 10, 100, 1,000 mg/l. Dilution water: Natural seawater, filtered (0.45 µm) to remove >95% of particulates. The dissolved oxygen level was 6.5-8.0 mg/l during the test. The total Cr concentration in the dilution water was 0.2 µg/l. Control response: 5.9% mortality. Endpoints: Survival of embryos and prezoea and hatching success. Comments: The survival at seven days and the hatching success (% hatch) were statistically significantly different ($p<0.05$) in all exposure groups when compared with controls. The mortality in the lowest concentration (o.o1 mg Cr/l) group was 33.1% and the percentage hatch in this group was 38.1% (the dose-response for percentage hatch was relatively poor, with 68.2%, 62.5% and 41.2% being seen at the next three Cr concentrations). A second experiment was carried out to investigate larval (prezoea) survival. Three trials were run using prezoea that had a) embryos and hatched larvae that had been exposed to Cr, b) embryos that had been exposed to Cr but hatched larvae had not been exposed, and c) embryos that had not been exposed to Cr but their hatched larvae had been exposed. These trials indicated that pre-exposure of embryos to Cr lead to a slightly higher resistance of the larvae to Cr compared to unexposed populations.	Macdonald et al, 1988
			7d LOEC (% hatch)	0.01	m	48h renew.	7.8	34‰		20	II		
Mysidopsis bahia	mysid shrimp	24h juvenile	38d NOEC (repro. brood size)	0.088	m	flow	8.0		30‰	22	II	No. of organisms: 5 animals/replicate, 6 replicates/concentration. Total loading was 30 animals in 76 litres. Test concentrations: 0.088 mg/l, 0.198 mg/l, 0.424 mg/l and 0.909 mg/l, plus control. Dilution water: Filtered (15 µm) natural seawater. Dissolved oxygen level not given although the flow through system used should have maintained an adequate level. The concentration of total Cr in the dilution water was <1 µg/l. Control response: 70% survival over 38 days. Days to first brood was 29 days. Number of young per female reproductive day was 0.84. Endpoints: Mortality and reproduction(time to sexual maturation, duration of embryonic development, brood size). Comments: The test was a 2 generation life-cycle test. In the test the animals were exposed until sexual maturity and then were redistributed to provide a consistent 2 male:3 female ratio. Although the control survival was a little low in this experiment, no statistically significant effects on survival or day to first brood was seen at any concentration. The brood size (number of young per female reproductive day) was significantly reduced at concentrations of 0.198 mg Cr/l and above.	Lussier et al, 1985
			38d LOEC (repro. brood size)	0.198					30‰	22	II		
			38d NOEC (mortality)	>0.909	m	flow	8.0		30‰	22	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Neanthes arenaceodentata	ragworm	1st gen. (P_1 - 10-30 segment stage)	LOEL (repro.)	<0.0125	m	1-3 week renew.	7.9		33.6 ‰	20	II	No. of organisms: 1 organism/replicate, 22 replicates concentration. Each organism of the parental generation (P_1) was placed in 3 litres of solution. Once the sex of the worms could be determined (~19-55 days), males were paired with females. The females naturally died after spawning leaving the males to incubate the eggs. The F_1 offspring were allowed to grow to 30-40 segments and 22 worms were subsampled and set up in a similar manner to the parental generation. The remaining offspring were used in a 7-day acute toxicity test (see above). The same procedure was then applied to the F_2 offspring. Test concentrations: 0.0125, 0.025, 0.050, 0.100 and 0.200 mg Cr/l plus control. Dilution water: Filtered (filter paper) natural seawater. The mean dissolved oxygen concentration during the test was 7.1 mg/l. The mean total Cr concentration in the dilution water was 1 µg/l. Control response: For the mean numbers of young per brood were 255 for the P_1 generation, 292 for the F_1 generation and 273 for the F_2 generation. Endpoints: Reproduction (brood size) Comments: A 440 day three generation lifecycle study. For the first generation (P_1 to F_1), eggs were never laid at the two highest concentrations tested (0.1 and 0.2 mg Cr/l). The lowest concentration tested (0.0125 mg Cr/l) showed a statistically significant ($p<0.05$) decrease in mean brood size relative to controls (133 against 255 in controls). The mean brood size at 0.025 and 0.05 mg Cr/l were also significantly reduced (146 and 78 respectively). For the second generation (F_1 to F_2), the mean brood size was significantly reduced at concentrations of 0.025 mg Cr/l and higher but not at 0.0125 mg Cr/l. For the third generation (F_2), the mean brood size was reduced compared to controls at all concentrations, but this reduction was only statistically significant at 0.05 mg Cr/l and above. Analysis for both total Cr and Cr(VI) carried out during the study indicates that concentrations were maintained during the study and that Cr(VI) was stable under the experimental conditions used. The mean measured Cr concentration in the 0.0125 mg/l nominal treatment was 0.013 mg/l. This is probably part of the study reported by Mearns et al (1976) below.	Oshida et al, 1981
		2nd gen.	NOEL (repro.)	0.0125	m	1-3 week renew.	7.9		33.6 ‰	20	II		
			LOEC (repro.)	0.025	m	1-3 week renew.	7.9		33.6 ‰	20	II		
		3rd gen.	NOEL (repro.)	0.025	m	1-3 week renew.	7.9		33.6 ‰	20	II		
			LOEL (repro.)	0.050	m	1-3 week renew.	7.9		33.6 ‰	20	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Neanthes arenaceodentata	ragworm	Parental gen. (30-40 segment)	NOEC (repro.)	≥0.0382	m	3 week renew.	7.76-8.40	33.6‰		20.8	II	No. of organisms: Used 90 animals/concentration in 50 litres of solution. The worms were allowed to grow for at least the first 45 days. Once the sex of the worms could be determined the males and females were paired. Females died naturally after spawning (~90 days after pairing) and the males were left to incubate the eggs. At this time the individuals and eggs were removed and placed in 3 litres of solution. After incubation had occurred for a further 23 days, the young worms (F_1 generation) produced were removed and exposed in 19 litres of solution. After all young worms had been counted the entire procedure was repeated for the F_1 generation, using 90 offspring from each of the Cr treatments. Test concentrations: 0.0026, 0.0045, 0.0098, 0.0166 and 0.0382 plus control. Dilution water: Sand-filtered natural seawater. The solutions were aerated during the test to maintain the dissolved oxygen level. The total Cr concentration in the dilution water was <0.001 mg/l. Control response: The number of spawning pairs and mean brood size were 22 and 323.3 respectively in the parental generation and 20 and 411.7 respectively in the F_1 generation. Endpoints: Time to spawning and brood size. Comments: A 309 day 2 generation lifecycle study. Appears to be a follow-on study from the Oshida, 1981 study to better define the NOEC values using more reproducing pairs. There were no significant ($p<0.05$) changes to the time to spawning in any Cr treatment group. No significant reductions in the mean brood size was seen in any treatment in the parental generation (the 0.0166 mg Cr/l group showed a significant increase in the mean brood size compared with controls). The response of the F_1 generation was similar to the parental generation except that a statistically significant decrease in the mean brood size was seen at the highest concentration tested (0.0382 mg Cr/l) The total Cr concentration was measured during the test. Earlier experiments had indicated that CrVI was stable under the 3 week renewal period used in the test.	Oshida and Word, 1982
		F_1 gen. (30-40 segment)	NOEC (repro.)	0.0166	m	3 week renew.	7.76-8.40	33.6‰		20.8	II		
			LOEC (repro.)	0.0382	m	3 week renew.	7.76-8.40	33.6‰		20.8	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Neanthes arenaceodentata	ragworm	10 mg (30-40 segment stage)	59d-LC_{50} (mortality)	0.200	m	1-3 week renew.	7.8-8.0	33.5‰		20	II	No. of organisms: 1 organism/replicate, 20 replicates/concentration. Each organism was placed in 100 ml of test solution. Once the sex of the worms could be determined (~19-55 days), males were paired with females where possible (not all worms could be paired due to unequal sex ratios). The females naturally died after spawning, leaving the males to incubate the eggs. The F_1 offspring were allowed to grow to 30-40 segments and then used for either acute tests (see above) or were set up in the same manner as the parents to observe the successive (F_2) generations. The overall length of the multigeneration study was >350 days. Test concentrations: 0.0125, 0.025, 0.050, 0.10 and 0.20 mg Cr/l plus control. Dilution water: Natural seawater. The dissolved oxygen concentration was maintained at >75% saturation throughout the test. The total Cr concentration in the dilution water was 0.5-1.0 µg/l. Control response: Mean time to spawning of parental (P_1) generation was 112 days. Mean brood size of P_1 generation was 255. Mean time to spawning of first (F_1) generation was 114 days. Mean brood size of F_1 generation was 329. Endpoints: Mortality, tube-building capabilities, behaviour and feeding activity, egg laying and brood incubation. Comments: This may be part of the same study as Oshida et al (1981) above. For the first generation (P_1 to F_1), eggs were never laid at the two highest concentrations tested (0.1 and 0.2 mg Cr/l). The lowest concentration that was tested (0.0125 mg Cr/l) showed a decrease in mean brood size relative to controls (133 against 255 in controls). The mean brood size at 0.025 and 0.05 mg Cr/l was also reduced (146 and 78 respectively). For the second generation (F_1 to F_2), although the mean brood size was again less than controls at all concentrations tested, this difference was only statistically significant at the 0.05 mg Cr/l concentration. A statistical "no effect" level for brood size was determined to be <0.0125 mg Cr/l for both generations. Result not used in assessment as effect >20%.	Mearns et al, 1976
			350d-LOEC (repro.)	<0.0125	m	1-3 week renew.	7.8-8.0	33.5‰		20	II		

Table C.2 continued overleaf

Table C.2 continued Summary of the ecotoxicological data for potassium dichromate to invertebrates.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.h	Test details	Reference
Praunus flexuosus	crustacean (mysid)		8d-LC_{50}	3	n	24h renew.		4.5‰		5	IV	No. of organisms: 20 animals/concentration. Test concentrations: 8, 16 and 32 mg/l plus control Dilution water: Natural seawater (27‰). This was diluted with tap water of low mineral content to given the desired salinity. Control response: The LT_{50} for controls was given as >300 days. Endpoints: Mortality. Comments: Study to investigate the effects of temperature and salinity on toxicity. Increased temperature (5 to 15°C) resulted in increased toxicity Increased salinity (4.5 to 22.5‰) generally resulted in decreased toxicity but there was evidence that the toxicity increased again at 27‰. This indicated that that the maximal survival of animals occurred at around 22.5‰, which is close to the iso-osmotic point for the species. The toxicity of Cr was thought to be related to a decrease in the ability of the animals to osmoregulate. As only three concentrations were tested many of the actual LC_{50}s reported are outside this range (8-32 mg/l) and so are more uncertain. The study also determined LT_{50} values (time to 50% mortality) at the various concentrations tested and these showed the same variation in toxicity with salinity and temperature as the LC_{50} values.	McLusky and Hagerman, 1987
			8d-LC_{50}	5	n	24h renew.		9‰		5	IV		
			8d-LC_{50}	5	n	24h renew.		9‰		15	IV		
			8d-LC_{50}	8	n	24h renew.		13.5‰		5	IV		
			8d-LC_{50}	7	n	24h renew.		13.5‰		15	IV		
			8d-LC_{50}	12	n	24h renew.		18‰		5	IIIb		
			8d-LC_{50}	7	n	24h renew.		18‰		15	IV		
			8d-LC_{50}	12	n	24h renew.		22.5‰		5	IIIb		
			8d-LC_{50}	8	n	24h renew.		22.5‰		15	IV		
			8d-LC_{50}	10	n	24h renew.		27‰		5	IIIb		
			8d-LC_{50}	5	n	24h renew.		27‰		15	IV		

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity (‰)
e) TLm = median threshold or tolerance limit - equivalent to LC_{50}
f) concentration converted from salt to chromium ion concentration
g) American Public Health Association. Standard Methods for the examination of water and wastewater
h) Val. = validity marking of the test (see main text)

Table C.3 Summary of ecotoxicological data for potassium dichromate to algae.

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp. (°C)	Val.[f]	Test details	Reference
ALGAE - freshwater													
Chlamydomonas reinherdi	green algae		10d-NOEC (biomass)	<0.010	n	static					IV	No. of organisms: 3 replicates/concentration. Tests carried out in 50 ml solution. Inoculum concentration not given. Test concentrations: 0.01 and 0.02 mg Cr/l plus control. Dilution water: Basal medium. Concentration of Cr in dilution water not given. Control response: Control showed essentially linear growth over the test period. Endpoints: Growth (biomass), determined by cell count. Comments: Growth was reduced at the lowest concentration tested at 6, 8 and 10 days. The first observations were made on day 6 and so no information is available on the effects over the first 6 days.	Zarafonetis and Hampton, 1974
Chlamydomonas sp.	green algae		10-day LOEC/ NOEC (growth rate)	0.5	m	static	6.8	68		15	II	No. of organisms: 6 replicates/concentration. The inoculum was 0.4 ml of a rapidly-growing batch culture added to a total volume of 4 ml. Test concentrations: 0.5, 1.0, 2.0 and 4.0 mg Cr/l plus control. Dilution water: Minimal nutrient medium, enriched with sodium silicate and vitamin B_{12}. The cultures were not bubbled or shaken during the experiment. The concentration of Cr in dilution water is not reported. Control response: Mean specific growth rate (h^{-1}) was 0.067 at 15°C and 0.071 at 25°C. Endpoints: Specific growth rate. Growth was monitored by optical density measurements, but direct cell counts were also made in some instances. Comments: The test was based on the USEPA Algal Assay Procedure. The inoculum was rapidly-growing and temperature-adapted. An initial decrease in growth rate was seen at all concentrations but algal growth rate started to recover after 4-6 days. The mean specific growth rate at 0.5 mg Cr/l was 0.052 h^{-1} at 15°C and 0.043 h^{-1} at 25°C. The statistical significance of these reductions is not given and so the NOEC/LOECs should only be considered approximate. The test duration is considered too long for exponential growth, so value not used in PNEC derivation.	Cairns Jr. et al, 1978.
			10-day LOEC (growth rate)	0.5	m	static	6.8	68		25	II		
Chlorella vulgaris	green algae		24h-EC_{50} (biomass) 24h-EC_{50} ([ATP])	0.264 0.46	n	static				20	IIIb	No. of organisms: 3-4x10^6 cells/ml Test concentrations: 6 levels, up to 0.8 mg/l Dilution water: Lefevre-Czarda medium, supplemented with trace elements as recommended in "Norme Expérimentale T90304. Essais des Euax, Détermination de l'Inhibition de Croissance de Scenedesmus subspicatus par une Substance". AFNOR, 1980, Paris. Control response: not presented Endpoints: growth (biomass) by optical density; inhibition of ATP induction Comments: AFNOR T90304, 1980. Initial cell numbers high, so exponential growth not certain over 96 hours - EC_{50} value increases with time (96 hour value 0.442 mg/l). 24 hour value probably most reliable. [ATP] - inhibition of ATP induction - used as a measure of growth inhibition.	Jouany et al, 1982

Table C.3 continued overleaf

Table C.3 continued Summary of ecotoxicological data for potassium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Chlorella vulgaris	green algae		72h-IC_{50} (growth)	0.47	n	static				20	II	No. of organisms: Initial inoculum was 1.5-3.0×10^6 cells ml in 10 ml solution. 3 replicates used per concentration. Test concentrations: 0.1, 0.2, 0.4, 0.6, 0.8 and 0.9 mg Cr/l. Dilution water: Lefevre-Czarda medium, supplemented with trace elements as recommended in "Norme Expérimentale T90304. Essais des Euax, Détermination de l'Inhibition de Croissance de Scenedesmus subspicatus par une Substance". AFNOR, 1980, Paris. Control response: Not given. Endpoints: Growth (biomass) by optical density and direct cell counts. Comments: Used two test methods: static - static test system and pseudodynamic - test solution topped up with toxic medium; no overflow, therefore, volume increased with time. Total chromium concentrations were measured in the water phase and the algal cells at the end of the experiment. The concentrations in the water phase were around 64-88% of the nominal concentrations.	Jouany et al, 1983
			72h-IC_{50} (growth)	0.12	n	pseudo dynamic				20	II		
			96h-IC_{50} (growth)	0.59	n	static				20	II		
			96h-IC_{50} (growth)	0.16	n	pseudo dynamic				20	II		
Chlorella pyrenoidosa	green algae		96h-NOEC (biomass)	0.1	n	static					II	No. of organisms: Inoculum concentration was 5×10^4 or 5×10^5 cells/ml. Test concentrations: 0.1, 0.5, 1.0, 2.0 mg Cr/l plus control. Dilution water: Not given. Control response: After 96 hours the control total dry weight of cells was 0.83 g/l, the total chlorophyll was 3.2% of dry weight cells and the total cell numbers were 5.4×10^6 cells/ml. Endpoints: Growth (dry weight cells, total chlorophyll, cell numbers) Comments: Tested under a 16:8 hours light:dark cycle and also under continuous light conditions. The results reported refer to tests under the 16:8 hours light:dark cycle. Similar results were obtained using both methods. The growth of algae was generally reduced compared to controls at concentrations of 0.5 mg Cr/l and above. The growth parameters at 0.1 mg Cr/l (total dry weight cells was 0.94 g/l, total chlorophyll was 3.3% of dry weight cells and the total cell numbers were 5.0×10^6 cells/ml) were similar to control values. Not statistical significance is given in the paper to the reduction in growth seen and so the NOEC is only approximate.	Meisch and Schmitt-Beckmann, 1979
Chlorella pyrenoidosa	green algae		10d-NOEC (biomass)	>0.02	n	static					IIIb	No. of organisms: 3 replicates/concentration. Tests carried out in 50 ml solution. Inoculum concentration not given. Test concentrations: 0.01 and 0.02 mg Cr/l plus control. Dilution water: Basal medium. Concentration of Cr in dilution water not given. Control response: Control showed essentially linear growth over the test period. Endpoints: Growth (biomass), determined by cell count. Comments: No effect on growth was seen at either concentration on days 2, 4, 6, 8 or 10. The first observations were made on day 2 and so no information is available on the effects over the first 2 days.	Zarafonetis and Hampton, 1974

Table C.3 continued overleaf

Table C.3 continued Summary of ecotoxicological data for potassium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Chlorella sp.	green algae		96h-NOEC (biomass)	0.1	n	static					IIIb	No. of organisms: Inoculum concentration was 5×10^4 or 5×10^5 cells/ml. Test concentrations: 0.1, 0.5, 1.0, 2.0 mg Cr/l plus control. Dilution water: Not given. Control response: After 96 hours the control total dry weight of cells was 0.56 g/l, the total chlorophyll was 4.5% of dry weight cells and the total cell numbers were 8.5×10^7 cells/ml. Endpoints: Growth (dry weight cells, total chlorophyll, cell numbers) Comments: Tests carried out with a wild strain. Tested under a 16:8 hours light:dark cycle and also under continuous light conditions. The results reported refer to tests under the 16:8 hours light:dark cycle. Similar results were obtained using both methods. The growth of algae was generally reduced compared to controls at concentrations of 0.5 mg Cr/l and above. The growth parameters at 0.1 mg Cr/l (total dry weight cells was 0.62 g/l, total chlorophyll was 4.1% of dry weight cells and the total cell numbers were 8.8×10^7 cells/ml) were similar to control values. Not statistical significance is given in the paper to the reduction in growth seen at the concentrations and so the NOEC is only approximate, although in this case it is clear that a large reduction in growth had occurred at 0.5 mg Cr/l.	Meisch and Schmitt-Beckmann, 1979
Cyctotella meneghinian a	diatom		5d-LOEC (growth rate)	~0.5	m	static	6.8	68		5	IIIb	No. of organisms: 6 replicates/concentration. The inoculum was 0.4 ml of a rapidly-growing batch culture added to a total volume of 4 ml. Test concentrations: 0.5, 1.0, 2.0 and 4.0 mg Cr/l plus control. Dilution water: Minimal nutrient medium, enriched with sodium silicate and vitamin B_{12}. The cultures were not bubbled or shaken during the experiment. The concentration of Cr in dilution water is not reported. Control response: Mean specific growth rate (h^{-1}) was 0.064 at 5°C 0.076 at 15°C and 0.198 at 25°C. Endpoints: Specific growth rate. Growth was monitored by optical density measurements, but direct cell counts were also made in some instances. Comments: The test was based on the USEPA Algal Assay Procedure. The inoculum was rapidly-growing and temperature-adapted. An decrease in growth rate was seen at all concentrations. The mean specific growth rate at 0.5 mg Cr/l was 0.028 h^{-1} at 5°C, -0.001 h^{-1} at 15°C and -0.27 h^{-1} at 25°C. The statistical significance of these reductions is not given and so the LOECs should only be considered approximate, although it is clear that severe growth inhibition occurred with 0.5 mg Cr/l at 15°C and 25°C.	Cairns Jr. et al, 1978.
			5d-LOEC (growth rate)	<0.5	m	static	6.8	68		15	II		
			5d-LOEC (growth rate)	<0.5	m	static	6.8	68		25	II		

Table C.3 continued overleaf

Table C.3 continued Summary of ecotoxicological data for potassium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Euglena gracilis	green algae		10d LOEC (growth rate)	26-102	m	static	3			23	IV	No. of organisms: 2×10^6 cells added to 50 ml of solution (4×10^4 cells/ml). Test concentrations: 26, 51, 77, and 102 mg Cr/l, plus control. Dilution water: Lactate medium. Concentration of Cr in dilution water was not given. Control response: Given graphically. Control growth reached plateau (~3×10^6 cells/ml) after 2-3 days. Endpoints: Various stages of growth (lag-phase free of division, exponential phase and plateau phase) determined by particle counter. Comments: All concentrations tested had no effect on the growth rate, but did increase the lag phase before growth commenced in a dose-related manner. Analysis of test medium for both total Cr and Cr(VI) after 24 hours indicated that <10% of the chromium was present as Cr(VI).	Brochiero et al, 1984
Euglina gracilis	green algae		144h-NOEC (biomass)	4.5							IIIb	No. of organisms: Actual inoculum concentration was not given but was <5×10^5 cells/ml. Test concentrations: 1.5, 3.0, 4.5, 7.5 and 9.0 mg Cr/l, plus control. Dilution water: Not given. Control response: Given graphically. Growth reached around 3×10^6 cells/ml after 144 hours. Endpoints: Growth (cells counted by particle counter), photosynthesis rate and respiration rate. Comments: Concentrations between 1.5 and 9.0 mg Cr/l inhibited growth, chlorophyll content and oxygen evolution, but the effects were transient at 4.5 mg Cr/l and less. The total cell counts at 72-96 hours at 1.5, 3.0 and 4.5 mg Cr/l were less than controls but by 144 hours they were similar to controls. It was thought that toxicity was due to interference of nucleic acid and protein metabolism. The statistical significance of the findings is not given.	Fasulo et al, 1983.
Lyngbya sp.	blue-green algae		18d- LOEC/ NOEC (growth rate)	~0.1	m	static	6.8	68		15	II	No. of organisms: 6 replicates/concentration. The inoculum was 0.4 ml of a rapidly-growing batch culture added to a total volume of 4 ml. Test concentrations: 0.1, 1 and 10 mg Cr/l plus control. Dilution water: Minimal nutrient medium, enriched with sodium silicate and vitamin B_{12}. The cultures were not bubbled or shaken during the experiment. The concentration of Cr in dilution water is not reported. Control response: Mean specific growth rate (h^{-1}) was 0.207 at 15°C, 0.278 at 25°C and 0.291 at 35°C. Endpoints: Mean specific growth rate. Growth was monitored by direct dry weight analysis at the end of the 18 day period. Comments: The test was based on the USEPA Algal Assay Procedure. The inoculum was rapidly-growing and temperature-adapted. The mean specific growth rate was slightly reduced compared to controls at 0.1 mg Cr/l at 15°C (growth rate 0.193 h^{-1}) and 25°C (growth rate 0.230 h^{-1}) but not at 35°C (a higher concentration of 1 mg Cr/l was needed to cause a light reduction at 35°C (growth rate 0.285 mg/l) . The statistical significance of these reductions is not given and so the NOEC/LOECs should only be considered approximate. The duration of the test is considered too long to include the result in the PNEC derivation.	Cairns Jr. et al, 1978
			18d- LOEC/ NOEC (growth rate)	~0.1	m	static	6.8	68		25	II		
			18d- LOEC/ NOEC (growth rate)	~1.0	m	static	6.8	68		35	IIIb		

Table C.3 continued overleaf

Table C.3 continued Summary of ecotoxicological data for potassium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Navicula seminulum	diatom		acute EC_{50}	0.187-0.308				45			IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985).	A.N.S., 1960
			acute EC_{50}	0.254-0.442				171					
Nitschia linearis	diatom		120h-EC_{50} (biomass)	0.208	n	static		soft			IIIa	No. of organisms: Organism inoculated into 150 ml flask. Initial concentration not given. Test concentrations: Not given. Several controls were run. Dilution water: Synthetic soft dilution water. Dissolved oxygen was 5-9 mg/l throughout the test. The concentration of Cr in dilution water is not given. Control response: Not given. Endpoints: Total cell counts at end of test (total biomass produced). Comments: A higher 120h-EC_{50} of 7.8 mg/l was obtained using potassium chromate.	Patrick et al, 1968.
Scenedesmus pannonicus	green algae		96h-EC_{50} (growth)	0.91[e]							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Growth (cell multiplication). Comments: Test carried out in accordance with OECD guidelines and "Degradability, ecotoxicity, and bio-accumulation. The determination of the possible effects of chemicals and wastes on the aquatic environment. Government Publishing Office, the Hague, 1980". Only a summary of the results is reported.	Adema et al, 1983
			96h NOEC (growth)	0.11[e]							IIIa		
Scenedesmus pannonicus	algae	log-phase	96h NOEC (biomass)	0.11[e]	n	static				23	II	No. of organisms: 3 replicates/concentration. The initial inoculum was ~1.5×10^6 cells in 150 ml solution. Test concentrations: Range of concentrations with a dilution factor of $\sqrt{10}$ between concentrations, plus control. Dilution water: Minimal nutrient medium. The Cr concentration in dilution water is not given. Control response: Not given. Endpoints: Growth (biomass) Comments:	Slooff and Canton, 1983; Van Leeuwen, 1990

Table C.3 continued overleaf

Table C.3 continued Summary of ecotoxicological data for potassium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Selenastrum capricornutum	green algae	exponetially growing cultures	IC_{50} (P-uptake rate)	0.21[e]	n	batch	8.0	24		25	II	No. of organisms: Inoculum was 1×10^3 cells/ml. Each test included at least 5 controls and two replicates of each test concentration. Test concentrations: 6-8 concentrations plus controls. Dilution water: ISO Standard growth medium, modified to given a N:P ratio of 56 so that phosphate was the limiting nutrient. The Cr concentration in dilution water is not given. Control response: Average specific growth rate in control cultures was 1.75 d^{-1} Endpoints: Specific growth rate and specific phosphate uptake rate. Comments: Used the USEPA bottle test method "The Selenastrum capricornutum Prinz Algal Assay Bottle Test. Experimental Design, Application, and Data Interpretation Protocol. EPA-600/9-78-018, 1978". IC_{10} (P- uptake rate) was 0.14[e] mg/l, which did not differ greatly from results for biomass growth rate (72h-IC_{10} = 0.11[e] mg/l).	Nyholm, 1991
			72h-IC_{50} (growth rate)	0.99[e]	n	batch	8.0	24		25	II		
			72h-IC_{10} (growth rate)	0.11[e]	n	batch	8.0	24		25	II		
Selenastrum capricornutum	green algae		96h-EC_{50} (biomass)	0.217	m		5.6-8.9				II	No. of organisms: Inoculum was 1×10^4 cells/ml. Test concentrations: 7 concentrations in the range ~0.06-0.4 mg Cr/l. Dilution water: Algal assay medium. The Cr concentration in the dilution water was not given. Control response: Not given. Endpoints: Total yield (biomass) Comments: Used a USEPA method "Protocol for bioassessment of hazardous waste sites. EPA-600/2-83-054, 1983."	Greene et al, 1988
Selenastrum capricornutum	green algae	exponential growth	72h-EC_{50} (growth rate)	0.233-0.235[e]	n	batch	8.1			24-26	II	No. of organisms: Inoculum was either 1×10^3 or 1×10^4 cells/ml. Test concentrations: Not given. Dilution water: Used standard algal assay medium. The Cr concentration in the dilution water was not given. Control response: Not given. Endpoints: Growth rate. Comments: Used the USEPA bottle test method "The Selenastrum capricornutum Prinz Algal Assay Bottle Test. Experimental Design, Application, and Data Interpretation Protocol. EPA-600/9-78-018, 1978". Results expressed for Weibull, probit and logit analysis are complimentary. The EC_{10} ranged between 0.010-0.012, with the Weibull method giving the lowest value.	Christensen and Nyholm, 1984; Christensen et al, 1983
			72h-EC_{10} (growth rate)	0.010-0.012[e]	n	batch	8.1			24-26	II		

Table C.3 continued overleaf

Table C.3 continued Summary of ecotoxicological data for potassium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Scenedesmus subspicatus	green algae	exponential growth	72h-EC_{10} (growth rate)	0.64[e]	n	static	8.0			24	I	No. of organisms: Inoculum concentration was 1×10^4 cells/ml. Test concentrations: A series of concentrations in the range 0.028-3.5 mg/l with a 1:2 dilution between concentrations, plus controls. Dilution water: Algal growth medium (full details given). The concentration of Cr in the dilution water was not given. Control response: After 72h, algae still in process of logarithmic growth; at end of 96h in stationary phase. A 16 fold increase in the cell numbers was achieved within 72 hours. The pH increased by 1.3 units during the test. This was within the acceptable range of the protocol. The validity criteria for the controls given in the test protocol were met. Endpoints: Growth rate and cell yield (biomass). Comments: Used German test procedure DIN 38 412, part 9 (1988). 48h and 72h EC_{10} based on growth inhibition (cell growth rate) was 0.74[e] and 0.63[e] mg/l, respectively. Large difference between EC values from growth and biomass; no other substances in test had such differences, so results not used in PNEC derivation.	Kuhn and Pattard, 1990
			72h-EC_{50} (growth rate)	4.6[e]	n	static	8.0			24	I		
			72h-EC_{10} (biomass)	0.032[e]	n	static	8.0			24	I		
			72h-EC_{50} (biomass)	0.13[e]	n	static	8.0			24	I		
			96h-EC_{10} (biomass)	0.039[e]	n	static	8.0			24	IIIb		
			96h-EC_{50} (biomass)	0.12[e]	n	static	8.0			24	IIIb		
Scenedesmus quadicuada	green algae		5-day LOEC (growth rate)	~0.5	m	static	6.8	68		15	IIIb	No. of organisms: 6 replicates/concentration. The inoculum was 0.4 ml of a rapidly-growing batch culture added to a total volume of 4 ml. Test concentrations: 0.5, 1.0, 2.0 and 4.0 mg Cr/l plus control. Dilution water: Minimal nutrient medium, enriched with sodium silicate and vitamin B_{12}. The cultures were not bubbled or shaken during the experiment. The concentration of Cr in dilution water is not reported. Control response: Mean specific growth rate (h^{-1}) was 0.165 at 15°C, 0.240 at 25°C and 0.249 at 35°C. Endpoints: Specific growth rate. Growth was monitored by optical density measurements, but direct cell counts were also made in some instances. Comments: The test was based on the USEPA Algal Assay Procedure. The inoculum was rapidly-growing and temperature-adapted. A decrease in growth rate was seen at all concentrations at 15°C, but only at concentrations of around 1-2 mg Cr/l and above at 25°C and 1 mg/l and above at 35°C. The mean specific growth rates at these concentrations were 0.130 h^{-1} (at 0.5 mg Cr/l) at 15°C, 0.220 h^{-1} and 0.229 h^{-1} (at 1 and 2 mg Cr/l) at 25°C and 0.206 h^{-1} (at 1 mg Cr/l) at 35°C. The statistical significance of these reductions is not given and so the NOEC/LOECs should only be considered approximate.	Cairns Jr. et al, 1978
			5-day LOEC/ NOEC (growth rate)	~1.0-2.0	m	static	6.8	68		25	IIIb		
			5-day LOEC/ NOEC (growth rate)	~1.0	m	static	6.8	68		35	IIIb		
Scenedesmus sp.	green algae		NOEC	0.5							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985).	Staub et al, 1973

Table C.3 continued overleaf

Table C.3 continued Summary of ecotoxicological data for potassium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Scenedesmus sp.	green algae		28h-NOEC (biomass)	0.7			7.5-7.8	12[o]		27	IIIb	No. of organisms: Not given. Test concentrations: Not given. Dilution water: May have used river water. Control response: Not given. Endpoints: Growth (biomass) Comments:	Bringmann and Kühn, 1959
13 algal species		log-phase	median 14d-EC_{100}	0.35[e]						20	IV	No. of organisms: The growth experiments were carried out on 250 µl cultures on microtitration plates. The inoculum gave an chlorophyll a concentration of 19 ng/ml. Four replicates/concentration. Test concentrations: 14 concentrations were used with a factor 0f 0.5 between concentrations. The range covered was 4.2 orders of magnitude. Dilution water: Inorganic medium Z8 at 10% strength. Control response: Not given (not clear if a control was run). Endpoints: Growth inhibition was estimated by visual inspection after 14 days to identify the lowest concentration tested causing 100% growth inhibition. Comments: Study tested sensitivity of 13 algal species to 19 compounds. Range of 14d-EC_{100} =0.05-5.7 mg/l. The LC_{50}s for the individual species tested (Chlamydomonas dysosmos, Chlorella emersonii, Kirchneriella contorta, Monoraphdium pusillum, Scenedesmus obtusiusculus, Selenastrum capricornutum, Klebsormidium marinum, Raphidonema longiseta, Bumilleriopsis filiformis, Monodus subterraneus, Tribonema aequale, Synechococcus leopoliensis and a "LPP.sp (Cyanophyta, Oscillatoriales).	Blanck et al, 1984
ALGAE - saltwater													
Microcystis pyritera	blue-green algae		5d-LOEC	1.0							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only reported in EPA (1985). A 10-20% inhibition of photosynthesis at 1 mg Cr/l over 5 days	Bernhard and Zattera, 1975

Table C.3 continued overleaf

Table C.3 continued Summary of ecotoxicological data for potassium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Olisthodiscus luteus	photoflagellate		10d-NOEC (growth rate)	0.05	n	static	8.0			20	IV	No. of organisms: Inoculum concentration was 770 cells/ml. 3 replicates/concentration. Test concentrations: 20, 10 and 0.05 mg Cr/l, plus control. Dilution water: Sterilised, filtered (0.5 µm) natural seawater, supplemented with minerals and vitamins. The concentration of Cr in the dilution water was not determined. Control response: Growth rate was 0.74 cell divisions/day. Endpoints: Growth rate (cell divisions/day) based on cell counts at 10 days and initial inoculum concentration. Comments: Used natural sea water. The same results are quoted as both mg/l and µg/l and this, and the wide spacing of concentrations used, means that the NOEC is not reliable. The test was carried out both with (11.7 µm/l) and without EDTA in the growth medium. A statistically significant (P=0.05) decrease in growth rate was seen at concentrations of 10 mg Cr/l and 20 mg Cr/l without added EDTA but no effects were seen at any concentration with EDTA.	Mahoney, 1982.
Skeletonema costatum	diatom	log-phase	120h NOEC (biomass)	0.35[e]	n	static	8.25			20	IIIb	No. of organisms: Inoculum concentration was 1×10^4 cells/ml. Each concentration was replicated once and the control was replicated 3 times. Test concentrations: A rangefinding test was carried out to determine the range of 5 or more concentrations to be tested in the definitive test. A controls was also run. Dilution water: Used a revised ASP 12 growth medium. Full details are given. The concentration of Cr in the dilution water are not given. Control response: Not given. Endpoints: Growth (biomass). Measured change in total cells/ml compared with controls with a Coulter counter Comments: Test method based on "Marine Algal Assay Procedure. Bottle Test. Eutrophication and Lake Restoration Branch, Pacific Northwest Environmental Protection Laboratory. USEPA, 1974".	Cowgill et al, 1989
			120h-EC_{50} (biomass)	5.2[e]	n	static	8.25			20			
Skeletonema costatum	diatom	exponential growth	4h-EC_{10} (photosyn.)	0.95-1.03[e]	n	static	8.0	20‰		15	IIIb	No. of organisms: Inoculum concentration 1×10^4 cells/ml. Each concentration was tested in triplicate and 3-5 controls were run Test concentrations: 6-8 concentrations, plus control. Dilution water: Filtered natural seawater, supplemented with nutrients. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Inhibition of photosynthesis measured by ^{14}C-assimilation. Comments:	Ole Kusk and Nyholm, 1991
			4h-EC_{50} (photosyn.)	2.05-2.72[e]	n	static	8.0	20‰		15	IIIb		
			6h-EC_{10} (photosyn.)	0.39-0.57[e]	n	static	8.0	20‰		15	IIIb		
			6h-EC_{50} (photosyn.)	1.13-1.77[e]	n	static	8.0	20‰		15	IIIb		
			20h-EC_{10} (photosyn.)	0.046[e]	n	static	8.0	20‰		15	IIIb		
			20h-EC_{50} (photosyn.)	0.18[e]	n	static	8.0	20‰		15	IIIb		

Table C.3 continued overleaf

Table C.3 continued Summary of ecotoxicological data for potassium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Tetraselmis suecica	microalgae (prasinophyte)		5h-IC_{50}	92.5[e]	n					20	IIIb	No. of organisms: Not given. Use 360 µl of algal suspension and 10 µl of contaminant solution. Test concentrations: 0.1, 0.5, 5, 10, 25, 50, 75, 100, 150 and 200 mg $K_2Cr_2O_7$/l. Dilution water: Filtered (0.2 µm) natural seawater, with added nutrients. The water was sterilised before use. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Growth inhibition measured by cell esterase activity using a fluorimetric stain, fluorescein diacetate (FDA). Comments: An experimental test method. The IC_{50} quoted in the paper of 261.55 mg $K_2Cr_2O_7$/l is outside the range of concentrations reported to be tested.	Gilbert et al, 1992
Thalassiosira pseudonana	diatom	rapidly growing culture	EC_{50} (growth rate)	0.0021	n	static	8.5-9.5	0.32‰		20	IIIb	No. of organisms: 0.1 ml of inoculum culture was added to 30 ml solution. The total number of cells added was 2×10^4 (i.e. 667 cells/ml) in the experiments carried out at 3.2‰ and 6×10^4 (i.e. 2×10^3 cells/ml) in the experiments carried out at 0.32‰. Test concentrations: The concentrations tested were 0.1, 0.2, 0.5, 1, 2, 5 and 10 µM Cr (0.0052, 0.010, 0.026, 0.052, 0.104, 0.26 and 0.52 mg Cr/l) at 3.2‰ and 0.01, 0.02, 0.05, 0.1, 0.2, 0.5 and 1 µM Cr (0.00052, 0.0010, 0.0026, 0.0052, 0.010, 0.026 and 0.052 mg Cr/l) at 0.32‰. Controls were also run. Dilution water: Artificial estuarine water made by diluting standard ocean water with artificial freshwater growth medium. The Cr concentration of the dilution water was not given. Control response: The control growth rate was much lower in the 0.32‰ experiments (~0.7 day^{-1}) than in the 3.2‰ experiments (~2 day^{-1}), but the maximum yield in both experiments were similar Endpoints: Cell growth rate measured by fluorescence. Comments: Exposure period not given. The algal cultures were routinely maintained in 1‰ water before use in the test. The pH was 8.5 at the start of the test and reached 9.5 at the end of the test. The test investigated the effects of varying the sulphate concentration of the test medium on the toxicity. The "normal" sulphate concentration of seawater is around 29 mM at 33‰, but may be lower in freshwater and hence estuarine water. The EC_{50} was found to be strongly influenced by the sulphate concentration at both salinities. In the 3.2‰ experiments, the EC_{50} was 0.341, 0.198, 0.075, 0.034 and 0.021 mg Cr/l at sulphate concentrations of 2.90, 1.45, 0.58, 0.29 and 0.15 mM respectively. The "normal" sulphate concentration at 3.2‰ would be around 2.9 mM. Similarly, in the 0.32‰ salinity experiments the EC_{50} was 0.039, 0.012, 0.010, 0.0052 and 0.0021 mg Cr/l at sulphate concentrations of 0.38, 0.19, 0.08, 0.04 and 0.02 mM respectively. The "normal" sulphate concentration at 0.32‰ would be around 0.38 mM.	Riedel, 1984
			EC_{50} (growth rate)	0.0052	n	static	8.5-9.5	0.32‰		20	IIIb		
			EC_{50} (growth rate)	0.010	n	static	8.5-9.5	0.32‰		20	IIIb		
			EC_{50} (growth rate)	0.012	n	static	8.5-9.5	0.32‰		20	IIIb		
			EC_{50} (growth rate)	0.039	n	static	8.5-9.5	0.32‰		20	II		
			EC_{50} (growth rate)	0.021	n	static	8.5-9.5	3.2‰		20	IIIb		
			EC_{50} (growth rate)	0.034	n	static	8.5-9.5	3.2‰		20	IIIb		
			EC_{50} (growth rate)	0.075	n	static	8.5-9.5	3.2‰		20	IIIb		
			EC_{50} (growth rate)	0.198	n	static	8.5-9.5	3.2‰		20	IIIb		
			EC_{50} (growth rate)	0.341	n	static	8.5-9.5	3.2‰		20	II		

Table C.3 continued overleaf

Table C.3 continued Summary of ecotoxicological data for potassium dichromate to algae

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Thalassiosira aestivalis	diatom		72h-NOEC (morph.)	0.104				30‰		12	IV	No. of organisms: Not given. Test concentrations: Not clear. Dilution water: Filtered seawater, enriched with micronutrients. Control response: Showed normal cell growth. Endpoints: Studied the effects of metals on cell morphology. Comments: No effects reported at >1000 nM Cr (~0.104 mg Cr/l).	Thomas et al, 1980
Natural phytoplankton assemblage			4h-IC_{10} (photosyn.)	0.50-0.81[e]	n	static		9‰		15	IIIb	No. of organisms: Used natural algal populations present in seawater. Each concentration was tested in triplicate, and 3-5 controls were run. Test concentrations: 6-8 concentrations, plus control. Dilution water: Natural seawater, supplemented with nutrients. The seawater was filtered (100 µm) to remove zooplankton. Control response: Not given. Endpoints: Inhibition of photosynthesis measured by ^{14}C-assimilation. Comments:	Ole Kusk and Nyholm, 1991
			4h-IC_{50} (photosyn.)	7.8-8.8[e]	n	static		9‰		15	IIIb		
			6h-IC_{10} (photosyn.)	0.33-0.42[e]	n	static		9‰		15	IIIb		
			6h-IC_{50} (photosyn.)	4.2-5.5[e]	n	static		9‰		15	IIIb		
			20h-IC_{10} (photosyn.)	0.035-0.046[e]	n	static		9‰		15	IIIb		
			20h-IC_{50} (photosyn.)	1.5-1.6[e]	n	static		9‰		15	IIIb		
Natural phytoplankton assemblage		late log-phase	5 day-growth inhibition	0.0015-0.015	n					12-16	IV	No. of organisms: Natural concentration in water was used, along with a natural population supplemented with a late log-phase inoculum of Thalassiosira aestevalis that had been isolated previously from the water. Each treatment was replicated once only, but controls were replicated 2 to 6 times. Test concentrations: 30, 100, 300 and 1,000 nM Cr/l, (0.0015, 0.005, 0.015 and 0.05 mg Cr/l) plus control. Dilution water: Natural water supplemented with N, P and Si. The Cr concentration was not given. Control response: Differences greater than 20% of control average were considered significant. Endpoints: Growth rate based on cell fluorescence of chlorophyll a. Comments: Natural phytoplankton populations from Saanich Inlet, Canada were used. Slight inhibition of growth was seen at Cr concentrations of 30 and 300 nM (0.0015 and 0.015 mg Cr/l).	Hollibaugh et al, 1980

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity (‰)
e) concentration converted from salt to chromium ion concentration
f) Val. = validity marking of the test (see main text).

Table C.4 Summary of ecotoxicological data for potassium dichromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp. (°C)	Val.[f]	Test details	Reference
AQUATIC PLANTS - freshwater													
Lemna minor	duckweed		7d NOEC (growth rate)	0.11[e]	n	static				25	II	No. of organisms: 2 fronts/replicate, 2 replicates/concentration. Test concentrations: Range of concentrations with a dilution factor of √10 between concentrations, plus control. Dilution water: Reconstituted dilution water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Not given. Endpoints: Specific growth rate. Comments:	Slooff and Canton, 1983; Van Leeuwen, 1990
MICROORGANISMS													
Bacillus subtilis	bacteria	Asynchro-nous culture	10h- EC_{50} (growth rate)	4.6[e]						37	II	No. of organisms: Not given. Test concentrations: 2.0, 4.0, 5.0 and 7.0 mg Cr/l, plus control. Dilution water: Spizien growth medium. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Given graphically Endpoints: Inhibition of growth rate. Comments: Cr(VI) inhibited DNA synthesis resulting in increased generation time and decrease in cell division.	Ogawa et al, 1989
Chilomonas paramaeciu m	protozoa	log-phase	98-163h LOEC	1.0			6.3			10	II	No. of organisms: 2 replicates/concentration and 4 replicates for controls. The inoculum was 0.2 ml of log-phase culture added to a total volume of 6.2 ml. Test concentrations: 1.0, 2.0, 4.2, 5.5, 10.0, 18.0 and 50 mg Cr/l, plus control. Dilution water: Organic growth media (0.1 % tryptone, 0.2% yeast extract and sodium acetate in glass-distilled water). The dissolved oxygen concentration and concentration of Cr in dilution water are not reported. Control response: Not given. All results are expressed as % inhibition compared with control. Endpoints: Growth rate. Growth was determined by electronic particle counter. Comments: A very steep dose-response was obtained, making it difficult to determine the concentrations at which effects started to be seen. At 10°C, a concentration of 1.0 mg Cr/l caused a 10-50% reduction in growth rate, and all other concentrations caused >50% reduction in growth rate. At 20°C, the growth rate at a concentration of 2.0 mg Cr/l was similar to controls, but all higher concentrations caused a >50% reduction in growth rate. At 30°C, no effect was seen at 1.0 mg Cr/l, and concentrations of 4.2 mg Cr/l and higher caused a >50% reduction in growth rate (the 2 mg Cr/l concentration was not tested at this temperature).	Cairns Jr. et al, 1978
			44-48h NOEC	2.0			6.3			20			
			19-25h NOEC	1.0			6.3			30			

Table C.4 continued overleaf

Table C.4 continued Summary of ecotoxicological data for potassium dichromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Colpidium campylum	protozoa		24h-IC_{50} (growth)	2.8-4.6[e]			7.5-8.15				II	No. of organisms: Inoculum was 500 cells/ml. 3 controls were used. Test concentrations: Range of concentrations obtained either by serial or logarithmic dilutions of a stock solution. Dilution water: Used 3 dilution waters. Firstly a standard mineral medium was used. The second medium was the standard medium with 1/10 calcium concentration. The third medium contained 1/10 calcium and bicarbonate concentration. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: The different dilution waters had no significant effect on cell growth. Endpoints: Cell growth (biomass) and number of generations at 24 hours. Comments: Report from a workshop testing a method for growth inhibition test for protozoa. Mean results from approximately 100 experiments lay in the approximate range 2.8-4.6 mg Cr/l.	Dive et al, 1990
Escherichia coli	bacteria		24h-LC_{50}	3.5[e]	n					37	II	No. of organisms: Inoculum was 4×10^9 colony forming units/ml. All concentrations were run in duplicate. Test concentrations: 10, 20, 30, 40, 50, 60 and 100 mg Cr/l, plus control. Dilution water: Peptone water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Total biomass produced was 0.26-0.27 mg/ml. Endpoints: Growth (biomass). Comments: Potassium chromate more toxic than dichromate (24h-LC_{50} was 0.42 mg/l).	Gaur and Bhattacherjee, 1991
Escherichia coli	bacteria		14h-IC_{100} (growth)	10.4[e]			6.5			30	IIIb	No. of organisms: 0.14% Test concentrations: 10^{-6}, 10^{-5}, $5x10^{-5}$, $7.5x10^{-5}$, 10^{-4} M (as $K_cCr_2O_7$) Dilution water: $FeSO_4$-9K medium, pH adjusted. Control response: included on graphs Endpoints: growth inhibition, measured by optical density. Comments: no statistical information on results presented, so values for NOEC or 50% effect cannot be calculated. From graphs, 10% effect is at around $5x10^{-5}$ M (0.5 mg/l Cr) by rapporteur.	Wong et al, 1982
Escherichia coli	bacteria		6h-IC_{100}	9.6[e]						37	IIIb	No. of organisms: starting optical density 0.4-0.5 Test concentrations: no information Dilution water: liquid medium VB, supplemented with glucose (2%) and thymine (50 mg/l). Control response: included on graphs Endpoints: reduction in growth. Comments: no statistical information on results presented, so values for NOEC or 50% effect cannot be calculated. Paper comments that Cr(VI) at 9.6 mg/l caused a complete but gradual inhibition of growth. From graphs, all concentrations appear to reduce growth - lowest tested was equivalent to 0.35 mg/l Cr.	Ödberg-Ferragut et al, 1991

Table C.4 continued overleaf

Table C.4 continued Summary of ecotoxicological data for potassium dichromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Microcystis aeruginosa	bacteria	log-phase	4d NOEC (growth rate)	0.35[e]	n	static				23	II	No. of organisms: 3 replicates/concentration. The initial inoculum was ~1.5×10^6 cells in 150 ml solution. Test concentrations: Range of concentrations with a dilution factor of $\sqrt{10}$ between concentrations, plus control. Dilution water: Minimal nutrient medium. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Not given. Endpoints: Specific growth rate. Comments:	Slooff and Canton, 1983; Van Leeuwen, 1990
Microregma heterostoma	protozoa		28h NOEC	0.21			7.5-7.8			27		No. of organisms: not given (1 ml culture suspension in total of 10 ml test solution) Test concentrations: not given. Dilution water: filtered and pasteurised river water. Control response: reduction in turbidity in controls included Endpoints: threshold of reduction in feeding rate, measured by turbidity. Comments: organisms fed E coli; feeding activity leads to reduction in turbidity. Threshold is lowest concentration where turbidity is higher than that in the controls. This is interpreted as a NOEC, in line with threshold values in other papers by the same authors.	Bringmann and Kuhn, 1959
Myxobolus vanivilasae	protozoa	spores	less than 100% mortality 15% mortality	2.0% soln. 0.1% soln.							IIIb	No. of organisms: 250,000 - 300,000 spores/ml Test concentrations: 0.1, 0.25, 0.5, 1.0, 1.5 and 2.0% $K_2Cr_2O_7$ by weight. Dilution water: distilled water. Control response: no information Endpoints: spore death as shown by morphological changes. Comments: endpoint could be considered to be related to reproduction, but spores might be expected to be an insensitive life stage. Response varied little over the concentration range, with 20% mortality at the highest level tested. Taking LOEC/2 as the NOEC would give 0.35 g/l as Cr. Overall not considered relevant.	Seenappa and Manohar, 1983
Nostoc muscorum	cyanobacteria		15d-LC_{50}	20							IV	No. of organisms: not given Test concentrations: 10, 20 and 30 μg/ml and control Dilution water: Chu_{10} medium Control response: included on graphs Endpoints: survival, measured by plate colony counts Comments: no statistics presented. Study intended to look at effects of other substances on Cr toxicity in N_2-fixing cyanobacterium - may be counteracted by reducing substances (glutathione) and amino acids	Rai and Raizada, 1988
Photobacterium phosphoreum	bacteria		30min- EC_{50}	21[e]						15	II	No. of organisms: standard for Microtox Test concentrations: not given Dilution water: distilled water with 2% NaCl; pH not adjusted. Control response: not given Endpoints: reduction in light emission. Comments: Microtox test; saltwater organism.	Tarkpea et al, 1986

Table C.4 continued overleaf

Table C.4 continued Summary of ecotoxicological data for potassium dichromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Photobacterium phosphoreum	bacteria		30min- EC_{50} no pH adjustment pH adjusted	27[e] 200[e]							II	No. of organisms: standard for Microtox Test concentrations: not given Dilution water: 2% NaCl solution; tests conducted with and without neutralising the solutions. Control response: not given. Endpoints: reduction in light emission. Comments: Microtox test; saltwater organism.	Krebs, 1983
Pseudomonas aeruginosa	bacteria				n		7.0			37	IV	No. of organisms: not given Test concentrations: 0, 165 and 330 μmol l^{-1} in broth; 0, 82.5 μmol l^{-1} in succinate medium; 0, 165 μmol l^{-1} in M63 (all as potassium dichromate). Dilution water: Luric broth; succinate medium; M63 minimal medium (three series of experiments) Control response: given on graphs Endpoints: growth, measured by optical density. Comments: Cr-tolerant strain isolated from tannery sludge. Paper states that normal growth occurred at 165 mg/l in broth, but graphs indicate decreased cell numbers at this concentration. Results in the text do not match those in the graphs. No NOEC or EC values can be derived.	Khare et al, 1997.
Pseudomonas aeruginosa	bacteria										IIIb	No. of organisms: 3% inoculum of exponentially-growing cells. Test concentrations: 0-400 mg/l. Dilution water: liquid culture medium MYGP. Control response: on graphs. Endpoints: growth measured by optical density; oxygen uptake measured by Warburg apparatus. Comments: Cr tolerant bacteria isolated from effluent soil from a tannery. Results presented for adapted and unadapted organisms, but not clear whether unadapted came from a non-contaminated site. No statistical information presented. By eye from graphs, NOEC for unadapted organisms (for growth) is 20 ppm Cr, with LOEC 40 ppm (~30% effect) at 4 hours. For oxygen consumption, there is little effect at 10 ppm, significant (by eye) effects at 50 ppm.	Nair and Krishnamurthi, 1991a and 1991b
Pseudomonas fluorescens	bacteria	log-phase	7h NOEC (growth rate)	0.11[e]	n	static				22	II	No. of organisms: 3 replicates/concentration. The initial inoculum was ~10×10^{10} cells in 100 ml solution. Test concentrations: Range of concentrations with a dilution factor of √10 between concentrations, plus control. Dilution water: Artificial test water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Not given. Endpoints: Specific growth rate. Comments:	Slooff and Canton, 1983; Van Leeuwen, 1990

Table C.4 continued overleaf

Table C.4 continued Summary of ecotoxicological data for potassium dichromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Vibrio harveyi	bioluminescent marine bacteria	overnight culture	50 min- EC_{50}	2.2[e]	n	static	7.2			20-25	II	No. of organisms: not given Test concentrations: not given Dilution water: standard for assay with this organism. Control response: not given. Endpoints: reduction in bioluminescence Comments: assay similar to Microtox; marine organism.	Thomulka and Lange, 1997
Natural bacterioplankton			1h-EC_{50} (enzyme inhibition)	1.1[e]		static	7.8		170	20	IIIb	No. of organisms: no information. Taken from Rhine at Lobith, NL. Test concentrations: 1, 3.2, 10, 32, 100 mg/l as potassium dichromate. Dilution water: river water; properties in table are average values for Rhine at sampling site. Control response: described as variable in samples taken at different times of the year. Endpoints: thymidine uptake, phosphatase activity and protease activity. Comments: EC_{50} (phosphatase) ranged from 1.1 to 8.9 mg Cr(VI)/l; 30 min-EC_{50} (thymidine incorporation) ranged from 3.3 to 35 mg Cr(VI)/l; 1h-EC_{50} (protease inhibition) >35 mg Cr(VI)/l	Tubbing and Admiraal, 1991
Natural bacterioplankton (freshwater and saltwater)			2h-EC_{50}	7.4[e]							IIIb	No. of organisms: not given. Samples taken from coastal marine waters and from freshwater lakes. Test concentrations: 5-100 mg/l as potassium dichromate. Dilution water: natural waters as sampled. Control response: not given. Endpoints: thymidine incorporation, 2 hour exposure Comments: Results obtained for freshwater lakes were 39-87 mg/l and for coastal waters 21-123 mg/l, all EC_{50} values as potassium dichromate.	Riemann and Lindgaard-Jorgensen, 1990
AMPHIBIANS													
Bufo melanostictus	toad	tadpole	96h-LC_{50}	49.29		static	7.4	185	135	31	II	No. of organisms: 10 per concentration. Test concentrations: logarithmic series, 7-10 levels. Dilution water: well water (parameters included). Control response: not included. Endpoints: mortality. Comments: organism length 1.95 cm, weight 100 mg.	Khangarot and Ray, 1987a
Rana hexadactyla	frog	tadpole	96h-LC_{50}	100		Semi-static (24 h renewal)	6.1	200	27	15	II	No. of organisms: 10 per replicate, 3 replicates per concentration. Test concentrations: 7-10 in series. Dilution water: no details. Control response: not given. Endpoints: mortality. Comments: organism length 2 cm, weight 500 mg.	Khangarot et al, 1985

Table C.4 continued overleaf

Table C.4 continued Summary of ecotoxicological data for potassium dichromate to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp. (oC)	Val.f	Test details	Reference
Rana cyanophlyctia	Indian skipper frog	adult - female	96h-LC_{50}	81		Semi-static	7.2	65		26	II	No. of organisms: 10 per concentration. Test concentrations: no information. Dilution water: tap water. Control response: not given. Endpoints: mortality. Comments: average organism weight 29.7±2.4 g.	Joshi and Patil, 1991
Rana tigrina	common Indian frog	larvae	96h-LC_{50}	0.035[e]		static					IV	No. of organisms: 20 per concentration. Test concentrations: 0.05, 0.1, 0.25, 0.5, 1.0, 2.0 mg/l. Dilution water: distilled water. Control response: included. Endpoints: survival, gulf (gulp?) rate and heart beat over 144 hours Comments: results not clear in table; no statistics; poor survival in controls at later times.	Vyas et al, 1991
Xenopus laevis	clawed frog	<2 d	100d NOEC (mortality)	0.35[e]	n	static				20	II	No. of organisms: 75/concentration in 50 litres of solution. Test concentrations: Range of concentrations with a dilution factor of √10 between concentrations, plus control. Dilution water: Reconstituted dilution water. Dissolved oxygen level and Cr concentration in dilution water was not given. Control response: Not given. Endpoints: Mortality, development and growth. Comments:	Slooff and Canton, 1983; Van Leeuwen, 1990
			100d NOEC (growth)	1.1[e]	n	static				20	II		
			100d NOEC (develop.)	1.1[e]	n	static				20	II		

Notes: a) n = nominal concentration; m = measured concentration. If blank, no specific comment in the paper, assumed to be nominal.
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity (‰)
e) concentration converted from salt to chromium ion concentration
f) Val. = validity marking of the test (see main text).

References

The references for this appendix appear in the full reference list (Section 6) of the main report.

Appendix D Summary of aquatic toxicity data for ammonium dichromate

This appendix reviews the aquatic toxicity data for ammonium dichromate. Values which have been used in the risk assessment report are highlighted with light grey shading. The following paragraphs provide some information about the selection process; these apply to the overall data set for chromium (VI) and not all comments may apply to data in this particular appendix.

For short term test results, the values selected are the lowest for each species which come from tests with a validity marking of I or II. In some cases a number of valid results may have been produced by one study, using different experimental conditions (for example, hardness, salinity and temperature). For properties such as temperature and salinity the test conditions closest to the 'real' environment have been chosen (so avoiding high or low temperatures, and preferring tests at salinities similar to sea water); for hardness, the lowest test result is preferred as a range of hardness is found in natural waters. These 'rules' have been applied flexibly so as to allow interpretation of the individual studies.

For long term tests, all data from validity marking I and II have been selected, but some studies with marking IIIb have also been included. Multiple values have been taken from some studies, where a number of different endpoints were measured (for example, mortality, reproduction and growth). Where several measures of the same endpoint are reported in one study, values from longer exposure periods are generally preferred, with the exception of algal studies where the maintenance of exponential growth conditions is considered.

The further treatment of the long term data to derive the PNEC is described in the main risk assessment report. In some cases, notes on data not used in the PNEC derivation have also been included in the comments on the tests in the appendix.

Table D.1 Summary of the ecotoxicological data for ammonium dichromate

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp. (°C)	Val.[f]	Test details	Reference
FISH - freshwater - short-term studies													
Gambusia affinis	mosquitofish	adult females	24h-TLm	92[e]	n	static	5.7- 7.4		<100	18-20	IV	No. of organisms: 10 fish/concentration in 15 litres of solution. Test concentrations: 10, 18. 32, 56, 100, 180, 320, 560 and 1,000 mg/l as $(NH_4)_2Cr_2O_7$, plus control. The substance was weighed directly into the test tanks. Dilution water: Used pond water with a high turbidty (160-200 ppm tubidity). Aeration was used to maintain the dissolved oxygen level and the disperse the turbidity-producing soil. Concentration of Cr in dilution water not reported. Control response: Not given. Comments: Tail-rot disease was seen in the holding tank. The fish were treated with medication prior to use.	Wallen et al, 1957
			48h-TLm	87[e]	n	static	5.7-7.4		<100	18-20	IV		
			96h-TLm	56[e]	n	static	5.7-7.4		<100	18-20	IV		

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) concentration converted from salt to chromium ion concentration
f) Val. = validation marking of test (see main text)

References

The references for this appendix appear in the full reference list (Section 6) of the main report.

Appendix E Summary of aquatic toxicity data for chromic acid/chromium trioxide

This appendix reviews the aquatic toxicity data for chromic acid/chromium trioxide. Values which have been used in the risk assessment report are highlighted with light grey shading. The following paragraphs provide some information about the selection process; these apply to the overall data set for chromium (VI) and not all comments apply to data in this appendix.

For short term test results, the values selected are the lowest for each species which come from tests with a validity marking of I or II. In some cases a number of valid results may have been produced by one study, using different experimental conditions (for example, hardness, salinity and temperature). For properties such as temperature and salinity the test conditions closest to the 'real' environment have been chosen (so avoiding high or low temperatures, and preferring tests at salinities similar to sea water); for hardness, the lowest test result is preferred as a range of hardness is found in natural waters. These 'rules' have been applied flexibly so as to allow interpretation of the individual studies.

For long term tests, all data from validity marking I and II have been selected, but some studies with marking IIIb have also been included. Multiple values have been taken from some studies, where a number of different endpoints were measured (for example, mortality, reproduction and growth). Where several measures of the same endpoint are reported in one study, values from longer exposure periods are generally preferred, with the exception of algal studies where the maintenance of exponential growth conditions is considered.

The further treatment of the long term data to derive the PNEC is described in the main risk assessment report. In some cases, notes on data not used in the PNEC derivation have also been included in the comments on the tests in the appendix.

Table E.1 Summary of the ecotoxicological data for chromic acid/chromium trioxide to fish

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp (°C)	Val.[g]	Test details	Reference
FISH - freshwater - short-term studies													
Colisa fasciatus	not known	adult (5.23 g)	96h-LC_{50}	31.2[e]	n	static	7.6	170		25	II	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Tap water. The dissolved oxygen level was 7.67 mg/l. The Cr concentration in the dilution water was not given. Control response: Not given. Comments: Test carried out according to APHA[f] (1971 version). determinations. Liver glycogen decreased significantly over 3 to 96 hour test period; a significant hyperglycaemic response observed from 6 hours to 96 hours.	Nath and Kumar, 1988
Colisa fasciatus	not known	adult - female (5.12 g)	96h-LC_{50}	20.8[e]			7.3	120		25	II	No. of organisms: Not clear. Probably 12 fish/concentration. Test concentrations: Not given. Dilution water: Tap water. The dissolved oxygen level was 6.8 mg/l. The Cr concentration in the dilution water was not given. Control response: Not given. Comments: Total erythrocyte count, number of red blood cells, and hematocrit values significantly elevated in exposed fish; erythrocyte sedimentation rate, total leukocyte count, and number of small lymphocytes significantly lower in exposed fish. Hematological stress responses observed at 90h exposure to sub-lethal levels of CrO_3 (i.e. 18.2 mg Cr/l[e]).	Srivastava et al, 1979
FISH - freshwater - long-term studies													
Carassius auratus	goldfish	embryo-larval	7-d LC_{50}	0.66	m	12h renewal	7.4	195		22	II	No. of organisms: Minimum of 150 eggs/concentration was used. Test concentrations: Exposure concentrations were initiated in the range 10 to 100 ppm and continued at 2 to 10 fold dilutions until survival of the experimental animals equalled or approached that of controls. A total of 10 to 14 concentration used, plus control. Dilution water: Source of water not given. Dissolved oxygen level was maintained near saturation by continuous aeration. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Mortality Comments: Exposure maintained from fertilisation to 4 days post hatching, giving a total exposure period of 7 days. Control adjusted LC_1 and LC_{50} values calculated by probit analysis. Anomalous survivors were counted as lethals. The significance of the LC_1 values is questionable.	Birge, 1978
			7-d LC_1	0.0081	m	12h renewal	7.4	195		22	IV		

Table E.1 continued overleaf

Table E.1 continued Summary of the ecotoxicological data for chromic acid/chromium trioxide to fish

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp (oC)	Val.g	Test details	Reference
Micropterus salmoides	largemouth bass	embryo-larval	8d-LC_{50}	1.17	m	12h renewal	7.2-7.8	93-105		19-22	II	No. of organisms: Minimum of 100 eggs/concentration was used. Test concentrations: Not given. Dilution water: Source of water not given. Dissolved oxygen level was maintained near saturation by continuous aeration. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Mortality. Comments: Exposure maintained from fertilisation to 4 days post hatching, giving a total exposure period of 8 days. Control adjusted LC_1 and LC_{50} values calculated by probit analysis. Anomalous survivors were counted as lethals. The significance of the LC_1 values is questionable.	Birge et al, 1978
			8d-LC_1	0.011	m	12h renewal	7.2-7.8	93-105		19-22	IV		
Oncorhynchus mykiss	rainbow trout	embryo-larval	28d-LC_{50}	0.18	m	12h renewal	7.2-7.8	104		12-13	II	No. of organisms: Minimum of 150 eggs/concentration was used. Test concentrations: Exposure concentrations were initiated in the range 10 to 100 ppm and continued at 2 to 10 fold dilutions until survival of the experimental animals equalled or approached that of controls. A total of 10 to 14 concentration used, plus control. Dilution water: Source of water not given. Dissolved oxygen level was maintained near saturation by continuous aeration. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Mortality Comments: Exposure maintained from fertilisation to 4 days post hatching, giving a total exposure period of 28 days. Control adjusted LC_1 and LC_{50} values calculated by probit analysis. Anomalous survivors were counted as lethals. The significance of the LC_1 values is questionable.	Birge, 1978; Birge et al, 1978; Birge et al, 1981.
			28d-LC_1	0.019	m	12h renewal	7.2-7.8	104		12-13	IV		

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) concentration converted from salt to chromium ion concentration
f) American Public Health Association. Standard Methods for the examination of water and wastewater
g) Val. = validity marking of test

Table E.2 Summary of the ecotoxicological data for chromic acid/chromium trioxide to aquatic invertebrates

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp (°C)	Val.[g]	Test details	Reference
INVERTEBRATES - saltwater - short-term studies													
Capitella capitata	polychaete worm	larvae	96h-LC_{50}	8.0	n		7.8				II	No. of organisms: The test with juveniles used 20 larvae/concentration in 15 ml solution. The test with adults used 1-2 animals/replicate, 10 replicates/concentration. The loading rate was 1-2 animals in 100 ml. Test concentrations: 0.05, 0.1, 0.5, 1, 5 and 10 mg Cr/l, plus controls. Dilution water: Filtered natural seawater. The dissolved oxygen level and Cr concentration are not given. Control response: Not given. Endpoints: Mortality. Comments:	Reish et al, 1976
		adults	96h-LC_{50}	5.0	n		7.8				II		
Neanthes arenaceodenta	ragworm	juvenile	96h-LC_{50}	>1.0	n		7.8				IIIb	No. of organisms: 1 animal/replicate, 10 replicates/concentration. Loading rate was 1 animal in 100 ml solution. Test concentrations: 0.1, 0.2, 0.3, 0.4, 0.5 and 1 mg Cr/l, plus controls. Dilution water: Filtered natural seawater. The dissolved oxygen level and Cr concentration are not given. Control response: Not given. Endpoints: Mortality. Comments: The concentration range tested is inappropriate.	Reish et al, 1976
		adults	96h-LC_{50}	>1.0	n		7.8				IIIb		
INVERTEBRATES - saltwater - long-term studies													
Capitella capitata	polychaete worm	adult	28d-LC_{50}	0.28	n		7.8				II	No. of organisms: The test used 1-2 animals/replicate, 10 replicates/concentration. The loading rate was 1-2 animals in 100 ml. Test concentrations: 0.05, 0.1, 0.5, 1, 5 and 10 mg Cr/l, plus controls. Dilution water: Filtered natural seawater. The dissolved oxygen level and Cr concentration are not given. Control response: Not given. Endpoints: Mortality. Comments:	Reish et al, 1976
Ctenodrilus serratus	polychaete worm	adult	21d-LOEC (~25% reduction in pop. size)	0.05	n		7.8				II	No. of organisms: 4 animals/replicate, 10 replicates/concentration. Loading rate was 4 animals in 20 ml solution. Test concentrations: Used 0.05, 0.1, 0.5, 1.0, 2.5 and 5.0 mg Cr/l, plus control. Dilution water: Filtered seawater. The dissolved oxygen level and Cr concentration are not given. Control response: The population at 21 days was 188. Endpoints: Size of population at 21 days. This will combine both parent mortality and effects on reproduction. Comments: The size of population was found to be statistically significantly (p=0.05) reduced at all Cr concentrations. The population at 0.05 mg Cr/l was 142 (~76% of control). The 96h-LC_{50} for this species is between 2.5 and 5.0 mg Cr/l (the exact value was not given in the paper).	Reish and Carr, 1978

Table E.2 continued overleaf

Table E.2 continued Summary of the ecotoxicological data for chromic acid/chromium trioxide to aquatic invertebrates

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ ma	Test method	pH	Hard.b/ Sal.d	Alk.c	Temp (oC)	Val.g	Test details	Reference
Neanthes arenaceodenta	ragworm	juvenile	28d-LC_{50}	0.70	n		7.8				II	No. of organisms: 1 animal/replicate, 10 replicates/concentration. Loading rate was 1 animal in 100 ml solution. Test concentrations: 0.1, 0.2, 0.3, 0.4, 0.5 and 1 mg Cr/l, plus controls. Dilution water: Filtered natural seawater. The dissolved oxygen level and Cr concentration are not given. Control response: Not given. Endpoints: Mortality. Comments:	Reish et al, 1976
		adult	28d-LC_{50}	0.55	n		7.8				II		
Ophryotrocha diadema	polychaete worm	adult	21d-NOEC	0.5	n		7.8				II	No. of organisms: 4 animals/replicate, 10 replicates/concentration. Loading rate was 4 animals in 20 ml solution. Test concentrations: Used 0.05, 0.1, 0.5, 1.0, 2.5 and 5.0 mg Cr/l, plus control. Dilution water: Filtered seawater. The dissolved oxygen level and Cr concentration are not given. Control response: The population at 21 days was 97. Endpoints: Size of population at 21 days. This will combine both parent mortality and effects on reproduction. Comments: The size of population was found to be statistically significantly (p=0.05) reduced at concentrations of 1.0 mg Cr/l and above. The populations seen at lower Cr concentrations were also less than controls, but these effects were not considered to be statistically significant.	Reish and Carr, 1978

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) concentration converted from salt to chromium ion concentration
f) American Public Health Association. Standard Methods for the examination of water and wastewater
g) Val. = validity marking of the test (see main report)

Table E.3 Summary of the ecotoxicological data for chromic acid/chromium trioxide to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp (°C)	Val.[f]	Test details	Reference
AMPHIBIANS - freshwater - short-term studies													
Rana cyanophlyctis	Indian skipper frog	adult	96h-LC_{50}	43[e]	n	24h renew.	7.2	65		26	II	No. of organisms: 10 animals/concentration, in 2 litres solution. Test concentrations: Not given. A control was run. Dilution water: Tap water. The dissolved oxygen concentration was 7.0 mg/l. The Cr concentration of the dilution water was not given. Control response: Not given. Endpoints: Mortality. Comments: 96h-LC_{50} for potassium and sodium dichromates were 81 and 85 mg/l respectively.	Joshi and Patil, 1991
AMPHIBIANS - freshwater - long-term studies													
Ambystoma opacum	marbled salamander	embryo-larval	8d-LC_{50}	2.13	m	12h renewal	7.2-7.8	93-105		19-22	II	No. of organisms: Minimum of 35 eggs/concentration was used. Test concentrations: Not given. Dilution water: Source of water not given. Dissolved oxygen level was maintained near saturation by continuous aeration. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Mortality. Comments: Exposure maintained from fertilisation to 4 days post hatching, giving a total exposure period of 8 days. Control adjusted LC_1 and LC_{50} values calculated by probit analysis. Anomalous survivors were counted as lethals. The significance of the LC_1 values is questionable.	Birge et al, 1978
			8d-LC_1	0.017	m	12h renewal	7.2-7.8	93-105		19-22	IV		
Gastrophryne carolinensis	narrow-mouthed toad	embryo-larval	8d-LC_{50}	0.030	m	12h renewal	7.4	195		22	II	No. of organisms: Minimum of 150 eggs/concentration was used. Test concentrations: Exposure concentrations were initiated in the range 10 to 100 ppm and continued at 2 to 10 fold dilutions until survival of the experimental animals equalled or approached that of controls. A total of 10 to 14 concentration used, plus control. Dilution water: Source of water not given. Dissolved oxygen level was maintained near saturation by continuous aeration. The concentration of Cr in the dilution water was not given. Control response: Not given. Endpoints: Mortality Comments: Exposure maintained from fertilisation to 4 days post hatching, giving a total exposure period of 7 days. Control adjusted LC_1 and LC_{50} values calculated by probit analysis. Anomalous survivors were counted as lethals. The significance of the LC_1 values is questionable.	Birge, 1978
			8d-LC_1	0.001	m	12h renewal	7.4	195		22	IV		

Table E.3 continued overleaf

Table E.3 continued Summary of the ecotoxicological data for chromic acid/chromium trioxide to other organisms

Species	Common name	Lifestage	Endpoint	[CrVI] mg/l	n/ m[a]	Test method	pH	Hard.[b]/ Sal.[d]	Alk.[c]	Temp (°C)	Val.[f]	Test details	Reference
MICROORGANISMS													
Unknown	rumen bacteria		2h-IC_{50}	69.7							IV	No. of organisms: Not clear. Test concentrations: Appear to have use 11 concentrations covering the range <10% inhibition to >90% inhibition.. Dilution water: Not given. Control response: Control rate of gas evolution was 59.4 µl/g min. Endpoints: Inhibition of fermentation rate, as measured by *in vitro* gas evolution. Comments: IC_{50} refers to fermentation rate. Sub-inhibitory effects on various bacterium observed to occur at 80-200 mg/l; growth inhibitory effects at 200 mg/l. The results are of little relevance to the environmental assessment.	Forsberg, 1978
Escherichia coli	bacteria		24h-EC_{50}	260[e]							IIIa	No. of organisms: Not given. Test concentrations: Not given. Dilution water: Not given. Control response: Not given. Endpoints: Not given. Comments: Summary of results only is available. The LC_{50} is reported as 500 mg CrO_3/l.	Roth, 1996

Notes: a) n = nominal concentration; m = measured concentration
b) Hard. = hardness as mg $CaCO_3$/l
c) Alk. = alkalinity as mg HCO_3^-/l
d) Sal. = salinity
e) concentration converted from salt to chromium ion concentration
f) Val. = validity marking of test (see main text)

References

The references for this appendix appear in the full reference list (Section 6) of the main report.

Appendix F Summary of aquatic toxicity data from chromium (III)

The available toxicity data for chromium(III) has been derived mainly using the water soluble forms (chromic chloride, chromic nitrate and chromium potassium sulphate). In the environment, chromium(VI) is likely to be reduced to chromium(III) species that are much less soluble, and hence bioavailable, than the forms of chromium(III) used in these tests. When the more insoluble forms of chromium(III) (e.g. chromium hydroxide sulphate and dichromium trioxide) have been tested, they have generally shown no effects on aquatic organisms at concentrations up to their effective water solubility.

From the available toxicity data, it appears that chromium(III) is less toxic in hard water and saltwater than in soft water.

Table F.1 Summary of the ecotoxicological data for chromium(III) to fish

Species	Method	Chemical tested	Hardness (mg/l)	Endpoint (mg Cr/l)	Reference
FISH - freshwater - short-term (48-96h) studies					
Anguilla rosttrata (American eel)	S; M	-	55	LC_{50} = 13.9	Rehwoldt et al, 1973
Brachydanio rerio (zebra fish)	N	Dichromium trioxide	-	96h-NOEC >6,840	IUCLID, 1999
	M	Dichromium trioxide	-	96h-NOEC >0.001*	
Brachydanio rerio (zebra fish)	SS	Chromium hydroxide sulphate	-	96h-NOEC >3,130	IUCLID, 1999
Carassius auratus (goldfish)	S; N	Chromium potassium sulphate	20	96h-LC_{50} = 4.1	Pickering and Henderson, 1966
Fundulus diaphanus (banded killifish)	S; M	-	55	LC_{50} = 16.9	Rehwoldt et al, 1972
Cyrprinus carpio (common carp)	S; M	-	55	LC_{50} = 14.3	Rehwoldt et al, 1972
Lepomis gibbosus (pumpkinseed)	S; M	-	55	LC_{50} = 17.0	Rehwoldt et al, 1972
Lepomis macrochirus (bluegill)	S; U	Chromium potassium sulphate	20	96h-LC_{50} = 7.46	Pickering and Henderson, 1966
Leuciscus idus (ide)	N	Dichromium trioxide	-	48h-NOEC >684	IUCLID, 1999
Leuciscus idus (ide)		Chromium hydroxide sulphate	-	96h-LC_{50} = 157 (effects may have been due to pH changes)	IUCLID, 1999
Marone americana (white perch)	S; M	-	55	LC_{50} = 14.4	Rehwoldt et al, 1972
Marone saxatillis (striped bass)	S; M	-	55	LC_{50} = 17.7	Rehwoldt et al, 1972
Oncorhynchus mykiss (rainbow trout)	FT; M	Chromic nitrate		LC_{50} = 24.1	Hale, 1977
Oncorhynchus mykiss (rainbow trout)	S; N	Chromic chloride	44	LC_{50} = 11.2	Bills et al, 1977; Markin, 1982.
Oncorhynchus mykiss (rainbow trout)	FT; M	Chromic nitrate	26	LC_{50} = 4.4	Stevens and Chapman, 1984
Pimephales promelas (fathead minnow)	S; U	Chromium potassium sulphate	20	96h-LC_{50} = 5.07	Pickering and Henderson, 1966
			360	96h-LC_{50} = 67.4	
Pimephales promelas (fathead minnow)	FT; M	Chromium potassium sulphate	203	LC_{50} = 27-29	Pickering (unpublished)
Poecillia reticulata (guppy)	S; N	Chromium potassium sulphate	20	96h-LC_{50} = 3.33	Pickering and Henderson, 1966

Table F.1 continued overleaf

Table F.1 continued Summary of the ecotoxicological data for chromium(III) to fish

Species	Method	Chemical tested	Hardness (mg/l)	Endpoint (mg Cr/l)	Reference
FISH - saltwater - short-term (48-96h) studies					
Fundulus heteroclitus (mummichog)	S; U	Chromic chloride		LC_{50} = 31.5	Dorfman, 1977
FISH - freshwater - long-term studies					
Brachydanio rerio (zebra fish)	early life stage	Chromium hydroxide sulphate	-	30d-NOEC >313	IUCLID, 1999
Oncorhynchus mykiss (rainbow trout)	early life stage	Chromic nitrate	26	NOEC = 0.050 LOEC =0.157 MATC = 0.089	Stevens and Chapman, 1984
Pimephales promelas (fathead minnow)	life-cycle	Chromium potassium sulphate	203	NOEC = 0.75 LOEC = 1.4 MATC = 1.03	Pickering (unpublished)

Note: *effective solubility limit in the test medium
S = static test system
FT = flow-through test system
SS = semi-static test system
N = nominal concentrations
M = measured concentrations

Table F.2 Summary of the ecotoxicological data for chromium(III) to aquatic invertebrates

Species	Method	Chemical tested	Hardness (mg/l)	Endpoint (mg Cr/l)	Reference
INVERTEBRATES - freshwater - short-term (48-96h) studies					
Crustaceans					
Asellus aquaticus (sowbug)	-	Chromic chloride	-	48h-EC_{50} = 937 96h-EC_{50} = 442	DOSE, 1993
Crangonyx pseudogracilis (amphipod)	-	Chromic chloride		48h-EC_{50} = 388 96h-EC_{50} = 291	DOSE, 1993
Daphnia magna (water flea)	-	Chromic chloride	-	24h-EC_{50} = 111	DOSE, 1993
Daphnia magna (water flea)	S; N	Chromic chloride	-	EC_{50} = 1.2	Anderson, 1948
Daphnia magna (water flea)	S; M	Chromic nitrate	52	EC_{50} = 16.8	Chapman et al (unpublished)
			92	EC_{50} = 27.4	
			110	EC_{50} = 26.3	
			195	EC_{50} = 51.4	
			215	EC_{50} = 58.7	
Gammarus sp. (amphipod)	S; M	-	50	EC_{50} = 3.2	Rehwoldt et al, 1973
Orconectes limosus (crayfish)	S; M	Chromic chloride	-	EC_{50} = 6.6	Boutet and Cheismemartin, 1973
Insects					
Caddis fly (unidentified)	S; M	-	50	EC_{50} = 58	Rehwoldt et al, 1973
Chironomus sp. (midge)	S; M	-	50	EC_{50} = 11.0	Rehwoldt et al, 1973
Damselfly (unidentified)	S; M	-	50	EC_{50} = 43.1	Rehwoldt et al, 1973
Ephemarella subvaris (mayfly)	S; N	Chromic chloride	44	EC_{50} = 2.0	Warnick and Bell, 1969
Hydropsyche bettoni (caddis fly)	S; M	Chromic chloride	44	EC_{50} = 64.0	Warnick and Bell, 1969
Molluscs					
Amnicola sp. (snail; embryo)	S; M	-	50	EC_{50} = 12.4	Rehwoldt et al, 1973
Amnicola sp. (snail; adult)	S; M	-	50	EC_{50} = 12.4	Rehwoldt et al, 1973
Annelids					
Neis sp. (worm)	S; M	-	50	EC_{50} = 9.3	Rehwoldt et al, 1973
INVERTEBRATES - saltwater - short-term (48-96h) studies					
Crassostrea virginica (eastern oyster)	S; U	Chromic chloride		EC_{50} = 10.3	Calabrese et al, 1973
Ophtyotrocha diadema (polychaete worm)	S	Chromic chloride	32‰	48h-EC_{50} = 100	Parker, 1984

Table F.2 continued overleaf

Table F.2 continued Summary of the ecotoxicological data for chromium(III) to aquatic invertebrates

Species	Method	Chemical tested	Hardness (mg/l)	Endpoint (mg Cr/l)	Reference
INVERTEBRATES - freshwater - long-term studies					
Daphnia magna (water flea)	life-cycle	Chromic nitrate	52	NOEC = 0.047 LOEC = 0.093 MATC = 0.066	Chapman et al (unpublished)
			100	NOEC = 0.129 LOEC = 0.291 MATC = 0.193	
			206	NOEC <0.044*	
Daphnia magna (water flea)	21-day repro.	Chromic chloride		NOEC = 3.4	Kühn et al, 1989; DOSE, 1993
INVERTEBRATES - saltwater - long-term studies					
Neanthes arenaceodentata (ragworm)	mulit-gen.	Chromic chloride		NOEC >50.4	Oshida et al, 1976 and 1981

Note: * effects were thought to be due to ingestion of precipitated chromium in particulate matter
S = static test system
FT = flow-through test system
N = nominal concentrations
M = measured concentrations

Table F.3 Summary of the ecotoxicological data for chromium(III) to other organisms

Species	Chemical tested	Method/comment	Endpoint (mg Cr/l)	Reference
ALGAE				
Chlorella pyrenoidosa	Chromium potassium sulphate	Biomass Cell no.	5d-NOEC >2 5d-NOEC 0.1	Meisch and Schmitt-Beckmann, 1979
Selenastrum capricornutum	Chromic chloride	Biomass	96h-EC_{50} = 0.32	Greene et al, 1988
Scenedesmus subspicatus	Chromium hydroxide sulphate	Oxygen production inhibition	24h-NOEC > 0.313	IUCLID, 1999
BACTERIA				
Activated sludge	Chromium hydroxide sulphate	ISO 8192 - Inhibition of oxygen consumption	3h-NOEC >3,130	IUCLID, 1999
Azobacter vinelandii (soil bacterium)	Chromic chloride	Growth inhibition over 4 days	LOEC/NOEC ~ 0.26	Ueda et al, 1988
Fusarium oxysporum (soil fungus)	Chromic chloride	Growth inhibition over 27 hours	NOEC > 6.5	Ueda et al, 1988
Pseudomonas fluorescens	Dichromium trioxide		24h-NOEC >6,840	IUCLID, 1999
Pseudomonas fluorescens	Chromium hydroxide sulphate		24h-NOEC >313	IUCLID, 1999

Note: see Appendix VII for data on toxicity of chromium (III) to soil processes.

The toxicity data included in the tables have been largely taken from existing reviews.

References

The references for this appendix appear in the full reference list (Section 6) of the main report.

Appendix G Summary of soil process toxicity data from chromium (III)

Data on the toxicity of chromium (III) to soil processes have been taken from the review by Crommentuijn et al (1997). The values used in this risk assessment were selected from those presented in Table 4.4 of Appendix IV in the Crommentuijn review, applying the following criteria. Values for the NOEC or EC_{10} which were reported directly were used as NOEC values. Where an EC value for an effect between 10 and 20% was reported, a NOEC of half the EC value was taken. Effect levels greater than 20% were not used. Where results from different exposure periods were reported for the same study, the result from the longest available exposure matching the above criteria was taken. In one case, a NOEC and an EC_{10} value were presented for the same study and duration; in this case the geometric mean of the two values was used. The basic data are presented in Table VII.1. This includes the original values where the effect was between 10% and 20% (ie before division by two), and the values for different durations.

The selected values were used to determine a PNEC value for soil processes using the statistical extrapolation method. The log NOEC values were fitted to a normal distribution. The Kolmogorov-Smirnov test did not reject the hypothesis, that the log NOEC values came from a normal distribution. A plot of the observed and expected cumulative frequencies is included as Figure VII.1. The result of the statistical extrapolation calculation is a HC_5-50% value of 5.9 mg/kg. For comparison, the HC_5-95% value is 2.1 mg/kg.

The data cover a range of processes: arylsulphatase, nitrification, N-mineralisation, phosphatase, respiration and urease. A plot of the distribution of the different processes is presented in Figure VII.2. This shows that there are no processes clearly more sensitive than others. The two lowest values relate to arylsulphatase, but the two highest values are also for the same process, and there are other values for this process in the data set as well. Only the two lowest values are below the HC_5 - 50% value derived. In this case it is considered that an assessment factor of 1 is sufficient, hence the PNEC for soil processes with chromium (III) is 5.9 mg/kg

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Table G.1 Toxicity of chromium (III) to soil processes (after Crommentuijn et al, 1997)

Process	Soil type	pH	% Organic matter	% clay	Temp (°C)	Exposure time	Endpoint	Result (mg/kg dw)	Reference
Arylsulphatase	sand	7.7	1.6	2	20	18 m	EC_{10}	2.1	Hanstra and Doelman, 1991
	sandy loam	5.1	5.7	9	20	6 w	EC_{10}	(46)	
						18 m	EC_{10}	1.0	
	silty loam	7.4	2.4	19	20	18 m	EC_{10}	83	
	clay	6.8	3.2	60	20	6 w	EC_{10}	(43)	
						18 m	EC_{10}	276	
	sandy peat	3.0	12.8	5	20	6 w	EC_{10}	(3338)	
						18 m	EC_{10}	2730	
Nitrification*		7.2	2	17	30	21 d	NOEC	100	Denneman and Van Gestel, 1990
N-mineralisation		5.8	4.4	23	30	20 d	EC_{20}	260[a]	
		6.6	5	45	30	20 d	EC_{15}	260[a]	
		7.8	6.4	30	30	20 d	EC_{13}	260[a]	
Phosphatase (acid)	Webster	5.8	4.4	23	37	1.5 h	NOEC	130	Juma and Tabatabai, 1977
Phosphatase (alkaline)	Okoboji	7.4	9.3	34	37	1.5 h	EC_{14}	130[a]	
Phosphatase	sand	7.7	1.6	2	20	6 w	EC_{10}	(1092)	Doelman and Haanstra, 1989
						18 m	EC_{10}	723	
	sandy loam	6	5.7	9	20	6 w	EC_{10}	(2782)	
						18 m	EC_{10}	858	
	silty loam	7.4	2.4	19	20	6 w	EC_{10}	(728)	
						18 m	EC_{10}	280	
	clay	7.5	3.2	60	20	6 w	EC_{10}	(52)	
						18 m	EC_{10}	2153	

Table G.1 continued overleaf

Table G.1 continued Toxicity of chromium (III) to soil processes (after Crommentuijn et al, 1997)

Process	Soil type	pH	% Organic matter	% clay	Temp (°C)	Exposure time	Endpoint	Result (mg/kg dw)	Reference
	sandy peat	4.4	12.8	5	20	6 w	EC_{10}	380	
Respiration	sandy loam	5.1	5.7	9	20	8 w	EC_{10}	(5)	Dennemann and Van Gestel, 1990
						10 m	NOEC	(148)	
						10 w	EC_{10}	(7)	
						43 w	EC_{10}	6	
	silty loam	7.4	2.6	19	20	21 m	EC_{10}	86[b]	
						21 m	NOEC	182[b]	
	sandy peat	4.3	12.8	5	20	19 m	EC_{10}	71	Dennemann and Van Gestel, 1990
	clay	6.8	3.2	60	20	19 m	NOEC	400	
Urease	sand	7.7	1.6	2	20	6 w	EC_{10}	(1880)	Doelman and Hanstra, 1986
						18 m	EC_{10}	390	
	silty loam	7.4	2.4	19	20	6 w	EC_{10}	(2050)	
						18 m	EC_{10}	890	
	clay	7.5	3.2	60	20	18 m	EC_{10}	350	
	sandy peat	4.4	12.8	5	20	6 w	EC_{10}	360	
	Harps	7.8	6.4	30	37	2 h	NOEC	26	Denneman and Van Gestel, 1990
	Luton	6.8	7.4	30	37	2 h	EC_{17}	260[a]	
	Okoboji	7.4	9.3	34	37	2 h	EC_{19}	26[a]	

Notes: All results based on measured concentrations and on added amount of chromium. All involved addition of chromium (III) chloride except for *, where chromium (III) sulphate was used.
( ) - values in parentheses not used in the statistical extrapolation, as a value from a longer exposure under the same conditions is available.
a - NOEC determined as $EC_x/2$, as $x \leq 20$ for use in the extrapolation.
b - geometric mean of the two values used in the extrapolation.

Figure G.1 Statistical extrapolation cumulative frequencies

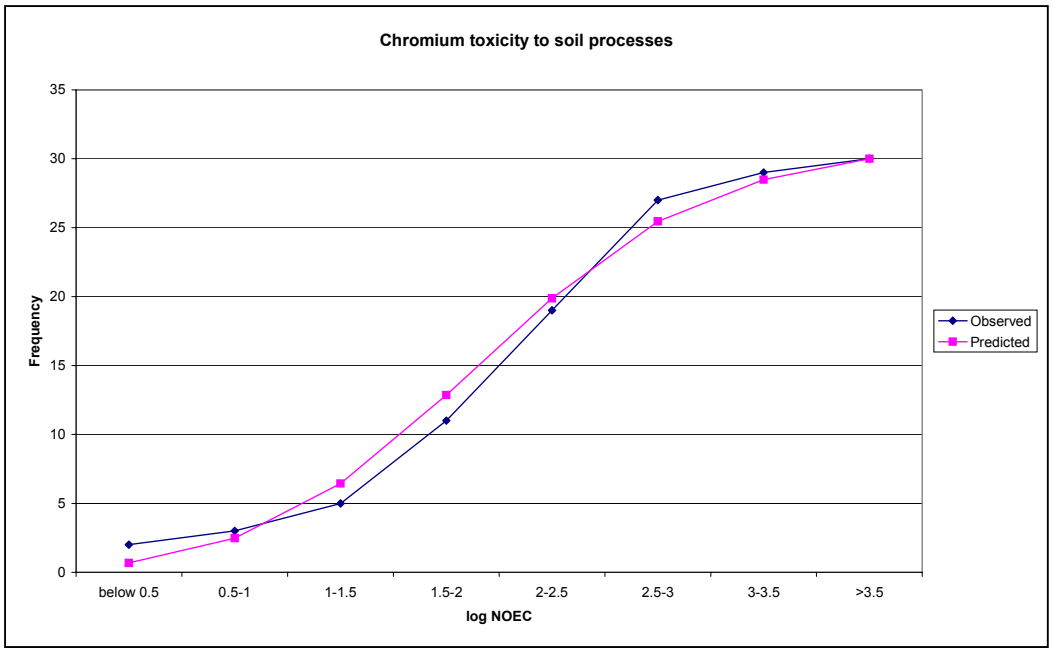
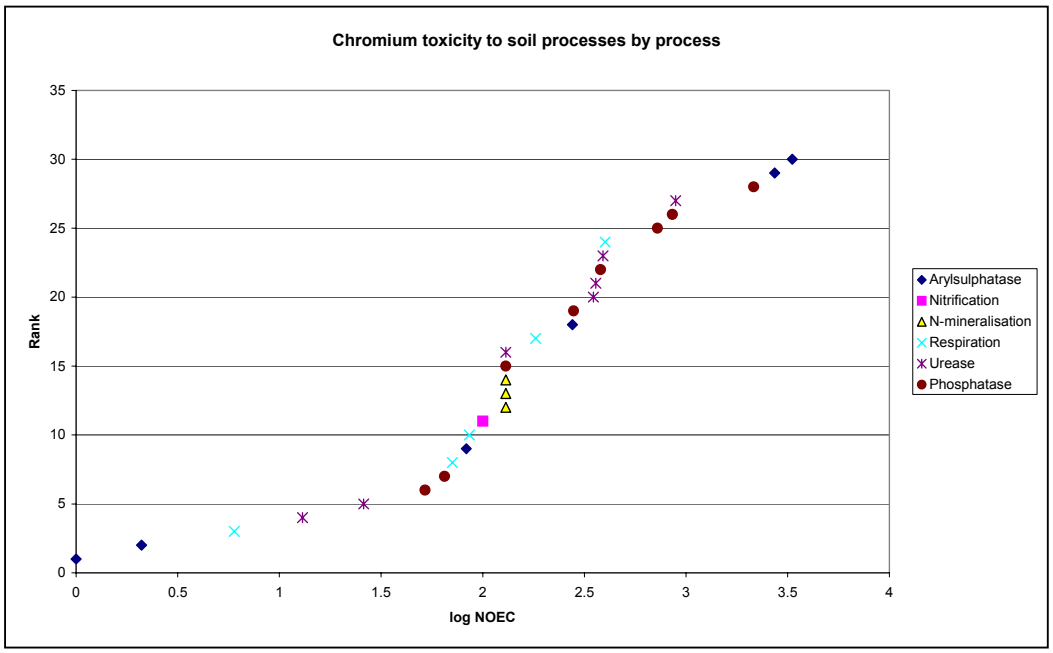


Figure G.2 Distribution of process NOECs



Appendix H Quantitative Risk Assessment for Chromium (VI) Compounds

A submission by The Netherlands

The studies of Mancuso, 1975 and Mancuso, 1997 are considered suitable to be used as point of departure for calculation of

- the additional lifetime cancer risk per unit of exposure and
- the concentration of chromium in air associated with a cancer risk of 0.25 in humans, i.e., the HT25.

Since the U.S. EPA used also the Mancuso study of 1975 to derive an air unit cancer risk for Cr (VI), the data from the EPA cancer risk analysis were adopted to be used as starting point to calculate the HT25 for life time and occupational conditions of exposure. Using a low-dose linear extrapolation model for estimation of the cancer risks, the EPA calculated for chromium compounds a lifetime air unit risk of $1.2 \cdot 10^{-2}$ per $\mu g/m^3$. The occupational and lifespan exposure conditions included exposure period default values of 40 years, 8 hrs/day, 5 days per week, 48 weeks per year and 75 years, 24 hrs/day, 365 days/year respectively (U.S. EPA, 1998).

Based on these data a life time exposure of 1 $\mu g/m^3$ Cr (VI) involves an additional lifetime lung cancer risk of $1.2 \cdot 10^{-2}$. This risk is calculated from the total chromium concentration in the chromate plant. The EPA noted that the use of total chromium as a surrogate for hexavalent chromium could result in an underestimation of the risk by no more than 7 times. On the other hand, EPA noted that underestimation of plant exposures and of smoking habits in the workers could lead to an overestimation of the risk of roughly 4 times (U.S. EPA 1998). Overall, the Mancuso study is considered to give the best possible estimate of the cancer risk (U.S. EPA 1998).

For non-threshold carcinogens it is assumed that the HT25 can be derived from the incidence per $\mu g/m^3$ by linear extrapolation. Starting from an incidence of 1.2×10^{-2} per $\mu g/m^3$ the following HT25 values are derived,

HT25 (lifespan conditions of exposure)[7] = 21 $\mu g/m^3$

HT25 (occupational conditions of exposure)[8] = $20.8 \cdot 8.5$ $\mu g/m^3$ = 177 $\mu g/m^3$

Conclusion

Based on the HT25 for occupational conditions of exposure, it can be calculated that the occupational exposure data listed in **Table 4.15** are associated with lifetime cancer risks > $1 \cdot 10^{-4}$. The highest and lowest reasonable worst-case estimations, i.e., 0.05 and 0.001 mg/m^3 being associated with risks of $7 \cdot 10^{-2}$ and $1.4 \cdot 10^{-3}$ respectively.

Therefore, it is concluded for all scenarios listed in **Table 4.15** that they entail a substantial cancer risk, i.e., conclusion (iii).

CONSULTED LITERATURE

U.S. EPA, 1998.

7 Lifespan conditions of exposure: 75 years, 24 hours/day, 7 days/week, 52 weeks/year

8 Occupational conditions of exposure: 40 years, 8 hours/day, 5 days/week, 48 weeks/year

Toxicological review of hexavalent chromium, August 1998

U.S. EPA IRIS , 1998
Substance file – Chromium(VI); CASRN 18540-29-9

European Commission

EUR 21508 EN **European Union Risk Assessment Report**
Chromium trioxide, sodium chromate, sodium dichromate, ammonium dichromate, potassium dichromate,Volume 53

Editors: S.J. Munn, R. Allanou, K. Aschberger, F. Berthault, O. Cosgrove, M. Luotamo, S. Pakalin, A. Paya-Perez, G. Pellegrini , B. Schwarz-Schulz, S. Vegro.

Luxembourg: Office for Official Publications of the European Communities

2005 – IX pp., 416 pp. – 17.0 x 24.0 cm

Environment and quality of life series

The report provides the comprehensive risk assessment of the substances Chromium trioxide, sodium chromate, sodium dichromate, ammonium dichromate, potassium dichromate. It has been prepared by the United Kingdom in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to humans and the environment, laid down in Commission Regulation (EC) No. 1488/94.

The evaluation considers the emissions and the resulting exposure to the environment and the human populations in all life cycle steps. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic, terrestrial and atmospheric compartment has been determined. For human health the scenarios for occupational exposure, consumer exposure and humans exposed via the environment have been examined and the possible risks have been identified.

The risk assessment for chromium trioxide, sodium chromate, sodium dichromate, ammonium dichromate and potassium dichromate concludes that there is a risk to the aquatic, terrestrial compartments and micro-organisms in the sewage treatment plant.There is no concern for the atmosphere.

A need for further information for the environment with special attention to sediment has also been identified. This conclusion also applies to indirect exposure of predators through the mussel-based food chain. At present it is not proposed to carry out any further work – this will be reviewed once the risk reduction strategy has been developed.

The human health risk assessment for chromium trioxide, sodium chromate, sodium dichromate, ammonium dichromate and potassium dichromate concludes that there is at present concern for workers, consumers and humans exposed via the environment. For workers additional information is needed in order to characterise the risk. For consumers and human exposed via the environment the risk assessment concludes that a risk cannot be excluded as the substance is identified as a non-threshold carcinogen. The risks though are low and this should be taken into account when considering the feasibility and practicability of further specific risk reduction measures.

The conclusions of this report will lead to risk reduction measures to be proposed by the Commissions committee on risk reduction strategies set up in support of Council Regulation (EEC) No.793/93.

It should be noted that this assessment and therefore the conclusions presented do not address possible risks to human health as a result of exposure to Cr(VI) in cement, nor does it address the possibility of exposure to Cr(VI) in leather goods and wood imported into the EU

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chromium trioxide, sodium chromate, sodium dichromate, ammonium dichromate and potassium dichromate

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