ANNEX XV DOSSIER

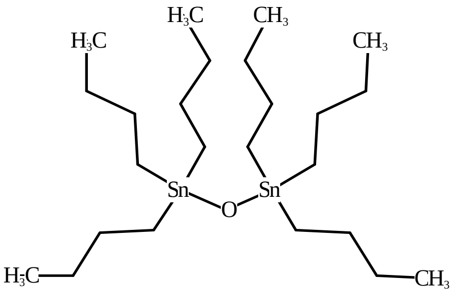
PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A PBT SUBSTANCE

Substance name: Bis(tributyltin) oxide

EC number: 200-268-0

CAS number: 56-35-9

Structural formula:



It is proposed to identify the substance as a PBT according to Article 57 (d).

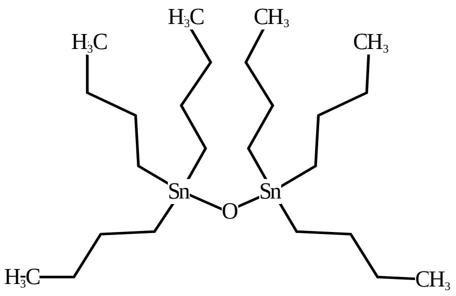
Summary of the evaluation:

Bis(tributyltin) oxide is considered as a PBT substance. Tributyltin, to which the substance transforms in the aqueous environment, fulfils the P, B and T criteria. Furthermore, bis(tributyltin) oxide fulfils the T criterion for human health due to the hazard classification of tributyltin compounds. Bis (tributyltin) oxide has been discussed in the TC NES subgroup on identification of PBT and vPvB substances, and the subgroup concluded that the substance fulfils the PBT criteria, see http://ecb.jrc.it/esis/index.php?PGM=pbt

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name:	Bis(tributyltin) oxide
EC Number:	200-268-0
CAS Number:	56-35-9
IUPAC Name:	
Molecular Formula:	C24H54OSn2
Structural Formula:	



Molecular Weight:	596.12
Synonyms:	TBTO; Hexa-n-butyldistannoxan; Bis(tri-n-butylzinn)oxid; Tri-n-butylzinnoxid

1.1 Purity/Impurities/Additives

Impurities as reported by CDCh (2003) are:

Di-n-butyltin oxide	ca. 0.5 % w/w
Tetra-n-butyltin	ca. 1.2 % w/w
Tetra-n-butyl-1,3-di-(2-ethyl-hexyl)-di-stannoxane	ca. 1.3 % w/w

1.2 Physico-Chemical properties

Table 1 Summary of physico-chemical properties.

REACH ref Annex, §	Property	Value	Comments
VII, 7.1	Physical state at 20 C and 101.3 Kpa	liquid, metallic, organometallic	European Commission (2000)
VII, 7.2	Melting / freezing point	< - 45 °C	Chapman and Hall (1984) as cited in GDCh (2003)
VII, 7.3	Boiling point	220-230 °C at 13 hPa	Chapman and Hall (1984) as cited in GDCh (2003)
VII, 7.5	Vapour pressure	0.00000085 – 0.00016 hPa at 20 °C	Blunden et al. (1984) as cited in GDCh (2003)
VII, 7.7	Water solubility	0.090 mg l^{-1} at 25 °C 100 mg l^{-1} 0.73 mg l^{-1} (at pH 6.0-6.6; distilled water) 4.0 mg l^{-1} (at pH 7.0; 20 °C; distilled water) 18-71.2 mg l^{-1} 3-10 mg l^{-1} (artificial seawater)	WSKOW v1.41 WSKOW v1.41, exper. database (data not evaluated) Maguire et al. (1983) as cited in GDCh (2003) Maguire et al. (1983) as cited in GDCh (2003) The range of several sources as cited in GDCh (2003) Blunden et al. (1984) as cited in GDCh (2003)
VII, 7.8	Partition coefficient n-octanol/water (log value)	4.05 (estimated) 3.84 3.31 3.2 (pH 6.0, at 20 °C) 3.8	KOWWIN v1.67 KOWWIN v1.67, exper. database (data not evaluated) CITI (1992) as cited in GDCh (2003) Maquire et al. (1982) as cited in GDCh (2003) Laughlin et al. (1986) as cited in GDCh (2003)
	Dissociation constant	6.25 6.51	GDCh (2003); for tributyltin cation OECD (2007); for unspecified tributyltin compound

It is noted, that the results of water solubility and logKow –tests are significantly dependent on the pH where the tests have been conducted.

2 MANUFACTURE AND USES

Not relevant for this type of dossier, see section 9.2 for information.

3 CLASSIFICATION AND LABELLING

The classification of tributyltin compounds (no CAS entry) in Directive 67/548/EEC applies for TBTO:

T; R25	Toxic if swallowed
T; 48/23/25	Toxic; danger of serious damage to health by prolonged exposure through inhalation and if swallowed
Xn; R21	Harmful in contact with skin
Xi; R36/R38	Irritating to eyes and skin
N; R50-53	Very toxic to aquatic organisms. May cause long-term adverse effects in the aquatic environment

4 ENVIRONMENTAL FATE PROPERTIES

4.1 Degradation (P)

4.1.1 Abiotic degradation

Maguire et al. (1984 as cited in GDCh, 2003) and Laughlin et al. (1986 as cited in GDCh, 2003) expect that TBTO dissociates in aqueous solution forming a hydrated tributyltin (TBT) cation. According to data compiled by GDCh (1988), TBTO forms in seawater mainly TBTCl, TBTOH, an aqueous complex ($TBTOH_2^+$) and calcareous compounds ($(TBT)_2CO_3$). Also WHO (1990) reports, that tributyltins are present in seawater and normal conditions as three species (hydroxide, chloride and carbonate). The speciation of tributyltin cation is dependent on the pH, anion content and temperature (WHO, 1990).

The C-Sn bonds of TBTO are stabile against hydrolysis under environmental conditions (CDCh, 2003) but this bond can be cleaved under UV-radiation at 290 nm according to Navio et al. (1993 as cited in GDCh, 2003). WHO (1990) reviews similar study results on photodegradation in water under various conditions. Photodegradation of TBT can be expected to be a relevant removal pathway in the environment only in very shallow clear waters and in the first few centimeters layer of the water column. Aquatic photodegradation is not considered to have relevant impact on the overall persistency of TBT in the environment.

Indirect photochemical degradation in the atmosphere is considered to be fast based on the estimated half-life of 4.5 hours for the reaction with OH-radicals using AOP v1.91 (24 h day^{-1}; $5*10^5$ OH^- cm^{-3}). It is noted, however, that due to the very low volatility of TBTO, atmospheric degradation is not a relevant route of degradation for this substance.

4.1.2 Biotic degradation

Degradation half-lives from experiments with natural micro-organism populations under aerobic conditions in aquatic systems are between 4 and 225 days and describe mainly primary degradation and not complete mineralisation (GDCh, 1988). In the studies reviewed by WHO (1990), half-lives from several days to several months in water have been determined for different test temperatures and including both pre-adapted (polluted) and non-adapted water samples.

Only few studies are available on sediment; the degradation half-life in these studies is > 1-15 years. Studies in highly polluted areas show, that after a certain concentration has been reached, no further TBT degradation occurs (GDCh, 2003).

Springborn Laboratories (1995b, as cited in GDCh, 2003) has reported on an aerobic degradation test with ^{14}C-TBTO and sandy loam soil. A nominal test concentration of 1.15 mg TBTO kg^{-1} dw and a test temperature of 25 ºC were employed. Half-life for primary degradation was estimated to be 114 days (323 days corrected to 12 ºC according to the TGD), whereas the main degradation product was identified as dibutyltin and monobutyltin as a minor product. The recovery at day 365 of the experiment was still 80 % (at the start 100 %). Springborn Laboratories (1994 as cited in GDCh, 2003) determined a half-live of 130 days (368 days corrected to 12 ºC according to the TGD) for primary degradation of ^{14}C-TBTO in anaerobic conditions in a test similar to the aerobic soil test.

4.1.3 Other information

4.1.4 Summary and discussion of persistence

TBTO is subject to transformation when dissolved to aqueous solution. Different tributyltin (TBT) species form as dissolution products, whereas the species formed depend mainly on the pH but also on other abiotic conditions. TBT is expected to be stabile to abiotic degradation in the normal environmental conditions.

Experimental half-lives of tributyltin compounds in water between 4 and 225 days have been reported by GDCh (1988) and between several days to several months by WHO (1990). According to GDCh (2003), the few studies available on degradation in sediment showed degradation half-lives of > 1-15 years.

In a soil degradation study an aerobic half-life of 114 d at 25 ºC was estimated corresponding to 323 d at 12 ºC.

4.2 Environmental distribution

4.2.1 Adsorption

Sorption behaviour of TBTO was investigated by Springorn laboratories (1995a as cited in GDCh, 2003) in a system consisting of seawater and sandy sediment (OC of 1.8 %) in volume ratio of 10:1. The partitioning coefficient between water and sediment was determined to be 28 after the establishment of the equilibrium within 48 hours. A Koc was estimated to be 2650. As the test was conducted in seawater (pH > 7 assumed), TBTO has been mainly present in non-dissociated form of tributyltin (e.g., TBTOH). The Koc at pH < ca. 6.5 can be assumed to be lower than at pH around 7 to 8 due to the predominance of the cationic, more hydrophilic form of tributyltin at pH ca. < 6.5.

The partitioning coefficient can be expected to vary along the whole range of environmentally relevant pH due to the speciation behaviour of TBT. Ma et al. (2000 as cited in GDCh, 2003) observed partitioning in water-sediment sorption tests using tributyltin chloride as test substance and adjusting individual test systems to a pH between 1.5 and 11.5. Partitioning between porewater and water was highest within pH of 7.5 – 8 decreasing below and beyond this range.

For the comparison, Koc for predominantly hydrophobics is predicted at 2400 based on the logKow of 4.05 according to the TGD. PCKOWIN v1.66 predicts a Koc of 3.7×10^{7} for TBTO, but it is likely, that this program does not take into account the transformation of TBTO to TBT in water. PCKOWIN v1.66 predicts for tributyltin (CAS 20763-88-6) a Koc of 9950 and for tributyltin chloride (CAS 56573-85-4) and tributyltin hydroxide (CAS 1067-97-6) a Koc of 15 010.

Based on the information described above, TBTO (more precisely its aqueous transformation product TBT) is expected to be very slightly mobile in sediment and soil in the pH-range of ca. 6.5 to 8 based on the experimental and estimated adsorption coefficients and its dissociation behaviour. The adsorption potential to sediment and soil can be expected to be significantly lower at pH < 6.5 and pH > 8.

4.2.2 Volatilisation

Based on the vapour pressure provided in Table 1, TBTO has a very low volatility. An estimated Henry’s Law coefficient has been reported to be 2×10^{-5} kPa mol^{-1} (GDCh, 1988) indicating that the substance is only slightly volatile from aqueous surfaces. Volatilisation to air is therefore assumed to be not a relevant route of distribution for TBTO.

4.2.3 Long-range environmental transport

Due to the fast estimated atmospheric degradation and the very low volatility, TBTO is not expected to be susceptible to long-range transport via air in vapour phase.

4.3 Bioaccumulation (B)

It is noted, that due to the transformation of TBTO in aqueous solution to TBT species, and as TBTO cannot be analysed in aqueous solution (GDCh, 2003; WHO, 1990), the experimental results presented generally refer to TBT.

4.3.1 Screening data

Due to the dissociation behaviour of tributyltin cation, it can be expected, that its bioaccumulation potential is lower at pH –range below its pKa (ca. 6.5), whereas its undissociated, more hydrophobic forms (TBTOH and TBTCl) predominate at a pH-range above this value up to the point where an anionic species is formed.

4.3.2 Measured bioaccumulation data

Experimental bioaccumulation data of various aquatic species have been reviewed by, e.g., WHO (1990) and GDCh (2003 and 1988).

BCFs for whole fish in experiments using TBTO as test substance at levels below its water solubility and an appropriately long exposure time (8 weeks) have been reported by Yamada and Takayanagi (1992, as cited in GDCh, 2003) for *Pargus major* (11 000), *Mugil cephalus* (3 000) and *Rudarius ercodes* (3 600) and by Ward et al. (1981 as cited in WHO, 1990) for *Cyprinodon variegatus* (2 600). Metabolism seems to take place in fish according to several studies, where additional butyltin compounds have been analysed (e.g., Ward et al., 1981 as cited in WHO, 1990). Depuration half-lives in the study of Yamada and Takayanagi (1992, as cited in GDCh, 2003) were between 7 and 29 days.

Among invertebrates, annelids and crustaceans exhibit bioaccumulation factors around 1000, while molluscs and particularly predatory prosobranchs have had concentration factors of 10 000 to 100 000 in a variety of laboratory and field studies (GDCh, 2003).

4.3.3 Other supporting information

Data not reviewed for this report.

4.3.4 Summary and discussion of bioaccumulation

Based on the reviews of WHO (1990) and GDCh (2003), experimental BCFs in whole fish > 2000 were determined in studies with appropriately low test concentrations and long exposure periods. Bioaccumulation potential of molluscs and prosobranchs seems to be even higher based on various field and laboratory studies. Due to the dissociation behaviour, high bioaccumulation potential is generally expected at pH > 6.5, whereas in the acidic range a lower bioaccumulation potential can be anticipated due to the predominance of the ionised, more hydrophilic form of tributyltin.

Similarly, in the basic pH –range, the accumulation potential is expected to decrease from the point, where anionic species of TBT start to dominate.

5 HUMAN HEALTH HAZARD ASSESSMENT

Data not reviewed for this report.

6 HUMAN HEALTH HAZARD ASSESSMENT OF PHYSICO-CHEMICAL PROPERTIES

Data not reviewed for this report.

7 ENVIRONMENTAL HAZARD ASSESSMENT

7.1 Aquatic compartment (including sediment)

Endocrine effects have been observed amongst various aquatic species, the review of which has been provided, e.g., in GDCh (2003), RPA (2003) and Vos et al. (2000).

A large dataset exists for TBT with standard acute and chronic studies at three trophic levels. The lowest reliable chronic NOEC for TBT was identified in the risk assessment of organotin compounds (RPA, 2003 and 2005) to be 0.06 µg Sn l^{-1} for *Daphnia magna* (Kühn et al., 1989 as cited in RPA, 2003). This corresponds to ca. 0.15 µg TBT l^{-1}.

Based on the review of European Commission (2005), the mollusc species *Nucella lapillus* (dog whelk) is the most sensitive species to tributyltin compounds. A NOEC of 0.001 µg l^{-1} was obtained in a 360-d study looking at imposex. European Commission (2005) derived a SSD curve using 24 NOECs in total from several species of fish, crustaceans, molluscs, insects and echinoderms. A 5th percentile of the SSD was calculated to be 0.00083 µg TBT l^{-1}. The highest NOEC-value of the data used for the SSD was 18 µg TBT l^{-1} from a 4-day test with *Chlorella pyrenoidosa*.

7.1.1 Toxicity test results

7.1.1.1 Fish

Acute toxicity

Long-term toxicity

7.1.1.2 Aquatic invertebrates

Acute toxicity

Long-term toxicity

7.1.1.3 Algae and aquatic plants

7.1.2 Sediment organisms

Data not evaluated for this report.

7.1.3 Other aquatic organisms

Data not evaluated for this report.

7.2 Terrestrial compartment

Data not evaluated for this report.

7.3 Atmospheric compartment

Data not evaluated for this report.

8 PBT AND vPvB

8.1 PBT, vPvB assessment

Persistence: Bis(tributyltin) oxide (TBTO) transforms in aqueous solution to tributyltin (TBT). The form in which TBT is present in the environment, depends much on pH, but also on other abiotic conditions. Various degradation studies in water show half-lives between few days to several months. Half-lives of > 1- 15 years have been observed in sediment degradation experiments. It is considered that TBT fulfils the P criterion.

Bioaccumulation: Experimental reliable BCFs are available for four fish species and they all are > 2000. The bioaccumulation potential is expected to be dependent on the pH of the exposure medium. At pH of ca. < 6.5 bioaccumulation potential is based on the speciation of TBT lower than around pH 7. In the basic pH –range, bioaccumulation potential decreases when the anionic species of TBT start to predominate. Accumulation of TBT compounds to invertebrates has been observed in various studies. The accumulation/concentration factors in certain molluscs have been observed in a range of 10 000 to 100 000. It is considered that TBT fulfils the B criterion.

Toxicity: A large data set on standard and non-standard long-term effect studies is available for TBT compounds. NOECs are generally in the range of < 1 to several ten µg TBT l^{-1}. In addition to the very high toxicity in relation to conventional toxicity end-points, TBT compounds elicit effects in the endocrine systems of aquatic organisms at the ng to µg TBT l^{-1} –level. TBT compounds are considered to fulfil the T criterion for ecotoxicity. Furthermore, TBTO fulfils the T criterion for human health through the hazard classification of tributyltin compounds (T; R48/R23/R25).

Summary: Tributyltin, the aqueous transformation product of bis(tributyltin) oxide, fulfils the P, B and T criteria. Furthermore, bis(tributyltin) oxide fulfils the T criterion for human health due to the hazard classification of tributyltin compounds. Bis(tributyltin) oxide is considered to be a PBT substance.

9 INFORMATION ON USE AND EXPOSURE ALTERNATIVES AND RISKS

9.1 Information on exposure

A risk assessment according to EU guidance has been conducted for TBT in the frame of the work of RPA (2005 and 2003). An impact assessment of potential restrictions on the marketing and use of certain organotin compounds is in process RPA (2007). These reports contain relevant information on uses and exposure in the EU. Further information on use and exposure has been obtained from the SPIN database (Substances in Preparations In Nordic countries) and several monitoring reports.

Two producers/importers have provided data under Regulation 93/793/EEC. TBTO among other triorganostannic compounds have been formerly used as biocides in antifouling paints and coatings and for other biocidal uses.

In the frame of Directive 76/769/EEC (amended by Regulation 782/2003/EC), the use of organostannic compounds (no CAS or EINECS entry) is forbidden in the following uses :

1. as substances and constituents of preparations when acting as biocides in free association paint.
2. as substances and constituents of preparations which act as biocides to prevent the fouling by micro-organisms, plants or animals of:
   (a) all craft irrespective of their length intended for use in marine, coastal, estuarine and inland waterways and lakes;
   (b) cages, floats, nets and any other appliances or equipment used for fish or shellfish farming;
   (c) any totally or partly submerged appliance or equipment.
3. as substances and constituents of preparations intended for use in the treatment of industrial waters.

Regulation (EC) No (782/2003) of the European Parliament and the Council also prohibits the use, as from 1 July 2003, of organotin compounds as biocides in anti-fouling systems on EU ships and, as from 1 January 2008, on any ship entering EU waters. The International Maritime Organisation (IMO) has also agreed a global phase out of TBT in shipping, which will enter into force in Spetember 2008.

According to RPA (2007) antimicrobial products are produced based on tributyltin oxide and tributyltin maleate (formulated at concentrations around 1% and 25% respectively and generally further diluted by mixing with other ingredients). These products are sold only to industrial customers for use in manufacturing (and are not sold to consumers, nor are they sold for apparel applications). Applications for these products include:

- polyurethane foam, where it is added during the ‘blowing’ process and is subsequently incorporated into the polymer matrix;

- incorporation into various other polymers that are used for products such as flooring, tiles and carpeting;

- back-coating of textiles used in upholstery (co-applied with a polymeric binder on the rear of the fabric); and

- a small amount used in treatment of feather and down.

In the review of the Biocidal Products Directive, these 'non-notified' uses should cease before 1 September 2006. TBTO will not be evaluated under the Biocides Directive (98/8/EEC), as no data submissions were provided within the deadlines set under the Review Programme of the Directive. Hence, any potential biocidal use of TBTO under Annex I of the Biocides Directive is not in sight. The Biocidal Products directive does, however, not apply to imported TBTO-containing preparations, if the preparation is not within the definition of a biocidal product, nor does it apply to imported articles treated with TBTO as a biocide.

Further marketing and use restrictions are currently being considered in the framework of directive 76/769/EEC (to be included in Annex XVII of REACH from 1 June 2009) concerning a. o. all tri-substituted compounds (including TBTO) so that these shall not be placed on the market or used in articles. The proposed restrictions covers the use in articles and not as preparations.

Tri-substituted organotins are also used as intermediates in the production of other chemicals. Releases may be possible in connection with the production sites or from residuals/impurities in the final products.

Tributyltin compounds (CAS 688-73-3) are identified as "hazardous priority substances" under the Water Framework Directive (2000/60/EU). The objectives of this regulatory instrument apply in principle to any use of these compounds.

According to ESPA (2005), tributyltin compounds are not used as stabilisers in plastics, as they are not technically applicable for this use. However, tributyltins can be present as impurities in mono- and dibutyltin stabilisers for plastics, but their content is voluntarily controlled by industry to ≤ 0.67 % (as tin) (OECD, 2007). This impurity presumably originates from tributyltin compounds used as intermediates for the stabiliser production, not from TBTO. Tetra-substituted tins used as an intermediate contain significant amounts of tri-substituted tins according to RPA 2007.

Use volumes and releases:

Organotin quantities sold in the EU-15 MS were ca 19,000 t in 2002 (RPA 2005). The quantities estimated for tri-substituted organotins for 2002 (table 2.2; copied from RPA 2005) were < 100 t /yr for biocides, 1,250 t/yr for biocides in antifouling paints, pesticides 100 t/yr and for synthesis <150 t/yr. It is also noted that "*ETINSA has adviced that the total quatity of tri-substituted tins for use as an intermediate in 2004 was substantially higher than the estimate for 2002. Although not clarified, this could perhaps* *be because the quantities present in tetra-substituted tins were excluded*.” As of 2001, less than 100 t/yr of tri-substituted organotins were used as biocides in wood preservatives, primarily in the UK, France and Spain with an quantity of less than 50 t /yr of TBTO .

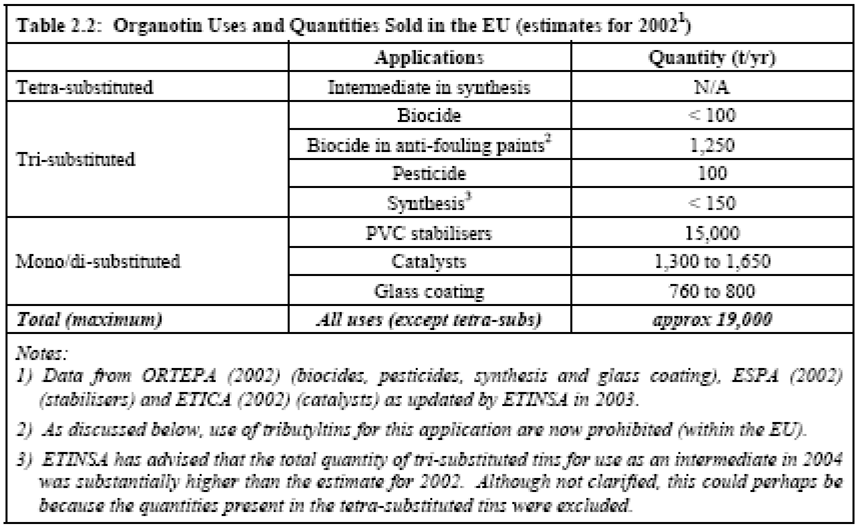


Table 2.2: Organotin Uses and Quantities Sold in the EU (estimates for 2002[1])

	Applications	Quantity (t/yr)
Tetra-substituted	Intermediate in synthesis	N/A
Tri-substituted	Biocide	< 100
	Biocide in anti-fouling paints[2]	1,250
	Pesticide	100
	Synthesis[3]	< 150
Mono/di-substituted	PVC stabilisers	15,000
	Catalysts	1,300 to 1,650
	Glass coating	760 to 800
Total (maximum)	*All uses (except tetra-subs)*	*approx 19,000*

Notes:

1) Data from ORTEPA (2002) (biocides, pesticides, synthesis and glass coating), ESPA (2002) (stabilisers) and ETICA (2002) (catalysts) as updated by ETINSA in 2003.

2) As discussed below, use of tributyltins for this application are now prohibited (within the EU).

3) ETINSA has advised that the total quantity of tri-substituted tins for use as an intermediate in 2004 was substantially higher than the estimate for 2002. Although not clarified, this could perhaps be because the quantities present in the tetra-substituted tins were excluded.

Recent information on the total use of TBTO in the Nordic countries has been derived from the SPIN database. While no quantities have been reported for Sweden and Finland from 2000, high amounts of TBTO have been used in Norway 786 t (2001) followed by Denmark 68 t (2001), see figure 1 below. The main industrial use registered for TBTO in the last years is the manufacture of “other transport equipment”, namely “building and repairing of ships and pleasure and sporting boats”. However high amounts of TBTO (> 800 t/a) have also been used in 2000-2001 in Norway and Denmark for “manufacturing of chemicals and chemical products”. Figure 2 shows that even if the total amount is significantly decreased in Denmark, the number of preparations has increased.

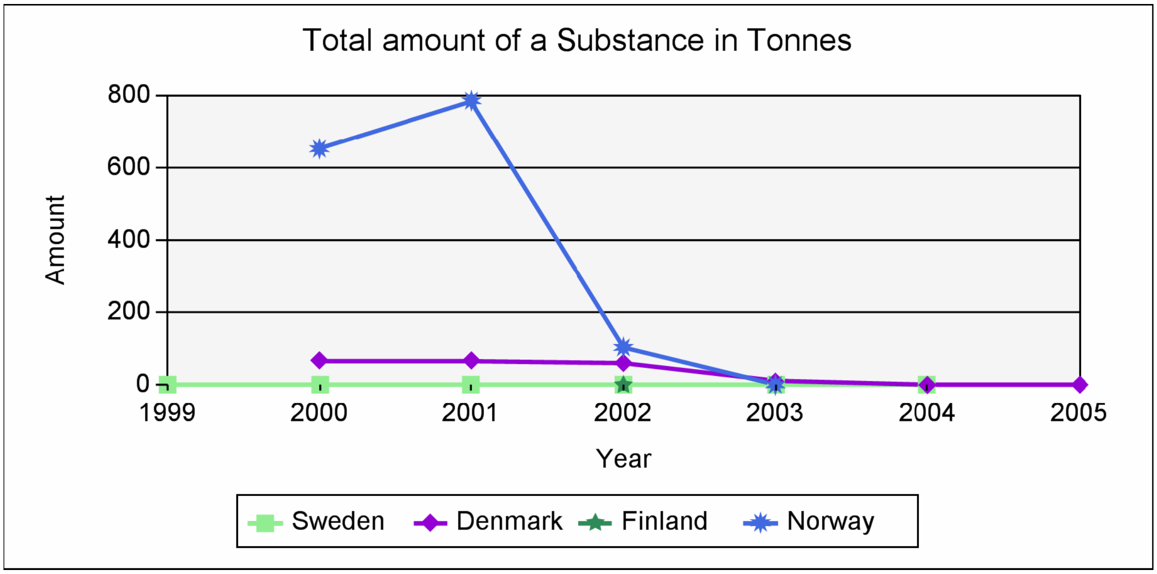


Figure 1: Total amount of a TBTO in tonnes in Nordic countries

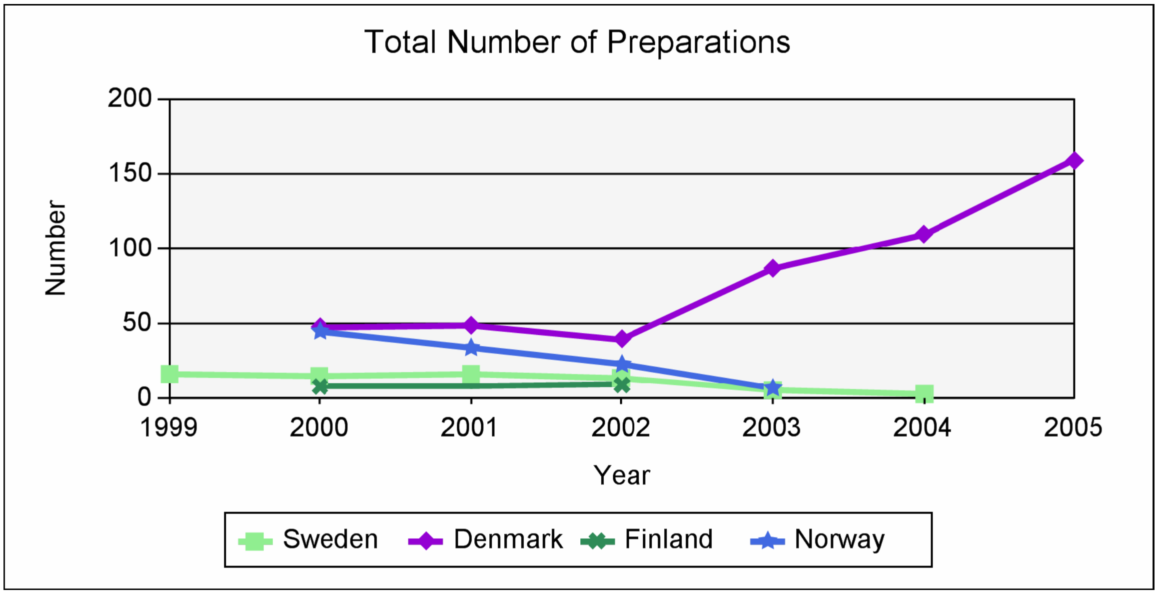


Figure 2: Total number of preparations containing MTBO

The major previous releases of tri-substituted tin compounds related to antifoulant and biocide uses and these have ceased as a consequence of the restrictions imposed on the uses. Run-off from shipping docks not properly managing their discharges may continue for some years. Contaminated sediments will remain a source for resuspension of the compounds as well.

Release figures from remaining commercial uses are not readily available. Total discharges reported by Germany, Portugal, Spain and the UK to EPER in 2001 and 2004 indicate discharges of organotin compounds of 1.6 and 3.4 tonnes respectively, it is unclear exactly which compounds that have been reported. The reported discharges related mainly to the metal industry, the basic organic chemicals industry and the pulp and paper industry. This may indicate that discharges from regulated point sources may not be negligible.

Measured levels in the environment:

A compilation of monitoring data have been performed in risk assessment studies on targeted consumer applications of certain organotin compounds RPA (2005). Additional information from certain Norwegian and Austrian monitoring reports has been added. Measured data on TBT, DBT and MBT are referred. Levels of DBT and MBT may result of degradation of TBT. It has to be recognised that e.g. DBT is used in substantial amounts as stabilisers in PVC and therefore has its own source of emission.

Water compartment (including sediment):
Summer *et al* (1996), in their review of the available data, refer to measured concentrations of mono and dibutyltin compounds which were thought to relate mainly to degradation of tributyltin from use on boats as an anti-fouling paint.

Hoch (2001) provides a review of concentrations of various organotin compounds found in the environment. However further investigation showed that higher values (for sediments) are readily available and an example has been included together with the results from Summer et al (1996)) in table 3.46, copied from RPA 2005.

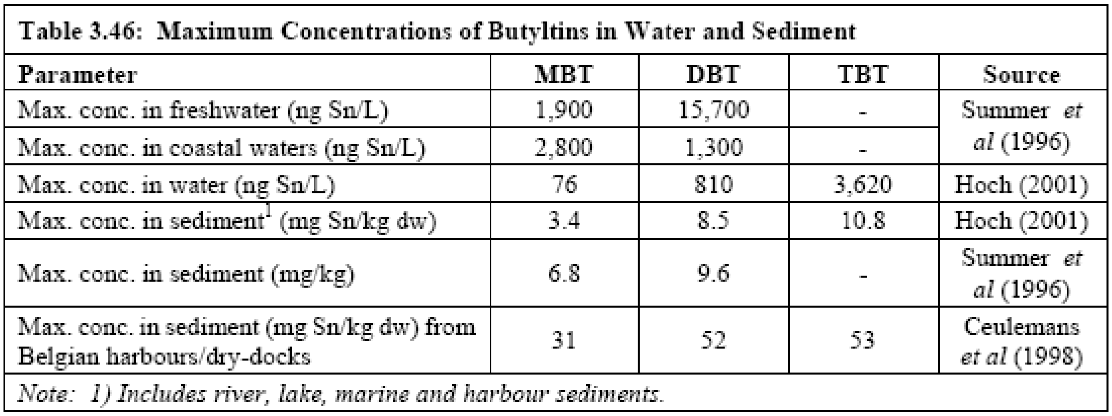


Table 3.46: Maximum Concentrations of Butyltins in Water and Sediment

Parameter	MBT	DBT	TBT	Source
Max. conc. in freshwater (ng Sn/L)	1,900	15,700	-	Summer *et al* (1996)
Max. conc. in coastal waters (ng Sn/L)	2,800	1,300	-	
Max. conc. in water (ng Sn/L)	76	810	3,620	Hoch (2001)
Max. conc. in sediment[1] (mg Sn/kg dw)	3.4	8.5	10.8	Hoch (2001)
Max. conc. in sediment (mg/kg)	6.8	9.6	-	Summer *et al* (1996)
Max. conc. in sediment (mg Sn/kg dw) from Belgian harbours/dry-docks	31	52	53	Ceulemans *et al* (1998)

Note: 1) Includes river, lake, marine and harbour sediments.

In a review of TBT monitoring data (BUA, 2003) from the late 1980s/early 1990s, typical median values of around 50 ng TBT/L were found in rivers, lakes, estuaries and coastal waters at various locations in Germany, UK, France, Italy, Netherlands and Switzerland with typical maximum values of over 1,000 ng TBT/L found in marinas. More recent data from France for 2001 shows levels of butyltins (dominated by MBT) to be generally in the range 0-10 ng Sn/L in rivers which have negligible boating. However, considerable monthly variations were observed leading to occasional higher values due, perhaps, to the periodic use of TBT biocides in agriculture and/or the local leather industry. DBT and TBT were also detected in sediment samples at concentrations of, typically, 1-5 µg Sn/kg (together with higher concentrations of MBT).

There is a general consensus that TBT concentrations in surface waters significantly declined in many water bodies following the enactment of TBT legislation in various countries such as Japan (Japanese Ministry of Environment, 2001; Sekizwa *et al*, 2003), Switzerland (Fent & Hunn, 1995), the United States (Hall *et al*, 2000), and the United Kingdom (Waldock *et al*, 1999). Areas where concentrations have not declined as rapidly are generally limited to marinas and other areas where larger ships are permitted to dock.

Declining trends in sediment TBT concentrations were also identified after TBT legislation was enacted. However this trend was most pronounced at locations with very high initial TBT concentrations. Nevertheless, there are indications that in many German rivers, TBT sediment concentrations are now below 0.005 mg TBT/kg dry weight (BUA, 2003).

Similar findings for both seawater and sediment are reported for the coastal waters (including harbours and marinas) of Mediterranean countries (UNEP, 2002). Furthermore, UNEP (2002) reports that “the large predominance of the organotin degradation products over the parent compounds in the Western Mediterranean suggests that there are almost no recent inputs of these compounds” (referring to TBT and TPT).

Terrestrial Compartment

Work by Huang *et al* (2004) in upland forested sites in Germany indicates MBT, DBT and TBT surface concentrations of up to 30, 0.6 and 0.1 µg Sn/kg dw respectively which decrease with soil depth.

Waste Water Treatment

Concentrations of butyltin compounds in sewage sludge from waste water treatment plants (WWTPs) have also been measured. Values reported are up to 0.77 and 2.22 mg/kg dry weight (Summer *et al*, 1996). Fent (1996) presents results from a number of Swiss plants which demonstrate that butyl organotins are progressively removed during waste water treatment as shown in table 3.47, copied from RPA 2005. Fent (1996) notes that the available data for Switzerland suggest that the concentrations remained constant over the mid-1980s to the mid-1990s.

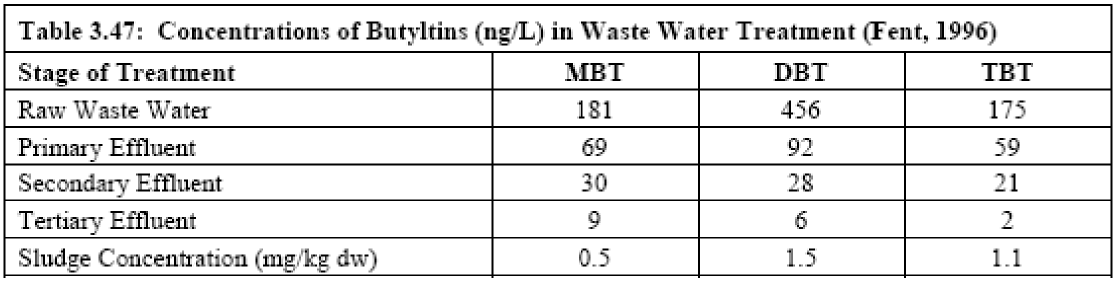


Table 3.47: Concentrations of Butyltins (ng/L) in Waste Water Treatment (Fent, 1996)

Stage of Treatment	MBT	DBT	TBT
Raw Waste Water	181	456	175
Primary Effluent	69	92	59
Secondary Effluent	30	28	21
Tertiary Effluent	9	6	2
Sludge Concentration (mg/kg dw)	0.5	1.5	1.1

Sampling from 158 German sewage plants in 2001/02 suggests a decline in sludge concentrations compared to those reported above (as reported in BUA, 2003). The results are summarised in Table 3.48, copied from RPA 2005.

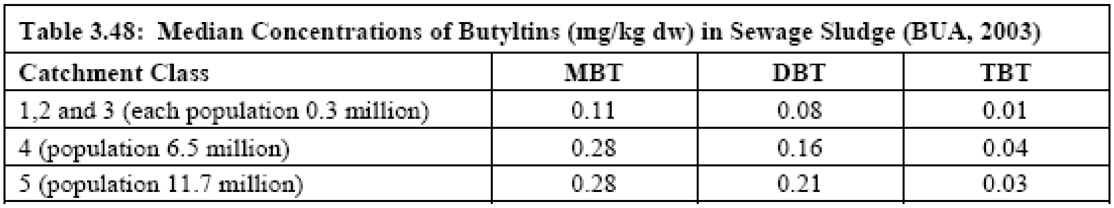


Table 3.48: Median Concentrations of Butyltins (mg/kg dw) in Sewage Sludge (BUA, 2003)

Catchment Class	MBT	DBT	TBT
1,2 and 3 (each population 0.3 million)	0.11	0.08	0.01
4 (population 6.5 million)	0.28	0.16	0.04
5 (population 11.7 million)	0.28	0.21	0.03

In Norway (Aquateam, 2006) sewage sludges from four municipal sewage treatment plants have been analysed for organotin compounds in 2006. Arithmetic mean values ranged from 52 µg/kg dry weight to 35 µg/kg dry weight for TBT, the results are comparable to levels measured in Sweden in 2002. Analysis of sewage sludge of STPs in Sweden (Sternbeck et al., 2006) shows levels of 20-410 µg/kg dry weight in 1993 compared to 10-96 µg/kg dry weight in 2002, indicating a decrease of TBT in sewage treatment sludge in Sweden from 1993 to 2002.

In Austria 17 sewage treatment plants (14 municipal, 3 industrial) have been analysed for organotin compounds in 2001. Maximum levels of TBT, DBT and MBT of 0.09, 2.0 and 0.53 mg /kg dw respectively in dried sewage sludge are reported by Gangl et al (2001).

Biosphere

Numerous studies have reported levels of butyltins in the biosphere particularly in fish and other aquatic organisms.

BUA (2003) summarises a range of studies of TBT levels found in organisms in Europe's rivers, lakes, estuaries and coastal waters during the 1990s with values typically ranging from around 50 to 5,000 µg TBT/kg fresh weight. The highest values were found in bivalves in marinas in Switzerland with maximum values 9,000 µg TBT/kg fresh weight.

Lower values are reported by Harino *et al* (2005) for the levels of butyltins found in various organisms taken from the Mersey Estuary (Liverpool) in 1997. In all cases, DBT concentration were lower than TBT (and MBT). The mean values were 14.4, 4.0 and 10.8 µg/kg fresh weight for MBT, DBT and TPT respectively suggesting that much of the organotin contamination has decayed.

In deep-sea fish from the Mediterranean in 1996, levels of butyltins were measured in various organs (Borghiand & Porte, 2002). Highest levels were found in the liver with total butyltin concentrations of up to 174 µg Sn/kg liver fresh weight. Although there was great variation amongst species, DBT tended to be more prevalent than TBT (and MBT).

Bortoli *et al* (2003) report rank concentrations in the order TBT, DBT and MBT among samples of six species from 12 locations in the Lagoon of Venice (in 1999/2000) although there is great variation amongst the results. The highest total butyltin levels were found in the mollusc, *M. galloprovincialis*, with mean/max levels of 2,000/8,000 µg/kg dw.

BgVV (2000) reports levels of up to 15 µg DBT/kg fresh weight in crab (from German samples taken in 2000) and up to 940 µg TBT/kg fw in Zebra mussel (from German samples taken in 1999).

Green and Ruus (SFT, report to be published) report levels of up to 2.7 mg TBT /kg dw in 1997 in blue mussels in the inner Oslofjord (Norway), see figure 3. However a decline can be registered to 0.28 mg TBT /kg dw in 2005. Also in the outer Oslofjord varying levels of 0,22-0,02 mg TBT /kg dw have been detected during the monitoring period 1997-2005.

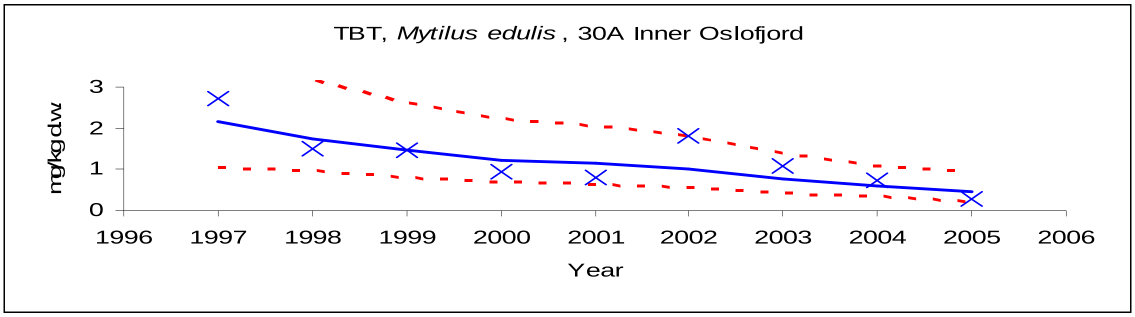


Figure 3: TBT levels in blue mussels in inner Oslofjord , Norway

EFSA (2004) reports that samples of fish and fishery products (intended for human consumption) from several EU countries contain higher levels of organotins in "seafood other than fish” than in fish. For DBT, mean values of 52 and 5.1 µg/kg fresh weight were reported for “other than fish” and fish respectively. For TBT, the corresponding mean values are 60 and 17 µg/kg fresh weight respectively. Since much of the underlying data come from Germany and date from 2000 (SCOOP, 2003), this suggests a decline in DBT/TBT concentrations from the earlier data (again with a German focus) reported in BUA (2003).

Generally low levels of butyltins have been found in humans. Studies in Japan (Takahashi *et al*, 1999) and Denmark (Nielsen and Strand, 2002) produced similar results for butyltins in human livers (although the Japanese concentrations were higher). In both studies, TBT was not detected but significant levels of DBT (up to 76 µg/kg in Japan) and, to a lesser extent, MBT (up to 22 µg/kg in Japan) were detected.
Kannan *et al* (1999) found butyltins (MBT/DBT/TBT) in most of the 32 blood samples from people in Michigan with levels of up to 100 µg/L. However, analysis of more recent eight samples from Germany (Lo *et al*, 2003) found only traces of TBT in human blood (and no MBT/DBT). Similarly, in a sample of 91 volunteers (Meijer *et al*, 2004) across the Netherlands:

- no-one had levels of DBT above the MDL of <0.1 µg DBT/kg blood;
- only 3 had levels of TBT above the MDL of <0.1 µg TBT/kg blood; and
- only 3 had levels of MBT above the MDL of <0.1 µg MBT/kg blood.

DBT and TBT (and MBT) have been detected in house dust. Santillo *et al* (2003) reports maximum DBT and TBT levels in UK samples of 0.66 and 0.31 mg Sn/kg dust respectively whilst Fromme *et al* (2005) report maximum levels of up to 2.85 and 0.03 mg Sn/kg dust for DBT and TBT respectively in Berlin apartments. Al Bitar (2004) reports higher levels from the homes and offices of MEPs in Brussels, with maximum values of 3.11 and 1.02 mg Sn/kg dust for DBT and TBT respectively. Uhl et al (2004) report maximum levels of TBT, DBT and MBT in house dust from apartments and offices in Austria of 0.26, 24 and 20 mg/kg dust.

9.2 INFORMATION ON ALTERNATIVES

No information has been available on identified alternatives

10 OTHER INFORMATION

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