TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVB SUBSTANCES

RESULTS OF THE EVALUATION OF THE PBT/VPVB PROPERTIES OF:

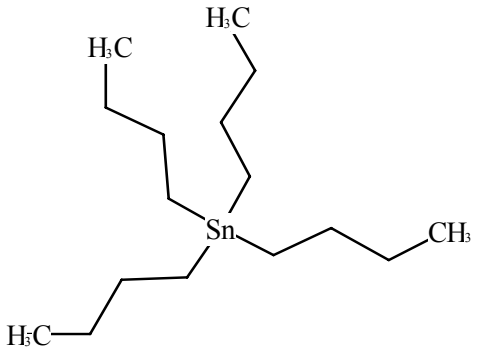
Substance name: Tetrabutyltin

EC number: 215-960-8

CAS number: 1461-25-2

Molecular formula: C16H36Sn

Structural formula:



Summary of the evaluation:

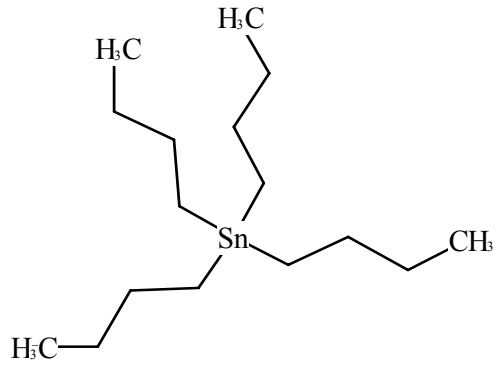
Tetrabutyltin is considered as a substance containing a PBT impurity and as a substance forming a PBT substance.

Pure tetrabutyltin is considered as a PBT –substance based on screening data. The substance fulfils the screening P/vP criteria, the screening B criterion and the screening T criterion. However, based on an experimental bioaccumulation study, in combination with a weight of evidence approach taking into account molecular size and solubility, it can be concluded that tetrabutyltin itself is most probably not meeting the B criterion. Tetrabutyltin forms tributyltin, which is a PBT substance (see PBT summary fact sheet nr. 95). Furthermore, technical grade tetrabutyltin contains tributyltin in a concentration of 15-30 %.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name: Tetrabutyltin
EC Number: 215-960-8
CAS Number: 1461-25-2
IUPAC Name: Stannane, tetrabutyl-
Molecular Formula: C16H36Sn



Structural Formula:
Molecular Weight: 347.18
Synonyms: TTBT (abbreviation); Stannane, tetrabutyl-; Tetra-n-butyltin; Tetrabutylstannane; Tin, tetrabutyl-

1.1 Purity/Impurities/Additives

According to Parametrix, Inc (2003) tetrabutyltin contains tributylethyltin, tributyltin chloride, dibutyltin dichloride and tributyl-2-ethylhexylthin dibutyl-2-ethylhexylthi chloride. The concentrations of these impurities are not mentioned by Parametrix, Inc (2003). According to ETINSA (2003), tetrabutyltin contains as impurity 15-30 % tributyltin. This latter substance is considered a PBT substance (see summary fact sheet nr. 95).

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	liquid	

	and 101.3 kPa		
VII, 7.2	Melting / freezing point	-97 °C	Secondary sources cited in Parametrix, 2003 (data not evaluated)
VII, 7.3	Boiling point	127-145 °C at 10 mmHg ca. 140 °C at 10 hPa	Secondary sources cited in Parametrix, 2003 (data not evaluated)
VII, 7.5 VII, 7.7	Vapour pressure	0.0014 hPa at 20 °C (1) 0.016 mmHg at 25 °C (= 0.021 hPa)	Witco GmbH, 1989 as cited in European Commission, 2000 (data not evaluated) MPBPWIN v1.40 using BP of 269.7 °C (data not evaluated)
VII, 7.1	Water solubility	< 96.4 µg/l at 20 °C (2) [8.8 mg/l at 20 °C] (3) 11.5 µg/l at 25 °C 0.034 µg/l at 25 °C 0.14 µg/l at 25 °C	Crompton Corp., 2004 Schering AG as cited in Parametrix, 2003 (data not evaluated) Estimated (WaterFrag) Estimated (WSKOWWIN with the use of ClogP value) Estimate from Log Kow (WSKOW v1.41)
VII, 7.8	Partition coefficient n-octanol/water (log value)	[> 5.18] (4) 10.01 9.37	Crompton Corp., 2004 Estimate (ClogP v5) Estimate (KOWWIN v1.67)
	Dissociation constant	-	

(1) The used method is not clear, so nothing can be stated about the role of impurities in this determination.

(2) Based on the study report it is not possible to estimate how close the actual value would be of the unbounded result.

(3) Method OECD 105, pH ca. 6.2; .analysis method ICP spectrometry, which determines the total conc. of tin in the medium .Hence the result has probably been caused mainly by the more soluble impurities contained in TTBT

(4) Method OECD 107, analysis method GC-FID. It is noted, that the test method is not suitable for this compound, as the predicted log Kow is > 5.

2 MANUFACTURE AND USES

One producer has provided information under Regulation 93/793/EEC. According to ETINSA (2003) and RPA (2005), tetrabutyltin is used in Europe solely as an on-site and transported intermediate for the manufacture of mono- and dibutyltin stabilizers and the number of sites where the substance is used is less than 10 sites in Europe. According to RPA (2005), tetra-substituted organotin compounds are produced at two sites in Europe.

3 CLASSIFICATION AND LABELLING

The substance is not classified under Directive 67/548/EEC.

4 ENVIRONMENTAL FATE PROPERTIES

4.1 Degradation (P)

4.1.1 Abiotic degradation

Indirect photochemical degradation in the atmosphere is considered to be fast based on the estimated half-life of 6.8 hours for the reaction with OH-radicals using AOP v1.91 (24 h day^{-1}; $5*10^5$ OH^- cm^{-3}).

Crompton Corp. (2004) reported on a hydrolysis test according to OECD 111. Tetrabutyltin was tested in the definitive test at pH 4 and pH 7 at a temperature of 50 ± 0.5 ºC. Tetrabutyltin concentration was monitored using GC-FID. The nominal test concentration was 0.04 mg/l, which was probably too high considering the estimated water solubility and the standard requirements (initial conc. must be lower than half of the solubility). No significant disappearance was observed at pH 7 in the definitive test over a time period of 160 hours and pH 9 (pretest result). At pH 4, a decrease was observed, but the authors concluded that the decrease at pH 4 was more probably caused by the fact, that the test was carried out at the limit of analysis accuracy.

4.1.2 Biotic degradation

A reliable ready biodegradability test according to OECD 301 D resulted in 2% degradation (measured as BOD) at a test concentration of 2 mg/l in 28 d using domestic sludge as inoculum. Chloroform was used as solvent (stock solution concentration 56 mg TTBT/ml). Purity of TTBT was 99.93%.

Another OECD 301 D –test showed < 10 % degradation in 28 days. A test concentration of 2 mg/l and adapted domestic sludge inoculum were employed (Schering AG, 1994).

It is noted, that the study reports were not available to the Rapporteur for evaluation.

BIOWIN v4.02 provides the following estimates: BIOWIN2 = 0.99; BIOWIN3 = 3.6 and BIOWIN6 = 0.00.

4.1.3 Other information [1]

In a field monitoring study investigating the consequences of an unintended spill containing mainly tetrabutyltin and tributyltin, both tetrabutyltin and tributyltin disappeared with half-lives in the order of 20 to 40 days from river bed sediment. The initial concentration of tetrabutyltin was > 10 000 µg/kg in surface water sediments in depositional areas downstream of the release. The disappearance of the higher butylated tin species was monitored by analyzing with HPLC-MS the concentration in sediment samples in 1-3 following years after the spill. The disappearance coincided with the emergence of di- and monobutyltin and especially inorganic tin (Landmeyer et al., 2004). It is noted, that the conditions of this study are not comparable with the conditions of degradation simulation tests, as the concentrations after the spill were significantly higher than in normal environmental conditions. However, the study suggests that tetrabutyltin is dealkylated via tributyltin to di- and monobutyltins and finally to inorganic tin (no actual mass balance was presented to confirm the route).

[1] For example, half life from field studies or monitoring data

4.1.4 Summary and discussion of persistence

Tetrabutyltin is considered based on two available standard (OECD 301 D) ready biodegradation tests not readily biodegradable. The substance is not readily biodegradable based on the QSAR – predictions, although not persistent, either. Disappearance has been observed in a field monitoring study at very high concentrations in sediment of freshwater bodies after a spill. The study also suggests that tetrabutyltin is degraded to tri-, di- and monobutyltins and finally to inorganic tin. No hydrolysis was observed in an OECD 111 –test. It is concluded, that tetrabutyltin based on the present data is expected to be persistent in normal exposure situations, although it is likely that the substance undergoes dealkylation at an unknown (slow) rate.

4.2 Environmental distribution

Data on pure tetrabutyltin have not been reviewed for this report.

4.2.1 Adsorption

4.2.2 Volatilisation

4.2.3 Long-range environmental transport

4.3 Bioaccumulation (B)

4.3.1 Screening data

The estimated log K_{ow} for tetrabutyltin is around 10 (see Table 1).

4.3.2 Measured bioaccumulation data

CERI (2003; cited also with CITI, 2003) reports on a flow-through bioconcentration test according to OECD 305 with *Cyprinus carpio* (average weight: 24.1 g, average total length: 9.6 cm, average lipid content: 3.8%). Nominal test concentrations of 0.5 and 5 µg/l were introduced using HCO-40 as dispersant. Purity of the test material was reported as 95.2%. The exposure concentrations were measured during the exposure period of 12 weeks and remained within 80 % of the nominal concentration. Test temperature was 25 ± 2 ºC, and analysis was carried out with GC-MS. The BCFs were determined as the relation of the measured exposure concentrations and measured concentrations in fish at weeks 2, 3, 4, 6, 8, 10 and 12 and they ranged between 38 and 97 for the higher exposure level and between 127 and 310 for the lower exposure level (see Figure 4.1). A re-analysis of the data shows:

- a very good fit of the data especially at the lower concentration of ca. 0.44 µg/l.
- a dynamic BCF value of 293 L/kg at the lower concentration and a BCF value of 80 L/kg at the higher concentration

The fact that the BCF values between the two concentrations that differ by a factor of 11 are only different by a factor of 3.7 could mean that the solubility in at least the lowest concentration is not

exceeded. If in the highest test concentration the solubility is used instead of the aqueous concentration, equal BCF values would be obtained with an approximate water solubility of 1.3 µg/l, which is in the range of the estimated water solubilities in Table 1.

From visual inspection of the figure and assuming a linear uptake during the first two weeks of exposure, an uptake rate constant k_1 can be deduced of ca 100 l/kg/d and ca 33 l/kg/d for the low and high exposure concentrations, respectively. These values are a little lower but quite comparable to what would be expected for fish of this weight (190 l/kg/d). When taking the half-life of 2.4 weeks an uptake rate constant k_1 of 0.50 l/kg/d in the lowest test concentration and 0.20 l/kg/d in the highest test concentration can be deduced. These latter values are quite low compared to what would be expected for fish of this weight (190 l/kg/d). This **could** be caused by either a large overestimation of the real aqueous concentration (solubility is much lower than the exposure concentrations) or both the low uptake and depuration rate constants are caused by a slow diffusion across the membranes. The latter assumption is a plausible one as the estimated log K_{ow} values are in the range of the cut-off value for limited uptake.

To clarify the uncertainty with regard to the BCF study (and some results of toxicity experiments as well), the water solubility of the compound needs to be determined more accurately.

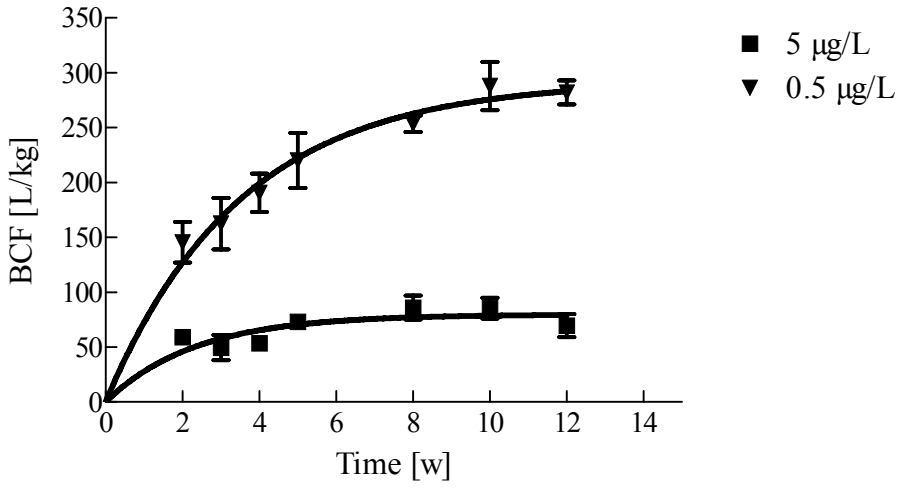


Figure 4.1 BCF during the OECD 305 flow-through bioconcentration test.

4.3.3 Other supporting information[2]

No data available.

4.3.4 Summary and discussion of bioaccumulation

The predicted log K_{ow} –values (9.37 and 10.01) are at the borderline of the indicator trigger of 10 for limited uptake. The assessment of bioaccumulation is hampered by the difficulty to measure

[2]For example, measured concentrations in biota

water solubility and log K_{ow} accurately. The available OECD 305 bioconcentration test with fish gave BCF-values up to 310, but the test is not considered reliable as the actual water solubility of the substance is not known.

5 HUMAN HEALTH HAZARD ASSESSMENT

Data not reviewed for this report.

6 ENVIRONMENTAL HAZARD ASSESSMENT

6.1 Aquatic compartment (including sediment)

6.1.1 Toxicity test results

6.1.1.1 Fish

Acute toxicity

Table 6.1 Available data on acute toxicity of tetrabutyltin to fish. For references, see Parametrix Inc. (2003).

Organism	Test duration	Method	Result	Analytical	Comments	Reference
Pimephales promelas	96 h	USEPA	LC/EC50 = 45.2 µg/l	Gas-liquid chromatography	Flow through exposure regime. A stock solution (98 µg/l) was prepared and the test was conducted using a liquid-liquid equilibrator. Test concentrations were analyzed daily by gas liquid chromatography. Analytical method recovery was 92.3%.	Geiger et al. 1990
Pimephales promelas	96 h	USEPA and NJDEP[1]	LC50 = 185 µg/l	None	Static test. Nominal concentrations tested. Stock solution prepared in acetone. No analytical confirmation of exposure concentrations. Authors reported that the 96h LC50 is between 100 and 300 ppb. It is noted, that the result is not reliable, as the LC50 is above the expected water solubility.	Princeton Aqua Science 1982
Oryzias latipes	48 h	OECD 203	LC50 = 5.21 mg/L	None	Nominal concentrations tested. Stock solution prepared in DMSO. Study was conducted for 96 hours, but only the 48 hour results are reported. No information on control and test organism response, replication, control water characteristics or exposure conditions. Final concentration of vehicle not provided. It is noted, that the result is not reliable, as the LC50 is far above the expected water solubility.	Nagase et al. 1991

Organism	Test duration	Method	Result	Analytical	Comments	Reference
Leuciscus idus	24 h	DIN 38 412, Teil 15	LC50 = 9 μg/l	GC-FID	Filtered saturated solution. The aqueous solution was acidified with 47% hydrobromic acid and extracted with 0.1% tropolon in toluene. Extracts were derivatized with pentyl-magnesium bromide and methylmagnesium chloride, dissolved in Grignard compound and heated. Limits of detection in water were 0.3-1.5 μg/l. Details of the toxic effects were not reported other than the lethal concentration. In the study it is indicated that the toxicity might be partly attributed to tributyltin impurities	Steinhaeuser et al. 1985

[1]New Jersey Department of Environmental Protection

Long-term toxicity

No data available.

6.1.1.2 Aquatic invertebrates

Acute toxicity

Table 6.2. The available data on the toxicity of tetrabutyltin to invertebrates. For references, see Parametrix Inc. (2003).

Organism	Test duration	Method	Result	Analytical	Comments	Reference
Daphnia magna	48 h	OECD 202	EC50 = 1.3 mg/L	GC/MS	Stock solution prepared in 1% Tween 80-acetone. Widely variable relationship between nominal and measured concentrations noted. TTBT was of 99.93 % purity (0.07% tributyltin chloride). The study is considered as not reliable as the EC50-value is ca. 1000 higher than the expected water solubility.	Schering AG 1995
Daphnia magna	24 h	OECD 202	EC50 = 1.55 mg/L	None	Nominal concentrations used. Stock solution prepared in acetone. Actual test concentrations and control response not reported. The study is considered as not reliable as the EC50 is ca. 1000 times higher than the expected water solubility.	Vighi and Calamari 1985

Organism	Test duration	Method	Result	Analytical	Comments	Reference
Daphnia magna	24 h	DIN 38 412, Teil 11	EC50 = 2 μg/l	GC-FID	Filtered saturated solution. The aqueous solution was acidified with 47% hydrobromic acid and extracted with 0.1% tropolon in toluene. Extracts were derivatized with pentyl-magnesium bromide and methylmagnesium chloride, dissolved in Grignard compound and heated. Limits of detection in water were 0.3-1.5 μg/l. Details of the toxic effects were not reported other than the lethal concentration. In the study it is indicated that the toxicity might be partly attributed to tributyltin impurities.	Steinhaeuser et al. 1985

Long-term toxicity

No data available.

6.1.1.3 Algae and aquatic plants

Table 6.3. The available data on the toxicity of tetrabutyltin to algae. For references, see Parametrix Inc. (2003).

Organism	Test duration	Method	Result	Analytical	Comments	Reference
Skeletonema costatum (marine diatom)	72 h	Not reported	$EC_{\mu}50$ = 49.7 μg/l	None	Nominal concentrations tested. Two tests conducted. Test substance dissolved in acetone.	Walsh et al. 1985

6.1.2 Sediment organisms

No data available.

6.1.3 Other aquatic organisms

Data available for micro-organisms were not reviewed for this report.

6.2 Terrestrial compartment

No data available.

6.3 Atmospheric compartment

No data available.

7 PBT AND vPvB

7.1 PBT, vPvB assessment

Persistence: Tetrabutyltin meets the P/vP criteria based on screening data. No degradation was observed in two OECD 301 D –tests for biodegradation and in a hydrolysis test according to OECD 111. The additional field data showing rapid degradation in sediment after a spill are not applicable to typical environmental conditions. Aerobic degradation of butyltins in the environment follows subsequent debutylation of the substance. This indicates that for tetrabutyltin the first substance to be formed is tributyltin. Tributyltin is a PBT –substance (see PBT summary fact sheet nr. 95).

Bioaccumulation: Tetrabutyltin fulfils the B criterion based on screening data (estimated log Kow is ca. 10). However, the estimated log K_{ow} indicates limited uptake. The available OECD 305 –test results with *Cyprinus carpio* provided BCFs up to 310, but the reliability of the results cannot be confirmed in the lack of accurate information on the water solubility. However, given the QSAR estimates for the water solubility it is likely that at least the results of the BCF determined at the lower aqueous concentration are not hampered by non-dissolved substance in the aqueous phase.

Toxicity: The substance fulfils the T criterion based on screening data. Acute ecotoxicity data are available for fish, invertebrates and algae, which all show L(E)C50–values below 0.1 mg/l. As in one reliable study the EC50 of 2 µg/l for daphnids and LC50 of 9 µg/l for fish were observed, it is also likely that the definitive T criterion could be considered as fulfilled. However, the values contain some uncertainty, as the purity of the test material was not provided for the study with the lowest results and the substance may have contained some tributyltin, which is highly toxic.

Other: The technical grade tetrabutyltin contains tributyltin as an impurity in a concentration of 15-30 %.

Summary: Tetrabutyltin fulfils the screening P/vP criteria, the screening B criterion and the screening T criterion. However, based on a weight of evidence approach considering an experimental BCF study in combination with estimates for the water solubility and molecular size, the B criterion is most likely not met for the parent substance tetrabutyltin. The substance forms tributyltin, which is a PBT–substance (see PBT summary fact sheet nr. 95), at an unknown rate. Additionally, technical grade tetrabutyltin contains 15-30 % tributyltin.

It is concluded, that pure tetrabutyltin is considered as a PBT–substance as a substance forming a PBT-substance. The technical grade tetrabutyltin is additionally considered as a substance containing a PBT-substance as an impurity.

OTHER INFORMATION

The information and references used in this report were mainly taken from the following sources:

European Commission, 2000. IUCLID Dataset, Tetrabutyltin, CAS 1461-25-2, 18.2.2000.

Parametrix Inc. (2003). IUCLID dataset, tetrabutyltin (CAS 1461-25-2), prepared for the Organotin Environmental Programme (ORTEP) Association Stabilizer Task Force; last update 27.3.2003.

Other sources:

CERI, 2000. Chemicals Evaluation Research Institute (CERI) - Japan. CAS No. 1461-25-2, [Tetrabutyltin]. http://www.ceriji.or.jp/ceri_en/index_e.html (accessed June 24, 2000).

CITI, 2003. Additional information on the METI –tests provided to ECB on 7.10.2003.

Crompton Corp., 2004. Tetrabutyltin (CAS No. 1461-2-2): Determination of general physico-chemical properties. SPL Project number 445/448, 20.10.2004.

ETINSA, 2003. European Tin Stabilizers Association at European Stabilizer Producers Association. Letter to B. Hansen, 14 February 2003 for the PBT assessment.

Landmeyer JE, Tanner TL and Watt BE, 2004. Biotransformation of Tributyltin to Tin in Freshwater River-Bed Sediments Contaminated by an Organotin Release. ES&T 38, 4106-4112.

RPA, 2005. Risk assessment studies on targeted consumer applications of certain organotin compounds. Final Report – September 2005. Prepared for the European Commission by Risk & Policy Analysts Limited (RPA).