ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

March 25, 2008

MEMORANDUM

SUBJECT: Revised Environmental Fate Assessment of TBT for RED

Case No.: 2620 **DP Barcode: D350671**

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Chemical Name	PC Code	CAS#	Common Name
bis(tri-n-butyltin) oxide	083001	56-35-9	Tributyl tin oxide, TBTO
tributyltin benzoate	083106	4342-36-3	TBTB
tributyltin maleate	083118	4027-18-3	TBTM

(Data for TBTB and TBTM are limited, but the TBTO fate data were used to support the TBTM. No fate data were available for TBTB.

Environmental Fate Science Chapter and Fate Assessment for the active ingredients in Case # 2620 are submitted for Reregistration.

ENVIRONMENTAL FATE SCIENCE CHAPTER

EXECUTIVE SUMMARY

Tributyl tin oxide is an anti-fouling and antimicrobial preservative. Based on the available labels and information from the registrants, it is used for wood treatment, cooling towers, material preservatives (e.g. interior grout, coatings), veterinary establishments and farm animal premises, and textiles. There are also uses in sonar domes and oceanographic instruments. TBTB also is used as a materials preservative, and TBTM is used in sponges, rubber, carpet backing, polyurethane foam, and other related materials.

The only outstanding environmental fate data requirement is leaching from treated wood.

The chemical structures of tributyltin oxide, tributyltin maleate, and tributyltin benzoate are as follows in Figure 1, 2, and 3, respectively.

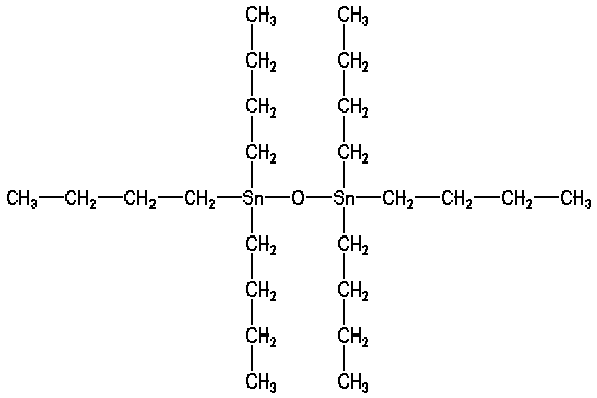

Figure 1. Structure of TBT Oxide

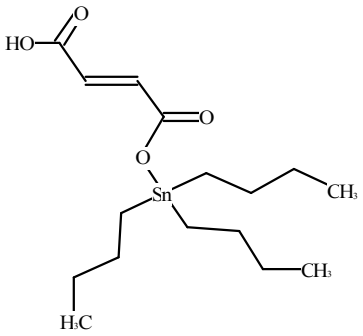

Figure 2. Tributyltin maleate

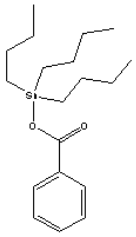

Figure 3. Tributyltin benzoate

Fate Characteristics of TBTO, TBTM, and TBTB

TBT oxide has limited solubility in water (0.09 mg/L), a high log P (log Kow, 3.84), and a vapor pressure of 7.8×10^{-6} mm Hg. The Henry's law constant is 6.8×10^{-5} atm m^3 mol^{-1}. Based on these values, TBT is normally associated with sediment in the presence of water, has high bioconcentration potential (low water solubility and high log P), and is not expected to volatilize from water (vapor pressure and Henry's Law). Degradation occurs primarily by microbial metabolism and in aerobic conditions.

TBT maleate (monomer) has limited solubility in water (4.mg/L), a high log P (log Kow, 3.79), and a vapor pressure of 1.7×10^{-7} mm Hg. The Henry's law constant is 1.4×10^{-7} atm m^3 mol^{-1}. Based on these values, TBT is normally associated with sediment in the presence of water and has high bioconcentration potential, and is not expected to volatilize from water (vapor pressure and Henry's Law). Degradation occurs primarily by microbial metabolism and in aerobic conditions.

TBT benzoate has limited solubility in water (2.6×10^{-1} mg/L), a high log P (log Kow, 4.69), and a vapor pressure of 1.3×10^{-6} mm Hg. The Henry's law constant is 2.8×10^{-6} atm m^3 mol^{-1}. Based on these values, TBT is normally associated with sediment in the presence of water, has high bioconcentration potential, and is not expected to volatilize from water. Degradation occurs primarily by microbial metabolism and in aerobic conditions.

Chemical reactions degrade TBTO to TBT ion, which degrades very slowly. Tributyltin oxide degrades by hydrolysis (freshwater and saltwater) to TBT ion which forms dibutyl tin (parent minus a butyl group, DBT (MRID 41557801). Like hydrolysis, the TBT ion is essentially stable to photodegradation in water at pH 5, 7, and 9 and in saltwater even though a photosensitizer was used to enhance photodegradation (MRID 41557802). TBTO data was used to support TBT maleate, but no fate data were submitted for TBTB.

Degradates

The primary breakdown product from chemical reactions and flooded conditions is dibutyl tin, but in non-flooded topsoil, the primary degradate is CO_2. Chemical reactions degrade TBTO to TBT ion, which degrades very slowly. Tributyltin oxide degrades by hydrolysis (freshwater and saltwater) to TBT ion which forms dibutyl tin (parent minus a butyl group, DBT). TBT ion is essentially stable, but there is an apparent equilibrium between TBT ion and DBT, with about 15-18 (freshwater) and 16-23 (saltwater) times more than TBT than DBT. These are average ratios of TBT ion and DBT. No other degradates were formed (MRID 41557801). Like hydrolysis, the TBT ion is essentially stable to photodegradation in water at pH 5, 7, and 9 and in saltwater even though a photosensitizer was used to enhance photodegradation. TBT was 15-18 times greater than DBT in freshwater, and 10-11 times greater in saltwater, with no other degradates present (MRID 41557802). The smaller TBT/DBT ratios in photodegradation were consistent with the hydrolysis results. TBTO data was used to support TBT maleate, but no fate data were submitted for TBTB.

Metabolism

Degradation in aerobic conditions is faster than in anaerobic conditions, and requires microbial activity. All aquatic metabolism studies were conducted using saltwater, not freshwater. In filtered and irradiated seawater, TBT ion was stable. In non-filtered seawater (aerobic aquatic metabolism), TBT degraded with a dark control adjusted half-life of 6.5 days with degradation in both lighted and dark conditions. In an anaerobic aquatic metabolism study (saltwater and nitrogen atmosphere), TBT was stable in sterilized water. The half-life of TBT in aerobic aquatic metabolism (saltwater, oxygen atmosphere) was 4.5 days. DBT reached about 50 % of parent concentration and hydroxylbutyl tin reached about 15 %. In an aerobic aquatic metabolism study (saltwater), the dark control adjusted half-life of TBT was 4.3 days with degradation in both dark control and irradiated samples. DBT was the only significant degradate. In the same study volume, the aerobic and anaerobic half-lives were 5-6 (sediment, saltwater, and oxygen atmosphere) and 24 (sediment, saltwater, and nitrogen atmosphere) days, respectively. Degradation is faster in salt water than fresh water (MRID 41024501). In water:sediment systems from Puget Sound (seawater, MRIDs 43831801, 43984201), TBT oxide was essentially stable (half-life of 506 days) and virtually all present in sediment. Water residues did not exceed 3 % of applied. These results are consistent with the tight sorption to soil. Sediment bound residues increased in the studies.

In non-flooded soil (aerobic soil, the top layer of soil), the half-life of TBT oxide was 127 days. Complete mineralization to CO_2 and non-extractable residues was observed. There were no significant non-volatile metabolites. These results are consistent with the straight chains of carbon in TBT that are systematically converted to CO_2 (MRID 43737401)

Persistence in the Environment

TBT ion is generally persistent in the environment and sorbed tightly to soil and suspended/ bottom sediment. Water exposures are expected to be small relative to sediment residues.

Leaching

Sorption to soil and sediment is a significant route of dissipation in the environment. The Kads values ranged from 7 to 157 ml/g with Koc values of 650 to 16,600 (MRID 43979701). Kads values relate sorption to whole soil, while the Koc represents sorption to the organic carbon content of the soil. Sorption is related to organic carbon content which is consistent with the structure and chemical content of TBT. However, desorption back into the water phase ranged from 17 to 70 % which is inconsistent with the metabolism studies. The desorption in the batch equilibrium studies was likely due to the fact that the soil and water were being shaken, which removed the compound. In metabolism studies, the soil:water systems are not shaken.

Bridging

Bridging for the different TBT containing compounds was conducted using data from TBTO.

TBTO data were used for TBTM, but no fate data were cited for TBTB. However, the fate of these compounds is expected to be similar and therefore no fate data for TBTB are required.

Bioconcentration

Bioconcentration in fish is an important route of dissipation in the environment. In MRIDs 41668901 and 41811501, the bioconcentration factors ranged from 13-100 for fillet (edible), 30-1800 for viscera (non-edible), and 21-2210 for whole bluegill sunfish. The reported depuration rates varied between the studies, with 50 % depuration occurring by 17-18 days for fillet, 10-14 days for viscera, and 13-15 days (whole body) (MRID 41668901). In MRID 41811501, the percent depuration by 21 days was 61 (fillet), 75 (viscera), and 66 (whole body). The results of these studies are consistent with desorption in batch equilibrium studies. In sheepshead minnows (MRID 92172011), bioconcentration factors of 1810, 2120, and 4580 were observed for fillet, head, and viscera, respectively. The percent depuration in 28 days was 74, 80, and 64, respectively. Within 7 days, 52 % depuration occurred.

The octanol/water partition coefficient Kow is very high and TBT shows a remarkable tendency to bioaccumulate. The bioaccumulation in various tissues can be from 200-fold to 6000-fold. This is attained by exposure to 1.25 ppb at the most and 0.15 ppb at the least.

With such high Kds as noted above, it has been estimated that TBT levels in the sediments need to be only 120 ng/g to give an interstitial water value of 10 ng/L, which is enough to give rise to chronic effects in salt water species. In actuality, it is both the desorbed TBT and the sediment bound TBT that contribute to the bioaccumulation and bioavailability in saltwater organisms.

According to the World Health Organization, the bioconcentration factors in various aquatic species are as high as 60,000X with most being less than 6,000X. The depuration half-life in mollusks for organic tin was 40 days and 25 days for total tin. The excretion rates in sheepshead minnow by 20 days were 74 % in muscle and 80 % in internal organs. The literature data are consistent with the guideline study data.

Aquatic Monitoring

Long-term near coastal monitoring was required in support of the antifouling paint uses of TBTO and several other TBT derivatives no longer registered by EPA. While the monitoring program was plagued by poor recoveries, sample contamination, and other difficulties, the Agency was able to utilize some of the information that was collected. Monitoring data were summarized in the June 2001 EFED risk assessment (Rexrode and Spatz, 5/11/01) and in MRID 45487301. Annual monitoring results and difficulties in the monitoring program were also reported to Congress. Based on the monitoring, residues in sediment were greater than in water which is consistent with the results of the metabolism studies and leaching studies in soil. Most sediment samples contained less than 10 ng/l in pore water, which is the level of concern for chronic effects. However, some samples ranged as high as 109 ng/l. DBT and monobutyl tin (MBT) were present in most samples. No monitoring has been conducted which targets the non-

antifouling uses of TBT.

Bioconcentration in Aquatic Organisms

Bioconcentration and bioaccumulation were observed in a variety of aquatic organisms, including birds, bivalves, sea otters and sea lions, clams and mussels, tuna, harbor porpoises, and sharks. Most of the measured concentrations were found at parts-per-billion levels, but some reached the parts-per-million level. The liver of the different animals contained the highest levels of total butyltins, but much of it was converted to DBT. Blubber generally contained more TBT than DBT. Many of the animals studied were either dead, stranded, or caught in harbors, indicating that these exposures may represent high-end concentrations. However, some animals were taken from areas with lower exposure and had lower concentrations.

Strand and Jacobsen (2005) studied the accumulation potential of tributyltin and triphenyl tin in two species of seaweed, four species of invertebrates, four species of fish, five species of birds, and two species of mammals. They reported butyltin concentrations of 60-259 ng/g (parts-per-billion, ppb) wet weight as tin in flounder, 12-202 ng/g in elder duck, and 134-2283 ng/g in harbor porpoises in Danish coastal waters. Triphenyl tin (including degradates) were found in most of the samples with the highest concentrations in flounder (9.8-74 ng/g), cod (23-28 ng/g), and great backed gulls (19-24 ng/g).

Strand et al. (2005) studied butyltin concentrations in the liver of 35 harbor porpoises which were found or caught along the Danish North Sea and the Inner Dutch waters, in addition to three porpoises from West Greenland. In harbor porpoises, butyltin concentrations in the livers were 68-4605 mg/kg (parts-per-million, ppm), and these tended to increase with age. Butyltin concentrations in stranded porpoises were higher than caught ones.

Diez et al (2002) studied tributyltin and phenyltin in harbor sediments from the Western Mediterranean Sea. Butyltins in commercial harbors that were attributed to large vessels averaged 5 ug/g (ppm). In waters used for recreational boating and fishing, the average level of tributyl tin was 1.0 ug/g. Phenyltin derivatives (monophenyl tins) averaged 45-945 ng/g (ppb) in sediment.

Strand and Asmund (2003) studied the accumulation and effects of TBT and degradates in marine mollusks from West Greenland. The highest TBT concentration (254 ng/g) was found in the bivalve *Mytilus edulis* from Nuuk harbor, but significant TBT was also found in bivalves from the other harbors. Low levels of TBT were found outside the harbors. Imposex (masculinazation) of neogastropods (e.g. *Buccinum*) was observed in the harbors, but not outside the harbors.

Jacobsen and Asmund (January 2000) studied butyltin concentrations in the bivalve *Mytilus edulis* (Blue mussel) and in marine sediments near Nuuk in Greenland. TBT was detected in the bivalves at approximately 1 ug/kg (wet weight, ppb) as tin. In sediments, TBT concentrations ranged from 1 ug/kg to 172 ug/kg (dry weight).

Chandrinou et al. (February 2007) studied organotin levels in five bivalve species. These included *Mytilus galloprivinciallis* (Mediterranean mussels), *Venus gallina* (stripped venus), *Modiola barbatus L*. (bearded horse mussels), *Pecten jacobeus* (scallops), and *Callista chione* (hard clans) in seven areas of the Aegean Sea near Greece between August 2001 and January 2003. The geometric means of the different butyltins were 17.1 ng/g (ppb) of TBT, 18.8 ng/g (dibutyltin),7.8 ng/g (MBT), and 13.0 ng/g for triphenyltin. The lowest concentrations were observed in Mediterranean mussels due to growth in water column in fish farms. The highest concentrations were observed in free-ranging species collected from fishing grounds.

Madhusree et al. (September 1997) studied the concentrations of butyltin compounds in harbor porpoise (*Phocoena phocoena*) collected from Turkish coastal waters of the Black Sea. Total butyltin compounds in the liver were in the range of 89-219 ng/g (ppb) wet weight. DBT residues were higher than TBT, suggesting that TBT degrades to TBT in the liver.

Kannan et al. (1998) studied butyltin residues in southern sea otters (*Enhydra lutris nereis*) found dead along California coastal waters. The body organs included the liver, kidney, and brain. Hepatic concentration of total butyltin compounds (TBT, DBT, and MBT) ranged from 40 to 9200 ng/g (ppb). When the 9200 ng/g concentration was removed as an outlier, the mean liver concentrations were 1090 $\pm$ 1560 ng/g. Total butyltin concentrations in kidney and brain were in the ranges of 4-430 (mean of 160 $\pm$ 140 ng/g) and 2.7-140 (mean of 61 $\pm$ 56 ng/g). Female sea otters contained approximately twice the levels of male otters. Most butyltin residues were TBT, indicating recent exposure. Sea otters are bottom feeders and eat invertebrates such as mollusks and gastropods, which accumulate butyltins from bottom sediment.

Kim et al. (1996) studied the characteristics of butyltin accumulation and its biomagnification in steller sea lion (*Eumetopias jubatus*) from 1976-1985 in Alaska and 1994-1995 in Hokkaido, Japan. Liver concentrations in sea lions from Alaska (19 ng/g, ppb) was much lower than those from western and eastern Hokkadio (150 and 220 ng/g). DBT residues were higher than TBT. The biomagnification factors of total butyltins in stellar sea lions (mean of 0.6) indicate that this specie is unlikely to biomagnify butyltins due to rapid degradation and excretion.

Kannan et al (July 1996) studied the butyltin concentrations in bottlenose dolphins (*Tursiops truncates*), bluefin tuna (*Thunnus thynnus*), and blue shark (*Prionace glauca*) collected from Italian coast of the Mediterranean Sea in 1992-1993. Concentrations of total butyltin in the liver of dolphins (1200-2200 ng/g, ppb) were an order higher than in blubber (48-320 ng/g). TBT was present more in the blubber, while DBT was higher in the liver. Butyltin concentrations in bluefin tuna were lower than in dolphins, with TBT highest in the muscle and DBT in the liver. Concentrations of butyltins in blue sharks were lower than those in dolphin and tuna, with the kidney having the highest concentrations. TBT was the predominant form of butyltin derivatives in the tissues of shark.

Data Gaps: See Table below.

Environmental Fate Data Requirements for TBTO, TBTM, and TBTB Technical			
OPP Guideline	**Data Requirement**	**MRID No.**	**Data Requirement Status**
161-1	Hydrolysis	41557801	Satisfied
161-2	Photodegradation in Water	41557802	Satisfied
161-3	Photodegradation on Soil	00074584 00074585 00125042	Not required
162-1	Aerobic Soil Metabolism	43747401	Satisfied
162-2	Anaerobic Soil Metabolism	No data	Not required[1]
162-3	Anaerobic Aquatic Metabolism	41024501 43831801	Satisfied
162-4	Aerobic Aquatic Metabolism	41024501 43984201	Satisfied
163-1	Adsorption/Desorption	43979701	Satisfied
OECD 305	Bioaccumulation in Fish	41668901 41811501 92172011	Satisfied
840.1100	Monitoring/Aquatic Field Dissipation Study	45487301, May 2001 EFED review	Satisfied
No guideline	Leaching from treated wood	No data	Required

[1] May be satisfied by the anaerobic aquatic metabolism studies (MRIDs 41024501, 43831801)

BIBLIOGRAPHY

161-1 Hydrolysis (835.2110)

MRID	Citation Reference
41557801	Pisigan, R.; Liu, L.; Zavala, P. (1989) Hydrolysis of Bis(Tributyl- tin) Oxide in Water: Lab Project Number: 3903019. Unpublished study prepared by Environmental Science & Engineering, Inc. 54 p.

161-2 Photodegradation-water (835.23210)

MRID	Citation Reference
41557802	Liu, S.; Zavala, P.; Gensheimer, G. (1990) Photodegradation of Bis- (Tributyltin) Oxide in Water: Lab Project Number: 3903021. Un- published study prepared by Environmental Science & Engineering, Inc. 69 p.

162-1 Aerobic soil metabolism (835.3300)

MRID	Citation Reference
43737401	Schocken, M. (1995) Tributyltin Oxide--Determination of Soil Metabolism Under Aerobic Conditions at 25 (degrees) C: Final Report: Lab Project Number: 95-1-5658: 12442.0193.6155.760. Unpublished study prepared by Springborn Labs, Inc. 69 p.

162-3 Anaerobic aquatic metab. (835.3400)

MRID	Citation Reference
41024501	Lee, R. (1988) Degradation of ?carbon 14|-Bis(Tri-n-Butyltin) Oxide in Coastal Waters and Sediments Under Aerobic and Anaerobic Conditions. Unpublished study prepared by Skidway Institute of Oceanography. 24 p.
43831801	Schocken, M. (1995) Tributyltin Oxide--Determination of Anaerobic Aquatic Metabolism at 25 (degrees) C: Final Report: Lab Project Number: 95-5-5879: 12442-0193-6158-755. Unpublished study prepared by Springborn Labs, Inc. 78 p.

162-4 Aerobic aquatic metab. (835.3100)

MRID	Citation Reference
41024501	Lee, R. (1988) Degradation of ?carbon 14|-Bis(Tri-n-Butyltin) Oxide in Coastal Waters and Sediments Under Aerobic and Anaerobic Conditions. Unpublished study prepared by Skidway Institute of Oceanography. 24 p.
43984201	Schocken, M. (1995) Tributyltin Oxide--Determination of Aerobic Aquatic Metabolism at 25

(degrees) C: Final Report: Lab Project Number: 94-9-5462: 12442-0193-6157-750. Unpublished study prepared by Springborn Labs, Inc. 72 p.

163-1 Leach/adsorp/desorption (835.1220)

MRID	Citation Reference
43979701	Mao, J. (1995) Tributyltin Oxide--Determination of the Adsorption and Desorption Properties: Final Report: Lab Project Number: 94-9-5476: 12442.0193.6154.710: 55-1807-05. Unpublished study prepared by Springborn Labs, Inc. 82 p.

164-2 Aquatic field dissipation (no guideline)

MRID	Citation Reference
45487301	Simmons, R.; Kluck, M.; Bennett, J. et al. (2001) Annual Report for the Long-Term National Monitoring Program for Tributylin and Its Primary Degradation Intermediates: Year 8, 1999-2000: Lab Project Number: 55-1807-07 (8A). Unpublished study prepared by Parametrix, Inc. 3412 p.

165-4 Bioaccumulation in fish (850.1730)

MRID	Citation Reference
41668901	Stuerman, L.; Lochhaas, C.; Young, B. (1990) Uptake, Depuration and Bioconcentration of (carbon 14)-Bis(tri-n-butyltin) Oxide by Bluegill Sunfish (Lepomis macrochirus): Lab Project No. 38561. Unpublished study prepared by Analytical Bio-Chemistry Labora- tories, Inc. 453 p.
41811501	Gendusa, T.; Brancato, M. (1990) Steady State Tissue Concentrations of Tributyltin and its Degradation Intermediates in Bluegill Sunfish (Lepomis macrochirus) Following Tributyltin Uptake and Depuration: Lab Project Number: Final Report: ES-7387. Unpublished study prepared by Texas A & M University, Parametrix, ABC Labs. 40 p.
92172011	Ben-Dyke, B. (1990) M&t Chemicals, Inc. Phase 3 Summary of MRID 00140824. Bioaccumulation and Chronic Toxicity of Bis(tributyltin) Oxide: Tests with a Saltwater Fish. Prepared by EG&G, Bionomics. 6 p.

165-5 Bioaccum-aquatic non-target (850.1850)

MRID	Citation Reference
45487301	Simmons, R.; Kluck, M.; Bennett, J. et al. (2001) Annual Report for the Long-Term National Monitoring Program for Tributylin and Its Primary Degradation Intermediates: Year 8, 1999-2000: Lab Project Number: 55-1807-07 (8A). Unpublished study prepared by Parametrix, Inc. 3412 p.

Other data sources

Chandrinou, S., A.S. Stasinakis, N.S Thomaidis, A. Nikolaou, and J.W. Wegener. (February 2007). Distribution of organotin compounds in the bivalves of the Aegean Sea, Greece. Environment International 33: pp. 226-232.

Diez, S., M. Abalos, and J.M. Bayona. February 2002. Organotin contamination of sediments from the Western Mediterranean enclosures following 10 years of TBT regulation. Water Research 30:pp. 905-918.

Jacobsen, J.A. and G. Asmund. January 2000. TBT in marine sediments and blue mussels (Mytilus edulis) from central-west Greenland. The Science of the Total Environment 245:pp. 131-136.

Kannan, K., S. Corsolini, S. Focardi, S. Tanabe, and R. Tatsukawa. July 1996. Accumulation pattern of butyltin compounds in dolphin, tuna, and shark collected from Italian coastal waters. Archives of Environmental Contamination and Toxicology 31:pp. 19-23.

Kannan, K., K.S. Guruge, N.J. Thomas, S. Tanabe, and J.P. Giesy. 1998. Butyltin Residues in Southern Sea Otter (Enhydra lutes nereis) found Dead along California Coastal Water. Environ. Sci. Technol. 32:pp. 1169-1175.

Kim, G.B., S. Tanabe, R. Tatsukawa, T.R. Loughlin, and K. Shimazaki. May 1996. Characteristics of butyltin accumulation and its biomagnification in Stelle Lion (Eumetopias jubatus). Environmental Toxicology and Chemistry 15:2043-2048.

Madhusree, B., S. Tanabe, A.A Ozturk, R. Tatsukawa, N. Miyazaki, E. Ozdamar, O. Aral, O. Samsun, and B. Ozturk. September 1997. Contamination by butyltin compounds in harbor porpoise (Phocoena phocoena) from the Black Sea. Fresenius' Journal of Analytical Chemistry 3598:pp. 244-248.

Rexrode, M. and D. Spatz. May 11, 2001. EFED Response to Request for Update on Tributyltin (TBT) Environmental Risk Characterization

Strand, J. and G. Asmund. May 2003. Tributyl tin accumulation and effects in marine mollusks from West Greenland. Environmental Pollution 123:pp. 31-37.

Strand, .J and J.A. Jacobsen. November 2005. Accumulation and trophic transfer of organotins in a marine food web from Danish coastal waters. Science of the Total Environment 350: pp. 72-85).

Strand, J., M.M. Larsen, and C. Lockyer. November 2005. Accumulation of organotin compounds and mercury in harbor porpoises (Phocoens phocoens) from the Danish water and West Greenland. Science of the Total Environment 350:pp. 59-71.

World Health Organization (1990)Tributyltin compounds, Environmental Health Criteria 116.