Marine Antifoulants: Tributyltin

Case Study # 8

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for

CHEM 301: Aqueous Environmental Chemistry

Materials Included in this Reading Package:

1. Organotin Environmental Programme (ORTEP) Association, 'Definitions of Common Terms Used in the Shipping/Antifoulant and Toxicology Industries', http://www.ortepa.org/pages/b2.htm accessed 14/11/2006

2. Adapted from: Open Chemist.net, 'Organotin Compounds in the Environment', edited by Joachim Nuyttens, http://openchemist.net/chemistry/show.php?id=analytical&story=env001 accessed 14/11/2006

3. Taken from: European Environment Agency, 'Tributyltin (TBT) antifoulants: a tale of ships, snails and imposex', http://reports.eea.europa.eu/environmental_issue_report_2001_22/en/issue-22-part-13.pdf, accessed 15/11/2006

4. Stumm, Werner, and James J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. 1996. 3. 631-632.

5. International Maritime Organization (IMO), 'Focus on IMO – Anti-fouling Systems', http://www.imo.org/includes/blastDataOnly.asp/data_id%3D7986/FOULING2003.pdf accessed 14/11/2006

6. Georgia Reproductive Specialists, 'Pollution causes female snails to become male', http://www.ivf.com/snail.html, accessed 15/11/2006

7. Greenpeace, 'TBT: A Global Problem for the Marine Environment', http://archive.greenpeace.org/toxics/reports/tbtfactsheet.html, accessed 15/11/2006

8. U.S. Environmental Protection Agency, ‘Ambient Aquatic Life Water Quality Criteria for Tributyltin (TBT) – Final’, http://www.epa.gov/waterscience/criteria/tributyltin/tbt-final.pdf accessed 14/11/2006

Further References:

International Programme on Chemical Safety, ‘Environmental health criteria 116; Tributyltin Compounds’, by S. Dobson and R. Cabridenc, http://www.inchem.org/documents/ehc/ehc/ehc116.htm accessed 15/11/2006

Extension Toxicology Network Pesticide Information Profiles, ‘Tributlytin (TBT)’, http://extoxnet.orst.edu/pips/tributyl.htm accessed 15/11/2006

Innovations, ‘Copper in Third-Generation Antifoulants for Marine Coatings’, by William H. Dresher, http://www.copper.org/innovations/2000/09/antifoulant_story.html accessed 15/11/2006

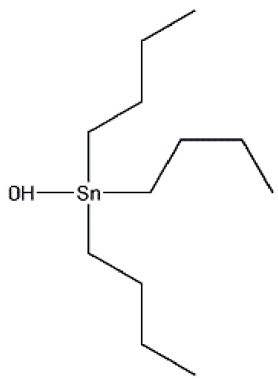
Table 1: Antifoulant Definitions

Ablative Paint	A rosin-based paint in which the film is dissolved at a slow rate in sea water after immersion, exposing a biocide (e.g., copper compound) which is released after dissolution and diffusion from the film. Although the thickness of the film of these types depletes over time, the paint film does not show smoothing characteristics in-service on ships
Antifoulant	Coatings applied to the portion of a hull below the waterline to discourage marine animals and plants that would otherwise adhere to it
Bioaccumulation	Chemical taken up by an aquatic organism directly from water and food, including sediment
Biocide	Active substance intend to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on, any harmful organism by chemical or biological means (e.g., pesticide, herbicide, algaecide, or fungicide)
Bioconcentration	The process whereby there is a net accumulation of a chemical directly from water into aquatic organisms resulting from direct uptake from the water, but not food
Biomagnification	The process by which the tissue concentration of a bioaccumulated chemical increases as it passes up the food chain through at least two trophic levels (minimum of three involved)
Booster biocides	An industry term for biocides targeting individual types of fouling organisms (e.g., algae, slime) added to paint formulations
Copolymer	A polymer derived from more than one species of monomer (groups of molecules which can undergo polymerization to the essential structure of a macromolecule)
Fouling	With respect to ships, the growth of shell, tissue, and microorganisms on immersed surfaces such as ship hulls. This may include organisms such as bryozoa, tubeworms, tunicates, microorganisms, algae, barnacles, and mussels
Free-association	A type of antifouling paint in which the biocide is not chemically bound and leaches freely from the paint. The initial release is rapid and uncontrolled and declines steadily from the paint such that the antifouling performance of the paint diminishes with time
Leaching rate	The rate at which a biocide is released from an antifouling paint into the water (e.g., 4 µg of biocide per square centimeter of hull per day)
Silicone SPC	New paint types based on polymers with alkylsilane groups
Volatile Organic Compounds (VOC's)	Organic chemicals used in industrial solvents (e.g., acetone) used in paint application that have tended to evaporate readily. Many of these compounds are associated with carcinogenic and chronic toxicity.

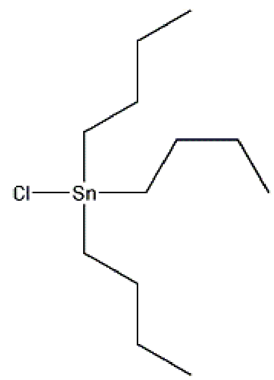
Taken from: Organotin Environmental Programme (ORTEP) Association, 'Definitions of Common Terms Used in the Shipping/Antifoulant and Toxicology Industries', http://www.ortepa.org/pages/b2.htm

What is Tributyltin anyway?

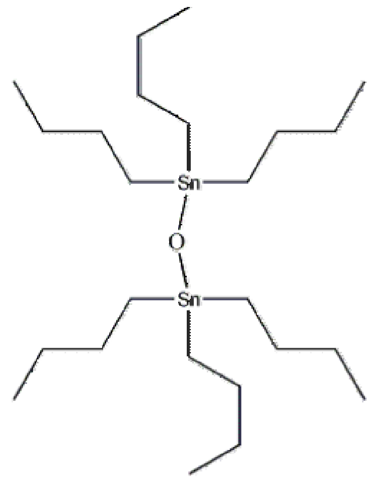
Tributyltin (TBT) is an organometallic compound, commonly used as an antifouling agent in marine paints. It is very toxic and can persist in the environment from days years as one of the species below:



Tributyltin Hydroxide
(predominant species in seawater)

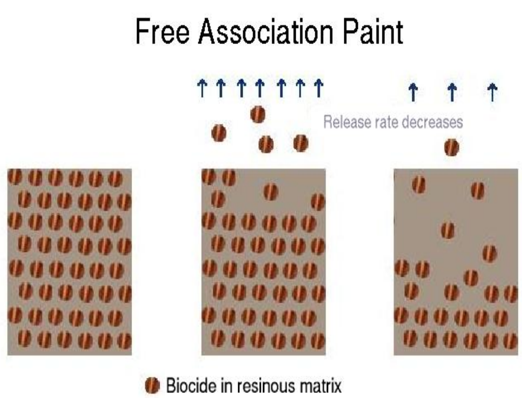


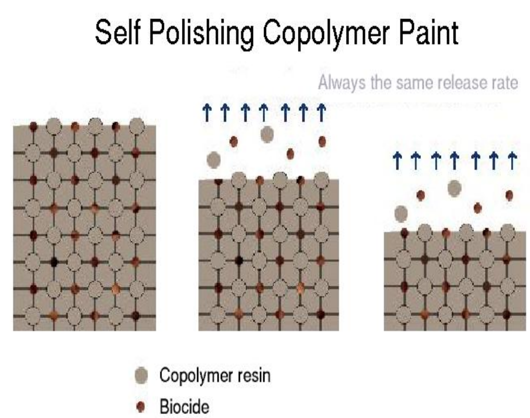
Tributyltin Chloride
(~3% in seawater)



Tributyltin Oxide
(minor species)

TBT is often used as a booster biocide along with cuprous-oxide, which has replaced more toxic lead, arsenic, organo-mercury compounds in antifoulant paints. These paints are of two distinct types: free association and copolymer paints. Free association paints allow their biocides to leach freely into the water at an uncontrolled rate. In copolymer paints the biocide is chemically bound and is released slowly as the paint's surface weathers.





Adapted from: Open Chemist.net, 'Organotin Compounds in the Environment', edited by Joachim Nuyttens, http://openchemist.net/chemistry/show.php?id=analytical&story=env001

Table 2: History of global TBT regulation

Early 1970s	Rapid increase in the use of TBT antifouling paints on vessels of all sizes and first reports of imposex in marine snails (Blaber, 1970; Smith, 1971)
1976–81	Repeated failure of larval settlement leads to near collapse of oyster fishery, Arcachon Bay, France
1982	France introduces legislation prohibiting the use of TBT paints on small vessels
1985	First controls introduced in United Kingdom limiting concentrations of TBT in paints
1986	Bryan *et al*. (1986) report widespread imposex in dogwhelks on southern coast of United Kingdom, linked to TBT
January 1987	United Kingdom announces further restrictions on TBT content of applied antifouling paint
May 1987	United Kingdom introduces ban on retail sale of TBT paint for use on vessels < 25 m and on fish cages
June 1987	PARCOM Recommendation 87/1 calls for similar ban over entire convention area (Northeast Atlantic)
1988	United States introduces restrictions. Waldock *et al*. (1988) highlight significance of inputs from shipyards
1989	Restrictions introduced in Canada, Australia and New Zealand
1991	Harmonised ban on retail sale of TBT paint introduced at European Union level
1994	Early reports of imposex in whelks from offshore areas of North Sea linked to shipping activity
1995	Ministerial declaration of fourth North Sea conference (Esbjerg) commits to working for global phase-out of TBT paint within IMO
1997	Concept of global phase out of organotin containing paints agreed at MEPC's 40th session
1998	Draft mandatory regulations aimed at such a phase-out adopted. OSPAR (Convention for the Protection of the Marine Environment of the Northeast Atlantic) prioritises organotins for action to cease all releases. Cessation of all releases of organotins to marine environment, under OSPAR's hazardous substances strategy in 2020
November 1999	Deadlines for phase-out adopted under IMO Assembly Resolution A.895(21)
2001	Text of International Convention on the Control of Harmful Anti-fouling Systems to be finalised. In 2003 worldwide prohibition on new application of organotin antifoulants to all vessels and in 2008 the existing organotin antifouling coatings will be replaced on all vessels worldwide

Taken from: European Environment Agency, 'Tributyltin (TBT) antifoulants: a tale of ships, snails and imposex', http://reports.eea.europa.eu/environmental_issue_report_2001_22/en/issue-22-part-13.pdf

Pollution Causes Female Snails to Become Male

VANCOUVER, British Columbia (AP) **Female snails have been turning into males**, in certain polluted coastal harbors of British Columbia a researcher says. Snails undergoing the change, which some scientists think is caused by tin-based contaminants in the water, have been found by University of Victoria biologist Derek Ellis and his colleagues.

The females have been turning into males in harbors and marinas throughout the Strait Juan de Fuca, Ellis said.

"Most of the harbors on the west coast of Vancouver Island... show the same effect," he said.

'So we know that the whole of the southern B.C. coast is affected, or was when we looked."

Ellis said the phenomenon called imposex has affected almost all species of carnivorous snails. In some species *not only do the females grow a penis, but the ovaries turn into testicles.* In others, females that retain their ovaries are prevented from releasing eggs by the growth of a penis.

The animals die out because they cannot breed said Ellis, who has studied imposex in snails at several polluted locations around the world.

Adapted from: Georgia Reproductive Specialists, 'Pollution causes female snails to become male', http://www.ivf.com/snail.html

TBT: A Global Problem for the Marine Environment

Tributyltin (TBT) is an aggressive biocide that has been used in anti-fouling ship paints since the 1970s. The toxicity of TBT prevents the growth of algae, barnacles and other marine organisms on the ship's hull. TBT leaches from the paint and enters the marine environment. TBT accumulates in the sediment, in particular in areas with many ship movements, like harbours and ports. In addition, on shipping lanes in the open sea, the toxic effects of TBT are observed…

TBT is responsible for the disruption of the endocrine system of marine shellfish leading to the development of male sex characteristics in female marine snails. TBT also impairs the immune system of organisms and shellfish develop shell malformations after exposure to extremely low levels of TBT in the seawater. Recent studies conducted by the Dutch Institute for Marine Research and the Free University (VU) of Amsterdam reveal that sperm whales that live and feed in the deep ocean far from ports and shipping lanes have appreciable amounts of TBT and its breakdown products in their bodies. This indicates that TBT may be widely dispersed in the marine environment, including the deep oceans where sperm whales normally live and feed.

TBT and its degradation products have been isolated from a wide range of marine environmental samples. In many cases, a relationship between levels of environmental contamination and the intensity of shipping traffic can be detected. TBT has been found in the tissues of cetaceans, seals, sea otters and water birds in a wide range of locations around the world. Tissues and sediments sampled from areas with heavy shipping activity show the highest levels of contamination.

Adapted from: Greenpeace, 'TBT: A Global Problem for the Marine Environment', http://archive.greenpeace.org/toxics/reports/tbtfactsheet.html

Table 3: Equilibria of Trialkyltin Compounds

Reaction[a]	-log K (25°C)
$Me_3Sn^+ + H_2O \Leftrightarrow Me_3SnOH + H^+$	6.60
$Bu_3Sn^+ + H_2O \Leftrightarrow Bu_3SnOH + H^+$	6.2
$Me_3Sn^+ + Cl^- \Leftrightarrow Me_3SnCl$	0.17
$Bu_3Sn^+ + Cl^- \Leftrightarrow Bu_3SnCl$	0.37

[a]Me = methyl; Bu = butyl.

Taken From: Stumm, Werner, and James J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters

Table 4: Tributyltin (TBT) - harmful effects on the environment

Water and sediments	Tributyltin - organotin compound (TBT) is a broad spectrum algicide, fungicide, insecticide, and miticide used in anti-fouling paints since the 1960s. TBT is toxic to humans. TBT can be broke n down in water under the influence of light (photolysis) and micro-organisms (biodegradation) into less toxic di- and monobutyltin. Half-life varies from a few days to a few weeks, but decomposition is slower when TBT has accumulated in sediment - if oxygen is completely excluded, TBT half-life maybe several years. Therefore waters with heavily sedimented bottoms - such as harbours, ports, estuaries - are at risk of being contaminated with TBT for several years.
Shell malformations	TBT causes thickening of shells in sea oysters, caused by disturbance of calcium metabolism.
Imposex	Recorded in marine snails: females develop male sexual characteristics. Imposex has been recorded in 72 marine species. Concentration of just 2.4 nanograms of TBT per litre needed to produce sexual changes in dog-whelks, leading to sterility.
Marine mammals	Traces of TBT have been found in whales, dolphins and members of the seal family in the United States, south-east Asia, the Adriatic Sea and the Black Sea. The TBT is absorbed via the food chain.
Reduced resistance to infection	Research has shown TBT reduces resistance to infection in fish such as flounder and other flatfish which live on seabed and are exposed to relatively high levels of TBT, especially around areas with silty sediment like harbours and estuaries.

Taken from: International Maritime Organization (IMO), 'Focus on IMO – Anti-fouling Systems', http://www.imo.org/includes/blastDataOnly.asp/data_id%3D7986/FOULING2003.pdf

Table 5: Bioconcentration factors for various aquatic species

Species	[TBT] in water (µg/L)	Duration (days)	BCF	Reference
FRESHWATER SPECIES				
Zebra Mussel (*Dreissena polymorpha*)	0.0703	105	**17,483**	Becker-van Slooten and Tarradellas 1994
Guppy (*Poecilia reticulatus*)	0.54	14	**460**	Tsuda et al. 1990
SALTWATER SPECIES				
Snail (*Littorina littorina*)	0.488 - 0.976	182	**1,020 - 1,420**	Bauer et al. 1997
Atlantic Dogwhinkle (*Nucella lapillus*)	0.0038 - 0.268	249 - 408	**11,000 - 38,000**	Bryan et al. 1987
Blue Mussel (*Mytilus edulis*)	0.079 - 0.452	56	**10,400 - 37,500**	Salazar et al. 1987
Pacific Oyster (*Crassostrea gigas*)	0.1460 - 1.216	21	**1,874 - 6,047**	Waldock et al. 1983
Note: Some of the results listed are pooled from multiple studies on the same species and from the same research source.				

Adapted from U.S. Environmental Protection Agency, 'Ambient Aquatic Life Water Quality Criteria for Tributyltin (TBT) – Final', http://www.epa.gov/waterscience/criteria/tributyltin/tbt-final.pdf