

A Review to Determine State-of-The-Practice Treatment Technologies For Reducing Concentrations of Organotin Compounds in Wastewater

Messing, A. , L.M. Ramirez, and T. Fox, 1997

Executive Summary

The purpose of this study is to identify practical technology that can be used by shipyards to remove tributyltin (TBT) from large volumes of water to levels below 50 parts per trillion. This study is based on: (1) a review of scientific and engineering literature, (2) a review of U.S. Patents, and (3) a survey of manufacturers and users.

TBT based paints are the most popular antifouling paints used on the hulls of the global merchant fleet, and the market share of TBT is still growing despite its banning or partial banning in certain areas. Shipyards generate large volumes of TBT-laden washwater during normal drydock operations.

TBT has been found to be highly toxic in marine environments with observable environmental impacts at levels of parts per trillion. In 1997, after 10 years of study, The United States Environmental Protection Agency (U.S. EPA) proposed a national saltwater aquatic life criteria for TBT of 10 parts-per-trillion (62 CFR 42554, August 7, 1997). After the appropriate comment period, the standard chosen will become the basis for state water quality standards and water discharge permits throughout the U.S.

This study concludes:

1. There is no “off-the-shelf” technology directly applicable to shipyard waste streams that will reduce TBT levels in water below a concentration of 50 parts per trillion.
2. Because TBT is highly attracted to particulates in water, adsorption process may prove be the most effective means to reduce TBT concentration. It is suggested that technology such as Dissolved Air Flootation, and Activated Carbon adsorption are the best candidate technologies.
3. While there are accepted and practical water treatment technologies that may be effective in reducing TBT concentrations in waste streams, these technologies have not been applied to shipyard waste streams. It is recommended that practical trials be conducted as soon as possible.

Introduction

It is estimated that between 70% and 80% of the global merchant fleet has tributyltin (TBT) antifouling paint applied to their hulls. When these ships are dry-docked, shipyards can generate tens of thousands of gallons of TBT contaminated washwater. For twenty years a substantial global effort has been focused on qualifying the adverse ecological effects of TBT and other organotin compounds in aqueous environments, but very little work has been done to develop practical methods to remove TBT from wastewater streams. At this time U.S. shipyards have no practical guidance on any technology that can be employed to meet regulatory discharge limits. Responding to a written survey question about legislation limiting TBT concentrations in water or wastewater, Arcino Quiero Jr. of Newport News Shipbuilding states: “We are required by our VPDES [Virginia Pollution Discharge Elimination System] permit to submit to the DEQ [Department of Environmental Quality] quarterly progress reports and achieve compliance with final [discharge] limits, 50 ppt, within four years from the effective date of our permit, June 4, 2000.”[sic] This value is based on the current water quality criteria for TBT in Virginia waters. According to the Virginia Code (9VAC25-260-130) “[TBT] in freshwater shall not exceed 0.026 parts per billion (j.tg/l), and the concentration of tributyltin in saltwater shall not exceed 0.001 parts per billion (~.tg/l).”

Currently, the reduction of TBT concentrations has been accomplished by limiting or banning products that contain TBT (primarily anti-fouling paints). This control strategy of reducing TBT concentrations by limiting or banning TBT-containing products is a high priority in management guidelines suggested by international, federal and state agencies. The approach of reducing TBT concentrations by reducing the use of products containing this compound does not address the difficulties encountered by facilities that do not manufacture or use TBT-containing products, but come in contact with the substance from outside sources. There is very little published information concerning the treatment of TBT in wastewater.

The problem has become urgent. Two Virginia shipyards have water discharge permits that require compliance with Virginia's standard (50 ppt) within two years. Furthermore, US EPA in August, 1997, issued for comment a draft national standard. The Applied Marine Research Laboratory (AMRL) of Old Dominion University in conjunction with the Center for Advanced Ship Repair and Maintenance (CASRM) instituted a literature search to determine the state-of-the-art technological practices regarding the reduction of TBT concentrations in wastewater. The project has 3 components: (1) a search of scientific and engineering literature; (2) a search of patent literature; and (3) a survey of TBT users and manufacturers of the technology employed in industry. Manufacturers of TBT, industries that incorporate TBT into their products, state and federal regulatory agencies, and Regional Water Control Boards were also contacted by phone. Surveys were sent to shipyards, researchers, and industries to gain information concerning TBT disposal in waste streams. This report summarizes those findings.

After an extensive inquiry, several avenues of exploration that held promise did not yield the expected results. In particular, the Royal New Zealand Navy voluntarily implemented a waste water collection and treatment system of TBT for the effluent from the large dry-dock at the Devonport Base (de Mora, *etal.*, 1995). Inquiries to the naval attaché at the New Zealand Embassy in Washington, D.C., have not produced results in time for inclusion in this report. Also, the International Maritime Organization may be of help in finding suitable technology.

2

Legislative History

Tributyltin achieved notoriety during the early 1980s as a result of its use as an active biocide in antifouling paints. It was used as a substitute for organo mercury, arsenic or lead boosters in copper based paints or as the sole biocidal agent. It was once described as the most toxic substance ever deliberately introduced into the aquatic environment and caused damage by leaching from boat hulls and aquaculture cages into the water column (Goldberg, 1986). Particularly high concentrations occurred, therefore, in the vicinities of fish farms, harbors, marinas and other areas of high boat use.

The first evidence of the harmful effects of TBT come from Arcachon Bay on the west coast of France in the mid 1970's (Alziew, 1986). Oyster culture and pleasure boating are traditional activities there, and TBT contamination from boats was linked to high mortalities of oyster larvae and such severe malformations of the shells of adults that they were unmarketable.

Since that time, the adverse environmental effects of TBT have been studied extensively. A search of all TBT studies through 1995 found over 600 scientific papers.

As a result of all the attention, many countries have implemented a variety of laws controlling the release of organotin into the environment. Virtually all of the new regulations are directed toward the use of antifouling paint.

The first regulatory actions were adopted in France in 1982 when the government banned the application

of antifouling paints to hulls of most boats shorter than 25 meters (Abel, *et al.*, 1986)

Britain introduced regulations in 1985 controlling the TBT content and release rate in paints. A safe target goal of 20 µg/L was established. In 1987 this target was reduced to 2 µg/L (Vosser, 1987).

In the United States, the United States Environmental Protection Agency (US EPA) commenced a special review of TBT on antifouling in 1986. The Commonwealth of Virginia in 1987 enacted legislation similar to that already in place in Europe (Code of Virginia, Title 3.1). Maryland, California, Michigan and several other states followed suit. In 1988 the U.S. Congress passed the Organotin Act of 1988. It established interim restrictions on painting vessels shorter than 25m (except aluminum) and required paints to have a leach rate of no greater than 4.0 µg/cm²/day. It stated that the prohibition could remain in place until a final decision was issued by the administrator of the US EPA (U.S. Public Law, 1988)

In August 1997 the US EPA issued an "Ambient Water Quality Criteria Document for Tributyltin", for comment (US EPA, Federal Register). This document proposes a Final Chronic Value concentration of 0.01 µg/L and a Species Mean Acute Value of 0.61 µg/L.

Also, in 1997, the International Maritime Organization reviewed comments on a proposal to ban the application of TBT world wide. This ban to be effective 10 years after enactment. Action on this proposal is expected in 1998 (IMO, 1997).

3

CHAPTER 1 REVIEW OF PRIMARY MATERIAL

Literature Review

(Prepared by AISIRL)

Manufacturers of TBT, companies that incorporate TBT into their products, and researchers dispose of waste in one of four ways. Those companies and laboratories that use TBT in research quantities incinerate the hazardous waste components of the TBT waste stream in accordance with 40 CFR 260-263. This method destroys the organic component and renders the residue non-hazardous waste. Other companies transport their waste to US EPA permitted Treatment/Storage/Disposal facilities, also in compliance with 40 CFR 260-263. Many companies that incorporate TBT into their products (i.e., wood stains, paints) do not generate TBT containing hazardous waste. TBT is delivered in drums and is placed in holding vats. The only residual product associated with TBT is the drum in which it is delivered. The drums are triple rinsed in compliance with 40 CFR 260-263 and are, therefore, no longer subject to RCRA waste characterization. They are returned to manufacturer or are transported to a drum disposal unit. The rinseate is placed into the holding tank and incorporated into the product.

The major manufacturer of TBT in the United States, Elf-Atochem, recovers all waste generated. Solid and aqueous waste is transported to a tin recovery unit where it is incinerated at high temperatures to destroy any organic components. The resulting slag is sent to a smelting facility and is purified into tin ingots that are returned to the plant to be used in synthesizing more TBT. Another manufacturer located in Germany, Witco Corp., filters its waste and applies several separation processes. The resulting sludge is dried and placed in an approved landfill.

Numerous studies (Laughlin, *et al.*, 1986; Maguire and Tkacz, 1985; Randall and Weber, 1986) have demonstrated that TBT adsorbs to particulate material. This material can be organic or inorganic in nature. Monitoring conducted at a wastewater treatment plant in Zurich, Switzerland, indicated that a large portion of organotin species, including TBT, was removed after the primary clarifying treatment. Analysis indicated that 75% of the TBT was removed and had been transferred to the remaining sewage

sludge (Fent, 1996). Initial concentrations of TBT were between 64 and 217 ppt. Concentrations in the secondary effluent ranged from 7-47 ppt. After the secondary sedimentation treatment and aerobic treatment, 90% of the initial TBT concentration was removed from the wastewater. An additional filtration resulted in a 98% removal of the compound. Concentration ranges in the effluent were <1 .17 ppt. This plant is noted to be more efficient than most treatment facilities in Switzerland.

The Water Resources Division in the City of Livermore, California, monitors for TBT in their waste stream. They have a unique situation in that they are not near a coastal area and the TBT contamination originates from inland areas. Conclusions drawn by their personnel suggest that TBT is originating from water cooling towers, but this has not been confirmed. Procedures for treating wastewater at the Livermore facility start with the addition of iron (II) chloride to remove sulfides and to promote settling. Activated sludge is added and a secondary clarification step follows. Caustic in the form of sodium hydroxide is added to adjust the pH and then sodium hypochlorite is added as a disinfecting agent. Data seems to indicate that wastewater treatment protocols at this facility reduce TBT by 90% or more (Touray, personal communication). However, there is a considerable lag time between influent and effluent sampling and the residence time of the sewage was not stated. Therefore, the reduced concentration of TBT in the effluent may not directly correlate to the initial influent value.

4

If current wastewater technology proves useful in reducing TBT to acceptable levels by partitioning the compound to the solid phase, the resulting sludge may be a potential source of contamination. Sludge is often dumped at sea and it is also used as a fertilizer. If TBT is present in fertilizer, it may be transferred to soils. At sea, resuspension may occur and TBT may again become a contaminant to aquatic life (Page, 1996).

Sediment samples were collected near a shipyard located on the Fore River near South Portland, Maine, and analyzed for TBT (Page, 1996). Concentrations in the surface sediments ranged from 24-12,400 ng/g on a dry weight basis. Subsequent elutriate analysis determined that TBT was released into the water. The concentration was 0.14% of the total TBT in the sediment sample, suggesting that TBT is released slowly into the water. Even at a slow release rate, there is the potential for future contamination due to the fact that TBT contained in paint chips would be resistant to biodegradation and persist in the sediment. Also, deposit feeders could directly ingest TBT by feeding.

Degradation experiments have been conducted on sewage sludge under both aerobic and anaerobic conditions. (Fent, *et al.*, 1991). Calculated half lives of TBT in water using radio-labeled TBT are approximately 6-7 days (Seligman, *et al.*, 1988). The half life of TBT in the surface sediment is approximately 4-6 months (Stang, *et al.*, 1992). The degradation rates of TBT may be due to the high availability of nutrients in sewage sludge. The nutrients may be a preferred source of carbon for microbes as opposed to the carbon contained in TBT.

TBT degrades to dibutyltin (DBT) and monobutyltin (MBT) and eventually to tin ion. These compounds are less toxic to marine life than TBT. Fungal cultures and freshwater green alga demonstrate the ability to debutylate TBT to DBT and MBT. Diatoms and dinoflagellates also debutylate TBT. While degradation depends upon temperature and the presence of microorganisms, the microorganisms that biodegrade TBT may not be able to survive if the concentration of TBT is too high. Several papers describe microbial biofilms that accumulate TBT without subsequent degradation. No evidence has been found that these microbial methods have been used on a large scale for waste stream treatment.

5

A search of the U.S. Patent data base has been conducted to identify proprietary technology that can remove tributyltin or organotin, from aqueous streams to purity levels of <50 parts per trillion. The search found no turn-key technology that can accomplish this task.

The search was then widened to determine proprietary technology which can remove organic pollutants from aqueous streams to levels of parts per billion. This search produced a number of patents based on different technical approaches.

1. *Resin Beds*

A wide variety of cationic, anionic and non polar resins have been employed to purify water. Non-polar resins are effective for the removal of a wide range of organic pollutants.

- U.S. Patent 3,531,463 describes a process to remove phenols and chlorinated hydrocarbons contained in the effluent of a bleached Kraft pulp mill.

While the class of non-polar ion exchange resins have been found to absorb a wide range of organic pollutants, U.S. Patent 5,236,594 describes the benefits of using non-ionic polymeric resins, since these can be regenerated using solvents in which the pollutants are soluble. The preferred resins are products such as:

AMBERLIGHT® XAD	Rohm & Haas, Philadelphia, PA
Duolite ®	Chemical Process Co, Redwood, CA
Dialon ®	Mitsubishi Chemical Co, Tokyo, Japan

Water purity levels to 0.1 ppb (100 ppt) are claimed

U.S. Patent 3,853,758 describes the use of this type of resin to remove toxic organic pollutants from the effluent of a dye manufacturing plant. For best results contact times of 2-10 minutes are required. After treatment, pollutants can be extracted from the resin by mixing with solvents in ratio 1 volume of resin: 3 volumes solvent. Solvents can be methanol, acetone, dichloromethane, chloroform, diethyl ether and ethyl acetate.

2. *Activated Carbon*

Effluent treatment using activated carbon has been found to remove a wide range of organic pollutants from water. A search using key words “activated carbon” and “water purification” revealed in excess of 400 patents issued since 1973. Activated carbon is not selective and removes most organic compounds from water. It cannot be easily regenerated and spent carbon must be disposed by incineration or in an appropriate land fill.

U.S. Patent 5,399,263 describes a water purifier for supplying high purity water with a low organic carbon content. The purifier consists of a multibed purification cartridge having several layers of activated carbon and both cationic and anionic ion exchanger resins. It is claimed that water with a total organic carbon contents of up to 100 ppb (100,000 ppt) is produced.

6

U.S. Patent 4,007,116 describes a process for purification of wastewaters using activated carbon in a moving fluidized bed arrangement. Granular activated carbon is moved in through the bed in counterflow to the water stream, so as to continuously introduce fresh activated carbon particles at the top of the bed to compensate for using carbon withdrawn at the bottom. Organic carbon contents of 1 ppb (1000 ppt) are claimed.

Activated carbon can be manufactured in a number of different ways and in different forms. We have

identified 381 U.S. Patents issued since 1973 describing different processes of preparation, manufacture, and method of use for this product.

3. *UltravioletLight*

Ultraviolet light has been used to remove organic compounds, and in some cases microbes, from water. The mechanism for removal of organic pollutants is the partial breakdown of the organic molecule by UV and subsequent removal of the disassociation products by some other means.

U.S. Patent 5,302,356 discloses an ultrapure water treatment system comprising a 185 nm UV light source in conjunction with a catalytic filter made of a polymeric porous material with a photoactive catalytic coating. The UV light, catalyst and air act to convert organic contaminants to carbon dioxide.

U.S. Patent 5,061,374 describes a process where-by water is treated in a succession of water treatment steps comprising: mineral filter, mixed ion exchange resin bed, UV light source, a reverse osmosis stage and fine ultrafiltration stage. Final water purity is claimed to be 1 ppb (1,000 ppt).

4. *Ultrafiltration*

Many organic contaminants including TBT are attracted to particulates in water. The principle behind ultrafiltration systems is to remove the contaminants by removing the particulates from the water.

Several patents employ ultrafiltration as the final stage of a water purification sequence. U.S. Patents 5,376,281 and 5,302,356 both describe the use of ultrafiltration in conjunction with ultraviolet light.

5. *Bio!ogical!Degradation*

Many industrial effluent streams are treated successfullyby microbial degradation.

U.S. Patent 5,653,883 describes a method of removing organic contaminants from water by microbial degradation in a stirred tank system having a powdered or granular media for biofilm support.

Biodegradation will not take place if the pollutant concentration is so high as to poison the microbes. U.S. Patent 5,653,883.

7

Survey of Manufacturersand Users of TBT

Approximately 150 questionnaires were mailed to several research facilities and laboratories, a manufacturer of TBT, and industries that either incorporated TBT into their products or came in contact with TBT containing products. Sixteen questionnaires were returned. Researchers and laboratories comprise nine of the respondents and industries comprise the remaining seven (see Appendix D).

The only company that monitored for TBT is the manufacturer, Elf-Atochem. Generated waste is sent to a tin~recovery unit. All solid and aqueous waste is incinerated at high temperatures, which destroys the organic portion. The resulting slag is delivered to a smelting facility and the tin is recovered as purified ingots to be used in further TBT synthesis.

Companies that incorporate TBT into their products do not monitor for TBT because they do not generate a wastewater stream. Washdowns from TBT holding tanks and rinses from TBT drums are incorporated into the product. Mr. Algimantas Pliodzinskas, the Health and Safety Coordinator at Hempel Coatings (USA), Inc., a marine paint manufacturer, states that “any residue which cannot be utilized in their product is sent for disposal through fuel blending for cement kilns. All TBT containing paint products or raw materials are in a combustible form suitable for fuels blending.”

None of the respondents from companies that incorporate TBT into their product were aware of any legislation in their respective regions that would regulate TBT discharge. Mr. Pliodzinskas stated that organotins are “by definition pesticides and are to be disposed of in accordance with federal, state and local regulations. RCRA regulations do not specifically list tin or TBTs as specific hazardous wastes.”

Most industries (primarily shipyards) that come in contact with products containing TBT are required to monitor for the compound. TBT monitoring is one of the requirements of the National Pollutant Discharge Elimination System (NPDES) permit. National Steel and Shipbuilding Company in San Diego, CA, currently monitors for TBT in the water column surrounding the facility, but not in its own discharge. A discharge of TBT can only occur at pier side at their establishment. Once their NPDES permit is renewed, however, TBT in the shipyard discharge will be monitored as well. This firm does not use any paints containing TBT unless a customer specifically requests it.

To reduce possible TBT contamination when applying 181-containing paints, Halter Marine Group, Inc. places plastic sheeting on the ground underneath the area to be painted. The plastic is moved from section to section to reduce the quantity of plastic used. This material is analyzed and disposed as a hazardous waste if necessary. Any sludges or solids such as paint suits, brushes, etc. are disposed in a similar fashion if found to be contaminated. When TBT-containing coatings are removed from vessels, the material is contained via “environmental screens” with a shade factor of 90% or more. These screens reduce off-site particulate migration. If the vessel is in dry-dock, “the screens and a temporary steel birm [sic] or wall of 12-18 inches is placed in areas to block any residual runoff.” (Appendix C) Norfolk Shipbuilding and Drydock Corporation (NORSHIPCO) has recently employed carbon-bed technology, but 181 concentrations in wastewater after treatment were 2 ppb; this concentration does not meet the proposed 50 ppt regulation. Still another facility manages its waste according to RCRA waste disposal guidelines.

A feasibility study was conducted by U.S. Filter for Newport News Shipbuilding with guidance from Rohm & Haas and the College of William and Mary Virginia Institute of Marine Sciences. A series of

8

resins was developed for the removal of copper in the effluent, but cost limitations did not allow further study to determine the efficiency of TBT removal.

There are several opinions concerning minimizing the hazards of TBT. One respondent wrote only that Best Management Practices need to be instituted. Suggestions from other respondents include entraining the wastewater and treating it, but details were omitted, and finding alternative sources of anti-foulants. It is understood that new anti-foulants might not be as effective as TBT, but the toxicity to the environment would be less. One shipyard representative stated that if a satisfactory solution for controlling TBT is determined, the rest of the world must adhere to these policies. If not, then contamination would persist despite the efforts to minimize the hazard TBT represents to aquatic life.

Research facilities that responded to the survey monitor for TBT at their respective laboratories or for clients, but do so for research purposes and not for compliance with any regulations. Each laboratory monitors in a slightly different fashion. Some laboratories directly sample and chemically analyze aqueous waste for clients or at their own facility. Others observe the emergence of imposex in biota as a biomarker for the presence of TBT in local coastal waters. Waste from these laboratories is quite small and is either incinerated or sent to a waste handling facility. Researchers have several suggestions for reducing TBT concentrations in water that range from containing initial waste and disposing of it at high temperatures, filtering contaminated water through an organic phase to which TBT will bind, or using biodegradation and biosorption techniques. NuTECH Enterprises, Inc., a waste disposal unit in Oceanside, California, has had success in reducing concentrations of other organometallic substances by using biodegradable quaternary surfactants. This company is willing to conduct experiments to determine

if this technology would be suitable for removal of TBT.

Most of the respondents do not know of any legislation enacted or pending that limits TBT concentrations in water. The exceptions are those respondents from Virginia and the United Kingdom (UK). The UK has an environmental quality standard of 2-3 ng/L in seawater - far more stringent than any standard in the U.S. at this time. Opinions on minimizing the hazard posed by TBT vary from banning the substance entirely, enforcing strict containment procedures by employing closed systems in dry docks, developing less toxic alternatives, to conducting a cost/benefit analysis of the use of TBT versus the impact of TBT on marine ecosystems.

9

CHAPTER 2 DISCUSSION (Prepared by CASRISI)

Discussion of Practical Alternatives for Removal of TBT from Water

There is no "off-the-shelf technology" that can be directly used by shipyards to achieve TBT discharge concentrations of <50 ppt.

Due to the very low volatility of TBT compounds, significantly lower than that of water, air stripping is not expected to be of value for removal of TBT from water.

Manufacturers of TBT use incineration to destroy TBT or recycle the TBT in waste streams into new product. These approaches are impractical in shipyards where TBT is dissolved in tens or hundreds of thousands of gallons of wash-water.

Reduction of aqueous TBT concentrations by sewage treatment has been demonstrated at a number of facilities around the world. Adsorption of TBT onto activated sewage sludge is significant. Typical results show influent TBT concentrations of >200 ppt and effluent concentrations of 50-100 ppt. However, one sewage facility in Zurich, which employed an extra treatment step, achieved an effluent concentration of 2 ppt (Fent, 1996). Shipyard effluents can contain >50,000 ppt TBT (Personal Communication with Tom Beacham from NORSHIPCO). This level is sufficiently toxic to suppress all microbial activity in activated sewage sludge (Muller, *et al.*, 1989).

Other technologies may be more directly applicable to shipyards than the technology used in water treatment facilities. The next section describes several approaches that may be more applicable to the removal of TBT from shipyard waste streams.

Technical Approaches Most Likely to Succeed

1. Dissolved Air Floatation (DAF)

TBT appears to be highly attracted to particulates in the water. Estimates of the water-solid coefficient range from 1,000 - 10,000 on a weight basis. For instance, Maguire *et al.* (1985) found a partition coefficient of 2180 ± 350 for TBT in water and sediment of Toronto harbor.

A Dissolved Air Floatation system can take advantage of this phenomenon to reduce TBT concentration in water by, perhaps, 1,000 times.

Control of pH may be important. Muller *et al.* (1989) showed solubility of TBT in water was minimum at a pH of 6.

Absorption processes may be able to reduce TBT concentrations to less than 50 ppt. In one sewage plant in Switzerland, TBT levels in water were reduced from 181 ppt to 9 ppt mainly by sedimentation in the primary classifier and subsequent treatment steps (Fent 1996).