Tributyltin Antifouling Paints:
Introduction & Overview

FOR THE OCEAN'S '87
INTERNATIONAL ORGANOTIN SYMPOSIUM

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1.0. INTRODUCTION

The Ocean's '87 International Organotin Symposium has been organized to bring together researchers from many disciplines, regulators and policy and decision makers from across the world to discuss and review data, studies and results. This Introduction and Overview Section has been prepared to aid those from non technical backgrounds gain a quick introduction and grasp of the technical and environmental issues and aspects, and vice versa for the technical person to be introduced to the policy and regulatory issues. We apologize for including a section from the previous introductory material (types/action/chemistry of organotin antifoulant paints) which was published in the Ocean's '86 Proceedings. However, we have added to it summaries of studies conducted in France and England, including a section on monitoring and research needs. Lacking a summary paper on monitoring data in theSymposia to compliment Rexrodes paper (this Volume) on ecotoxicity data, we quickly prepared a summary table of monitoring data (including data from papers in this volume (see Table 1). It's unfortunate that the findings of EPA's Special Study will not be available in time to be summarized or reprinted as a background paper(s) in this Volume. However, their ongoing studies will last several years with a series of publications to be issued.

The goals of these Organotin Symposia are to provide a forum for the exchange of research findings, methods and wisdom gained from studying organotin compounds. Another goal is to publish in one Volume many of the papers that have been published as technical reports or in a wide array of scientific and nontechnical literature and government reports. Such publications often are poorly disseminated or difficult to retrieve from computer data bases. A third goal is to provide a forum for the exchange of regulatory strategies among states and nations.

We believe that significant advances have occurred in our understanding of the toxicity and fate and behavior of organotin compounds in the environment in the past 3-4 years, and we are very fortunate that the MTS and IEEE as professional societies have been so far sighted as to host these Symposia. Also without the funding and support of the U.S. Navy, EPA, and NOAA, these Symposia and
Proceedings would not have been possible. Lastly within the Executive Committee, the contributors to the success of these Symposia are the Co-Chairmen who solicited papers from across the world and developed panels or sessions, and/or funding sources and that have brought these Symposia together.

1.1 Fouling Organisms

"Bottom fouling has been the mariner's curse ever since man first set sail" (Russell, 1967). The growth of marine organisms on boat bottoms has been a war between man and organism. The early Phoenicians even nailed copper strips to the hulls of their ships to inhibit the growth of fouling organisms, such as barnacles and sea weeds. Because they rowed or sailed their boats, they learned pretty quick that the smoother the boat bottom, the easier to row or sail and the faster the boat. In times of naval action this meant that one could either catch another vessel or get away from another vessel. It was the single most important factor to a Navy in the days of sail. Unfortunately for today, it is just as important to an aircraft carrier who has to launch aircraft while underway at 40 knots.

The growth of barnacles, seaweeds, or tubeworms on a boat bottom is referred to as "fouling." This fouling produces roughness that increases turbulent flow, acoustic noise and drag. A 10 micron (0.0001 mm) increase in average hull roughness can result in a 0.3 to 1.0 percent increase in fuel consumption. For large vessels (bulk carriers), fuel costs can amount to as much as 50 percent of the total operating costs. For example, the 1985-86 fuel bill (one of the world's largest ships) was $17 million (U.S. dollars).

For the U.S. Navy (which has ships having bottom (wetted hull) areas as great as 150,000 square feet) maintaining a fouling-free bottom becomes a major task. In tropical oceans, the Navy has found that ships may begin to experience significant bottom fouling in less than one year if painted with copper-based antifoulant paints as compared to the 5-7 years if painted with tributyltin (TBT) based antifoulant paints.

The Navy calculates, that if the entire fleet (600 ships) were painted with TBT antifoulant paints, that the fuel avoidance costs would exceed 110 million dollars annually (calculated with fuel costing approximately $16/barrel). In commercial shipping, fishing, and private boating, this could add another $300 to 400 million in fuel savings. The wasting of 1/2 billion dollars of fuel becomes fuelish, particularly when one realizes that this is almost 2 billion gallons of fuel per year, lost forever to this Nation. Fouling also represents increased wear on propulsion machinery, increases vulnerability to acoustic sensing systems, and increased down time and cost for hull scraping, cleaning, and painting.

1.2 Types of Antifoulant Paints

Wooden ships have been recorded to have been covered in lead sheets to prevent the action of boring and fouling organisms (as early as 300 BC). In the 17th and 18th centuries, the use of copper on boat bottoms was found to be more effective to prevent fouling. Cuprous oxide paints were introduced and widely used by the turn of the century. A wide range of biocides have been used in boat bottom paints. Organo-mercury compounds and stereoarsenicals were used until the 1970's to increase the biocidal properties of cuprous oxide paints. These compounds are no longer used in antifoulant paints because of their toxicity and environmental contamination problems.

An antifoulant paint consists of a film-forming material (matrix/binder/resin/medium) and a pigment. The film-forming material and pigment can affect the following paint properties: strength, flexibility, water absorption, and color. An antifouling paint is similar to any other paint (matrix plus pigment); however, the paint film is biocidal due to properties of either pigment or matrix. The antifoulant paint works by releasing small amounts of biocide at the paint surface that kill the settling stages of fouling organisms.

There are three types of antifoulant paints: (1) Conventional or referred to as "free association," in which the biocides are loose in the paint and are released by contact leaching; (2) soluble matrix and ablative; and (3) self-polishing, in which the biocides are added in free association or chemically integrated within a matrix as in the organotin copolymer paints. Types 1 and 2 are referred to as conventional paints, both use the biocide in the free association form.

Type 1 uses contact leaching to release the biocide. In this process, seawater percolates slowly through a tough usually insoluble paint matrix (see A and B in Figure 1). The biocides are added in the free association form and mixed into the paint and leach exponentially over time. This category of TBT antifoulant coatings has traditionally posed a problem of high early release rates with a shorter time period of protection from attachment and growth of fouling organisms. After a period of less than 2 years, the paint film ages, calcium carbonate (CaCO$_3$) clogs the microchannels in the paint surface and inhibits the release of biocide (see C in Figure 1), then the surface becomes biofouled. This calcareous fouling leaves a quantity of biocide that remains unused on the vessel hull, which must be removed prior to the next painting.

Figure 1 Contact Leaching Antifoulant Paints

![Figure 1 Contact Leaching Antifoulant Paints](image-url)
Type 2 is commonly referred to as an "ablative" (or shedding) paint. It is a slightly seawater soluble matrix paint that sheds during use—as the paint surface roughens, paint particles (very thin microlayers) peel off exposing a fresh supply of biocide (Figure 2). The biocides are added in the free association form, leaching exponentially with the release of biocide also being inhibited by the formation of surface insolubles. The lifetime of this paint is also about 2 years. In order to be effective, the vessel must be returned to the water before the paint film cures.

![Figure 2. Ablative Antifoulant Paint.](image1)

Type 3 antifouling paint is commonly referred to as a "self-polishing" copolymer paint. Developed in the early 1970s, the paint is hydrophilic (i.e., seawater does not enter into the paint matrix). The seawater/paint reaction layer occurs at the surface of the paint; the paint has an unstable release layer that gradually erodes (Figure 3). The paint formulation has biocide at very low levels in the biocide's free state. The paint works at the surface layer with a coating chemistry that promotes constant renewal of the surface layer. The TBT moiety is chemically bonded to a polymer backbone (e.g., TBT methacrylate copolymer). This bond is designed to be hydrolytically unstable under slightly alkaline conditions. Therefore, the biocide is released only by chemical hydrolysis of the tributyltin itself.

![Figure 3. Self-Polishing Copolymer Antifoulant Paint.](image2)

This paint formulation has several advantages: (1) release is governed by hydrolysis of the TBT group rather than dissolution of the paint particle and (2) the release rate is more effectively controlled (slowed down) by altering the polymer's water absorption characteristics. With the exception of the initial high release rate during the "conditioning" period (approximately the first month after the freshly painted hull is placed in the water), see Figure 4.

![Figure 4. Copolymer paint release rates.](image3)

These polymeric, film-forming resin coatings are characterized by a slow dissolution rate from ship hulls and thus are able to maintain a constant but prolonged, low release rate of antifouling toxicant. The controlled biocide release also gives the antifouling paint a controlled life span (the thickness of the initial application of the paint determines the life span). Current practices suggest that 5 to 7 years is the average life span. Also copolymer paints can be applied directly to the ship's hull surface without having to sandblast previous copolymer layers away; thus, reducing shipyard costs of grinding off old paint, and subsequently less TBT is used and wasted to the environment. Also workers are not exposed to TBT during paint removal.

1.3. ORGANOTIN COMPOUNDS

Organotin compounds are now one of the most studied group of organometallic chemicals, in terms of industrial and agricultural uses and applications. The first applied use was as a mothproofing agent in 1925. In 1932, organotin compounds were used for stabilizing chlorinated benzenes and diphenyls used in transformers and capacitors. This was followed by dibutyltin dilaurate and other dibutyltin salts in 1936 being used to stabilize polyvinyl chloride (PVC). The biocidal properties of organotin were first discovered in the 1950's by a group headed by G.J.M. van der Kerk at the Institute for organic Chemistry, T.N.O., Utrecht, Holland, under the sponsorship of the International Tin Research Institute in Greenford, Middlesex, England.

The largest use of organotin compounds today is in stabilizing PVC polymers. PVC is used extensively in the construction industry (flooring, fencing, and piping) and in the food-packaging industry (bottles and films). Exposure of PVC to heat or ultraviolet light for prolonged periods causes diminished optical clarity and undesirable coloration. Stabilizers are required if the endproducts containing PVC must be colorless or transparent, as in the case of bottles, films, or sheets used for food packaging. In the 1970s, about 10 percent of all PVC being produced was stabilized with organotin compounds. Following van der Kerk's discovery of the fungicidal
properties of organotin compounds, many agricultural and industrial bactericidal and fungicidal uses have been developed. Both triphenyltin hydroxide and triphenyltin acetate are used to control fungi that cause potato blight (leaf spot) on sugar beets, celery, carrots, onions and rice. Organotin compounds are also used as fungicides to prevent tropical plant diseases in ground nuts, pecans, coffee, and cocoa.

As an insecticide, triorganotin compounds have been used against houseflies, cockroaches, mosquito larvae, cotton bollworms, and tobacco budworms. They also act as chemosterilants and have antifeeding effects on insects.

In the early 1960s, two organotin compounds (tributyltin oxide and tributyltin fluoride) were first used as a molluscicide to kill several species of freshwater snails that were the intermediate hosts of the worms of the genus Schistosoma, which transmit the disease Schistosomiasis to humans. This immediately led to the use of tributyltin (TBT) as a paint additive in 1961 for its biocidal properties in antifoulant boat bottom paints.

Tributyltin compounds used in antifouling paints are chemically characterized by a tin (Sn) atom covalently bonded to three butyl (C₄H₉-) moieties. A representative TBT active ingredient, tri-n-butyltin fluoride, may be chemically describe by the following structural formulas for the undissociated (neutral) pure form or the active ingredient and for the water dissociated (positively charged) form:

\[ \text{H}_3\text{C}_4\text{Sn}-\text{C}_4\text{H}_9 \quad \text{Bu}_3\text{Sn}^+ \]

The toxicity of organotin compounds to aquatic organisms is thought to increase with the number of butyl substituents from one to three, and then to decrease with the addition of a fourth butyl group. In order to assess the fate of a particular tributyltin derivation in water, one must consider the dissociated active form, the TBT cation (Bu₂Sn⁺), and its major metabolites presumably formed by progressive debutylation to inorganic tin.

\[ \text{Bu}_3\text{Sn}^+ \rightarrow \text{Bu}_2\text{Sn}^{2+} \rightarrow \text{BuSn}^{3+} \rightarrow \text{Sn}^{4+} \]

Elemental or inorganic forms of tin (as in mineral deposits or tin can) appear to cause negligible toxicological effects in humans or wildlife. However, in contrast, the TBT's display an increased fat solubility and, consequently, enhanced ability to penetrate biological membranes, thereby posing a greater toxicity potential.

In the U.S., there are three major uses of triorganotin compounds: (1) as a wood preservative against wood-reducing fungi (such as Poria monticola, Coniophora olivacea, and Formos lividus) in bathrooms (shower stalls and flooring) and on decks and exterior siding and fences, (2) as a fungicide in the textile industry to control odor producing fungi in socks and under garments, and (3) as a biocide in antifoulant paints.

1.4. Nation-wide Production and Use

Approximately 250,000 - 300,000 lbs of TBT a.i are used in the U.S. in antifoulant paints annually. The U.S. Navy's use of TBT paints would increase the annual usage approximately 60,000 to 90,000 lbs a.i annually. A recent study funded by the EPA found only about 125 ship yards and boat yards in the U.S. painting with TBT paints. One of the largest U.S. ship yards, Newport News Shipbuilding in Newport News, Virginia has decided to turn down work, if it requires the use of TBT paints because of potential risk to employees that it does not wish to take.

2.0. Results of Studies in France and England

Excellent summaries have been prepared by Alzieu and Abel et al. (Ocean's 86 Proceedings) of the work in France and England. The U.S. studies have not been summarized in a similar manner, however, a summary is in preparation with NOAA funding (M.A. Champ, Principal Investigator) and will be available early in 1988.

2.1. Field Observations

The Pacific oyster (Crassostrea gigas) was introduced into France for oyster farming in 1968 to replace declining locally farmed oysters. In Arcachon Bay in France, growth anomalies in the development of C. Gigas larvae were first observed in 1976 in a small area of the Bay. By 1977, these anomalies were detected in the rest of the Bay. Early researchers noticed that there was an association between marinas or boat moorings and the occurrence of the shell malformations, and that the degree of shell thickness correlated well with the density of boats in the estuary, suggesting a relationship with increased use of TBT antifoulant paints. A stronger correlation was suggested when this tendency for shell thickening could be reversed by moving the oysters to an area far removed from boating activity. There were other problems than just growth and shell deformation, with some regions having little or no natural spat (settling oyster larval stage) fall, suggesting toxic effects to early oyster life stages. However, these biological field studies did not have chemical support data (measurements) for concentrations of TBT in the waters of these local areas where the shell deformities were found, making these correlations interesting but not valid. Similar observations were being observed in England but not as dramatic as first because it appears that the Pacific oyster is more sensitive to the toxicity of TBT than the
Chemical family: Organotins

Pesticide type: biocide, molluscicide, wood preservative and disinfectant.

Registrations: Antifoulant paints containing TBT compounds were initially registered in the early 1960's. There are over 300 TBT antifoulant paint formulations and over 60 manufactures.

Application sites: TBT's are use in antifoulant paints applied to ship and boat hulls as well as buoys, crabpots, fish nets, etc. TBT's are also registered as wood preservatives, disinfectants, and biocides for use in cooling towers, pulp and paper mills, breweries, leather processing facilities, and textile mills.

Paint formulations: TBT antifouling paints may be classified into two categories according to the way the TBT moiety is incorporated into the paint coating and subsequently released.

Free Association paints: In these conventional coatings, the TBT is physically incorporated into the paint matrix (which contains the pigment, water-soluble resins, and inert substances). This category of TBT antifoulant coatings has a high early release of TBT with subsequently shortened time period of protection from attachment and growth of fouling organisms.

Copolymer paints: In this category the TBT moiety is chemically bonded to a polymer backbone. The biocide is released only by chemical hydrolysis of the TBT itself. These paints are characterized by slow dissolution from ship hulls and thus achieve a constant but prolonged, low release of antifoulant toxicant.

Chemical names: Bis(tributyltin) oxide, Bis(tributyltin) dodecenyl succinate, Bis(tributyltin) sulfide, Tributyltin acetate, Tributyltin acrylate, Tributyltin fluoride, Tributyltin resinate, Tributyltin methacrylate, and copolymer, and Bis(tributyltin) adipate.

<table>
<thead>
<tr>
<th>TBT Acetate (ug/l)(PPM)</th>
<th>Effects on Reproduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>Inhibition of Fecundity</td>
</tr>
<tr>
<td>50</td>
<td>Inhibition of Segmentation</td>
</tr>
<tr>
<td>25</td>
<td>Partial Reduction of Segmentation</td>
</tr>
<tr>
<td>10</td>
<td>Absence of the Formation of Trocophores</td>
</tr>
<tr>
<td>3-5</td>
<td>Absence of Veligers - Malformation of Trocophores</td>
</tr>
<tr>
<td>1</td>
<td>Abnormal Veligers - Malformation of Trocophores</td>
</tr>
<tr>
<td>0.5</td>
<td>Numerous Anomalies - Total Mortality in 8 Days</td>
</tr>
<tr>
<td>0.2</td>
<td>Perturbation in Food Assimilation - Total Mortality After 12 Days</td>
</tr>
<tr>
<td>0.1</td>
<td>Normal D-Larvae: Slow Growth, Almost Total Mortality After 12 Days</td>
</tr>
<tr>
<td>0.05</td>
<td>Slow Growth; High Mortality Rate After 10 Days</td>
</tr>
<tr>
<td>0.02</td>
<td>No Observable Effect</td>
</tr>
</tbody>
</table>
European flat oyster (Ostrea edulis) which was introduced by the Romans. However, oyster farming of C. gigas was attempted and was quite unsuccessful in many areas of the U.K., particularly the estuaries of the Rivers Crouch and Roach on the east coast of England, which are two of the most highly TBT contaminated waters in the U.K. (Thain, 1986).

2.2. Laboratory Toxicity Studies

Subsequently a series of studies were conducted by the French at IFRMÉR (Institut Français de Recherche pour l'Exploitation de la Mer) by Alzieu and co-workers which is presented in Table 1, and by Waldock and Thain and co-workers at the Ministry of Agriculture, Fisheries and Food (MAFF) Fisheries Laboratory at Burnham-on-Crouch. The results of these studies demonstrated that TBT was an agent that could also cause oyster shell deformations.

2.3. Effects of Calcification Mechanisms in Oysters

The mechanisms of formation of shell anomalies in the growth and development of oysters has been studied by the French and they have found the formation of a series of chambers forming in between the layers of calcification within the shell, which is filled with a jelly-like protein. Analysis of the protein in this substance has shown a higher proportion of threonine and a smaller amount of serine, glycine, and aspartic acid compared to the usual composition of the normal calcification proteins. The components of this jelly-like substance does not appear to bind with the Ca^2+ or HCO3-. and when added to solution of CaCO3 slows down or prevents the formation of crystals of CaCO3. Leading to the conclusion that the formation of this gelatinous substance is an abnormal process which results in the perturbation of molecular genetic mechanisms (Alzieu, 1986). Figures 5 presents an example of the chambering effect in the upper valve of an oyster shell, from work at MAFF by Waldock and Thain. Wolniakowski et al. (this Volume) have recently found Pacific Oysters with similar deformations in Coos Bay, Oregon. South Slough is located adjacent to a boat yard that has used TBT paints for many years.

Figure 5. Abnormal oyster shell illustrating chambering and balling effect.

In the most acute malformations in Arcachon Bay, France, the thickening of the oyster shell (growth anomalies) was more rapid than its lengthwise growth, and the oyster took on a characteristic ball shape. These malformations were only observed in C. gigas and not in the European flat oyster (O. edulis). Figure 6. is a photo of a ball shaped oyster from Arcachon Bay, France.

Figure 6. Example of a Ball-shaped Oyster from Arcachon Bay, France

2.4. Imposex in the Common Dogwhelk

Populations of the common dogwhelk, Nucella lapillus, around the south-west peninsula of England were studied by Scientists of the UK Marine Biological Station (see Gibbs and Bryan, this Volume) for occurrence of "imposex" which is the superimposition of male characteristics notably a penis and a vas deferens, on female individuals of the species. These researchers found a high occurrence of imposex in populations close to centers of boating and shipping activities. The occurrence of imposex correlated significantly with the concentration of body tin in dogwells (up to 2 ug/g dry tissue). Laboratory studies have confirmed that exposure to TBT will induce imposex. The ecological significance is that the field observations of N. lapillus populations around south-west England indicate that those populations which exhibit marked imposex show signs of decline. They comprise fewer females than expected and juveniles and deposited egg capsules are scarce or absent, indicating a lowering of the reproductive capacity of those local populations. Also females examined had oviducts clogged with decomposing eggs that they could not release because the newly formed male reproductive tissues blocked these oviducts. Subsequent laboratory studies suggest that environmental concentrations of about 1 part per trillion (or 1 second in 31,000 years for comparison) seems to initiate imposex. The dog welks feed off rocky shore substrates, eating algae and other microscopic organisms, which become coated with high concentrations of surface micro layer transported TBT, and that this is a critical pathway of exposure to the dog welk, exposing them to abnormally higher levels of TBT. Levels in the surface micro layer have been found to be over 1000 times higher and in the water column below.
3.0. REGULATORY STRATEGIES

3.1. International

United Kingdom:

In January 1986, the UK enforced regulations that prohibit the retail sale and supply of antifouling paints containing organotin compounds where the total tin concentration is greater than 5.5% by weight in copolymer paints, or the total concentration in tin in other non-copolymer paints exceeds 2.5% by weight of tin. These regulations were meant to control use on small pleasure crafts, ban the sale of free-association paints containing high concentration of organotins, and to set an upper limit on organotins in copolymer paints. The Department of Environment (DOE) has taken steps to determine the effectiveness of this legislation. They have: (1) Set ambient water quality standards at 20 ng/l [ppt] (or 20 parts per trillion), (2) Set up a monitoring program, and (3) Instituted a research program to fill in data gaps.

Based on the results of the monitoring program, the DOE, in July, 1987, initiated a total ban on TBT paints for use on small boats because they found that the existing controls were not effective enough in reducing contamination to acceptable levels to protect sensitive species. The DOE lowered the water quality standard from 20.0 ppt to 2.0 ppt TBT (see Abel et al., this Volume for more information).

France:

In January 1982, France announced a ban on TBT paint containing more than 3% by weight organotin for boats less than 25 meters in length. Hulls made of aluminum or aluminum alloys were exempted from the ban.

Switzerland and Germany:

Both countries have banned all use of TBT in antifouling paints in freshwater environments.

3.2 U.S. Individual States

Virginia: Passed unanimously - [Article 5, Chapter 14, Section 3.1 - 249.22 through 249.26].

HJR190 [House Joint Resolution]. Memorializes Congress and EPA to cancel registration of TBT compounds used in free association paints, and to expand EPA's current review of pesticide registration of TBT used in antifouling paints to include all registered TBT compounds.

Urges Congress and EPA to support the states in their efforts to develop effective regional solutions to this issue.

HJR326 Requests the State Water Control Board to continue to act as expeditiously as possible in adopting a water quality standard sufficient to protect aquatic resources of the Commonwealth from toxicity and undesirable bioaccumulation from TBT compounds.

Requests that the Board coordinate its efforts with Maryland.

HB1603 Ban on sale or possession of TBT, except in commercial boat yards. TBT with acceptable leach rates can be used on vessels greater than 25 meters in length, or those which have aluminum hulls.

Requires public education program.

A person may distribute, sell, or apply TBT paint with acceptable leach rates if paint is sold in 16oz spray can for use on boat motors.

Virginia Department of Agriculture adopted Emergency Regulations that:

Defined acceptable leach rates for TBT paints at 5.0 microgram per square centimeter per day at steady state conditions.

Prohibited TBT paint on vessels less than 25 meters except aluminum hull boats. Vessels larger than 25 meters or aluminum hull boats may use TBT paint with acceptable leach rates.

Cancelled registrations of all TBT based paints except certified acceptable leach rate paints tested in accordance with EPA testing procedures.

Permited sale of TBT paints in 16oz. aerosol cans with acceptable leach rates, for use on outboard motors and lower units.

Regulations in effect until July 1, 1988, or until permanent regulations are adopted under the administrative process.

Maryland: Passed [Maryland State Code, Chapter 304].

SB499 Defines acceptable leach rates to be 1.0 nanogram per square centimeter per day at steady state conditions.

and

HB651

Bans the sale of possession or use of TBT antifouling paints except for commercial boatyards using TBT with acceptable leach rates on boats greater than 25 meters in length.

Permits sale and use of acceptable leach rate TBT paints if sold in a 16oz. spray can for outboard motors or lower units.
DOA may seize an antifouling paint used or possessed in violation of this bill.

Establishes maximum penalty of $2,500 fine for violation.

Directs the development of water quality standards for the concentration of TBT in waters of the state and the regulations of point sources releasing TBT in accordance with the water quality standard.

Directs the development of an education program to advise boaters, boatyards, marine suppliers, and other users of TBT paints.

Directs the publishing of a detailed list of antifouling paints in use in the state that contain TBT, and which have acceptable leach rates.

Washington: Passed

SB5978 Use and sale of TBT antifouling paint shall be prohibited on vessels less than 25 m in length. TBT paints with a leach rate of 5.0 micrograms per centimeter squared per day may be used on vessels over 25 m in length or with aluminum hulls. 16 oz. spray cans are exempted.

California: (In Hearings)

Assembly Bill 637: Use and sale of TBT antifouling paint shall be prohibited on vessels less than 25 m in length. TBT paints with a leach rate of 5.0 micrograms per centimeter squared per day may be used on vessels over 25 m in length or with aluminum hulls. 16 oz spray cans are exempted.

New Jersey:

In New Jersey Senator Pallone has introduced Senate Bill No. 2973 to regulate the use of TBT by regulating its sale. In this bill "no person may offer for sale any paint containing a tributyltin (TBT) compound." With a civil penalty of $500.00 for first offense and $1,000.00 for the second and subsequent offense. The bill states that "since less harmful alternatives exist, hardship from a total ban on the sale of paints containing TBT would be minimal."

3.3. U.S. Federal (EPA Special Review)

A pesticide product may be sold or distributed in the U.S. only if it is registered or exempt from registration under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), as amended (7 U.S.C. 136 et seq.). Before a product can be registered, it must be shown that it can be used without "unreasonable adverse effects on the environment" (FIFRA Section 3(c)(5)), that is, without causing any unreasonable risk to man or the environment. Taking into account the economic, social, and environmental costs and benefits of the use of the pesticide" (FIFRA Section 2(bb)). The Special Review (RAPAR-Rebuttable Presumptions Against Registration) Process (40CFR 162.11) provides a mechanism through which EPA gathers risk and benefit information about pesticides which appear to pose risks of adverse effects to human health or the environment which may be unreasonable. Through the issuance of regulatory support documents, EPA publicly sets forth its position, and invites pesticide registrants, Federal and state agencies, user and environmental groups, and any other interested persons to participate in the Agency's review process. If EPA determines that the risks appear to outweigh the benefits, then it can initiate action under FIFRA to cancel, suspend and/or modify the terms and conditions of registration.

On January 8, 1986, the EPA announced the initiation of a Special Review of all registered pesticide products containing TBT compounds used as additives in antifouling paints, that are applied mainly to boat and ship hulls to inhibit the growth of certain aquatic organisms. The decision to initiate the Special Review was triggered when EPA determined that the pesticidal use of these compounds resulted in TBT exposure to nontarget aquatic organisms at concentrations resulting in acute and chronic toxicity and, when applied as antifoulant paint, meet or exceed the risk criteria as described in 40 CFR 162.11. A review of the information used to make this decision was published in the "Tributyltin Support Document" (U.S. EPA, 1985).

In initiating the Special Review for TBT, the EPA identified significant gaps in the data bases supporting the registration of TBT as used in antifoulants. In order to obtain the data necessary to assess the risks and benefits, EPA plans to issue a series of Data-Call-In Notices (DCI's) to the registrants levying extensive data requirements to continue their registration pursuant to EPA's authority under FIFRA. Through the use of DCI's, EPA will request data under several areas: (1) chemical release rate studies of TBT from antifoulant paints. (2) product chemistry. (3) ecological effects, environmental fate. (4) worker exposure. (5) quantitative usage. (6) efficacy of TBT products. (7) specific toxicity tests with a wide range of organisms and (8) specific environmental monitoring data. For the release rate DCI, which was issued July 1986, a protocol for testing and chemically measuring release rates was developed in cooperation with the American Society for Testing and Materials (ASTM) which will provide information on daily release rates and 6-week cumulative release rates for different TBT paint products. Based on the rate of compliance with this DCI, about 300 (or 80%) of the registrations have been voluntarily cancelled [of the 359 total number of registrants] by the registrants. It is anticipated that it could take several years for the information requested by the DCI's to be collected and to be analyzed by EPA before the decision of the Special Review can be made. However, EPA's Office of Policy, Planning and Evaluation and the National Oceanic and
Atmospheric Administration's National Marine Pollution Program Office have joined together to produce a public information brochure for distribution with the assistance of the Coastal States Organization to registered boat owners in each state on "Safer Use of Boat Bottom Paints" because in the meantime its not known whether TBT presents an unreasonable hazard to marine life.

4.0. POLICY AND REGULATORY OPTIONS

There are four regulatory options that are available for policy & decision makers to consider: (1) Total ban of TBT in antifoulant paints. (2) Regulate by the length of vessels: such as prohibition on vessels less than 25 meters in length, with approval on all aluminum hull vessels. (3) Limit the amount of TBT (on a percentage basis) in the paint. and (4) Limit the release rate of TBT from the paint to the adjacent water column.

In the United States, no federal regulatory action has been taken for organotin compounds. However, public pressure is motivating states to ban or regulate the use of TBT as an active ingredient in antifoulant boat bottom paints and other uses which yield TBT in discharges waters (e.g. textiles). Since 1985, North Carolina, Maryland, Virginia, Oregon, Washington, and Michigan have passed TBT regulations. California, Alaska, New York and New Jersey have TBT bills pending in their legislatures. Fortunately many of these state bills are quite similar. Because if they were not, any regulatory action specific to individual states would be quite difficult to enforce and disruptive to interstate commerce.

In the Senate, a bill has been proposed focusing on regulating the release rate of TBT from the paint to the water column in an attempt to attain some determined minimal-effect level. In this bill (S. 428 - the "Tributyltin-Based Antifouling Paint Control Act of 1987"), the release rate for TBT has varied from 0.5 (+ 20%) micrograms of TBT per square centimeter of wetted hull surface area to 5.0 (+ 20%) micrograms per square centimeter, due to problems of uncertainty in analytical detection and precision. Unfortunately, the ambient concentrations of TBT in harbors, estuaries and lakes is a product of at least two key factors: TBT paint release rates and the total wetted surface area of TBT painted boat bottoms. Control of only one of these factors may not prove to be sufficient. Release rate regulatory controls can be overridden by boat density. Therefore the approach is a step in the right direction, but has a major flaw, making it quite difficult to lower ambient TBT concentrations using just release rate regulatory strategies.

The policy options being considered by the U.S. EPA were recently discussed by Dr. John Moore, the Assistant Administrator for Pesticides and Toxic Substances, in his presentation before the Subcommittee on Environmental Protection, Committee on Environment and Public Works of the U.S. Senate, April 29, 1987. Dr. Moore suggested that he envisioned a two-phase regulatory process, based upon results of initial monitoring programs carried out in selected estuaries and the information obtained from the EPA Data Call In (DCI) Notices on release-rate test data. Dr. Moore reported that EPA will be in a position to make a preliminary regulatory decision by fall 1987. At the Hearing, Dr. Moore felt that it would be "premature to speculate on specifics" but that "these measures will most likely involve the initiation of actions to restrict or cancel, the registrations of antifouling paints, based on release-rate or other criteria as appropriate. As the long-term ecological effects and environmental fate data become available over the next four years, and as additional monitoring data are accumulated, the Agency might refine its interim decision, including the imposition of more stringent restrictions, if necessary." Dr. Moore also discussed the progress EPA’s Office of Water is having in developing water quality criteria with regard to TBT. This work is being carried under Section 304(a) of the Clean Water Act. The EPA follows a prescribed set of guidelines in deriving criteria. These guidelines establish a minimum required data set, and define the methods for assessing the data. Generally, it requires about two years to develop a criteria document. Carr et al. (this Volume) are currently preparing the necessary assessments for determining the water quality criteria for TBT. Dr. Moore felt that it was quite possible that a water quality advisory would be issued in the mean time. The TBT advisory criterion for continuous concentration (chronic) for salt water can range from 3 to 60 ng/l (part-per-trillion) if one selected specific data sets and eliminates non conforming experiments (problems with controls, etc.). If one does not reject any of the available toxicity data in making the water quality criteria calculations, the numbers that are generated for the water quality advisory suggest that the "Criterion Maximum Concentration" (CMC) could be on the order of 1.6 ng/l for salt water and 26 ng/l for freshwater.

The lower value is very close to the limit of analytical detection and therefore could be very difficult to regulate.

5.0. RESEARCH AND MONITORING INFORMATION NEEDS

In July 1986, the NOAA's National Marine Pollution Program Office (NMPO) sponsored an Interagency Workshop (NOAA, NAVY and EPA) with leading researchers from across the country on Aquatic Monitoring and Analysis for Organotin Compounds, which was held at the U.S. Naval Academy in Annapolis, Maryland. The purpose of the Workshop was to identify analytical and field methodological problems and research needs. The proceedings of the Workshop consists of background papers and two subgroup reports (Landy, et al., 1986). Participants at the workshop identified data collection and research and monitoring needs for organotin compounds in aquatic environments. The purpose of the
Workshop was to provide a forum for discussing field and laboratory methodologies for sampling activities that were beginning at the state and federal levels. At that time, sampling programs were being developed in Chesapeake Bay by the States of Maryland (DNR) and Virginia (VIMS) and EPA's Chesapeake Bay Program, and in California, by Goldberg at SCRIPPS, by Stephenson at the Moss Landing Marine Laboratory, and by the Department of Environmental Quality in Oregon. Since the NMFOPO Workshop, groups at the state, Federal and international levels have meet in the U.S., the U.K., and France to identify information needs for research, monitoring, and toxicity studies with regard to TBT. Recommendations that have come out of these meetings are summarized below.

Research and monitoring needs that have been identified as important to policy and decision-making are:

- Advanced analytical methodologies or protocols for the determination of ultratrace butyl- and mixed butylmethyltin species (TBT and metabolites) at the parts-per-trillion levels in marine and estuarine waters and in tissues and sediments
- Certified TBT reference standards or materials for calibration and intercalibration of analytical methods for water, sediment and tissues, as a mixed reference material for TBT and its metabolites.

A wide array of fate and behavior questions with regard to TBT and its metabolites in marine and estuarine waters need answers:

- Identification and quantification of critical pathways (surface microlayer, water column, and sediments) of exposure of marine and estuarine organisms to TBT and metabolites
- Quantification of sediment sorption-desorption kinetics and partitioning coefficients.
- Quantification of specific and critical pathways and flux rates of TBT and metabolites from various antifoulant paint sources to suspended sediments, bottom sediments, pore waters and to the water column and specific concentrating mechanisms such as in the surface microlayer (see Harris and Cleary, and Stang and Seligman, and Cleary and Stebbing, this Volume, and Maguire and Tkacz, in press).
- Bioavailability (and rates) of TBT and its metabolites to marine and estuarine organisms from various antifoulant paint source functions (paint, dust, chips, ships, etc.).
- Uptake rates and degradation rates of TBT and metabolites by key organisms in lower trophic levels from both water and sediments (see Thain et al., this Volume).

Bioconcentration/bioaccumulation levels (BCFs) for TBT and metabolites by key organisms in lower trophic levels from both water and sediment, and subsequent biomagnification potential to higher trophic level organisms. The concentrations of organotin species in several key species of birds should be studied (gulls, terns, and oyster catcher to name a few).

- Biological and chemical degradation rates of TBT and metabolites in marine and estuarine waters (under a wide range of salinities and temperatures) and anaerobic sediments, and relationships between the relationship and importance of photosynthetic organisms in enhancing TBT degradation rates.

- Roll and function of the surface microlayer in concentrating, distributing, and degrading TBT and its metabolites, and relative exposure risk to neustonic organisms from contact with the surface microlayer.

Development and field evaluation of ecosystem (estuarine) distribution models and field validation of models predictive capability to estimate the fate and behavior of TBT and its metabolites in marine and estuarine systems in the field or through controlled ecosystem type studies such as in the Marine Ecosystems Research Laboratory (MERL) at the University of Rhode Island.

Many of the monitoring studies conducted to date have focused on "what" the condition is (as in terms of concentrations of TBT in marinas or downstream of boat yards or dry docks) and not on processes or on the "why" a particular concentration was measured at the station sampled. These studies need to have specific testable hypotheses, they need to have sampling strategies developed which focus on statistical requirements that have been set to meet the needs of both research objectives and regulatory applications, and not to provide newspaper cannon fodder.

Toxicity Information

Organotins are a rapidly growing class of biocidal compounds as new industrial and agricultural uses and applications develop. These compounds have widely diverse combinations of structurally distinct covalent chemical species, which are sufficiently long-lived to yield unique biological toxicological effects. A recent important finding of Hinga (this Volume) was that TBT's half life was only 3.5 days which is very significant as related to toxicity studies. The toxicity of organotins is dependent upon the valence of the tin atom and the organic moieties that are attached to it. Secondly, this toxicity is modified (either direction) by the physicochemical properties of the conformational structure of these organic moieties. As a rule, in general, increased molecular volumes is highly correlated with acute
organotin cytotoxicity. Recent studies have correlated the specificity of organotin molecular structure with cellular toxicity, which could lead to the possibility of creating organotin compounds which are toxic to specific or selected target organisms. Therefore future research in ultratrace (ug/l) molecular specification will facilitate new organism specific biocides.

Most of the toxicity studies conducted over the past 5 years have used nominal (one-initial dose) exposure concentrations in which the test organisms were exposed to initial test concentrations and not continuous concentrations that are quantified at selected time periods. These nominal tests (usually static, not flow through) are of limited value when conducted in the ng/l (parts per trillion) levels. Laboratory analytical studies conducted in the parts per million range have found up to 70% of test solution was absorbed to test containers. Also poor analytical sensitivity and precision in the low parts per trillion range have impacted wide spread acceptance of the results of these toxicity tests. It is very good to see groups such as the National Bureau of Standards, FREMER, University of Maryland, BSAEM, and the Moss Marine Laboratory taking active leadership in developing new methodology, conducting intercalibration studies and developing and testing reference materials (see Stephenson et al., Michel, Matthias et al., Humphrey and Hope, this Volume).

Through the various series of national and international meetings, the following recommendations have been made with regard to toxicity studies:

- Toxicity tests should focus on low level physiological endpoints through chronic-full life cycle exposure testing, including reproductive success, growth, metabolism, immunotoxicity, calcification mechanisms, and immune suppression rather than mortality as measured by short-term 96 hr bioassay tests (see White and Champ, 1983).

- Development and testing of hypotheses of modes of toxic action for organotin compounds in representative trophic levels and in sensitive marine organisms (such as molluscs). These studies also need to identify and follow the continuum of biological response (toxicant) from successful conteration to the overwhelming of homeostatic mechanisms.

- For the purposes of removing (dredging) highly contaminated bottom sediments, a series of toxicity studies employing benthic organisms and some assessment of releases of TBT and its metabolites to the water column are needed. These tests need to be more than just tests with available sediments, the tests need to use spiked sediments (4 or 5 ranges) and to be run for perhaps 60 days, because of the part-per-trillion test levels.

- On site bioassays using ambient water from selected high boat use areas are needed to validate effects observed in the field and in specific laboratory tests. Also representative large-volume toxicity tests, such as pp. CAN be conducted with the MSRL (Marine Ecosystem Research Laboratory at the University of Rhode Island) are needed to validate standard 96 hr laboratory toxicity tests, as well as to investigate population effects on plankton.

- Due to the high sensitivity of mollusks to TBT and its metabolites, long-term chronic studies should be first conducted extensively with mollusks to investigate effects on gametogenesis, settlement of spat, growth, calcification, and reproduction through all life stages.

6.0. ACKNOWLEDGMENTS

Figures 1-4 are from Anderson and Dalley (Ocean's '86 Proceedings. We thank David F. Bleil for his review comments on this manuscript.

7.0. BIBLIOGRAPHY


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### TABLE 1. ENVIRONMENTAL CONCENTRATIONS OF ORGANO Tin COMPOUNDS.

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Canada

- **Fresh Water**
  - Water, 1980-85, microlayer, 0.01-24.9
  - Subsurface, 0.01-18.1

- **Locations**
  - Sediment, 0.01-10.0 ng/kg
  - Subsurface, 0.01-2.01

- **Highest readings**
  - Sediment, 2 cm

- **Highest readings at Canadian site, 1982-85**
  - Vancouver Harbor: 0.01-0.04 ug/l
  - Fraser River: 0.01
  - Thunder Bay: 0.01-0.08
  - Nipigon River: 0.04
  - Turkey Lake: 0.05-0.09
  - Sault Ste. Marie: 0.11-1.68
  - St. Clair River: 0.02
  - Whitby: 0.10-1.72
  - Port Hope: 2.34
  - St. Lawrence River: 0.01-0.05
  - Detroit River-USA: 0.07
  - Ottawa River: 0.01-0.52

- **Highest readings in Canada, 1982-85**
  - Lake St. Clair: 0.01-0.10
  - Kingston: 0.05-0.10
  - Whiteside: 0.01-0.20
  - Kingston: 0.05-0.10

- **Lake Superior, 1981**
  - 0.02

- **Turkey Lake, 1981**
  - 0.05-0.08

- **Sault Ste. Marie, 1981**
  - 0.29

- **Sudbury, 1981**
  - 0.25-3.81

- **St. Clair River, 1981**
  - 11.9-60.7

- **L. St. Clair Mar., 1981**
  - 11.9-60.7

- **Port Credit, 1981**
  - 0.84

- **Whitby Harbor, 1981**
  - 0.05

- **St. Lawrence River, 1981**
  - 9.7

France

- **Arsenal Bay, 1982**
  - 0.20 organotin

- **LeVigne Bay, 1985**
  - <0.15 organotin

- **LeHillie Bay, 1985**
  - <0.15 organotin

UK

- **Comber to England, 1984**
  - Tyne

- **Plymouth, 1984**
  - <0.10-0.88 ug/l

- **Devon, 1984**
  - <0.10-0.88 ug/l

- **Yealm, 1984**
  - <0.10

- **Cromwell, 1982**
  - <0.10-0.13 ug/l

- **Cromwell-England, 1982**
  - 0.43-12.0 ug/l

- **Bramshill Marina, 1982**
  - <0.03-0.08

- **Essex Marina, 1982**
  - <0.03-0.08

- **West Mersea Marina, 1982**
  - 0.21-0.29

- **Farnham Marina, 1982**
  - <0.03-0.17

- **Burnham-on-Crouch, 1982**
  - <50 ng/l-1300 ng/l

- **Sutton Harbor, 1982**
  - <50 ng/l-1300 ng/l

- **Seawater Solubility, 1987**
  - 200 ng/l

- **U.K., 1986**
  - <0.02-2.00 ug/l

- **Sediment**
  - GF-AAD

- **Surface microlayer**
  - 20-1000 ng/l

- **Organotin**
  - Waldock & Miller (1982)

- **Organotin**
  - Waldock et al. (Ocean's '87)

- **Organotin**
  - Schatzberg (Ocean's '87)

- **Organotin**
  - Cleary et al. Ocean's '87