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Research Needs Concerning Organotin Compounds Used in Antifouling Paints in Coastal Environments

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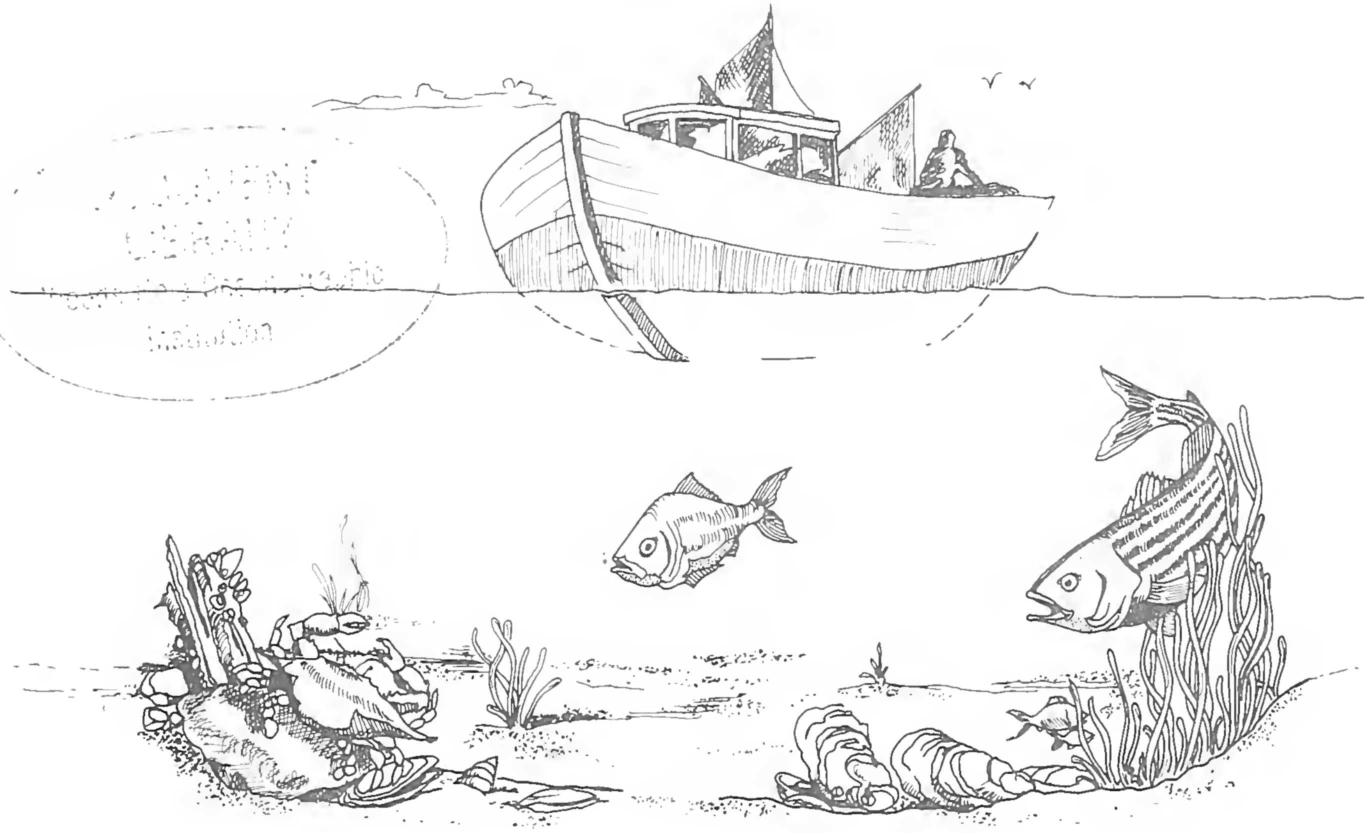

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
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Research Needs Concerning Organotin Compounds Used in Antifouling Paints in Coastal Environments

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March 1988

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INTRODUCTION

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CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

This Introduction has been prepared to aid those from non-technical backgrounds to gain a quick introduction and grasp of the technical and environmental issues and the policy and regulation associated with the use of organotin compounds as additives (biocides) in antifoulant paints.

Since the first days of sail, mariners have been battling fouling--the growth of barnacles, seaweeds, tubeworms, and other organisms on boat bottoms. The Phoenicians, realizing that smoother bottoms translated into easier rowing and faster sailing, nailed copper strips to the hulls of their ships to inhibit fouling.

In naval actions, the cleaner, faster vessels often escaped stronger forces or caught up to weaker ones. Thus fouling was an important factor to navies in the days of sail. Although copper strips went by the boards long ago, fouling prevention remains important today, as aircraft carriers launch aircraft while underway at 40 knots, supertankers crisscross the oceans, and fishing boats fish in coastal and oceanic waters.

In 1985, however, when the Navy proposed painting its ships with efficient antifouling paints that are widely used by commercial and pleasure craft, it focused scientific and political attention on the effects of these paints in the marine environment. Edward D. Goldberg, Professor of Chemistry at Scripps Institution of Oceanography, has stated on several occasions that TBT, the active ingredient of these paints, is the most toxic compound man has intentionally introduced into the marine environment.

Since the widespread use of TBT-based paints began in the early 1970's, evidence shows that TBT paints harm many forms of marine life other than fouling organisms, including economically important species such as oysters. The effects on untargeted species have attracted increasing international concern. A number of countries have adopted policies regulating or restricting TBT use. Several states in this country also have taken action, and federal regulation of TBT by Congress has been signed into Law (P.L. 100-333), as we discuss later. Meanwhile, one of the largest U.S. shipyards, Newport News Shipbuilding in Newport News, Virginia, has decided to turn down work that requires the use of TBT paints because of potential risks to employees' health.

The use of tributyltin paints on commercial ships, fishing vessels, and private boats could add another $300 to $400 million in fuel savings annually. Hence, the stakes riding on tributyltin paints amount to almost 2 billion gallons of fuel lost forever, or saved for future use, each year. These figures do not include the sums that would be saved from the decreased wear on propulsion machinery and the decreased down time for hull scraping, cleaning, and painting that would result from the use of TBT paints.

1.1.1 Fouling Organisms

"Bottom fouling has been the mariner's curse ever since man first set sail" (Russell, 1987). The growth of marine organisms on boat bottoms has been a war between man and organism; typical examples of fouling organisms are shown in Figure 1.1.

The growth of barnacles, seaweeds, or tubeworms on a boat's bottom is referred to as "fouling" (Figure 1.2). 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 of the Q.E. II (one of the world's largest ships) was $17 million (US dollars).

Figure 1.1 Marine Fouling. (Photo from a painting by Lisa Haderlie Baker, Lawrence Hall of Science, University of California at Berkeley. Copyright 1980 by the Regents of the University of California, courtesy National Science Teachers Association, the Carolina Biological Supply Company, Oceanus - The International Magazine of Marine Science and Policy and Ms. Lisa Haderlie Baker.

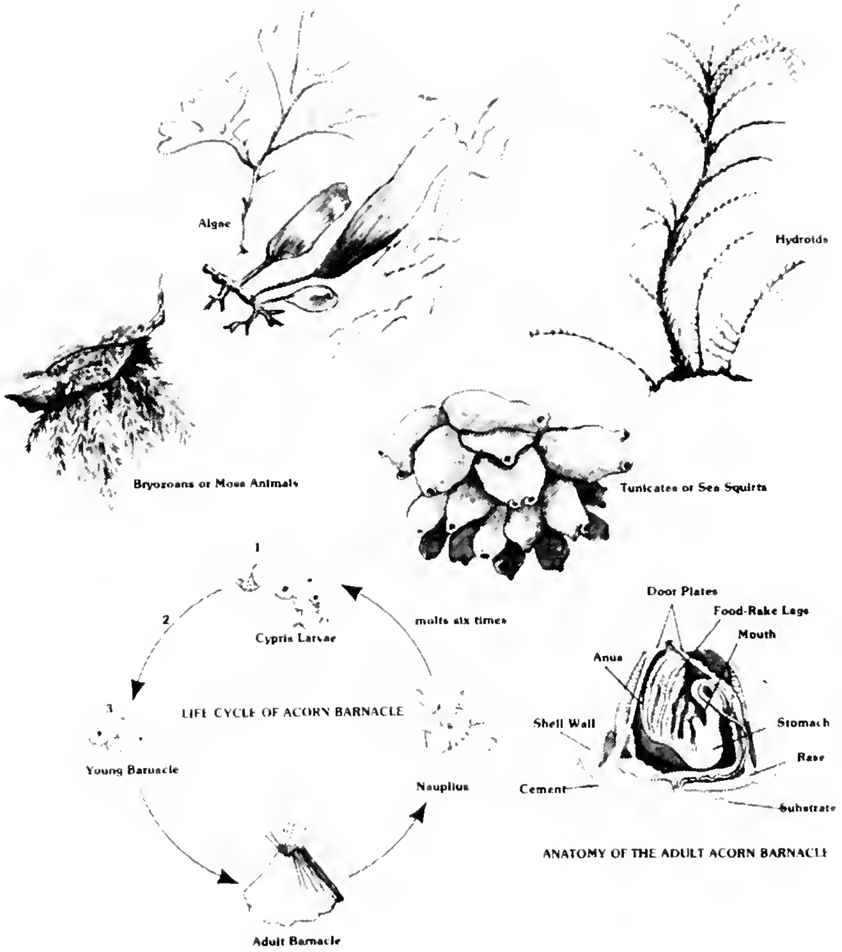


Figure 1.2 The marine hitchhikers. Depicted are examples of the animals and plants that grow on underwater surfaces such as ship hulls--resulting in marine biofouling. Ships are most susceptible to fouling when they are in port. How sedentary marine organisms are transported to colonize new surfaces is illustrated by the life cycle of the acorn barnacle at the bottom left: 1) free-swimming larvae must attach to a substrate in order to develop and feed. If they do not attach, they will die in a matter of days; 2) the larvae produce a strong, long-lasting adhesive for attaching themselves to substrates; 3) the larvae attaches head first, forming a conelike shell around itself, and uses its feet to propel food into its mouth. The anatomy of the resulting adult is shown at the bottom right. From a drawing by Lisa Haderlie Baker, courtesy of the National Science Teachers Association, the Carolina Biological Supply Company, and OCEANUS, the International Magazine of Marine Science and Policy.

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, the new fuel avoidance costs would exceed $110 million annually (calculated with fuel costing approximately $16/barrel).

1.1.2 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 this century. 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 ("free association") uses contact leaching to release the biocide. In this process, seawater percolates slowly through a tough insoluble paint matrix, see Figure 1.3. The biocides are added in the free association form and are mixed into the paint. They leach exponentially with time. This category of TBT antifoulant coatings has traditionally posed a problem of high early release rate with subsequently shortened 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, then the surface becomes biofouled. This leaves a quantity of biocide that remains unused on the vessel hull, which must be removed prior to the next painting. The removed paint film must be properly disposed of or it may then be a source of environmental contamination. The usual response of the recreational boater and small commercial operator to calcarious fouling of the paint film is to abrade the surface or remove the paint film and reapply. There may be a significant amount of TBT remaining in the film when the fouled film is removed. There have been few studies directed to the extent to which the old paint film is a source of TBT to the environment. The British Royal Yachting Association, in close consultation with other concerned fisheries associations and the Department of the Environment, produced a public education document directed at controlling the introduction of old paint into the coastal waters.

In about one half of the 1987 registered paint formulations, tributyltin is mixed with copper compounds. By the nature of the mixture, these paints are free association types. An example of this is a vinyl copper formulation which uses a very low (1%) TBT in the film as an antibacterial-antislime agent which increases the effectiveness of the copper oxide, the primary antifouling material. Other example mixed free association formulations include:

a) a formula having -- 2.5% TBT and 16% copper.

b) a series of blue and green paints having -- TBT content ranging from 13.3% to 15.7% depending on the paint color selected. Tributyltin is colorless and is used in higher percentages in colors other than the red shades which copper produces.

On the basis of paint surface exposure to the environment, the painted areas covered with free association paints account for a little more than one third of the total bottoms painted (Lucas & Williams, 1987).

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 1.4). The biocides are added in the free association form, leaching exponentially over time. The release of biocide also is inhibited by the formation of surface insoluble. The lifetime of this paint is about 2 years.

Type 3 antifouling paint is commonly referred to as "self-polishing" copolymer paint. Developed in the early 1970's, the paint is hydrophobic (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 1.5). The paint formulation has biocide at very low levels, which are released at the surface layer.

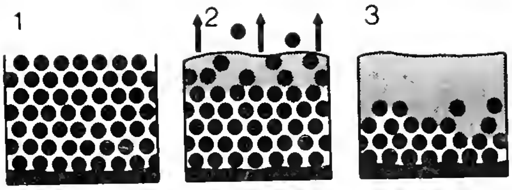


Figure 1.3 In free-association paints, the TBT molecules are leached from a permeable matrix by seawater percolating through the paint.

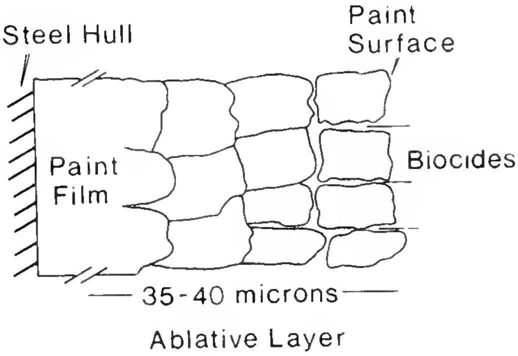


Figure 1.4 Ablative paints use a less permeable matrix that gradually flakes off exposing new leaching surfaces.

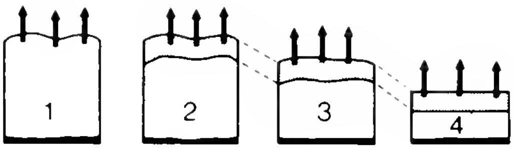


Figure 1.5 In copolymer paints, the TBT is part of an impermeable matrix, and is released through a chemical reaction with seawater at the paint surface. New TBT is exposed by gradual erosion of the paint.

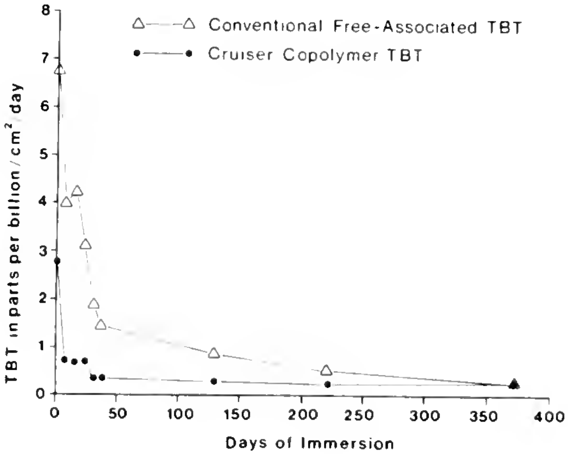


Figure 1.6 Except for an initial spike of rapid release, copolymer paints show a lower release rate than free-association paints. (Figures 1.3 through 1.6 are from Anderson and Dalley, 1986).

The coating chemistry 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.

This controlled release process has two major advantages: (1) release is governed by hydrolysis of the TBT group rather than dissolution of paint particles, and (2) the release rate is more effectively controlled (slowed down) by altering the polymer's water absorption characteristics.

Compared to Type 1 or 2 paints, these polymeric, film-forming resin coatings are also characterized by an initial higher release rate (with free association higher than copolymer) during the "conditioning" period (approximately the first month after the freshly-painted hull is placed in the water), followed by a constant low release rate of antifouling toxicant (Figure 1.6). A portion of this high initial release rate is due to unbound (free) TBT in the paint. Paint manufactures have indicated that these levels should drop for the copolymer paints as better quality control practices are implemented. The controlled biocide release also gives the antifoulant paint a controlled life span (the thickness of the initial application of the paint determines the life span). Current data suggest that 5 to 7 years is the average life span of an application of copolymer TBT paint. 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 removing old paint, and subsequently less TBT is released into the environment as spent paint waste.

1.1.3 Organotin Compounds

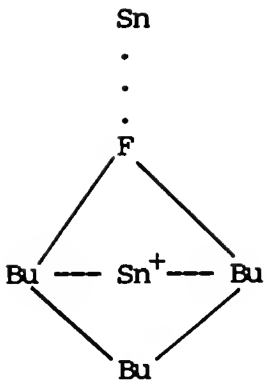
Organotin compounds are now one of the most studied groups of organometallic chemicals, in terms of industrial and agricultural uses and applications. The first applied use was as a mothproofing agent in 1925. In 1932, organotin compounds were used for stabilizing chlorinated benzenes and the diphenyls used in transformers and capacitors. This was followed by dibutyltin dilaurate and other dibutlytin salts in 1936 being used to stabilize polyvinyl chloride (PVC). The biocidal properties of diverse organotin molecules 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, employing diorganotin moieties. 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 end products containing PVC must be colorless or transparent, as in the case of bottles, films, or sheets used for food packaging. In the 1970's, 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 and that these properties were dependent upon the influence of the number and kind of organic groups bonded to tin, 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 peanuts, 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.

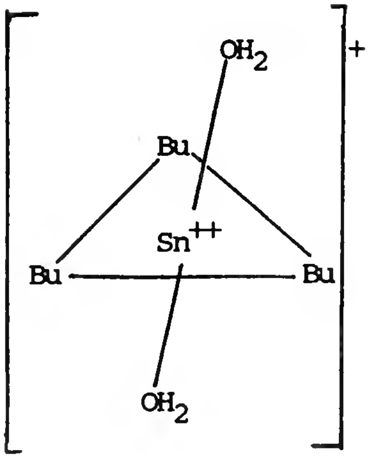
In the early 1960's, two organotin compounds (tributyltin oxide and tributyltin fluoride) were first used as a molluscicides to kill several species of freshwater snails that were the intermediate hosts of the worms of the genus Schistosoma, which transmit the disease Schistosomiasis to humans. This immediately led to the use of tributyltin (TBT) moiety 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 (C_4H_9-) moieties. A representative TBT active ingredient, tri-n-butyltin fluoride, may be chemically described by the following structural formulas for the undissociated (neutral) pure form or the active ingredient and for the water dissociated (positively charged) form.



Neutral Undissociated Free Association

TBTF in Paint Matrix



Aquated TBT Cation in

Water Media

Figure 1.7 Dissociation of TBT Ion in Water

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 to derivation in water, one must consider the dissociated active form, the TBT cation (Bu_3Sn^+), and its major metabolites presumably formed by progressive debutylation to inorganic tin (Brinckman, 1981).

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.

1.2 SUMMARY OF FEDERAL ACTIVITIES

The Navy's decision to implement fleet-wide (approximately 600 ships) use of organotin based antifouling paints precipitated regulatory activities in the U.S. Congress and in the legislatures of several states (these will be discussed in greater detail in Chapter II). On January 8, 1986, the U.S. Environmental Protection Agency (EPA) announced the initiation of a Special Review of all registered pesticide products containing TBT compounds used as additives (biocides) in antifouling paints applied 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 in antifoulant paints resulted in TBT exposure to nontarget aquatic organisms at concentrations resulting in acute and chronic toxicity and, meet or exceeded 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, EPA identified significant gaps in the technical information needed to support the registration of TBT used in antifoulant paints. To obtain the information necessary to assess the risks and benefits of TBT use, EPA has issued a series of Data Call in Notices (DCI's) to the registrants levying extensive data requirements to continue their registration. On October 1, 1987, EPA proposed certain restrictions on the use of TBT antifouling paints (EPA, PD 2/3, 1987). Upon review of comments submitted in response to this regulation proposal, EPA projects that final regulations will be issued in the fall of 1988.

In an attempt to stimulate self regulatory activities by boat owners, EPA's Office of Policy Analysis (of the Office of Policy, Planning and Evaluation - OPPE) and the National Oceanic and Atmospheric Administration's National Marine Pollution Program Office (NMPPO) have joined together to produce a self regulation - public information leaflet for distribution with the assistance of the Coastal States Organization and the States to registered boat owners. The leaflet provides guidance on the proper use and disposal of antifoulant paints, plus the potential risks to both humans and the environment from improper use and exposure to TBT and other biocides in antifouling paints.

1.3 PURPOSE OF THIS REPORT

This technical report is in response to NOAA's National Marine Pollution Program Office's request for a study entitled: Research Needs Concerning Organotin Compounds in Coastal Environments. This study is to provide the National Ocean Policy Board with the technical and policy information required to support the mandated role of the Federal Government to evaluate, monitor, and control the adverse effects from the use of organotin compounds used as additives (biocides) in antifoulant boat paints.

The report has been prepared in five chapters which review and summarize: (1) organotin based antifoulant paints, (2) legislative responsibilities of Federal agencies with respect to evaluating, monitoring, and regulating the use of organotin compounds in vessel antifouling paints, and proposed or pending or enacted legislation by individual U.S. states and by other Nations. (3) the usage patterns of TBT antifouling paints, (4) the status of scientific knowledge, and (5) research needs and recommendations concerning TBT in coastal waters.

Chapter II

LEGISLATIVE RESPONSIBILITIES OF GOVERNMENT AGENCIES FOR RESEARCH AND MONITORING AND A DESCRIPTION OF CURRENT FEDERAL PROGRAMS

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2.1 INTRODUCTION

The purposes of this chapter are to: 1) identify legislated responsibilities of Federal agencies with respect to evaluating, monitoring, and regulating the use of organotin compounds in vessel antifouling paints, 2) summarize the proposed or pending or enacted legislation by individual U.S. States and by other Nations to reduce the environmental impact from use of TBT in antifoulant paints, and 3) identify and delineate current Federal and State research, development, monitoring programs and activities. This will enable better Federal coordination of all activities associated with organotin compounds which is a purpose of the of the National Ocean Pollution Planning Act.

2.2 MAJOR STATUTES AFFECTING FEDERAL AGENCY ROLES

The Federal mandate with regard to the use of organotin compounds as additives or biocides in antifouling boat bottom paints comprises one Federal Act specific to organotin antifouling paints, HR.2210, which is now known as P.L. 100-333, the "Organotin Antifouling Paint Control Act of 1988." As this report goes to press, the legislation has been signed by the President on June 16, 1988. This legislation will be discussed in a later section (Sec. 2.3.1.1) of this report. The legislative responsibilities of Federal agencies with respect to organotin compounds are summarized in Table 2.1 and discussed in the following sections.

2.2.1 Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

This Act provides for the identification of environmental problems, the setting of water quality standards for toxic substances and the monitoring of environmental concentrations of toxicants for the purposes of regulating toxic substances. Power to develop and implement regulations under this Act are given to EPA. 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 (RPAR-Rebuttable Presumptions Against Registration) Process (40 CFR 162.11) provides a mechanism through which EPA gathers risk and benefit information about pesticides which appear to pose unreasonable risks of adverse effects to human health or the environment. Through the issuance of notices and support documents, EPA publicly establishes its position

Table 2.1

Legislative Responsibilities of Federal Agencies With Respect to Tributyltin in the Coastal Environment

Federal Legislation	National Bureau of Standards	NOAA/Coastal & Estuarine Program	NOAA/National Marine Pollution Program Office	NOAA/Environmental Research Laboratories	DOD/Corps of Engineers	DOD/Navy	EPA/Office of Pesticide Program	EPA/Office of Water	EPA/Office of R&D and Laboratories
Federal Insecticide, Fungicide, Rodenticide Act [FIFRA]	X						X		X
Toxic Substances Control Act [TOSCA]							X		X
Clean Water Act					X	X		X	X
Resource Conservation Recovery Act [RCRA]				X	X		X		
Marine Protection Research & Sanctuaries Act [MPRSA]		X	X	X	X			X	X
National Ocean Pollution Planning Act		X	X						
Natl. Bureau of Standards (15 U.S.C. 272)	X								
National Environmental Policy Act (NEPA)						X			

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 a given pesticides registration. The EPA has selected to regulate the use of organotin compounds in antifouling paints under the legislative mandates of FIFRA.

2.2.2 Toxic Substances Control Act (TSCA)

The Toxic Substances Control Act (TSCA), P.L 94-469, establishes responsibilities for definition of problems caused by the presence of toxic substances in the environment, and for setting acceptable levels or standards to insure maintenance of acceptable water quality. Monitoring environmental levels, drafting of regulations concerning use of the toxic substance and the enforcement of these regulations is also provided by TSCA. Under TSCA, EPA has the authority to regulate the use of organotin compounds in the environment. At present, however, EPA finds FIFRA the preferred authority for the regulation of organotins.

2.2.3 Clean Water Act (CWA) and Amendments

The Federal Water Pollution Control Act of 1972 as amended by The Clean Water Act of 1977 (P.L. 92-500 and P.L. 95-217) are known as the Clean Water Act (CWA). The objective of this act is to restore and maintain the chemical, physical and biological integrity of the nation's waters. Regarding control of marine pollution, the Act provides for a water quality surveillance system for monitoring the quality of navigable waters including the contiguous zone (Section 104[a][5]. Although the major responsibility under this Act is the Administrator of the EPA, the Act expressly encourages other Federal, State and local agencies to cooperate in establishing National programs for the prevention, reduction, and elimination of pollution. This includes research, investigations, experiments, training, demonstrations, surveys, and studies relating to the causes, effects, extent, prevention, reduction, and elimination of pollution (Section 104[a][1]). The National Oceanic and Atmospheric Administration (NOAA) is directed to establish, equip, and maintain a water quality surveillance system for the purpose of monitoring the quality of navigable waters, the contiguous zone and the oceans. NOAA in Section 303 is also directed to engage in activities responsive to the establishment of water quality standards, and effluent discharge standards in Section 307 (a). The Act directs the Administrator of the EPA to identify and quantify the distribution of in-place toxic contaminants with emphasis on toxic substances in harbors and navigable waterways. The EPA Administrator is also authorized, acting through the Secretary of the Army, to make contracts for the removal and appropriate disposal of such materials from critical port and harbor areas (Section 115). Therefore, in the future, if the concentrations of organotin compounds should increase in estuarine bottom sediments faster than they degrade, it may become necessary to implement the regulatory process as developed for the disposal of contaminated dredged materials.

2.2.4 Occupational Safety and Health Act (OSHA)

With regard to organotins, the focus of the Occupational Safety and Health Act (OSHA), P.L. 91-596, would be on the health and safety of shipyard and marina workers and "do it yourself" boat owners exposed to organotin compounds during application or removal of antifouling paints. Research in the area of worker protection is being conducted by the Navy and by the paint companies. Evaluation of protection strategies to assure the safety of workers during the handling and use of TBT antifouling paints is being conducted by the Navy which includes hull sealing mobile spray paint enclosures, paint spray collection mechanisms and dry dock clean up means. Investigations are also underway by the Navy on disposal alternatives for spent paint film and grit resulting from the removal of spent paint films.

Worker exposure and TBT body burden studies have been conducted by M&T Chemical Corporation. Alternative worker protection coverings were also investigated in the study which was conducted in response to the Data Call in Notice (DCI) from EPA under FIFRA rather than under OSHA. The OSHA regulations for permissible paint exposure currently exist and no evidence has been uncovered to date that these regulations are being evaluated or revised. Any such revision would be unlikely until the conclusion of the EPA Special Review.

2.2.5 Resource Conservation and Recovery Act (RCRA)

As a result of the Clean Air Act, the Clean Water Act and other Federal and State laws respecting public health and the environment, greater amounts of solid waste (in the form of residues) have been created. Similarly, inadequate and environmentally unsound disposal practices for the disposal or use of solid waste have created greater amounts of air and water pollution and other environmental and public health risks. The Resource Conservation and Recovery Act (RCRA), P.L. 91-596, is for wastes classified as hazardous, and applies to all wastes which can cause harm to the environment or human health. With regard to organotin compounds, the waste products are the paint residues (chips, particles, dust, etc.) that arise from removing spent antifouling paint from boat bottoms by sand blasting, scraping, etc., that contains TBT. At present EPA does not have special disposal requirements for these waste materials, they can go with general solid wastes such a household wastes (trash and garbage) to sanitary landfills.

2.2.6 Marine Protection, Research and Sanctuaries Act (MPRSA)

The "Marine Protection, Research, and Sanctuaries Act of 1972" is commonly called the "Ocean Dumping Act", P.L. 92-532. In this Act Congress declared that it is the policy of the U.S. to regulate the dumping of all types of materials into ocean waters which would adversely affect human health, welfare, or amenities, or the marine environment, ecological systems, or economic potentialities. The dumping of wastes or toxic materials at sea is strictly regulated by the U.S. EPA and the London Dumping Convention of which the U.S. is a Contracting Party. This act is concerned with the disposal of contaminated dredged materials from waterways, harbors or marinas that would be contaminated with toxic materials. Under Title II, Section 201, NOAA, in coordination with the U.S. Coast Guard, and EPA is responsible for a comprehensive and continuing program of monitoring and research regarding the effects of the dumping of material into ocean waters. Under Section 202, NOAA is also responsible for a comprehensive and continuing program of research with respect to the possible long-range effects from exposure from contaminants This Act also assigns the Army Corps of Engineers (COE) with the authority to issue permits for the transportation of dredged materials for the purpose of disposal at sea (ocean dumping), "where it has been determined that the dumping will not unreasonably degrade or endanger human health welfare or amenities, or the marine environment, ecological systems or economic potential." In order to establish the potential environmental impact or risk from disposal of contaminated sediments, the Chief of Engineers is authorized to conduct a comprehensive program of research, study and experimentation relating to dredged material.

In this study, we were unable to find any data on the concentrations of TBT or the release of TBT absorbed to dredged sediments. However, the U.S. Navy has indicated that they have conducted some standard elutriate tests on a few selected harbor bottom sediments to estimate sediment release of TBT to the water column that would occur either during dredging or disposal.

The Ocean Assessments Division (OAD) in NOAA has been designated this responsibility and studies were initiated during 1987 by the Status and Trends Program.

2.2.7 National Ocean Pollution Planning Act (NOPPA)

The National Ocean Pollution Planning Act (NOPPA), P.L. 95-273, 1978 as amended, directs the Administrator of NOAA, in consultation with the Director of the Office of Science and Technology Policy of the Executive Office of the President, and other appropriate Federal officials to prepare and update biennially a comprehensive five-year plan for the overall Federal effort in ocean pollution research and development and monitoring (Section 4). It further directs the Administrator of NOAA to establish within NOAA a comprehensive, coordinated and effective ocean pollution research and development and monitoring program consistent with the five-year plan (Section 5) and to provide financial assistance for research and development and monitoring projects or activities which are needed to meet priorities of the five-year plan if these are not being adequately addressed by any Federal department, agency, or instrumentality (Section 6). Finally, the Act directs that the Administrator of NOAA shall ensure that results, findings and information regarding Federal ocean pollution research and development and monitoring programs be disseminated in a timely manner and useful form to Federal and non-federal user groups having an interest in such information (Section 8).

2.2.8 15 U.S.C. 272 (National Bureau of Standards Act)

Under this Act, the National Bureau of Standards (NBS) is authorized to: (1) cooperate with other Federal agencies in the establishment of standard detection and measurements practices, (2) maintain and develop National Standard Reference Materials for the measurement of chemical species, and (3) conduct comparative studies of laboratory procedures between governmental, commercial laboratories and educational institutions.

2.2.9 National Environmental Policy Act (NEPA)

The National Environmental Policy Act (NEPA), 91-190, declared a national policy which encourages productive and enjoyable harmony between mankind and his environment; to promote efforts which will prevent or eliminate damage to the environment and biosphere and stimulate the health and welfare of man; to enrich the understanding of the ecological systems and natural resources important to the Nation and established the Council on Environmental Quality (CEQ). This Act requires that all agencies of the Federal Government shall utilize a systematic, interdisciplinary approach which will insure the integrated use of environmental, social and economic information in planning and decision-making to assess the impact of mankind's activities on the environment, and that unquantified environmental amenities and values may be given appropriate consideration in decision-making along with economic and technical considerations. and that a detailed statement of the action, commonly referred to as an Environmental Impact Statement (EIS), which details the environmental impact of the proposed action, including identifying alternatives to the proposed action, and identification of any irreversible and irretrievable commitments of resources. The U.S. Navy prepared an Environmental Assessment (EA) which is the first step in fulfilling the requirements of NEPA and issued and Interim Finding of No Significant Impact (Interim FONSI) for the proposed fleetwide implementation of organotin antifouling hull paints (Federal Register, Vol. 50, No. 120, p. 25748). This decision was based on ten years of Navy studies and comprehensive environmental assessment (U.S. Naval Sea Systems Command, 1984). When the Navy issued its Interim FONSI, it made commitments to monitor initial implementation operations, continue environmental studies, and reassess in 1988 its decision to proceed with full fleetwide implementation (U.S. Naval Sea Systems Command, 1986).

2.3 REGULATORY ACTIONS PROPOSED OR PENDING WITH RESPECT TO ORGANOTINS IN THE COASTAL ENVIRONMENT

The following sections have been prepared to review and summarize Federal, State, and international regulatory actions proposed, pending or enacted.

2.3.1 Federal Regulatory Actions

Among the many regulatory options that are available for policy & decision makers to consider for the regulation of organotins in the aquatic environment, there are four which have or are currently receiving the most attention. These are: (1) total ban of organotins in antifoulant paints, (2) regulate the use of organotins 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.

2.3.1.1 U.S. Congress

Following the Navy's preparation of an Environmental Assessment in compliance with the National Environmental Policy Act and the Navy's subsequent determination that the fleetwide (600 ships) use of organotin antifouling paints would not have significant adverse environmental consequences in Navy harbours (Interim FONSI). A major controversy developed, which was spearheaded by scientists and environmentalists who were concerned that the impact of TBT on oysters that occurred in France and England could occur in the U.S. and particularly in the high oyster production areas of lower Chesapeake Bay, which were in the proximity of large naval facilities. These concerns rose from studies in England and France that were finding significant impacts to oyster populations exposed to TBT.

Also there were a series of scientific questions which at that time could not be answered: (1) what concentrations of organotin compounds in the environment were causing the demise of oyster populations (acute and chronic dose exposure levels, for TBT and its metabolites), (2) what were the degradation rates, fate and behavior of TBT and its metabolites in the environment, (3) what were the release rates of TBT in different types of antifoulant paints, and the processes that effected these release rates, and (4) what was the distribution of TBT and its metabolites in the environment and the processes that influenced these distributions. Therefore, immediately following Secretary of the Navy (John F. Lehman's.) statement, that the Navy would paint up to 50 ships with TBT in FY 86, Senator Paul S. Trible from Virginia introduced on November 12, 1985, the following into the Report of the Continuing Resolution for FY 86's Federal Budget: that "none of the funds appropriated by this joint resolution may be obligated or expended to carry out a program to paint any naval vessel with paint known by the trade name of Organotin or with any other paint containing the chemical compound tributyltin, until such time as the EPA certifies to the Department of Defense that whatever toxicity is generated by organotin paints as included in Navy specifications does not pose an unacceptable hazard to the marine environment." The Navy was comfortable with this restriction since they had planned to use the low release rate copolymer TBT paints, and figured that EPA would be able to quickly approve some of these paints.

However, Senator Trible's wording required EPA to certify that specific TBT paint formulations that the Navy wanted to use did not pose <u>an unacceptable hazard to the marine environment</u>. This in essence required that EPA had to analyze all of the toxicological and environmental data available to it from the DCI's and all other sources and to complete its Special Review Study (which could take several years) prior to giving the Navy permission to use a specific paint formulation. For fiscal years '87 and '88, this language was placed in the actual legislation of each year's Continuing Resolution. For more information on the concerns of Congress during this period, see the Senate Congressional Record dated February 2, 1987 - S1481; the Senate Hearing Record of the Committee on Environment and Public Works, April 29, 1987, S. Hrg. 100-89 (73-832); and the Hearing Record for the Oversight Hearings on Tributyltin in the Marine Environment of the Committee on Merchant Marine and Fisheries, September 30, 1986 (S. Hrg. 99-49).

Senator William Cohen of Maine joined Senator Trible in pushing through these Amendments to the Continuing Resolution Bills. Subsequently, Senators Trible and Cohen began to draft comprehensive legislation, first as S. 428 (February 2, 1987). The exact language in this Bill was also introduced in the House by Congressman Bateman (VA) as H.R. 1046 on February 9, 1987. Senate Hearings were held for Bill S. 428, by the Committee on Environment and Public Works (S. Hrg. 100-89). However, the Bill was never marked up. Senators Trible and Cohen on October 15, 1987 introduced Senate Bill S. 1788 which subsequently became the Senate legislative vehicle - the "Tributyltin-Based Antifouling Paint Control Act of 1987," This Bill was co-sponsored by Senators Mitchell and Chafee, and focused 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 discussions, during the drafting of this Bill, the TBT release rates proposed have varied from 0.5 (±20%) $ug/cm^2/d$ of wetted hull surface area to 5.0 (±20%) $ug/cm^2/d$, due to standardization of the release rate testing protocol.

A new Bill was also introduced in the House on April 29, 1987 by Mr. Jones and subsequently amended by Mr. Studds and which was entitled: "the Organotin Antifouling Paint Control Act of 1987." This Bill (H.R. 2210) had the following requirements: a release rate of "not more than 5.0 $ug/cm^2/d$, and prohibited use of organotin antifouling paints on any vessel less than 65 feet in length, except for aluminum hull vessels. This Bill became the House legislative vehicle, and began to be compared to the Senate legislative vehicle (S. 1788).

The following is a chronology of events associated with the passage of these Bills:

> November 9, 1987, House passed H.R. 2210 and sent to the Senate
>
> December 12, 1987, Senate passed H.R. 2210 with S. 1788 language inserted into the Bill in place of H.R. 2210 language.
>
> Staff negotiations for agreement on: 4.0 release rate (rather than 3.0 - Senate, or 5.0 - House), 25 meter length prohibition (rather than House 65 feet), six months for sale of existing stocks, and one year for application of existing stocks.

April 18, 1988, Senate Amended H.R. 2210 and Passed the Bill Back to the House, adding a section requiring a Water Quality Criteria Document from EPA by March 30, 1989.

May 24, 1988, House Agrees to Senate Amendment of H.R. 2210 and sends the Bill to the President for signature into law.

June 16, 1988, President signs P.L. 100-333.

The purpose of the Act is to reduce immediately the quantities of organotin entering the waters of the United States. In the Act, if signed into law by the President, there are two permanent sections, the 25 meter size requirement, and the prohibition of retail sale of TBT antifouling paint additives. The release rate portion of the bill has a duration that would be in effect until a final decision of the Administrator of the EPA regarding continued registration of TBT as an ingredient in antifouling paints takes effect.

The following paragraphs summarizes highlights of key sections and identifies specific regulatory aspects of the Act. The Act, may be cited as the "organotin Antifouling Paint Control Act of 1988."

Sec. 3. Definitions: The term "organotin" means any compound of tin used as a biocide in an antifouling paint." The term "vessel" includes every description of watercraft or other artificial contrivance used, or capable of being used, as a means of transportation on water."

Sec. 4. Prohibitions: "No person in any State may apply to a vessel that is less than 25 meters in length an antifouling paint containing organotin with the following exceptions: (1) the aluminum hull of a vessel that is less that 25 meters in length; or (2) the outboard motor or lower drive unit of a vessel that is less than 25 meters in length.

No person in any State may: (1) sell or deliver to, or purchase or receive from, another person an antifouling paint containing organotin; or (2) apply to a vessel an antifouling paint containing organotin; unless the antifouling paint is certified by the Administrator [of EPA] as being a qualified antifouling paint containing organotin, and (3) sell or deliver to, or purchase or receive from, another person at retail any substance containing organotin for the purpose of adding such substance to paint to create an antifouling paint.

Sec. 6. Certification: The Administrator shall certify each antifouling paint containing organotin that the Administrator has determined has a release rate of not more than 4.0 micrograms per square centimeter per day on the basis of the information submitted to EPA in response to its Data Call in Notices.

Sec. 7. Monitoring and Research of Ecological Effects: The EPA and NOAA shall monitor the concentrations of organotin in the water column, sediments, and aquatic organisms of representative estuaries and near-coastal waters in the U.S., until 10 years after the date of the enactment of this Act, and shall submit annual reports to Congress on the results of these studies. The Navy is required to provide periodic (not less than quarterly) monitoring of waters serving as the home port for any Navy vessel coated with an antifouling paint containing organotin to determine the concentrations of organotin in the water column, sediments, and aquatic organisms of such waters. The Navy shall continue existing Navy programs evaluating the laboratory toxicity and environmental risks associated with the use of antifouling paints containing organotin. To the extent practicable, the EPA shall assist States in monitoring waters in such States for the presence of organotin and in analyzing samples taken during such monitoring. A five year special report is required by EPA to Congress to assess the effectiveness of existing laws and regulations concerning organotin compounds in ensuring protection of human health and the environment, with recommendations for additional measures to protect human health and the environment.

Sec. 8. Alternative Antifoulant Research: The Navy and EPA shall conduct research into chemical and nonchemical alternatives to organotin antifouling paints.

Sec. 9. Water Quality Criteria Document: Not later than March 30, 1989, the Administrator shall issue a final water quality criteria document concerning organotin compounds pursuant to section 304(a) of the the Federal Water Pollution Control Act.

Sec. 10. Penalties: Any person violating sections 4 or 5 shall be assessed a civil penalty of not more than $5,000 for each offense.

Sec. 11. Other Authorities; State Laws: Nothing in this Act shall limit or prevent EPA from establishing a lower permissible release rate for organotin under other authorities.

Sec. 12. Effective Dates; Use of Existing Stocks: Existing (on the shelf) stocks of antifouling paints containing organotin and organotin additives that exist before the date of the enactment of this Act may be sold, delivered, or purchased up until 180 days of the enactment of this Act. Existing stocks of any antifouling paints containing organotin and organotin additives that exist before the date of the enactment of this Act may be applied for up to a time period not to exceed one year. In reality, this last section delays the effective starting date of the Act for one one year for the prohibitions that enact restrictions for specific release rates and boat lengths.

Regulation of TBT release rates in organotin antifoulant paints are a step in the right direction, however, we must not forget that the ambient concentrations of TBT in harbors, estuaries and lakes are a product of at least three key factors: (1) TBT paint release rates, (2) the total wetted surface area of TBT painted boat bottoms in a water body, and (3) flushing dynamics of a water body. The effectiveness of release rate regulatory controls may be overridden by increases in boat density. Control of only one of these factors may not prove to be sufficient.

2.3.1.2 U.S. Environmental Protection Agency

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 applied 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 technical information needed to support the registration of TBT used in antifoulant paints. To obtain the information 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 has requested data under several areas including: (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 or 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). The protocol provides 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 of the 359 registrations for TBT were voluntarily cancelled within several months.

On October 1, 1987, EPA proposed certain restrictions on the sale and use of TBT based antifouling paints. Specifically, the Agency proposed to:

(1) Cancel all TBT antifouling paint registrations which either exceed a short term cumulative release of 168 ug/cm^2/first 14 days or exceed an average daily release rate of 4.0 ug/cm^2/day.

(2) Prohibit the use of TBT antifouling paint on all non-aluminum hulled vessels under 65 feet in length and require appropriate paint label restrictions.

(3) Classify TBT antifouling paints as restricted use pesticides, restrict their sale to certified applicators and their use by persons under the direct supervision of an on-site certified applicator.

(4) Require additional label language and compliance with certain use directions pertaining to the removal and disposal of old paint prior to the application of new paint.

Pursuant to Section 304(a) of the Clean Water Act, EPA issued a water quality advisory in October 1987 (EPA, 1987), through the Criteria and Standards Division of the Office of Water Regulations and Standards (OWRS). Water quality advisories have been developed as an interim vehicle for transmitting the best available scientific information concerning the aquatic life and human health effects of selected chemicals for which information is needed quickly but for which sufficient data, resources, or time are not available to allow derivation of a national ambient water quality criteria. The TBT advisory issued by EPA (1987) reports that "if the measured or estimated ambient concentration of tributyltin (TBT) exceeds 26 ng/l in freshwater or 10 ng/l in salt water, the discharger, after consultation with an appropriate regulatory agency, should evaluate the available exposure and effect data and complete one or more of the following options within a reasonable period of time:

a. Obtain additional measurements of the ambient concentration.
b. Improve the estimate of the ambient concentration.
c. Obtain additional laboratory and/or field data on the effects of TBT on aquatic organisms and their uses so that a revised, and usually higher, aquatic life advisory concentration or a water quality criterion can be derived.
d. Conduct appropriate toxicity tests on the effluent.
e. Reduce the ambient concentration of TBT to an acceptable level.

OWRS is currently developing a water quality criteria document (a more permanent set of recommended guidelines than those in the advisory), and is under congressional mandate to have the criteria in place by March 31, 1989.

As a public information self regulatory risk communication action, EPA's Office of Policy Analysis of the Office of Policy, Planning and Evaluation and the National Oceanic and Atmospheric Administration's National Marine Pollution Program Office have cofunded Science Applications International Corporation to develop and prepare a public information leaflet similar to the United Kingdom's "Don't Foul It" for distribution with the assistance of the Coastal States Organization and private boating organizations to registered boat owners. The leaflet provides boat owners with guidance on proper use and disposal practices of TBT antifouling paints to reduce the risks to both humans and the environment from misuse. The University of Hawaii's Sea Grant Extension Service has prepared and distributed its own leaflet "Don't Foul Things Up" drafted from the UK and the EPA/NOAA leaflets (Tabata, 1988). The Department of Environmental Quality of the State of Oregon and the Oregon State Marine Board have prepared a "A Users Guide for Antifouling Paints" leaflet modified from the EPA/NOAA leaflet (Wolniakowski, 1988). Also a citizens group in the New England region (Westport, MA) has prepared and distributed its own public information leaflet "TBT Alert" (Westport River Watershed Alliance, 1987).

2.3.1.3 National Oceanic and Atmospheric Administration (NOAA)

In furtherance of the objectives of the National Ocean Pollution Planning Act (NOPPA), NOAA's National Marine Pollution Program Office (NMPPO) coordinated the development of an interagency (NAVY, EPA, NBS AND NOAA) Workshop on Organotins. This Workshop was held in July 1986. The Workshop brought together leading researchers from across the country on aquatic monitoring and analysis for organotin compounds. It 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 (Landy, et al., 1986) consists of background papers and two working subgroup reports. 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. With the resultant discussions leading to the Workshop participants identifying data collection, research and monitoring needs for organotin compounds in aquatic environments. These discussions were very valuable because sampling programs were being initiated 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.

In preparation for the next 5-year plan, NMPPO is currently directing the collection of information on various aspects of issues associated with the use of TBT based antifoulant paints. A broad scope of information is being collected from the open literature, gray literature and from direct contact with researchers in the field. The status of developments for the regulation of organotin antifouling paints both at the state and international levels is being monitored continuously and the results are being compiled for use in the preparation of the next 5-year U.S. Federal Marine Pollution Research Plan.

In September of 1987, the OCEANS '87 International Organotin Symposium was co-sponsored by an interagency effort of the following Federal agencies:

NOAA (NOAA's Ocean Assessment Division and the National Marine Pollution Program Office); U.S. Navy (Naval Sea Systems Command, Office of the Chief of Naval Research, the Naval Ocean Systems Center, David W. Taylor Naval Ship Research and Development Center and the Naval Research Laboratory); EPA (Office of Policy, Planning, and Evaluation, and the Office of Pesticide Programs); and the National Science Foundation. The Symposium was held September 28, to October 1, in Halifax, Nova Scotia, Canada.

2.3.2 U.S. State Proposed or Pending Regulatory Actions

State legislatures have not been inclined to wait for the EPA to complete its Special Review process before adopting regulations of their own. The legislatures of adjacent States have also made an effort to assure uniformity is areas such as acceptable release rates, [currently 5.0 $ug/cm^2/d$ is favored, except for the State of Maine which wants 3.0 $ug/cm^2/d$], size limit on vessels permitted to use the paint [25 meters is favored], exemptions for Aluminum hulls and exemptions for 16 oz. spray cans for aluminum propellers and outdrives.

Since 1985, Alaska, North Carolina, Maine, Maryland, New York, Virginia, California, Oregon and Washington have passed TBT legislation. New Jersey, Massachusetts, and Michigan have bills enacted or pending in their legislature to regulate TBT (Table 2.2). Delaware, Texas and Wisconsin have chosen to use regulations under existing statutes rather than introduce new legislation. 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 would be disruptive to interstate boating commerce. On the Pacific Coast, the Pacific Fisheries Legislative Task Force has been responsible for the uniformity in bills enacted in California, Oregon, Washington, Hawaii and Alaska.

The following sections are a summary of each States enacted or pending legislation as of January 1988.

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

- o 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.
- o Urges Congress and EPA to support the states in their efforts to develop effective regional solutions to this issue.
- o 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.
- Bans the sale or possession of TBT paints, except in commercial boat yards. TBT paints with acceptable leach rates can be used on vessels greater than 25 meters in length, or those which have aluminum hulls.
- Requires a public education program.
- Violations are Class I misdemeanors, paint in violation may be seized.

Virginia Department of Agriculture adopted Emergency Regulations that were enacted into law which:

- Defined acceptable leach rates for TBT paints at 5.0 ug/cm^2/d 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.
- Permitted sale of TBT paints (in 16 oz. aerosol cans) with acceptable leach rates, for use on outboard motors and lower units.
- Adopted under the administrative process to amend Code of VA [Feb. 27, 1987].

2.3.2.2 Maryland: Enacted [Maryland State Code Chapter 304].

- Defines acceptable leach rates to be 5.0 microgram per square centimeter per day at steady state conditions, determined in accordance with the U.S. Environmental Protection Agency Testing Procedure.
- A person may not distribute, possess, sell, offer for sale, apply, or offer for application any substance that contains TBT in concentrated form and that is labeled for mixing with paint by the user to produce an antifouling paint for use on a vessel.
- Bans the sale, distribution, possession or use of TBT antifouling paints except for commercial boatyards using TBT paints with
- acceptable leach rates on boats greater than 25 meters in length or that have aluminum hulls where the paint is applied only within the commercial boat yard.
- Permits sale to any person 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 and seizure of paint for violation.
- Directs the development of water quality standards by Dec. 1, 1988 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 by D.N.R. 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.
- Directs a study of possible toxic effects of motorized bottom paint scrubbing devices used in the waters of the state.

2.3.2.3 Washington: Enacted

- Use, sale, offer for sale or possession of antifouling paints containing TBT or other triorganotin is prohibited.
- Exceptions for 16 oz. or less spray cans having acceptable release rate tested according to EPA approved methods.
- Acceptable release rate is 5.0 ug/cm^2/day.
- Effective until EPA promulgates final regulations.

2.3.2.4 California: Enacted

- Use and sale of TBT antifouling paint or antifoulant coating or the importation of items coated with TBT shall be prohibited. TBT paints with a leach rate of 5.0 ug/cm^2/day may be used on vessels over 25 m in length or with aluminum hulls.
- 16 oz. spray cans having acceptable release rates are exempted.
- Vessels painted prior to January 1, 1988 are exempted.
- Controls any item immersed in water.
- Violation is a misdemeanor.
- Regulations promulgated by State Food & Agriculture Department supersede this law.

2.3.2.5 New Jersey: (In Hearings)

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, use or possess 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.
- Exceptions are granted to certified commercial marine owners/operators to purchase and apply TBT paints having an acceptable release rate to vessels over 25 meters length or which have an aluminum hull.
- Exceptions are also granted to anyone to purchase or apply paint containing TBT having an acceptable release rate in 16 oz. spray cans.
- An acceptable release rate is defined as 5.0 ug/cm^2/day or less.

2.3.2.6 Oregon: Enacted

- Sale or use of TBT or triorganotin compounds are restricted-use pesticides to be sold only to licensed dealers.
- State will develop a public education brochure to be distributed to owners of boats 20 ft. or longer.
- Use and sale of antifouling paints containing TBT or other triorganotin compounds is prohibited on boats less than 25 meters length.
- Boats with aluminum hulls and boats 25 meters or longer may use a paint having a release rate of 5.0 ug/cm^2/day.
- Exemption granted for 16 oz. spray cans for outboard lower drive units.

2.3.2.7 North Carolina: Enacted

- Water Quality Standard of 2 parts per trillion in salt water, and to 8 parts per trillion in fresh water.

2.3.2.8 Hawaii: Enacted

- In 1987, the State Department of Agriculture restricted the sale and distribution of paints that release more than 5 micrograms of TBT per square centimeter per day.

2.3.2.9 Alaska: Enacted

- Use, sale or importation of submergible TBT paint coated items is prohibited. Any item immersed in water.
- Use and sale of antifouling paint containing TBT is prohibited on boats less than 4,000 gross tons. Antifouling paints which have a release rate of 3.0 micrograms/cm^2/day or less may be used on boats having aluminum hulls and on boats over 4,000 gross tons.
- Exemptions are granted for boats painted or items imported or ordered before December 1, 1987. Exemptions for foreign vessels in the State less than 90 consecutive days, to U.S. Government vessels or to vessels having aluminum hulls.
- Exemption for TBT paints having acceptable release rate of 3.0 ug/cm^2/day to be applied to vessels over 4,000 gross tons or aluminum hulls.

2.3.2.10 Michigan: In Hearings

- Total prohibition of sale to all persons
- Use on any vessel prohibited.
- Violation is criminal, fines to $500/day.

2.3.2.11 Delaware: Regulations adopted under existing legislation.

- Sale, distribution, possession, application or offer to sell or apply TBT antifouling paint is prohibited.
- Exemptions are granted to commercial boatyard owners or ships agent to apply acceptable release rate paint to vessels over 25 meters length or vessels with aluminum hulls.
- Exemptions for 16 oz. spray cans of TBT paint to any person.
- Acceptable paint must be copolymer paint with a release rate of 5.0 ug/cm^2/day or less.
- Violation is criminal, fine to $1,000 and/or 6 months in prison.

2.3.2.12 Maine: Enacted.

- Sale, distribution, possession or application of TBT compounds is prohibited.
- Prohibition applies to vessels, lobster traps, fishing gear, moorings or piers.
- Exemptions granted for commercial boatyard owners/agents to apply paint having acceptable release rate to vessels longer than 25 meters or vessels having aluminum hulls.
- Exemptions granted for sale and use of 16 oz. spray cans of TBT antifouling paint.
- An acceptable release rate is 3.0 ug/cm^2/day or less.
- Violation is criminal offense, fine to $25,000/day

2.3.2.13 Massachusetts: Pending

- Distribution, sale, possession, offer of sale, use or application of organotin antifouling paints or TBT compounds to mix to produce antifouling paint are prohibited
- Vessels, lobster traps and fishing apparatus may not be coated.
- Exceptions granted for commercial boatyard owners or agents to purchase and apply paints having acceptable release rates to vessels longer than 25 meters or to vessels having aluminum hulls.
- An acceptable release rate is 3.0 ug/cm^2/day or less.
- Violation is a misdemeanor: fines $500 to $2,000 first offense, $2,000 second offense and subsequent offenses.
- Office of Coastal Zone Management and Bureau of Pesticides to develop public education program.

2.3.2.14 New York: Enacted

- Sale, use, application, or offer for sale of TBT antifouling paints are prohibited.
- Exceptions are granted for application to aluminum parts of vessels only. An acceptable release rate paint must be used and the vessel must be less than 25 meters long.

- o Exceptions granted to 32 oz. spray cans.
- o Exceptions granted to Department of Environmental Conservation for scientific research.
- o An acceptable release rate is defined to be between 1.0 and 5.0 $ug/cm^2/day$.
- o Violations are civil offenses, fines to $250.
- o Public education to comprise lists of banned and acceptable paints.

2.3.2.15 <u>Texas</u>: Regulation adopted under existing legislation.

- o Requires registration of sale of all antifouling products.
- o Sale of unregistered paints is prohibited.
- o Monitoring required.
- o Health and environmental effects study required.

2.3.2.16 <u>Wisconsin</u>: Regulation pending.

- o All persons will be required to have a permit to use or apply TBT compounds.

Table 2.2 presents a summary of key features of TBT regulatory legislation on a State by State basis for comparison.

2.3.3 <u>International Regulatory Actions</u>

2.3.3.1 United Kingdom

The first regulatory action in the UK to reduce the environmental impact of organotin compounds from antifouling paint was announced by the Environment Minister in Parliament on 24 July 1985. The action consisted of the five following steps: (1) the development of regulations to control the retail sale of the most damaging organotin containing paints [beginning 1 January 1986, they intended to ban the use of "free association" organotin-based paints by small boat owners, and to set the maximum levels for the organotin content of "copolymer" paints], (2) a notification scheme for all new antifouling agents, (3) guidelines for the cleaning and painting of boats coated with antifoulants, (4) propose the establishment of a provisional ambient environmental quality target (EQT) for the concentration of tributyltin in water [20 ng/l was proposed as the UK's EQT], and (5) coordination and further development of organotin monitoring and research programs so that the Government could assess the effectiveness of these regulatory actions at a later date.

The first legislation to control the retail sale of organotin based antifoulant paints was introduced on December 18, 1985, under the Control of Pollution (Antifouling Paints) Regulations of 1985, which came into force on 13 January 1986. These regulations were developed under Sections 100 and 104(1) of the Control of Pollution Act of 1974. They prohibited

Table 2.2
TBT Regulatory Legislation - State by State Comparison

	Legislative or Regulative Action-Status	Regulated Substance	Means to Control Release	Extent of Control	Exceptions	Acceptable Release Rate $ug/cm^2/day$	Penalty for Violation	Public Education	Duration of Law
Maine	Enacted	TBT cmpd.	Sale/use	Boat/gear	Al/25 M	3.0	Fine <$25K		Permanent
Mass.	Pending	Organotin	Sale/use	Boat/gear	Al/25 M	3.0	Fine <$2K	Inform.prog	
Rhode Is.	None								
Connect.	None								
New York	Enacted	TBT Paint	Sale/use	Boats	Al/<25 M	Rng 1-5	Fine <$250	Apr.list	Permanent
New Jersey	Pending	TBT Paint	Sale/use	Boats	Al/25 M	5.0	Fine <$1K		Permanent
Delaware	Adopted	TBT Paint	Sale/use	Any item	Al/25 M	5.0	Fine <$1K	Study	Permanent
Maryland	Enacted	TBT Cmpd.	Sale/use	Boats	Al/25 M	5.0	Fine <$3K	Inform.prog	Permanent
Virginia	Enacted	TBT Paint	Sale/use	Boats	Al/25 M	5.0		Inform.prog	Permanent
N. Carolina	Regs	TBT Cmpd		Discharge WQS 2.0 ng/l					Permanent
S. Carolina	None								
Alabama	None								
Florida	None								
Louisiana	None								
Texas	Adopted	All Paint	Register					Study	
California	Enacted	TBT Paint	Sale/use	Any item	Al/25 M	5.0			Until Regs.
Oregon	Enacted	Tri-organo	Sale/use	Any item	Al/25 M	5.0		inform.pr	
Washington	Enacted	Tri-organo	Sale/use	All pers.	Al/25 M	5.0			Until Regs.
Alaska	Enacted	TBT Paint	Sale/use	Any item	Al/4K GT	3.0			Permanent
Hawaii	Regs.	TBT Paint	Release Rate			5.0		Brochure	Permanent
Minnesota	None								
Michigan	Pending	TBT Paint	Sale	Any item	None	None	Fine <$5K		Permanent
Ohio	None								

U.S. Congress (Proposed Bills - January 1988)

Senate	Pending	Organotin	Sale/use	Boats	Al/25 M	3.0	Fine <$5K	USN/EPA/NOAA	Til EPA Reg
House	Pending	Organotin	Sale/use	Boats	Al/65 Ft.	5.0	Fine <$25K	EPA/NOAA	Til EPA Reg

the retail sale of antifouling paints containing organotin compounds if: (1) the total concentration of tin in dried copolymer paints exceeded 7.5% by weight of tin, or (2) the total concentration of tin in other non-copolymer [free association] paints exceeded 2.5% by weight of tin (The Control of Pollution (Anti-Fouling Paints) Regulations - Statutory Instruments No. 2011, 1985). These regulatory actions were enacted with the provision that they would be reviewed with the interim results of the comprehensive scientific studies that were being carried out by both government and non-government laboratories, which included studies on the distribution, fate and effects of TBT in the environment and laboratory toxicity studies.

During the 1986 boating season, a detailed monitoring program was conducted by the Ministry of Agriculture, Fisheries and Food (MAFF), (as proposed above) in oyster cultivation areas of 9 estuaries of England and Wales. These studies found that water column TBT concentrations still exceeded 20 ng/l [the UK proposed EQT] by up to ten times in six of the nine estuaries. An in-depth review of these data and additional data provided by other UK researchers led to the conclusion that the proposed EQT was not being met in areas of high boat densities. Also there were measurable environmental problems resulting from the use of TBT as an antifoulant on nets and pens used in salmon cultivation in Scotland (see Davies, 1987), and significant findings of imposex (sex changes of females to males) in dogwhelk populations (see Section 4.2.4 and Figures 4.3 and 4.4 this report). The finding of these high levels following regulatory actions led DOE in July of 1987 to initiate the total ban on the use of TBT in antifoulant paints on small boats and to revise the previous regulatory actions, because these results suggested that the existing controls were not effective enough in reducing TBT Water column concentrations to acceptable levels to protect sensitive species. The DOE has also suggested a lowering of the TBT water quality standard from 20.0 ng/l to 2.0 ng/l, but as of February 1988, no action has been taken. These new regulations, introduced in January 1987, reduced the maximum allowable tin content of copolymer paints from 7.5%. to 5.5% through The Control of Pollution ACT (COPA) of 1986, which amended the Control of Pollution Act of 1985 (the Antifouling Paints Regulations, of 1985) No. 2300, 1986). These prohibited the retail sale and the supply for retail sale of antifouling paints containing a triorganotin compound as well as the wholesale and retail sale of antifouling treatments containing such a compound. The ban also did not make any exceptions to accommodate vessels with aluminum hulls, outboard drives, parts or fittings, as have U.S. regulatory strategies. The DOE expected the paint companies to provide suitable products in the short term, and in fact both International Paints and Blakes are now marketing in the UK, paints, which they say are suitable for this use (AL27 and Lynx). These regulations came into force on May 28, 1987 (The Control of Pollution (Anti-Fouling Paints and Treatments) Regulations, 1987 - Statutory Instruments No. 783, 1987). It also should be noted that the control of pesticide regulatory actions in the U.K., has shifted from DOE to the Ministry of Agriculture, Fisheries and Food (MAFF) on July 1, 1987 through powers conferred to MAFF by sections 16(2) and 24(3) of the U.K. Food and Environmental Protection Act of 1985 and Regulation 5 of the Control of Pesticides Regulations 1986, as reflected in the Statutory Instruments No. 1510 (The Control of Pesticides Regulations, 1986).

The UK Government also enacted the Food and Environment Protection Act (FEPA) to ensure that in the future all antifouling agents of any kind would be screened in the same way as other pesticides under provision of Part III. This was coordinated with the Control of Pesticides Regulations of 1986 which provided for the statutory screening of antifouling paints beginning 1 July 1987. These regulations prohibit the advertisement, sale, supply, storage or use of any pesticide - including antifouling paints and treatments - unless approved by Ministers (see Able et al., 1986, 1987 for an in-depth historical perspective). The DOE has also revised (January, 1988) its "Don't Foul Things Up" Leaflet to draw again the attention of boaters to the likely environmental impact from organotin in antifouling paints in 1988 when they expect a large amount of TBT paint to be stripped off following the ban (January, 1988).

2.3.3.2 France

In January 1982, the France Ministry of Environment announced a temporary 2 year ban on TBT paint containing more than 3% by weight organotin for the protection of hulls of boats of less than 25 tons, for for both the Atlantic coasts and the English Channel, following the official recommendation issued by the "Evaluation Committee on Ecotoxicity of Chemical Substances". The decree of 16 September 1982 extended the ban to the whole coastal area and to all organotin paints, beginning October 1, 1982. These regulations also only allow the application of antifouling paints containing organotin to hulls of all boats and marine craft having an overall length of greater than 25 meters in length. Hulls made of aluminum or aluminum alloys were exempted from the ban.

2.3.3.3 Switzerland and Germany

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

2.3.3.4 Commission of the European Communities

The Commission of the European Communities on 1 February 1988 proposed an amendment for Council Directive (76/769/EEC) restricting the marketing and use of certain dangerous substances and preparations (COM(88) 7 Final - Brussels). The proposal lists "organstannic compounds" and restricts their use as substances and constituents of preparations intended for use to prevent the fouling by micro-organisms, plants or animals of: a) the hulls of boats of an overall length, as defined by 1SO 8666, of less than 25 meters, and b) cages, floats, nets and any other appliances or equipment used for fish or shellfish farming, and may be sold only to professional users in packagings of a capacity of not less than 20 liters.

Table 2.3 is a summary of the specific restrictions (such as % TBT in antifouling paint, or exemptions for specific vessel length, or for aluminum hulls) that have been implemented by regulatory action or legislation as international regulatory strategies, for the countries indicated.

2.4 CURRENT FEDERAL ORGANOTIN RESEARCH, DEVELOPMENT AND MONITORING PROGRAMS

A summary of the current programs of Federal agencies with respect to organotin in the coastal environment is presented in Table 2.4. Research is presented here in the sense of any systematic inquiry into any aspect of organotin detection, speciation, biological effect, distribution, fate and behavior in the environment, toxicity testing, new application methodology or new disposal methodology.

Monitoring is used here in the sense of any program of measurement employing previously developed methodology with the intention of determining some aspect of change or distribution over a unit of time (hours, days, months or years) in natural environments, or areas of application and/or removal of organotin antifouling paints, or simply recording over time, the volume of organotin antifouling paints sold or used (distribution and application patterns).

Development is used here in the sense of the improvement of a method for the detection, identification or quantification of organotin in: air, water, sediment, or tissue. Development also refers to the improvement of existing means to apply, remove, store or denature organotin antifouling active ingredients.

2.4.1 National Bureau of Standards

Research at the National Bureau of Standards (NBS) focuses on the comparisons of methodologies for quantitative molecular determination of the various species of organotins likely to be found in the environment. The ability to detect organotins-particularly butyltins at the part per trillion (ng/l) level reliably is essential to development of a successful regulatory strategy since biological evidence strongly indicate that adverse biological effects occur at or below the present ill-defined limits of reliable detection. Researchers at NBS have conducted a series of inter-laboratory intercalibration experiments with the Naval Ocean Systems Center (NOSC) on natural samples. NBS obtained very good agreement (generally within 20% of the mean values) on quantification of di- and tributyltin species in split, and shared samples from marine waters in the U.S. and U.K. The standards division of NBS is also currently developing very pure, dilute, aqueous solution of tributyltin and mixed solutions of di- and tributyltin to be tested as possible reference standard materials. Researchers at NBS have also investigated the degradation rates of tributyltin in Chesapeake Bay (from industrial areas of Baltimore Harbor, and marina areas near Annapolis).

Table 2.3

International Regulatory Strategies

	Legislation or Regulation	Restrict by boat use/type	Restrict by boat length	Aluminum hull exemption	Restrict by paint type	Restrict by weight % TBT in paint	Restrict by release rate $ug/cm^2/day$	Requires further research	Water quality standard in ng/L
United States	Enacted		65 Feet	yes			4.0	yes	FW 26/SW 10*
Canada	None								
Great Britain	Enacted		25 Meters	No	1987	5.5% Copolymer 2.5% Free Assoc.	No	yes	SW 2.0**
France	Enacted		25 Meters	yes		3.0% 1982			
Fed. Rep. Germany	Enacted								Ban in Fresh
Switzerland	Enacted								Ban in Fresh
Holland	None								
Denmark	None pending EEC joint act.								
Sweden	None								
Norway	None								
Mexico	None								
Japan	Regs adopted								

FW = Freshwater

SW = Saltwater

* = U.S. EPA Advisory (as a Recommendation to the States)

** = Proposed/Suggested (Not Adopted)

Agriculture Canada has advised the paint and coating industry that boat and ship antifouling paints are subject to registration under the Pest Control Products Act (February 12, 1987), and that manufactures of TBTO have formed a task force to provide additional data for evaluation by regional staff and federal advisors (Information Bulletin, Pesticides Directorate, Agriculture Canada, 87-7, Ottawa, Ontario).

The organotin research at NBS is solely conducted on a reimbursable basis with funding from four agencies, including (1) Transportation--Coast Guard, (2) Interior--Minerals Management Service, (3) Defense--Navy, and (4) Commerce--NOAA. An automated sampling methodology is currently being developed for the continuous analysis of organotin compounds with a detection limit of 5 ng/l with continuous measurement capability over complete tidal cycles.

2.4.2 National Oceanic and Atmospheric Administration

The principal office within NOAA having the responsibility for monitoring of organotin concentrations in the aquatic environment is the Ocean Assessments Division (OAD) within the National Ocean Service. The OAD is responsible for the NOAA Status and Trends Program (S&T) which is collecting water, sediment and tissue samples from a series of 150 coastal stations to establish the status and trends of specific contaminants over time. This program has added TBT and DBT to its sampling program in specific areas beginning in 1987.

The NOAA National Sea Grant College Program has sponsored a research study with organotins, testing for toxicity and sublethal effects with the Fiddler Crab (Uca Pugilator) and Killifish (Fungulus heterclitus) at Rutgers University (Weis et al., 1987a, b).

2.4.3 U.S. Environmental Protection Agency

The Environmental Protection Agency (EPA) Chesapeake Bay Program (CBP) initiated a small scale (500) sample monitoring program during the Summer of 1986. These samples were analyzed by EPA's Gulf Breeze Laboratory, which has a lower detection limit of 20 ng/l. The study was coordinated by the EPA Chesapeake Bay Liaison Office with the assistance of Dr. Lenwood Hall of Johns Hopkins University as a twenty week, small-scale sampling program to measure concentrations of tributyltin and dibutyltin at four selected harbor sites in Northern Chesapeake Bay: Annapolis, Solomons, Oxford and Plaindealing Creek. The survey concluded that sources of TBT measured in the harbor areas are directly linked to local boating and marina activity and specifically to TBT leachate from antifouling paints, and that the sampled harbors are a source to TBT to the estuarine environment beyond the boundaries of the harbors.' The highest average concentrations of TBT by site were found at Annapolis (70.6 ng/l) followed by Solomons (34.7 ng/l) Oxford (27.7 ng/l) and Plaindealing Creek (20.1 ng.1). It was concluded that these concentrations were high and sufficiently constant enough to pose a threat to organisms living in the harbor areas (EPA Chesapeake Bay Program, 1987). Improvements in instrumentation are underway to enable a larger monitoring program to be conducted in Chesapeake Bay.

In the near future, EPA will issue a Data Call In Notice requiring TBT registrants to conduct a three to four year study of U.S. waters. This study will provide baseline information on the extent and levels of TBT found around representative docks, marinas and other sensitive areas.

2.4.4 U.S. Navy

The Navy has initiated the monitoring of organotins - particularly tri- and dibutyltin species in several harbors where Navy ships are based. These include Chesapeake Bay where monitoring programs are in place in both the Maryland portion, principally around Annapolis and in the Severn River, and in the Virginia portion of the Bay, principally around Norfolk and the Elizabeth River. Between 1984 and 1986 organotin baseline measurements were made in Portsmouth, NH, New London/Groton, CN, Philadelphia, PA, Charleston, SC, and Mayport Basin and St. John's River, FL on the East Coast. On the West Coast, baseline surveys were conducted in Puget Sound, WA, San Francisco Bay. Los Angeles/Long Beach and San Diego Bay, CA, and Pearl Harbor, HI. Intensive monitoring has been conducted in San Diego, Pearl Harbor and the Norfolk region of Chesapeake Bay.

The Navy has had ongoing research and monitoring programs for TBT since the early 1980's. The current focus of the Navy studies is on the fate and behavior of organotin compounds and the subsequent biological effects of these compounds in ecosystems. Extensive research has been conducted by the U.S. Navy through the Naval Ocean Systems Center (NOSC) and the David W. Taylor Naval Ship Research and Development Center at Annapolis. Table 2.4 presents a listing of the research projects that the Navy has planned for the next several years.

Table 2.4

Federally Sponsored Organotin Research Projects for Federal Fiscal Years 1986-1988

U.S. Navy (for specific research descriptions, see NAVSEA, 1986):

Four major areas: (1) Harbor Monitoring and Modeling, (2) Analytical Methods, (3) Drydock Operations and Discharges, and (4) Environmental Studies. Specific Studies:

- Baseline Surveys of Navy Harbors
- Monitoring of Organotins in Navy Harbors During Initial Paint Implementation
- Monitoring of Organotins with Remotely moored, Automated Samplers
- In-Situ Organotin Release Rate Studies from Ship Hulls
- Harbor Modeling
- Improved Analytical Methods for Drydock Discharge Studies
- Improved Procedures for Measuring Organotin Release Rates
- Improved Analytical Methods for Water and Sediment
- Drydock Clean-up Technologies
- Reduce Drydock Waste Generation
- Drydock Wastewater Collection
- Drydock Discharge Monitoring
- Drydock Waste Treatment
- Organotin Degradation in Wastewater Treatment Plants
- Toxicity Studies
- Food Chain Effects
- Environmental Chemistry/Biochemistry of Butyltins

Table 2.4 (continued)

<u>EPA</u>:

- Provisional Aquatic Life Advisory Concentrations for Tributyltin
- Chesapeake Bay Monitoring Program for 4 selected Marinas

<u>NOAA</u>:

- Developmental Effects of TBT on the Fiddler Crab (<u>Uca Pugilator</u>) and Killifish (<u>Fungulus heterclitus)</u>
- Monitoring of TBT, DBT, and MBT at the Master Stations of the Status and Trends Program

2.4.5 Non Federal Programs

Dr. Edward Goldberg of the University of California (Scripps Institution of Oceanography) directed the collection and analysis of water, sediment and tissue samples from marina's up and down the coast of the State of California between February 1, to June 31, 1986, for tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT), (for actual data, see Goldberg, 1986 Data Report to the Sate Water Resources Control Board). These monitoring activities were sponsored by the University of California Toxic Substances Teaching and Research Program and by the State of California Water Resources Control Board, Sacramento, California (Goldberg, 1986 and Stallard et al., 1987). Researchers at the Moss Landing Marine Laboratory (Dr. Mark Stephenson) supplemented this study with water samples collected during the Spring and Summer of 1987 from California marinas and from Coos Bay, Oregon (see Stephenson et al., 1986; 1987 and Wolniakowski et al., 1987). Elsewhere on the West coast, the Department of Environmental Quality of the State of Oregon has received a grant from NOAA's National Estuarine Program Office to extensively study organotin concentrations is Coos Bay, beginning the Summer of 1988.

In the Northern portion of Chesapeake Bay, studies have been supported by the State of Maryland's Department of Natural Resources and the University of Maryland Center for Environmental and Estuarine Studies and by Johns Hopkins University (Hall et al., 1987). In the Southern Chesapeake Bay, a group from the Virginia Institute of Marine Science has been monitoring marinas, boatyards, creeks and the Elizabeth River and Hampton Roads Virginia areas (Huggett et al., 1986 and Unger et al., 1987).

2.4.6 Federal Coordination and Cooperation

There have been two major areas of Federal cooperation and coordination. The first was the formulation of an ad-hoc interagency committee which organized the Organotin Workshop that was hosted by NOAA's National Marine Pollution Program Office and was held at the U.S. Naval Academy in Annapolis, MD, during June 1986. The second has been the cooperative funding of the OCEANS '86 and '87 Organotin Symposia. The first symposium was held in Washington, D.C. September 23-25, 1986 and the second was held in Halifax, Nova Scotia, Canada September 28, to October 1, 1987. These Symposia have been funded jointly by Navy, EPA, NOAA and NSF.

The purpose of these Symposia were to bring together researchers from many disciplines, regulators, policy and decision makers from around the world to provide a forum for the exchange of research findings, methods used and to discuss and review data and results of studies and regulatory actions, and information necessary for policy and decision-making. Each symposium has a Proceedings of published papers that address scientific, management and regulatory aspects of TBT paints in the coastal environment

OCEANS '86 and '87 Proceedings). These Proceedings each have an Introduction and Overview Paper which has been prepared to aid those from non-technical backgrounds to gain a quick introduction and grasp of the technical and environmental issues. At OCEANS '88, in Baltimore, MD, a few organotin sessions will be held, to review the progress of monitoring studies. The Third International Organotin Symposia is being planned for the fall of 1989 and is scheduled to be held in Monaco, under the sponsorship of IAEA, MEDPOL, UNEP and several international organizations.

CHAPTER III

PRODUCTION AND PATTERNS OF TBT ANTIFOULING PAINT USE

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3.1 INTRODUCTION

This Chapter summarizes information on registrations and use patterns of organotin antifouling paints. Also included in this Chapter are sections which review paint application and removal practices as they serve to introduce organotin compounds into the marine environment. Antifouling paint formulations vary in the percent by weight of organotin compounds employed and in the manner or rate in which these compounds are made available (or released) to the environment. The variation in release rates of different paints is under extensive study by paint manufactures, the U.S. Navy, and the Environmental Protection Agency. Since EPA's Data Call-In Notice, nearly 80% of previous paint registrations have been voluntarily cancelled. Most of these have been free association or high release rate formulations. Therefore, past paint usage patterns may not give an accurate picture of future organotin introductions to the environment from paint formulations which remain registered.

3.2 WORLDWIDE PRODUCTION AND USE

Zuckerman et. al. (1978) estimated the annual world consumption of tin to be 84 x 10^6 kg; of this, 4.5 x 10^6 kg was in the form of organotin biocides (see Table 3.1). Estimates by Davies and Smith (1982), which are some what higher than Zuckerman's suggest that the use of organotin compounds in industry had risen to (30-35) x 10^6 kg by 1980. Of current production, about two-thirds is used for stabilization of PVC plastics and 7.8% for biocides, see Figure 3.1.

3.3 NATIONWIDE PRODUCTION AND USE

Dibutyltin bis(isooctyl mercaptoacetate) dominates the market, constituting 33 x 10^6 of the 65 x10^6 kg of alkyltin compounds produced between 1965 and 1976. This is because the major area of utilization (70% of total annual production) is as a heat stabilizer for rigid and semi-rigid PVC. Dioctyltin compounds are used only in PVC in contact with food; dibutyltin dilaurate is used as a catalyst in foam and elastomer production and as a poultry anthelmintic; and bis (tributyltin) oxide and tributyltin fluoride are used as biocides. Table 3.2 summarizes the number of organotin antifoulant paint registrants and the number of their products on the market at the time of the EPA Data Call In Notice (PD/1—July, 1987). When EPA published its PD/1, it was estimated in the document that in the U.S., that 250,000 pounds (113,600 kg) to 300,000 pounds (114,000 kg) of TBT compounds were used in antifouling paints annually. However, information supplied by registrants in response to the DCI revealed that the actual U.S. annual use of TBT in antifouling paints was approximately 624,000 gallons of paint with over one million pounds (450,000 kg) of TBT. Commercial vessels are the major users of TBT antifouling paints although 33 % is applied to recreational vessels (EPA, PD 2/3, 1987). Between 34,000 and 45,000 kilograms of the total is in the form of tributyltin-bis-oxide. The U.S. Navy's proposed fleet-wide (600 ships) use of TBT paints would increase the U.S. annual usage an additional 27,000 to 41,000 kilograms.

Figure 3.1

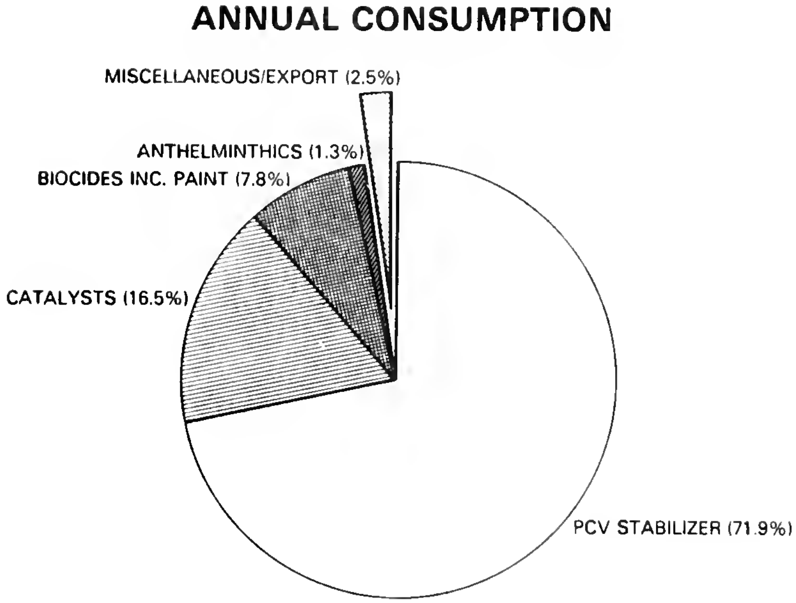
ANNUAL CONSUMPTION
MISCELLANEOUS/EXPORT (2.5%)
ANTHELMINTHICS (1.3%)
BIOCIDES INC. PAINT (7.8%)
CATALYSTS (16.5%)
PCV STABILIZER (71.9%)

Table 3.1
Estimated Annual U.S. Consumption of Selected Alkyltin Compounds By Use Area (after Zuckerman et al., 1978)[a]

ANNUAL CONSUMPTION (10^6 kg)

Year	PVC Heat Stabilizers	Catalysts	Biocides	Anthelmintics	Miscellaneous Excluding Exports	Total
1965	1.6	0.23	0.23	0.068	0.16	2.3
1966	2.6	0.32	0.27	0.073	0.15	3.4
1967	2.9	0.45	0.32	0.077	0.23	4.0
1968	3.5	0.64	0.36	0.082	0.24	4.8
1969	4.0	0.82	0.41	0.086	0.27	5.6
1970	5.0	1.0	0.50	0.095	0.26	6.9
1971	5.4	1.2	0.59	0.10	0.30	7.6
1972	7.1	1.4	0.68	0.10	0.073	9.4
1973	7.8	1.7	0.77	0.11	0.12	10.5
1974	7.4	2.0	0.91	0.11	0.086	10.5
1975	6.0	1.7	0.68	0.091	0.091	8.6
1976	7.3	2.3	0.91	0.12	0.091	10.7
1981	10-12	3.4	2.3	0.16	0.27	16.1-18.1
1986	13-15	4.5	4.5	0.23	0.45	22.7-24.7
TOTAL (1965-1976)	61	14	6.6	1.0	2.1	84

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[a] The original sources of data are Lapp (1976) and U.S. EPA (1977).

Table 3.2
Butyltin Compounds Tabulated By Number Of Antifouling Paint Registrations

CHEMICAL CODE	CHEMICAL NAME	NO. OF REGI-TRANTS	NO. OF PRODUCTS	NO. W/CU	NO. W/SN	NO. W./ SN + CU	NO.W/ OTHER
083001	Bis TBT oxide	37	161	81	11	12	8
083101	Bis TBT dodeceny succinate	1	13	8	0	0	0
083105	TBT acetate	3	3	0	0	0	0
083112	TBT fluoride	34	141	40	24	2	1
083113	Bis TBT sulfide	2	3	0	3	0	0
083114	TBT resinate	3	13	2	0	0	0
083117	Bis TBT adipate	2	9	2	0	0	0
083119(20)	TBT methacrylate	19	52	23	16	10	0
083121	TBT acrylate	1	1	1	0	0	0
	ALL TBT ANTI-FOULING PAINTS	102	396	157	54	24	9

Source: U.S. EPA, 1987.

Since tributyltin compounds were first registered in the U.S., in the early 1960's, the number of EPA registered formulations has grown to 364. Sixty-one manufacturers have one or more paint formulations registered for use.

The Navy estimates that, if the entire fleet were painted with TBT paint, the reduction in fuel costs would exceed $110 million annually calculated with fuel costing (also referred to as fuel avoidance costs) less than $16 per barrel, (U.S. NAVSEA, 1986). In commercial shipping, fishing, and private boating, this could add another $300 to $400 million in annual fuel savings. Table 3.3 (from Lucas and Williams, 1987) presents an estimate of the average area coverage (square feet) of paint coverage per gallon of paint by paint type and application firm type. Copolymer, ablative, and and self polishing paint designations have been combined due to the fact that users surveyed were not always able to discriminate whether the paint being applied was self polishing or not. Similarly if the paint did not designate the manner of incorporation of the Tributyltin as copolymer or self polishing, the paint was considered to be a free association type. More square feet covered per gallon means that the paint is usually applied in a thinner paint film. In most cases, free association paints are generally applied with the thinnest paint film possible because the spent paint film will have to be removed by mechanical means. Copper base paints are usually applied as a thicker film than free association TBT paints while self polishing copolymer paints are applied in the thickest film.

Another factor that affects quantity of TBT released from the paint to the environment is the degree of drying. Table 3.4 presents the degree of drying of the paint film in terms of the number of days between painting and water contact with the new paint film. The Gulf and Southern Pacific coasts have generally the shortest times between painting and launching. This may possibly be due to external factors such as the prevalence of good weather. However, the longer the paint film dries, the less antifouling biocide is released from the film.

Table 3.3
Antifouling Paint
Average Coverage in Square Feet per Gallon
by Paint Type and Applicator Firm Type

	Tributyltin		
Applicator Firm	Copolymer	Free Association	Other Antifouling
Ship building/repair	55	33	37
Boat building	0	0	60
Boat repair	15	35	35
Other	66	81	64
Total by paint type	49	69	58
Percentage of total	[29]	[37]	[33]

Source: Lucas and Williams, 1987.

Paint manufacturers specify a maximum time interval between painting and launching the hull in order to retain maximum antifouling effectiveness. Collecting drying time information is also essential to proper interpretation of the release rate studies mandated by the EPA Data Call In Notice.

3.4 Impact of EPA's DCI on Registration

Following EPA's issuance of the DCI, twenty antifoulant paint manufacturers have requested voluntary cancellation of 82 paint formulations rather than provide or fund the studies required by the Environmental Protection Agency's Data Call In Notice [DCI] (Moore, 1987). In addition, twenty one of the sixty one manufacturers holding EPA registrations for antifouling paint have indicated to EPA that they are conducting or intending to conduct studies of leach rates of their paints in compliance with EPA's DCI. Of the remainder, 30 manufacturers holding an aggregate of 139 registrations for antifouling paint formulations have not responded to the EPA DCI and have been sent a Notice of Intent to Suspend their paint registrations. An additional 10 manufacturers have

Table 3.4

Average Number of Days between Application/Water Contact (Degree of Drying)

Active Ingredient Type

	Tributyltin			
Reporting Domain	Copolymer/ Self-polishing	Free Association	Other	Undetermined
North Atlantic	6	6	4	0
Mid Atlantic	4	5	3	3
South Atlantic	2	2	1	0
Gulf Strata	2	2	2	82
South Pacific	1	2	1	2
Mid Pacific	2	3	5	5
North Pacific	10	2	1	6
Great Lakes	0	1	3	0
River Strata	1	2	1	1
Average Number of Days	3	4	3	18

Paints containing Tributyltin in one form or another comprise two thirds of all the exposed painted surface found in the Survey. Antifouling paints without Tributyltin made up the other third of the exposed surface.

Source: Lucas and Williams, 1987.

been sent a Notice of Intent to suspend their registrations because they have not filed a timely response to the EPA's DCI requirements even though they have indicated intent to comply. Of the 57 registered products that provided acceptable data to EPA's DCI Notice, only 29 products meet the proposed EPA release rate of 0.5 ug/cm^2/d (U.S. EPA, 1987).

The aggregate effect of the voluntary requests for cancellation and the Notice of Intent to Suspend registrations if carried out will be a reduction of 80% of the brand names available to the market place. However these brand names which are candidates for cancellation account for only half of the volume of antifouling paint production. Thus it is the less popular products which are being dropped. An equivalent increase in production can be anticipated by the more popular brands to capture the segment of the market place abandoned by the canceled registrations. Therefore, the cancellation of registrations may not have the effect of an equivalent reduction in the amount of TBT reaching the environment.

3.5 PATTERNS OF ANTIFOULANT PAINT USE AND RATES OF USE

Antifouling paint use by individuals does represent a significant portion of paint sold but is extremely difficult to assess with a survey method. Industrial establishments are the other major user of antifouling paint. The 1982 U.S. Census identified 2,500 to 2,600 non-military industrial establishments in the contiguous States which are likely to be applicators of antifouling paints. Of these nearly half build or repair ships or boats. Lucas and Williams (1987) conducted for EPA a survey of these shipyards and boatyards employing follow up procedures to increase the accuracy of the survey results. The results of their studies are summarized in the sections below.

3.5.1 Paint Use by Vessel Hull Composition

Table 3.5 presents the number of vessels painted, by the type of paint used and by the composition of the hull. The first number in each category is the probable number of vessels in the contiguous United States based on the sample survey proportions. The primary hull composition material painted with TBT containing bottom paints was found to be fiberglass or glass reinforced plastic (GRP). Fiberglass hulls comprise 77.3% of all the hulls painted with paints containing TBT. Wood composition hulls comprise 13.5 % of the hulls painted with tributyltin containing paints. Copper anti-fouling paints corrode aluminum hulls and outdrives rapidly and steel structures somewhat more slowly. An epoxy type isolation primer is normally used on metal hulls to prevent or control the effects of electrolysis which is due to the action of antifouling paints containing copper. Aluminum hulls (which have the most severe problem with electrolysis (when painted with antifouling paints other than TBT) represent only 2.3% of the hulls painted with Tributyltin antifouling paints.

Table 3.5

Number of Vessels Painted by Type of Hull and by Type of Antifouling Active Ingredient

		Active Ingredient Type		
		Tributyltin		
	Total # Vessels	Copolymer/ Self-polishing	Free Association	Undetermined Other
Type of Hull				
Iron/Steel	6,399	1,349	2,812	2,238
Aluminum	6,564	1,499	4,303	762
Wood	37,967	955	8,866	28,146
Fiberglass/ Plastic	217,842	43,406	97,010	77,426
Other	611	561	0	50
Undetermined	12,925	12	2,988	9,925

Source: Lucas and Williams, 1987.

3.5.2 Paint Use by Vessel Size Category

Figure 3.2 presents the distribution of the number of vessels painted with paints containing TBT by length of the vessel, utilizing data from Table 3.6. Sixty-two percent of the vessels painted with paints containing TBT are in the range of 28 to 65 feet. This size category will include the bulk of the pleasure boats which are not kept on a trailer. Pleasure boats smaller than 28 feet are more likely to be stored out of the water than the larger boats. Boats stored out of the water for extended periods of time are less likely to require the use of antifouling bottom paint. Figure 3.3 presents the relative proportion of the different paint types in use. Figure 3.4 illustrates the predominance of recreational vessels over all other vessel types.

Figure 3.2

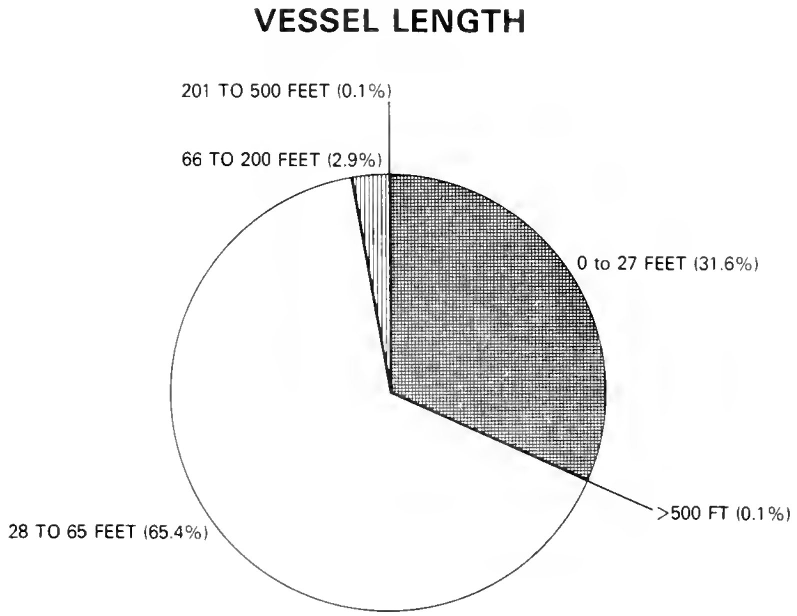

VESSEL LENGTH
201 TO 500 FEET (0.1%)
66 TO 200 FEET (2.9%)
0 to 27 FEET (31.6%)
>500 FT (0.1%)
28 TO 65 FEET (65.4%)

Table 3.6

Number of Vessels Painted by Length of Vessel and by Type of Antifouling Active Ingredient

		Active Ingredient Type		
		Tributyltin		
Length of Vessel	Total # Vessels	Copolymer/ Self-polishing	Free Association	Undetermined Other
0-27 feet	84,541	4,580	43,423	36,538
28-65 feet	175,146	42,039	63,584	69,523
66-200 feet	7,692	449	4,304	2,939
201-500 feet	154	35	25	94
501-800 feet	330	29	264	37
800+ feet	14	6	6	2
Undetermined	13,749	138	4,202	9,409

Source: Lucas and Williams, 1987.

Figure 3.3

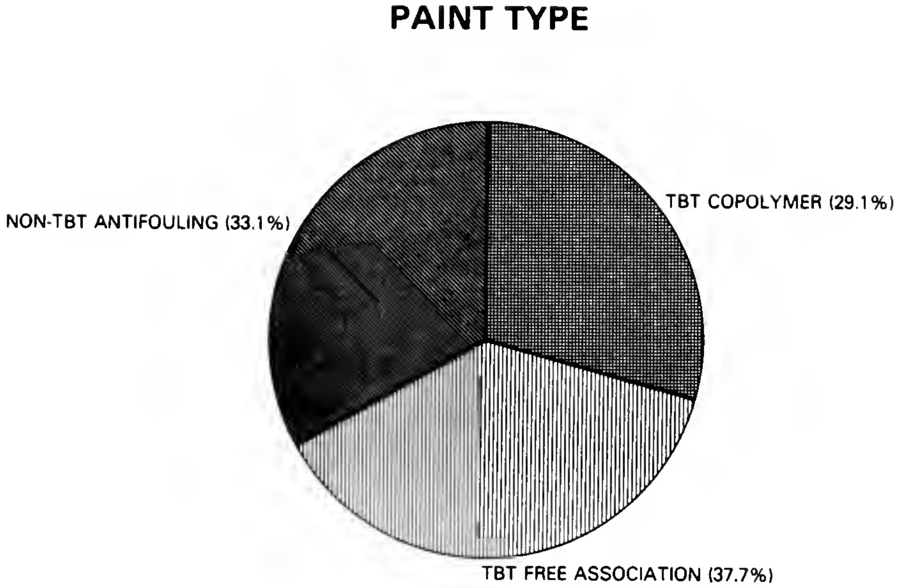
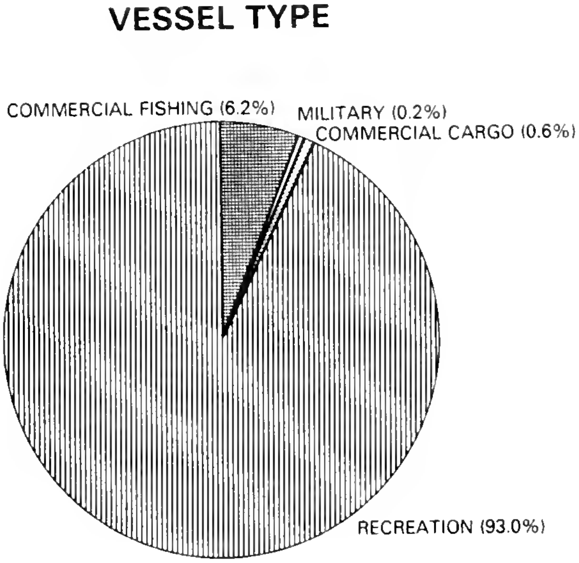

PAINT TYPE
NON-TBT ANTIFOULING (33.1%)
TBT COPOLYMER (29.1%)
TBT FREE ASSOCIATION (37.7%)

Figure 3.4


VESSEL TYPE
COMMERCIAL FISHING (6.2%)
MILITARY (0.2%)
COMMERCIAL CARGO (0.6%)
RECREATION (93.0%)

3.5.3 Paint Use by Vessel Type (Use Category)

Table 3.7 is a summary of types of painted vessels by use. The estimate of 260,710 recreational vessels outnumbers all other types of use. Eliminating TBT paint from recreational boats would eliminate 93% of the individual sources of TBT to the environment. However, recreational vessels are not uniformly distributed. The Atlantic Coast contains 42% of the recreational fleet, the Pacific Coast 28%, and the Gulf Coast 29%.

3.5.4 Paint Use by Region of Boating Activity

Fouling intensity increases with water temperature and length of the boating season. There are substantial differences in the fouling intensity depending on the level of nutrients in the water. Different paint formulations are available for use in the temperate regions and in the tropics. Table 3.8 lists formulations used in the different regions of the U.S.

Table 3.7

Number of Vessels Painted by Vessel Use Type, Firm Type, and Region

	Type of Vessel			
	Cargo	Commercial Fishing	Recreation	Military
Type of Firm				
Ship building/repair	1,265	290	687	290
Boat building	21	989	14,455	61
Boat repair	76	11,646	158,086	105
Other	279	4,486	87,483	70
TOTAL	1,653	17,448	260,710	546
Region				
North Atlantic	44	1,426	38,198	75
Mid Atlantic	62	4,402	63,175	13
South Atlantic	38	1,707	8,146	51
Gulf Strata	1,176	7,846	76,158	63
South Pacific	51	557	22,332	78
Mid Pacific	220	1,246	48,392	190
North Pacific	11	264	3,223	54
Great Lakes	0	0	158	22
River Strata	51	0	926	0
TOTAL	1,653	17,448	260,710	546

Source: Lucas and Williams, 1987.

Table 3.8
Estimated Annual Usage (Thousands of Gallons) of Antifouling Paint by Active Ingredient Type and Region
(Lucas and Williams, 1987)

	Total	North Atlantic Coast	South Atlantic/ Gulf Coast	Pacific Coast	Interior
Organotin* in Ablative or Self-Polishing Form with:					
Cuprous oxide	173.0	2.1	16.1	154.8	0.0
Copper thiocyanate	85.6	5.8	4.5	75.3	0.1
Tributyltin oxide	245.0	6.0	20.6	218.3	0.1
Tributyltin fluoride	0.7	0.08	0.05	0.3	0.3
Tributyltin methacrylate	217.7	7.7	19.2	190.4	0.4
Triphenyltin fluoride**	10.9	0.00	10.9	0.00	0.00
Organotin* in Free Association with:					
Copper (metallic)	12.8	0.9	0.2	11.5	0.2
Copper hydroxide	4.1	2.7	0.2	1.2	0.00
Cuprous oxide	246.6	28.3	33.4	185.0	0.00
Cuprous/cupric oxides	1.8	0.4	0.00	1.4	0.00
Pentachlorophenol	1.8	0.1	0.9	0.7	0.00
Tributyltin oxide	214.8	28.0	7.2	178.7	0.9
Tributyltin fluoride	158.8	7.3	34.0	116.9	0.5
Tributyltin sulfide	0.4	0.2	0.2	0.00	0.00
Organotin* in Undetermined Paint Type with:					
Copper salts of organic acids	4.1	4.1	0.0	0.0	0.0
Cuprous oxide	4.3	4.1	0.0	0.2	0.00
Diethyl diphenyl dichloroethane	0.3	0.3	0.00	0.00	0.00
Tributyltin oxide	0.4	0.3	0.00	0.5	0.0
Tributyltin acetate	0.5	0.48	0.0	0.2	0.0
Tributyltin fluoride	3.9	3.8	0.0	0.1	0.0
Tributyltin adipate	1.0	0.8	0.2	0.0	0.0
Non-organotin Paint Types	198.2	79.1	53.0	61.0	5.1

* Compound listed is the primary antifouling ingredient. Where an ingredient other than organotin is the primary ingredient, organotin is present in lesser amounts.

** A possible replacement for TBT. EPA has issued a DCI notice for information on the toxic effects of this chemical to non-target aquatic organisms.

It is interesting to note, that the application rate of copolymer paint applied in fresh water has been estimated to be about 1%. For antifouling paints with copper as the active ingredient, has been estimated to be about 2.7% (Lucas and Williams, 1987).

3.5.5 Paint Choice by Type of Vessel

The largest number of vessels coated with tributyltin are recreational vessels. Ninety two and a half percent of all the vessels surveyed by Lucas and Williams (1987) were recreational vessels and 60 percent of those vessels were painted with tributyltin antifouling paints. However, there are no good means to estimate the amount of painted surface area which is represented by this large recreational fleet, but the numbers of boats involved indicate that the recreational fleet is a significant source of TBT to coastal waters. This is true for several reasons. One, the large numbers of boats involved spread the sources of paint contact over a major portion of coastal water. There is hardly a creek or harbor near any metropolitan area which does not have several recreational boats berthed there. The second aspect of exposure of TBT by recreational boats is the infrequency of their use and lack of movement from the place where they are kept. The third significant factor involving recreational craft is their principal use to date of cheaper, high leach-rate, free-association commercial TBT paints.

One of the surprises of the Lucas and Williams (1987) survey is the relatively low percentages of cargo vessels which reported being painted with TBT copolymer/self polishing paint considering the publicized advantages of this paint type for reducing fuel costs and improving speed. Only 13% of the cargo vessels were reported being painted with self polishing copolymer paints as compared with 18% of the recreational boats, and free association was used on only 36% of the cargo vessels and 43% of the recreational boats surveyed. This data may have a unique bias because not many new commercial ships are being built in the U.S. at this time, and the omission of such would significantly lower the volume to organotin antifoulant paints used in the cargo vessel category surveyed.

3.5.6 Reasons for Using a Specific Paint

In Table 3.9, reasons for selecting a specific antifouling paint are reported using the particular paints classified by four categories. Customer request is a factor, but the main reasons relate to effectiveness of TBT versus low cost of other antifouling paints.

Table 3.9
Reasons for Use of Active Ingredient Types
as Stated by Percent of Firms

	ACTIVE INGREDIENT TYPE			
	Tributyltin			
Reason for Use	Copolymer/ Self-polishing	Free Association/ Other	Other	Undetermined
Hull Type	5.3	11.3	6.9	0.3
Cost	2.7	8.0	18.5	0.6
Product Effectiveness	42.5	43.0	0.1	21.9
Ease of Application	5.4	6.8	9.5	0.0
Color	4.4	8.2	12.3	0.0
Customer Request	23.6	31.0	32.8	2.1
Contract Specification	2.4	3.2	4.1	0.3
Other	1.1	2.3	2.3	0.0

Source: Lucas and Williams, 1987.

3.6 ANTIFOULANT PAINT APPLICATION AND REMOVAL PRACTICES

Shipyard and drydock practices typically require specialized painting equipment not available to the citizen boat owner. Use of specialized equipment encourages specialization in job assignments and training in the safe use of the equipment. The availability of this training provides the opportunity for more control over worker exposure and over the amount of organotin compounds released into the environment. There is far less knowledge of and control over the owner painting a boat in his driveway than there is on the commercial yard with a significant investment in equipment and higher public visibility. There have been no studies of the relative contribution of TBT to the environment from individual boat owners vs. commercial ship and boat yards.

The U.S. Navy requires the use of airless spray equipment by painting contractors painting Navy ships. Studies of the coating efficiency of spray painting found that 5% to 9% by weight of the paint went elsewhere than the hull being painted. Recommended means for preventing this overspray from reaching the environment include plastic film lining of the dry dock area prior to painting, and clean up by vacuum and wash down prior to reflooding the drydock. Developmental studies are being conducted by the Navy at Norfolk to develop a complete spray enclosure on a hi-lifter arm which will have a sealing skirt to the hull, to effectively contain any overspray or grit blasting residue.

3.6.1 Recommended Paint Application Practices

The Navy recommends the use of airless spray techniques as the preferred application method but is testing alternatives. The recommended application rate would be 12 to 16 mils dry film thickness or 12 mg of TBT per square centimeter of hull surface. This would apply approximately 400 kg of TBT on a 100 meter Navy ship having a typical 3.3×10^7 square centimeter wetted surface.

The Navy's safety requirements for protecting the health of the applicators is presented below (Chapter 631 of NAVSEA, 1983 Technical Manuals):

The basic safety requirements for applying organotin containing antifouling paints are as follows:

- o Workers within 25 feet of paint application or removal, must wear impervious disposable coveralls, taped at the wrists and ankles, disposable shoe covers, plastic or rubber gloves, and NIOSH-approved full face, air supplied respirators;
- o Only protected personnel may remain within the exposure zone (up to 100 feet from the spray);

- o Personnel 50 to 100 feet away from the work site must wear protective eyeware, gloves, disposal coveralls, and NIOSH-approved, full-face, organic vapor respirators; and

- o Shipyard Safety Officer and Industrial Hygienist shall be contacted for specific personnel precautions when spray application is planned.

The applicator exposure study conducted by M&T Chemicals Inc. (Envirosphere, 1986) at the Curacao Drydock Company found that the actual level of worker protection was found to vary because of work practices of the painters and their helpers. Principal difficulties were encountered in working in hot humid environments while completely sealed in air impervious suits without the addition of circulated air except for that provided directly for breathing. Other results derived from this study are: (1) pre-employment body burdens for organotin was found to be between 4 and 5 parts per billion, (2) air hoods are effective respiratory protection for keeping painters exposure to organotin below the OSHA Permitted Exposure Level (PEL), (3) dermal contact is more significant than inhalation as the route of worker exposure, and (4) worker urinary organotin levels quickly returned to pre-exposure levels after cessation of exposure to the organotin paints. These results were determined during the application of paint containing 3.2% tributyltin methacrylate, 1.3% tributyltin oxide, and 1.7% triphenyltin fluoride using airless spray equipment.

Application by brush is the preferred method for the small boat owner because of low capitol investment and low level of skill required for a satisfactory job. Some of the paint remains in the container, between 2.5% and 4.5% by weight according to US Navy Studies and some remains in brushes and cleaning rags. These are potential sources of TBT to the environment, if not properly disposed.

3.6.2 Recommended Paint Removal Practices

Various removal practices provide different risks of introducing TBT into the environment. Each practice offers different control possibilities. Removal of the paint film or portions of it may occur intentionally or unintentionally during wash down with a high pressure hose prior to seasonal storage or other work on the hull. US Navy studies have found that as much as 60 mg of TBT per square centimeter of hull surface can be washed into the environment with high pressure wash down of the paint (U.S. NAVSEA, 1984). The British Government and the Royal Yachting Association have also found that the use of high pressure wash down to be a source of TBT to the environment and have specifically recommended that the pressure of the power wash nozzles be monitored and adjusted to minimize the removal of the paint film during cleaning operations. Paint manufacturers in the U.S. recommend the use of high pressure wash down of antifouling paints as soon as the vessel is out of the water as a means of keeping the bioactivity of the paint as high as possible.

3.6.2.1 Sanding

This method is probably the most common used by the owners of small pleasure craft because of the low cost involved. Where wet/dry or water sandpaper is employed, the removed paint film can be washed into the public sewer or ground water. This paint removal practice may occur well inland of the waters edge if the boats are small enough to be put on a trailer and stored at a residence.

3.6.2.2 Sand or Grit Blasting

This is the method of choice in commercial yards because of its removal speed. Because of the size of the vessels involved, much of this work is done at or near the water's edge. Alternatives to grit blasting, investigated by the Navy, include cavitating high pressure water jets and high energy beams. In all types of surface preparation, the old paint, rust, and marine organisms are found mixed in the spent blasting media or liquid. Surface preparation methods comprise dry abrasive blasting, hydroblasting, wet blasting, water cone blasting, and chemical paint stripping. Surface preparation methods, other than dry blasting, are not common in the industry. Wet blasting and water cone blasting is confined principally to Navy ships having special coatings including TBT. Chemical paint stripping is rare and is used only on small localized areas made of more delicate materials.

Dry abrasive blasting (sandblasting, grit blasting), is the most common method of surface preparation. When employed, spent abrasive is the principal source of solids in the drydock discharge. Particle sizes of the used grit range from fine dust to whole bits of abrasive, approximately one-eight inch in diameter. Some of the spent grit falls directly into drainage gutters, especially if a ship is large and the hull sits over the drains. The potential also exists for the abrasive to be washed into the drains from storm runoff, shipboard wastewater discharges on the dock, hosing, seepage, or other sources of water to the dry dock. The spent grit is for the most part, settleable. In dry dock areas, it can be vacuumed up for proper disposal. Sometimes, sand is used as the abrasive, instead of utility slag or copper slag. Delicate equipment, such as sonar domes, are occasionally sand blasted. Aluminum-clad hulls are often blasted with sand instead of grit to minimize metal erosion during blasting.

The major pollution problem from hydroblasting (U.S. NAVSEA, 1984) is that the volumes of water used increase the potential that the paint and grit will be flushed into the drainage discharge. Since oxidation of the surface of the hull of the ship will prevent a good bond between the fresh paint and metal, rust inhibitors, which contain compounds such as sodium nitrite and diammonium phosphate, are used. However, hydroblasting is not preferred by ship repair facilities, because the resulting surface obtained is not as suitable for paint adhesion as the surface obtained by dry grit blasting.

3.6.2.3 Chemical Paint Stripping

Antifouling paint may be chemically stripped rather than grit blasted or sanded. The method is used by commercial yards for delicate equipment such as sonar domes, antennas and deck machinery. Small articles with an intricate surface may be dipped in some yards. The disadvantage of the process is that the resulting combination of paint and stripping chemicals often has the consistency of jelly or thin putty, is frequently caustic and difficult to handle. There is some anecdotal evidence that the methods is perceived as preferable or safer than hand sanding by the private boat owner (i.e. Washington Post editorial February 2, 1986 by Angus Phillips). Nevertheless, the chemical strippers have not gained wider popularity due to the tendency of the chemical to dissolve the gelcoat of fiberglass boats along with the old paint film.

3.6.2.4 Burning

Paint removal by heating is more frequently done on wooden hulls or metal hulls than on fiberglass hulls. A new technology has been developed by Laser Technologies in Ann Arbor, MI which uses lasers to burn the paint off large commercial ships. Laser Technologies claims that all the paint film is converted to vapor, that there is no solid residue to dispose of as is the case with grit blasting.

3.6.2.5 Paint Waste Disposal Practices

Spent paint containing toxic constituents is removed, along with iron oxide and dead marine organisms from ships during grit blasting and sanding. This residue is either collected or it will be washed, pushed or blown into uncovered drains or into coastal waters. The Navy has tested waste abrasive grit containing tributyltin employing the extraction procedure toxicity test and has determined that grit blasting waste is not a hazardous solid waste. The Environmental Protection Agency has reviewed the Navy findings and concurred with the Navy's determinations (U.S. NAVSEA, 1984). Therefore, blasting residue can be collected and disposed in an approval landfill.

3.7 QUESTIONS TO BE RESOLVED

Total antifouling paint production is well established. How much of the biocide reaches the environment and by what routes is a major unknown. A second unknown is what portion of the removed paint is still toxic, and what portion of that reaches the aquatic environment. Boat work tends to be performed where boats are kept. The relative contributions of boat maintenance and boat mooring as sources of butyltin into the environment needs to be investigated more thoroughly.

Total release of butyltin into coastal waters is a combination of the different leach rates of the different paints, and the area of paint exposed to the water. The degree to which the leached paint organotin materials is concentrated depends not only on the area of paint but on the relative mobility of the painted vessels. Many pleasure craft never leave the dock while commercial vessels remain immobile no longer than necessary.

CHAPTER IV

CURRENT STATE OF SCIENTIFIC KNOWLEDGE OF TRIBUTYLTIN IN COASTAL WATERS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

4.1 INTRODUCTION

This chapter is organized in subsections pertaining to selected categories of scientific knowledge as related to tributyltin antifouling paints. These sections are:

- Estimated release rates from antifouling paints.
- Toxicity to freshwater and marine organisms.
- Behavior and fate in the marine environment.
- Bioconcentration/bioaccumulation/biomagnification.
- Levels or concentrations found in marine environments.
- Laboratory analytical methodologies.
- Comparison of reporting units in the literature.
- Computer numerical modeling.
- Alternatives to organotin based antifoulant coatings.

An extensive literature search was conducted through the Dialog Information Service data bases comprising the files of METADEX Oceanic Abstracts National Technical Information Service, INSPEC (Physics, Electronics and Computing) COMPENDEX (Engineering and Technology), ISMEC (Engineering), Current Technology Index (UK Publications), World Aluminum Abstracts, BIOSIS Previews, Water Resources Abstracts, Aquatic Sciences and Fisheries Abstracts. For these searches, a comprehensive list of search terms and key words were developed in consultation with SAIC's information retrieval specialists and David S. Moulder, Head, Marine Pollution Information Centre, Marine Biological Association, Plymouth, United Kingdom.

The distribution by general categories of reviewed organotin literature is presented in Table 4.1 and an international organotin bibliography is presented in the Appendix. From reviewing this literature, it is evident that the bulk of the research effort to date has been in toxicology and bioaccumulation studies, primarily the former. Laboratory bioassay procedures are relatively easy to run and inexpensive when compared to field cause and effects studies and monitoring programs. Twenty percent of the reviewed studies have dealt with some aspect of monitoring, but only five percent have ended up as refereed publications. Most of the remainder were summary type articles referencing data reported from other studies. The two categories with the paucity of refereed publications or cited work were release rates from ships, and analysis of the severity of the problem. The following sections are a review of the available literature by selected categories.

Table 4.1
Distribution of Reviewed Organotin Literature by Selected Categories.

	Percent of Reviewed Publications		Percent of Reviewed Refereed Publications	
Topics	Number	Percent	Number	Percent
Release Rates from Ships	6	4	0	
Toxicity and Bio-accumulation	54	36	13	9
Behavior of Organotin in the Environment	22	15	6	4
Typical Levels of Organotin in the Environment	30	20	8	5
Chemical Analysis and Test Procedures	20	14	8	5
Alternatives to Tin Based Antifoulants	9	6	4	3
Severity of the Problem	8	5	2	1
TOTALS	192	100	41	28

4.2 TRIBUTYLTIN RELEASE RATES FROM ANTIFOULING PAINTS

The lack of acceptable (standardized) data estimating the release rates of organotin compounds from different antifouling paint formulations led EPA to issue a Data Call In Notice (DCI) to paint manufacturers in order to obtain this information (EPA, 1986). Over the next few years, the amount of information available on the release rates of various paint formulations will increase significantly. Table 4.2 is a summary of the release rate data that was available prior to EPA's DCI Notice.

4.2.1 Factors Effecting Tributyltin Release Rates from Painted Surfaces

The Navy has determined that the release rate of organotin compounds from antifouling paints from painted surfaces is dependent upon several factors: (1) the chemistry of the coating, (2) the chemistry of the seawater (particularly the pH and salinity), (3) the water temperature, (4) flow rate (vessel speed) and turbulence, (5) the extent of biological activity, and (6) the age of the paint film. Direct measurements (in-situ) of organotin release rates from ship hulls have been determined by researchers at NOSC for several paint formulations (see Table 4.2). Lieberman et al. (1985) have reported in-situ organotin release rates (measured from Navy ships at different locations) ranging from 0.33 to 2.8 $ug/cm^2/d$ of TBT. Laboratory studies of measurements of tributyltin release rates from antifouling paints on panels have been conducted by several Navy groups and have been found to range from less than 0.1 to 1.9 $ug/cm^2/d$ of TBT, see Table 4.3 from Desmatics (1984) who conducted the data analysis for the Navy.

To make direct TBT release rate measurements from ships, the U.S. Naval Ocean Systems Center (NOSC) developed an in-situ process to measure released organotin compounds from painted surfaces of ships. The protocol consists of using a polycarbonate half dome, which is held on the underwater surface of a ship hull by differential water pressure (Lieberman et al., 1985). As utilized, this device permits collection of water samples that can be analyzed to estimate release rates from aged as well as fresh paint coatings under representative environmental conditions (salinity, temperature, dissolved oxygen and other water quality parameters). The effect of bacterial and algal films on the paint surface, which may modify the rate of TBT release is thereby accounted for by using the in-situ device. The rate of water circulation through the device can be regulated to simulate different harbor conditions, vessel speeds or can be used to determine steady state release rates. The purpose of these studies was to determine the relative release rates of different paint formulations that the Navy had under consideration for fleetwide use. In the NOSC studies, tributyltin cation reported as the oxide was the form of butyltin which was measured by atomic absorption

Table 4.2

Tributyltin Release Rates in ug/cm^2/d as Measured Directly From Ship Hulls and Painted Panels.

Ablative Antifouling Formula		Navy Copolymer Formula	
ABC-2	0.33 to 2.8	CMP M5211F	1.6 to 2.0
SPC-254	0.18 to 0.31	CMP M5211S	2.4 to 3.2
SPC-4	0.40 to 1.7	CMP 58S	0.72 to 1.7

TBT Leach Rates in ug/cm^2/d, Determined by Utilizing Coated Panels Removed From Ships:

Paint formula	Months of Exposure length	Leach Rate (ug/cm^2/d)
ABC-2	12 months	1.7
	24 months	2.8

Source: Lieberman et al., 1985.

Table 4.3

Tributyltin Release Rates in ug/cm^2/day for U.S. Navy and Commercial Paint Formulations.

Navy Paint Formulation	Estimated Release Rates	Commercial Paint Formulation*	Estimated Release Rate
ABC-2/222	<0.035 ±<0.001	Takata LLL	0.56 ± 0.12
SPC-4	2.40 ± 0.781	Hemple 7695/7697	1.30 ± 0.31
SPC-9	1.36 ± 0.289	Sea Shield	[1.46-4.16] ± 0.93
SPC-20	0.525 ± 0.047		

* Use of trade names does not imply endorsement or criticism by NOAA/NMPPO, or SAIC.

Source: Desmatics Corp., 1984.

spectroscopy (HDAA Protocol). In the report by Desmatics Corp. (1984) on release rates of immersed panels coated with antifouling paint formulations under (conditions of controlled temperature and pH in laboratory circulation tanks) there is no mention of the time periods of exposure, or area from which the release rates were estimated.

In general, these release rate studies found relatively consistent values once past the 30 day initial stabilizing period when the vessel is first returned to the water after being freshly painted, except for one product. A paint formulation for which a range of values was reported rather than a measure of central tendency. In these studies, leach rates were measured periodically and were observed to decrease with increasing time of submergence of the panels with the exception of one data set. All tests found high variability between panels, indicating that further development of application and measurement methodologies was required. Consequently EPA and the D01.45 Subcommittee of the American Society of Testing and Materials (ASTM, August 1, 1986) have developed a standardized TBT release rate protocol to standardize the test conditions and procedures. The protocol was published as an attachment to EPAs Data Call in Notice (EPA, July 29, 1986). The standard unit that has evolved for estimating TBT release rates from antifouling paints is the ug/cm^2/d [micro gram of TBT release per cm^2 of wetted vessel bottom per day].

Schatzberg (1986) has investigated the release rates of different TBT paint formulations for up to 42 months (see Table 4.4) and determined TBT release rates for three different regions of the U.S. (i.e. Miami, Annapolis, and Hawaii), and found some regional differences, but they were not significant. However, Hall et al. (1986) studying the effect temperature on TBT release rates have reported a reduction in release rates by approximately one-fourth for a temperature change from 25°C to 10°C. (see Table 4.5).

4.2.2 Estimates of TBT Release Rates from Removed Spent Film and Waste Residues

One of the areas of concern as a source of TBT into the environment is the grit from sandpaper or sand blasting to remove a partially spent or fouled paint film. The grit contains some of the spent paint film and is thus a source of TBT if washed into the marine environment or if disposed in land fills. Schatzberg (1986) devised a soil lysimeter to investigate the rate of leaching of TBT from grit containing spent paint film.

Table 4.4
Tributyltin Release Rates in ug Sn/cm^2/d for Different Paint Formulations.

Coating Formulation Source	Coating Condition	Release Rate at 25°C (ug Sn/cm^2/d)	
		Mean	Std. Deviation
	Freshly painted, cured	15.4-4.4	----
M253	27 Months, Miami	2.5	0.55
DTNSRDC	27 Months, Miami	1.3	0.25
	42 Months, Annapolis	1.9	0.23
	Freshly painted, cured	10.0-3.3	----
M5211	27 Months, Miami	1.3	0.28
DTNSRDC	27 Months, Miami	1.2	0.46
	42 Months, Annapolis	1.6	0.30
SPC4	Fresh-85 Days in Measurement Tank	0.4	0.09
International Paint Company	Fresh-190 Days in Measurement Tank	0.4	0.12
F-170	Freshly paint, cured	12.9	2.80
	42 Months, Hawaii	1.5	0.19

Source: Schatzberg, 1986.

Table 4.5

Effect of Temperature on Tributyltin Release Rates.

Coating Formulation	Coating Condition	Temp C°	Release Rate (ug Sn/cm^2/d)	
			Mean	Standard Deviation
M5211	42 Months, Annapolis	25	1.6	0.30
		10	0.36	0.16
M253		25	1.9	0.23
		10	0.54	0.15

Source: Hall et al., 1986.

Tributyltin compounds are hydrophobic, only slightly soluble in seawater, and partition readily on to solid surfaces. In Schatzberg's study, three soil types were examined for their affinity for tributyltin compounds to determine leaching and soil disposal effectiveness. Table 4.6 presents results obtained with soil lysimeters and organotin-contaminated abrasive grit from Navy shipyards (Schatzberg, 1986). The study found that tributyltin compounds were strongly adsorbed by the three selected soil types. Similarly, strong adsorption of tributyltin compounds to particulate matter, suspended and bottom sediments has been found (see Valkirs et al., 1986; Stang, 1987).

4.2.3 Estimates of Potential Loadings of Tributyltin Released by Vessels to Lower Chesapeake Bay

One of the aspects of concern in the consideration of TBT released from vessels is the relative contribution of different vessel types, because they have different residence times in a specified location as well as different paint formulations (use) patterns. The following assumptions of vessel type (and use) versus expected preference of release rates paints were made by the Navy to estimate the quantities of TBT that would be released to the State of Virginia's coastal waters from all types of vessels (should the Navy implement fleetwide use of TBT antifouling paints):

o Commercial and fishing vessels would be painted with copolymer paints having a low release rate (due to desire of limited time for dry-dock maintenance).

o Recreational craft would be painted with high release rate free association paints (due to paint costs).

o Navy vessels would be painted with lowest release rate paints available, and that Navy ships would be painted on a 10 year implementation schedule.

Table 4.7 presents the Navy's estimates of the potential total loading of TBT in the Lower Chesapeake Bay, that would be released by all vessels, given full fleetwide implementation of low release rate copolymer paints over the next ten years (NAVSEA, 1986). The greatest uncertainty in the generation of these estimates is the proportion of recreational boat owners who are in fact using free association paints containing tributyltin as the principal antifoulant. The Navy has estimated that recreational vessels would add 66%, while Navy vessels in lower Chesapeake Bay would only add 4%. The Navy has made a similar estimate for the entire U.S. and determined that their contribution would be 2.5% of the total loading to U.S. waters using the following assumptions and data:

Table 4.6
Mean Leachate Tin Content (in ppb Sn) of Soil Lysimeters Before and After Grit Addition.

Lysimeter Number	Soil Type		Tin Content of Grit Type	Tin Content of Leach Water Before Grit Addition *		Tin Content of Leach Water After Grit Addition **	
				Mean	SD	Mean	SD
1	Topsoil	B	31 ppm	8	3	2	2
2		A	132 ppm	8	4	2	1
3	Clay	B	31 ppm	5	3	1	1
4		A	132 ppm	4	3	1	0
5	Sand	B	31 ppm	2	2	2	1
6		A	132 ppm	3	3	2	1

* After 5 weeks of flushing with distilled water.

** After 16 weeks of flushing with distilled water.

Source: Schatzberg, 1986.

Table 4.7

Estimates of Potential Annual Loading of Tributyltin Released by Vessels to Lower Chesapeake Bay.

Vessel Type	Painted Hull Area (ft^2)	Release Rate ($ug/cm^2/d$)	Estimated Vessel Residence Time (%)	Total Release (kg/yr)	Percent
Commercial Ships	8,616,517	1.0	10	495.0	27
Fishing Fleet	204,012	1.0	50	57.7	3
Recreational Craft	426,625	5.0	100	1209.5	66
U.S. Navy*	2,820,169	0.1	50	80.0	4
			Total:	1,842.2	

* Hypothetical 100% implementation in 10 years.

Source: Navy Data Submitted to Congress, and NAVSEA, 1986.

The U.S. has about 15 million small recreational boats, 68,000 pleasure yachts, and 87,000 commercial vessels. The total surface area needing antifouling paint on the pleasure yachts and commercial vessels (excluding small recreational boats) has been estimated to be approximately 440 million square feet. By comparison, the bottom hull area of the entire U.S. Navy Fleet is approximately 11 million square feet, or 2.5 % of the commercial vessels and private yachts.

It should be noted that these estimates do not consider in the calculation whether vessels are using low or high release rate paints, and that the percentages are comparative percentage boat bottom for indicated vessel types (which is the worst case example).

4.3 TOXICITY TO FRESHWATER AND MARINE ORGANISMS

This Chapter has been prepared as an overview and summary of simple bioassays and in-depth laboratory toxicity studies. In general, flow through and static bioassay procedures generally follow a well documented protocol, are laboratory oriented, and hence less expensive than field studies. Consequently this is the area where the organotin toxicity literature is richest, representing 38 percent of the toxicity papers reviewed. However, much of this earlier bioassay data is suspect, many of the studies were static (with one dosing) or static with daily renewal, or nominal (without actual chemical testing of test container concentrations - just calculated dosing). The problems of concern here deal with bioassays that were conducted at low ng/l levels in which absorption to test containers (walls, tubing, etc.) either greatly lowered actual exposure concentrations or in some cases (daily repeated dosing) increased exposure concentrations. The following sections present laboratory determined toxicity data for a large group of organisms arranged in rough phylogenetic order from bacteria to chordates.

4.3.1 <u>Fungi/Bacteria</u>

Tributyltin is used as a fungicide/bacteriacide to preserve wood exposed to water. Tributyltin has also been used to inhibit the growth of odor forming bacteria in clothing. Very little research has been done to euclidate the bacteria species which are most susceptible to tributyltin. Dooley and Kenis (1987) investigated <u>Photobacterium phosphorem</u>, a gram negative marine bacteria and found that tributyltin had the highest toxicity of all organotins. In general, they found that gram positive bacteria were more sensitive to tributyltin than gram negative bacteria. <u>Pseudomonas aeruginosa</u>, a gram positive bacteria, was found to debutylate TBT at sublethal concentrations. In contrast marine strains of gram negative bacteria have been shown to adsorb TBT to high concentrations on their outer membranes without degradation of metabolic inhibitors (G. Blair, personnel communication). Another interesting observation should be noted, researchers at NBS working with bacterial biofilms acquired from immersed TBT painted panels in the marine environment found that the bacteria in these biofilms were capable of uptaking TBT from seawater to concentrations of greater than 350 ng/l (Blair et al., 1987).

The following wood or cellulose degrading fungi have been shown to grow on an artificial estuarine salt media spiked with TBTO-Cl and to metabolize the compound: Coniophora puteana, Sistotrema brinkmanii, and Coriolus versicolor (Olson et al., 1986). Tributyltin has been found to be toxic to estuarine bacteria generally at concentrations as low as 5 ug/l using thymidine or glutamate metabolism methodology for toxicity assessment.

4.3.2 Phytoplankton/Zooplankton

Table 4.8 lists the algae for which EC_{50} values have been determined. Some of these algae have also been shown to metabolize and debutylate TBT. These algae include Ankistrodesmus falcatus, Skeletonema costatum, Coniophora puteana, and Trametes versicolor. To date, studies have not established effects of tributyltin on phytoplankton productivity or on zooplankton grazing. The most abundant and frequently the most important grazer in the zooplankton is the copepod. The only copepod to be tested so far has been the common estuarine species Acartia tonsa.

4.3.3 Crustaceans

The most sensitive of the crustaceans tested to date has been the marine Mysid Acanthomysis sculpta which demonstrated reproductive inhibition at 0.19 ug/l. The second most sensitive is the freshwater cladoceran Daphnia magna which shows serious behavioral changes at 5.0 ug/l. Laughlin and French (1980) have found a 90% decrease in growth of American lobster (Homarus americanus) larvae in static renewal studies at 1.0 ug/l TBTO. Toxicity studies in general with crustaceans have found that the effects level is occurring in the low parts per billion range (see Table 4.9). However, the results presented in this table are difficult to compare because of the differences in test protocols.

4.3.4 Shellfish

More studies have been conducted on the TBT toxic effects and mechanisms with shellfish than any other group, due to their commercial fisheries value and to the low threshold effects levels (ng/l). As a group they appear to be the most sensitive organisms that have been exposed to tributyltin.

Table 4.8
Toxicity Values for Algae Exposed to Tributyltin.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Indigenous algae sampled from Lake Ontario	TBT	Inhibitory effect on primary prod. at 0.1 ppb.	Nominal concentrations	Static	0.1, 1, 10, 100 ppb	Wong *et al*. (1982)
Ankistrodesmus falcatus (green algae)	TBTO	50% of original TBT was metabolized to DBT over 4-week period. Bioaccumulated 30,000-fold.	Measured concentrations GC-FPD	Static	20 ppb	Maguire *et al.* (1984)
Skeletonema costatum (Marine Diatoms)	TBTO	72 hr EC_{50} = 0.33 ppb.	ICAP	Static nominal (only stock measured)	0.5, 1.0, 5.0, 7.5, 10.0, 15.0, and 25.0 ppb	Walsh *et al.* (1985)
Thalassiosira pseudonana (Marine diatoms)	TBTO	72 hr EC_{50} = 1.33 ppb.	ICAP	Static nominal (only stock measured)	0.5, 1.0, 5.0, 7.5, 10.0, 15.0, and 25.0 ppb.	Walsh *et al.* (1985)
Pavlova lutheri, *Ounaliella tertiolecta*, *S. costatum*	TBTO	5 ppb killed cultured in 2 days. 0.1 ppb caused a reduction in growth.	FAAS	Static	5, 1, and 0.1 ppb	Beaumont & Newman (1986)

GC = Gas Chromatography.
FPD = Flame Photometric Detection.
ICAP = Inductively Coupled Argon Plasma.
FAAS = Flameless Atomic Absorption Spectrophotometry.

Source: EPA, 1987.

Table 4.9

Acute Toxicity Values for Crustaceans Exposed to Tributyltin.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Crangon crangon (Shrimp)	TBTO	Larvae 96-hr LC_{50}^{*} = 1.5ppb Adult 96-hr LC_{50} = 41 ppb.	Not reported	Static renewal every 24 hours	Not reported	Thain (1983)
Acartia tonsa (Copepod)	TBTO	72-hr EC_{50} = 2.1 ppb. 96-hr EC_{50} = 1.0 ppb 144-hr EC_{50} = 0.4 ppb.	Measured concentrations AAS	Static renewal every 24 hours,	0.3, 0.5, 1.0, 1.7, and 3.0 ppb	U'ren (1983)
Acanthomysis sculpta (Mysid shrimp juveniles)	TBT as leachate	96-hr LC_{50} = 0.42 ppb.	Measured concentrations AAS	Static renewal every 24 hours	0.25, 0.31, 0.43, 0.54, and 0.66 ppb.	Davidson *et al.* (1986)
Daphnia magna (Water flea)	TBTO	48-hr LC_{50} = 1.67 ppb. (1.01 to 2.5 ppb.)	Nominal concentration	Static	1.7, 3.0, 5.3, 7.1, and 13.3	M&T Chemical Company (1976)
Homarus americanus (Lobster larvae)	TBTO	90% decrease in growth at 1.0 ppb.	Nominal concentration	Static renewal every 48 hours	1.0, 5.0, 10.0, 15.0, and 20.0 ppb.	Laughlin and French (1980)
Acanthomysis sculpta (Mysid shrimp, juveniles, and mature females)	TBTO as leachate	Reproductive effects to mature females at 0.19 ppb. Growth effects noted at 0.25 ppb. NOEL** was 0.09 ppb.	Measured concentrations AAS	Flow-through for 63 days	0.03, 0.08, 0.25 0.38, and 0.48 ppb.	Davidson *et al.* (1986)

Table 4.9
(Continued)

Acute Toxicity Values for Crustaceans Exposed to Tributyltin.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Uca pugilator (Fiddler crab)	TBTO	Retardation of limb regeneration and ecdysis after 24-day exposure to 0.5 ppb. TBT.	Nominal concentrations	Static	0.5, 5.0, and 50 ppb.	Weis *et al.* (1987)
Palaemonetes pugia (Grass shrimp)	TBTO	Did not avoid TBT at 2.3 to 30 ppb.	Measured concentrations (FAAS)	Flow-through	2.3, 6.0, 9.6, 16.7, and 30.0 ppb.	Pinkney *et al.* (1986)
Rhithropanopeus harrisii (Mud crab larvae)	TBTO TBTS	Metamorphosis affected after exposure to 10 ppb. TBTO and 20 ppb. TBTS.	Nominal concentrations	Static renewal every 24 hours ppb.	TBTO: 0.5, 1, 5, 10, 15, and 25 ppb TBTS: 0.5, 1, 5, 20, 30, and 50 ppb.	Laughlin *et al.* (1982)
Daphnia magna	TBTC	At 0.5 ppb. TBTO daphnids displayed positive phototaxis, while organisms not exposed to TBTO showed a negative phototaxis.	Nominal concentrations	Static renewal every 48 hours	0.25, 0.5, 0.75 and 1.0 ppb.	Meador (1986)

* LC_{50} = Lethal Concentration to 50% of population

** NOEL = No Observed Effects Level

Source: EPA, 1987.

4.3.4.1 Field Studies

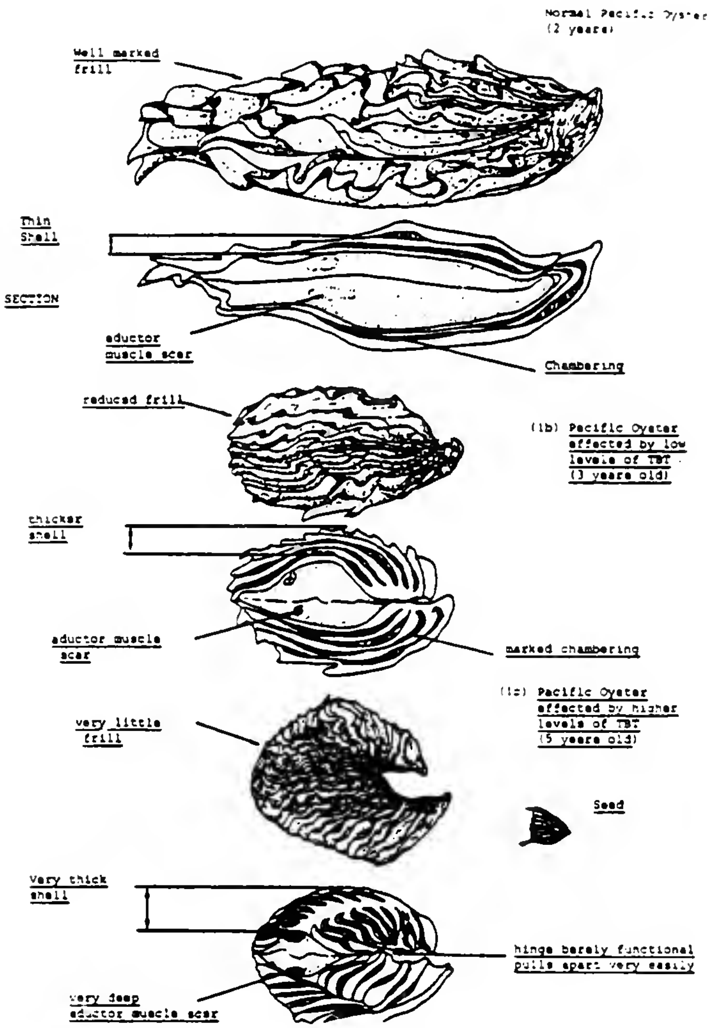
Abnormal growth effects were first noticed in the Pacific Oyster Crassostrea gigas in France. The Pacific oyster was introduced into France for oyster farming in 1968, to replace naturally declining locally farmed oysters. In France, growth anomalies in the development of C. gigas larvae were first observed in 1976 in a small area of Arcachon Bay. By 1977, these anomalies were detected in the rest of the Bay. The most obvious growth abnormality was the malformation of the valves, particularly the upper one (a balling effect). Early researchers noticed that there was a correlation between the number of marinas or boat moorings and the occurrence of the shell malformations (Alzieu, 1986). 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. Also there were other problems than just growth and shell deformation, some regions have little or no natural spat (settling oyster larval stage) fall, suggesting toxic effects to early oyster life stages. However, these biological field observations did not have supporting water column chemistry (TBT concentration data) for the waters of the local areas where the shell deformalities were found, making these correlations interesting but not convincing.

Similar observations were subsequently made on oysters from England collected from the Rivers Crouch and Roach, by Waldock and Miller (1983), Waldock et al. (1983, 1987). The Pacific oyster is far more sensitive to the toxicity of TBT than the European flat oyster (Ostrea edulis). 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).

The mechanisms of formation of shell anomalies in the growth and development of oysters has been studied by French and British scientists and they have found the development of a series of chambers in the shell which are formed as the layers of calcification are laid down within the shell. These chambers are filled with a jelly-like protein (see Figure 4.1, from Waldock and Thain, 1983). 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 with HCO^{3-}, on the exposed surface of the shell and when added to a solution of $CaCO_3$ TBT slows down or prevents the formation of crystals of $CaCO_3$. This suggests that the formation of this gelatinous substance on the inside surface of the oysters shell is an abnormal process which is the result of a perturbation of molecular genetic mechanisms (Alzieu, 1986). In the most acute malformations in Arcachon Bay, France, the thickening of the oyster shell

Figure 4.1

Abnormal Growth Effects in the Pacific Oyster.



Source: Thain and Waldock, 1983.

(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) present in the same waters.

Recently, examples of these same malformations were reported in the U.S. by Wolniakowski et al. (1987) in Joe Ney Slough and South Slough National Estuarine Research Reserve of Coos Bay Estuary, located near Charleston, Oregon (see Figure 4.2, from Wolniakowski et al., 1987). South Slough is located adjacent to a boat yard that has used TBT paints for many years. These examples of excessive shell thickness and chambering are the first oyster malformations reported in the U.S. However, it should be noted that definite chemical data were not available for South Slough when these deformed oysters were found, therefore, additional studies in South Slough are needed to validate these cause and effect relationships.

Figure 4.2

Pacific Oysters Collected in Oregon,
Demonstrating Abnormal Growth Effects.

(A) Pacific oyster (<u>Crassostrea gigas</u>) collected in South Slough, Oregon, in March 1987, showing ball shape.

(B) Upper valve of a Pacific oyster showing excessive thickness (top) and chambering (lower) when sectioned.

Source: Wolniakoski et al., 1983.

4.3.4.2 Laboratory Toxicity Studies

Extensive part per billion acute and chronic laboratory toxicity studies of TBT with oysters have been conducted in France and England (See Tables 4.10 and 4.11). Laboratory bioassays determined that concentrations of 9 ug/l TBT was lethal to half of the larvae of the Pacific Oyster exposed in 48 hours and that exposures to 2.4 ug/l would cause a significant reduction in the growth of the spat which had settled on a substrate. These same concentrations were also found to cause a significant reduction in the rates of growth of mussel spat Mytilus edulis, Clam spat Venerupis decussata and the spat of the European flat oyster Ostrea edulis. Studies reported by Alzieu (1986) from France were able to delineate embryogenesis and larval developmental effects over a range of TBT concentration exposures, see Table 4.12.

Other serious reproductive effects have been found in other molluscs which accounts for the demise of local populations in England of gastropods Nucella lapillus, (the dogwhelk) and Nassarius obsoletus (the mud snail). The dogwhelks are predators, feeding mainly on barnacles, mussels and limpets. Populations of the common dogwhelk, Nucella lapillus, around the South-West peninsula of England were studied by scientists of the UK Marine Biological Association for occurrence of "imposex" (imposed sex) 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 burdens of tin in dogwhelks (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 Nucella lapillus populations around South-West England indicate that those populations which exhibit marked imposex show signs of decline in numbers, populations contain fewer females than expected and that 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. The newly formed male reproductive tissues blocked these oviducts. Subsequently laboratory studies suggest that environmental concentrations of about 20 ng/l of TBT as Sn (56 ng/l TBT) seems to initiate imposex (Bryan et al., 1986; Bryan et al., 1987; Gibbs and Bryan, 1986; Gibbs and Bryan, 1987; Gibbs et al., 1987). See Figure 4.3, from Gibbs et al., 1987 for description of stages, and Figure 4.4 which is a photograph of a female dogwhelk which has developed three penises (photograph courtesy of P.E. Gibbs, U.K. Marine Biological Association).

Table 4.10

Acute Toxicity Values for Molluscs Exposed to Tributyltin.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Bivalves						
Crassostrea gigas (Pacific oyster larvae)	TBTO	48-hr LC_{50}* = 1.6 ppb.	Not reported	Static renewal every 48 hours	Not reported	Thain (1983)
Mytilus edulis (Mussel larvae)	TBTO	48-hr LC_{50} = 2.3 ppb.	Not reported	Static renewal every 48 hours	Not reported	Thain (1983)
Crassostrea gigas (Pacific oyster larvae)	TBTO	48-hr EC_{50} = 0.9 ppb. (0.4 to 1.9ppb)	Nominal concentrations	Static	0.1, 0.3, 0.6, 1.0, 3.2, and 5.6 ppb.	M & T Chemical Company (1977)
Gastropoda						
Biomphalaria and *Bulinus* (Mud snails)	TBTO	48-hr LC_{50} = 10 to 100 ppb.	Nominal concentrations	Static	Not reported	Duncan (1980)
Biomphalaria glabrata (Mud snail)	TBT	2-5 day study: oviposition inhibited at 10ppb. all snails died; 1.0 pb, 90% reduction; 0.1 ppb 50% reduction; 0.01 ppb NOEL.**	Nominal concentrations	Static	0.01, 0.1, 1.0, and 10 ppb.	Ritchie *et al.* (1974)

* LC_{50} = Lethal Concentration to 50% of population

** NOEL = No Observed Effects Level

Source: EPA, 1987.

Table 4.11

Chronic Toxicity Values for Molluscs Exposed to Tributyltin.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Bivalves						
Crassostrea gigas (Pacific oyster spat)	TBT methacrylate leachates	Significant reduction in growth at 0.24 ppb.	Measured daily for 3 weeks and every other day for the remainder of the experiment (M&T standard method FAAS).	Flow-through	0.24 ± 0.23 ppb for low-level and 2.62 ± 1.09 ppb for high level	Thain and Waldock (1985)
Mytilus edulis (Mussel spat)	TBT methacrylate leachates	Significant reduction in growth at 0.24 ppb	Measured daily for 3 weeks and every other day for the remainder of the experiment (M&T standard method FAAS).	Flow-through	0.24 ± 0.23 ppb for low-level and 2.62 ± 1.09 ppb for high level	Thain and Waldock (1985)
Venerupis decussata (Clam spat)	TBT methacrylate leachates	Significant reduction in growth at 0.24 ppb.	Measured daily for 3 weeks and every other day for the remainder for high level of the experiment (M&T standard method FAAS).	Flow-through	0.24 ± 0.23 ppb for low-level and 2.62 ± 1.09 ppb for high level	Thain and Waldock (1985)
Ostrea edulis (European oyster spat)	TBTO	At 0.06 ppb growth rate was severely curtailed after 10 days	Nominal concentration renewed every day	Static renewal 24 hours	0.02 to 2.0 ppb	Thain and Waldock (1985, 1986)

(Continued)

Chronic Toxicity Values for Molluscs Exposed to Tributyltin.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Crassostrea gigas (Pacific oyster spat)	TBTO	Spat grew poorly at TBT concentrations of 0.15 ppb; developed pronounced thickening of upper shell valve. Bioconcentration (flesh) after 56 days exposure to 0.15 ppb. was about 11400 fold.	Measured concentrations FAAS.	Static renewal 24 hours.	0.08 to 1.2 ppb	Waldock and Thain (1983)
Crassostrea gigas (Pacific oyster spat)	TBTF	30% mortality after 113 days exposure to 0.2 ppb and 100% mortality after exposure to 2.0 ppb after 30 days. Shell malformation (gel) at 0.2 ppb after 110 days	Measured total Sn.	Flow-through	0.2 ppb and 2 ppb	Alzieu et al. (1981)
Ostrea edulis (European Oyster spat)	TBT leachates	Predominance of maleness at 0.24 ppb and no differentiation at 2.6 ppb. No larvae released at these concentrations.	Measured for the first 5 days of exposure and on alternate days until completion.	Flow-through 75 days	0.24 and 2.6 ppb.	Thain (1986)
Mytilus edulis (Mussel larvae)	TBTO	15-day LC_{50} = 0.1 ppb	Measured concentrations	Static renewal every 72 hours	10.0, 1.0, and 0.1 ppb	Beaumont and Budd (1984)

Table 4.11
(Continued)
Chronic Toxicity Values for Molluscs Exposed to Tributyltin.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Crassostrea gigas (Pacific Oyster spat)	TBT acetate	1.0 ppb malformation of trochophores. 0.5 ppb larval anomalies after 8 days. 0.2 ppb perturbation in larval food assimilation. 0.1 ppb slow growth and total mortality after 12 days. 0.05 ppb slow growth high mortality after 10 days. 0.02 ppb no observable effect.	---------------	--------------	100 to 0.02 ppb	His and Roberts (1985)
Gastropoda						
Nucella lapillus (Dogwhelk snail)	TBTO	Bioaccumulation of 1.65 ppb. Imposex produced in the laboratory after exposure to 0.02 ppb as Sn. Findings corroborated in the field.	Measured concentrations. AAS	Flow-through 120 days	0.02 ppb TBT as Sn	Bryan et al. (1986)
Nassarius obsoletus	Alumacide TBT paint concentration as labeled.	Anatomical abnormality. Superimposition of male characteristics on female snails	Not reported	Paint on shell.	Not measured	Smith (1981)

Source: EPA, 1987.

Table 4.12

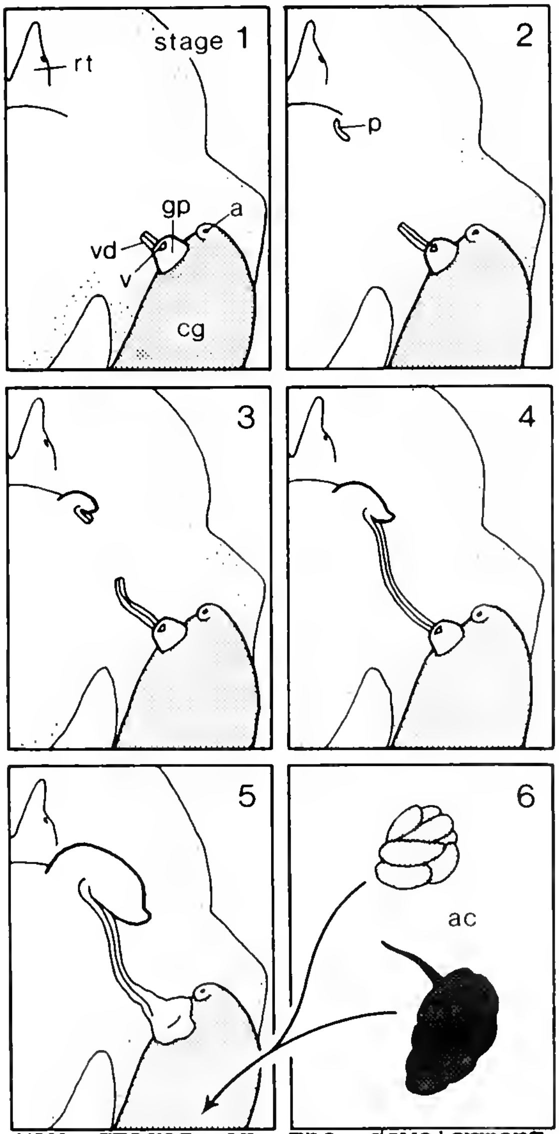
Embryogenesis and Larval Developmental Effects in *Crassostria gigas* Exposed to Tributyltin Acetate.

TBT Acetate (ug/1) (PPB)	Effects on Reproduction
100	Inhibition of Fecundity
50	Inhibition of Segmentation
25	Partial Reduction of Segmentation
10	Absence of the Formation of Trocophores
3-5	Absence of Veligers - Malformation of Trocophores
1	Abnormal Veligers - Malformation of Trocophores
0.5	Numerous Anomalies - Total Mortality in 8 days
0.2	Perturbation in Food Assimilation - Total Mortality after 12 days
0.1	Normal D-Larvae: Slow Growth, Almost Total Mortality after 12 days
0.05	Slow Growth; High Mortality Rate After 10 days
0.02	No Observable Effect

Sources: Alzieu, 1986, and His and Robert, 1985.

Figure 4.3

Development of Imposex (Male Organs) on Female Dogwhelks



Abbreviations:

a: anus

ac: aborted capsule masses

cg: capsule gland

gp: genital pupilla

p: penis

v: vulva

vd: vas diferens

Nucells lapillus. Six stages in the development of imposex from its initiation (stage 1) to sterilization (stage 5) and subsequent accumulation of aborted capsules in capsule gland (stage 6). A longitudinal cut of the mantle cavity roof is made to expose the genital system: see text for explanation.

Source: Gibbs et al., 1987.

Figure 4.4

Photograph of a Female Dogwhelk
Which Has Developed Three Penises.

Source: Photograph - Courtesy of P.E. Gibbs,
U.K. Maine Biological Association.

Imposex has also been reported to occur in Nassarius reticulans and Ocenebra erinacea and has been found to occur in the U.S. and in Europe (Smith, 1980, 1981; Bryan et al., 1987; Gibbs et al., 1987).

4.3.5 Fish

The most sensitive of the adult fish tested is the chinook salmon Oncorhynchus tshawytscha. Table 4.13 summarizes the acute toxicity values of tributyltin reported in the literature for fish by species. The least sensitive fish of those tested for acute effects is the mummichog Fundulus heteroclitus. Table 4.14 summarizes the sublethal effects of exposure of fish to low levels of tributyltin. Most of the effects studied have been histological or behavioral. The ability of fish to detect the presence of TBT has been suggested to be at or below the level at which the fish exhibits active avoidance behavior. Although the mummichog is relatively tolerant of TBT in terms of acute toxicity, the fish exhibited avoidance behavior at 1.0 ppb.

Table 4.13

Acute Toxicity Values for Fish Exposed to Tributyltin.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
FISH						
Oncorhynchus tshawytscha (Chinook salmon)	TBTO	96-hr LC_{50} = 1.5 ppb.	FAAS* measured concentrations	Static renewal	2, 4, 8, 16, 32, and 64 ppb.	Short and Thrower (1986)
Lepomis macrochirus (Bluegill)	TBTO	96-hr LC_{50} = 7.6 ppb. (5.6 to 10 ppb.)	Nominal concentrations	Static	5.6, 7.5, 10.0, and 14.0 ppb	M & T Chemical Company (October 1976)
Salmo gairdneri (Rainbow trout)	TBTO	96-hr LC_{50} = 6.9 ppb. (6.27 to 7.8 ppb.)	Nominal concentrations	Static	4.1, 5.3, 6.8, 8.8, and 11.0 ppb	M & T Chemical Company (June 1978)
Ictalurus punctatus (Channel catfish)	TBTO (7.3 to 20.0 ppb.)	96-hr LC_{50} = 12.0 ppb.	Nominal concentrations	Static ppb.	7.5, 14.0, 18.0, 24.0 and 28.0 (September 1976)	M & T Chemical Company
Fundulus heteroclitus (Mummichog)	TBTO	96-hr LC_{50} = 24.0 ppb.	Nominal concentrations	Static	32.0, 42.0, and 56.0 ppb	M & T Chemical Company (September 1976)
Cyprinodon variegatus (Sheepshead minnow)	TBTO acetone-methanol	21-day LC_{50} = 0.96 ppb. Total mortality at 3.2 ppb. at 14 days.	AAS** measured concentrations	21-day flow-through acute testing	0.33, 0.63, 0.70, 1.5, and 3.2 ppb	Ward et al. (1981)

* FAAS = Flameless Atomic Absorprtion Spectrophotometry

** AAS = Atomic Absorption Spectrophotometry

Source: EPA, 1987.

Table 4.14
Chronic Toxicity Values for Fish Exposed to Tributyltin.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Salmo gairdneri (Rainbow trout)	TBTO	24-hr EC_{50}* = 31 ppb (loss of positive rheotaxis). Levels from 5850 to 11.7 ppb TBTO resulted in damage to gill epithelium. At 11.7 ppb there was a flattening of bile duct columnar epithelial cells and separation from connective tissue after 5-day exposure. Destruction of corneal epithelium occurred after 7-day exposure to 11.7 ppb.	Not reported	Continous flow stainless steel	5850 to 11.7 ppb	Chilamovitch and Kuhn (1976)
Salmo gairdneri (Rainbow trout)	TBTC	Fish exposed to 0.2 and 1.0 ppb TBTCl for 110 days experienced a dose-related decrease in growth rate. NOEL** was established at <0.2 ppb. Hyperplasia & diminished glycogen content in liver. Erythrocyte count and hemoglobin concentration were reduced in blood.	Nominal concentrations	110-day continuous-flow	0, 0.2, 1.0, and 5.0 ppb	Seinen *et al.* (1981)

Table 4.14
(Continued)
Chronic Toxicity Values for Fish Exposed to Tributyltin.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Fundulus heteroclitus (Mummichog)	TBTO	Avoidance occurred at 1.0 to 3.7 ppb	Measured concentrations AAS*	Flow-through	1.0, 3.7, 8.0 and 13.8 ppb	Pinkney et al. (1985)
Morone saxatilis (Juvenile striped bass)	TBTO	Avoidance occurred at 24.9 ppb	Measured concentrations AAS	Flow-through	4.5, 6.4, 12.4, 14.7, and 24.9 ppb.	Hall et al. (1984)
Brevorrtia tyrannus (Atlantic menhaden)	TBTO	Avoidance occurred at 5.5 ppb	Measured concentrations AAS	Flow-through	2.7, 5.5, and 9.1 ppb	Hall et al. (1984)
Cyprinodon variegatus (Sheepshead minnow)	^{14}C -TBTO	Mortality of F_1 generation during 28 days posthatch was noticeably high for TBTO parental exposure levels 0.24 ppb.	Liquid scintillation counting	Flow-through 21 days	0.14, 0.16, 0.24 and 0.45 ppb acetone	Ward et al. (1981)
Oncorhynchus tshawytscha (Juvenile Chinook salmon)	TBTO	Bioaccumulation in liver, brain and muscle tissue of 4300-, 1300-, and 200- fold, respectively.	Measured concentrations AAS	Static 96 hours	7.0, 3.5, and 0.52 ppb	Short and Thrower (1986)

* EC_{50} = Effective Concentration for 50% of the poipulation [effect produced is other than death]

** NOEL = No Observed Effects Level

* AAS = Atomic Absorption Spectrophotometry

Source: EPA, 1987.

4.4 BEHAVIOR AND FATE OF ORGANOTIN COMPOUNDS IN THE MARINE ENVIRONMENT

Tributyltin and the other butyltin moieties are poorly soluble in water and are strongly lipophilic. In the marine environment TBT will preferentially dissolve in polar molecular films in the surface microlayer. Concentrations have been reported in the surface microlayer several orders of magnitude above ambient water column values (Brinckman et al., 1986; Cleary et al., 1987). TBT also adsorbs to particulate matter suspended in the water column. The partitioning of organotins between the water fraction and the particulate fraction is currently under investigation. The tendency to adsorb on particulates is influenced by the composition of the particles, whether alive or dead and by the nature of the charge interactions with certain clay materials (Valkirs, et al., 1987; Unger et al., 1987). In laboratory studies with high quantities of sediments, once the particulate material settles out, TBT concentrations in the water column were lower, and bottom sediment TBT concentrations increased which subsequently may become available to the benthic fauna. Although this area has been little studied to date, Maguire and Tkacz (1985) have demonstrated that benthic oligochaetes can take up and metabolize TBT associated with sediment. The body burden of these worms is thus potentially available to bottom feeding fish.

4.4.1 Surface Microlayer

The sea surface microlayer is a naturally occurring surface film in relatively calm water, about 30 Angstroms thick, is polar in nature and readily accumulates lipophilic compounds. Organotins are strongly lipophilic and have a high octanol to water partition coefficient and will readily bind to the lipid monolayer at the air-water interface. Cleary and Stebbing (1987) have characterized tributyltin concentrations in the water column and the surface microlayer. They found organotin levels in the surface microlayer up to 27 times greater than in the subsurface water samples. Maguire et al. (1982) found concentrations in the surface microlayer of 2 times subsurface water. They found high organotin concentrations in the surface microlayer both in the summer of 1986 and the spring of 1987 in both estuarine and freshwater environments. Table 4.15 summarizes surface microlayer concentrations found in Canada, the U.S. and England. These microlayer concentrations are not directly comparable, because each study was conducted with a different sampling instrument. An indication of the degree of variability introduced by the different sampling methods can be seen in the measurements taken in the same waters at the same time with the Garrett screen and the glass plate samplers. The forces adhering the surface film to the sampler surface are different in the two cases. Also the thickness of the surface film removed are different between the two samplers. The glass plate sampler removes a layer 60 to 110 microns thick while the screen removes a 280 to 300 micron thick layer.

Concentrations (ng Sn/1) of Tributyltin
in Surface Microlayer and Subsurface Water Samples.

Sample Location	Reference	TBT in Subsurface Water (ng/l)	TBT in Surface Microlayer (ng/l)	Sampling Method	Microlayer Thickness (um)
Canada					
Great Lakes	Maguire et al., 1982	<4-1187	<4-24927	Rotating drum	~60
USA					
Chesapeake Bay	Hall et al., 1986	<8-468	<8-186	Teflon sheet	~30
San Diego Bay	Valkirs Per Comm.	4-72	24-100	Glass plate	
Great Bay Esturary	Donard et al. 1986	<2	306	Glass plate	~40-70
England					
Devon and Cornwall	Cleary & Stebbing 1987	<8-289	24-1069	Garrett screen	~280-300
Devon and Cornwall		9-300	119-3620	Glass plate	~40-70
Essex		11-41	17-91	Garrett screen	~280-300
Essex		17-22	163-550	Glass plate	~40-70
Norfolk		8-396	89-522	Garrett screen	~280-300
Norfolk		8-396	166-1600	Glass plate	~40-70

Source: Cleary and Stebbing, 1987

4.4.2 Degradation by Biota

Within the water column, the primary means of degradation of organotin compounds is likely to be planktonic algae or other microorganisms. Thain (1987) and Lee et al. (1987) have found that degradation of TBT did not occur in natural water where filtration had been used to remove all organisms. In the presence of light, diatoms appear to be a significant agent for the degradation of TBT (Lee, 1987). In Atlantic coastal waters, the chain forming diatom Skeletonema costatum has been identified as the most common TBT debutylating agent. Thain et al. (1987) found that microalgae were able to degrade 1/2 of available TBT in 6 days at 20°C but at 5°C the same degradation took 60 days. The species of algal cells present, as well as ambient temperature and light intensity, all appear to affect the rate of TBT degradation. In the absence of light, bacteria become the principal organism for the degradation of TBT in natural waters. Because of the number of variables involved, a high diversity in half life periods are reported in the literature, ranging from a half life of several months to 3.5 days. The lowest estimate was developed at the Marine Ecosystem Research Laboratory (MERL) using ^{14}C labeled tributyltin introduced into the enclosed ecosystem containing natural water, plankton, sediment and benthic organisms from Narragansett Bay (Hinga et al., 1987). They found a first order removal rate constant of 0.20/day or a half life of 3.5 days.

It is not known at this time if dissolved organotins form complexes with the lipids and detritus in the microlayer and thus become biologically more available to filter feeders or deposit feeders or whether the presence of such high concentrations may be biologically significant from a toxicity perspective. The neuston (floating and swimming) comprises organisms who inhabit the surface microlayer. These organisms include microbial populations, and the eggs and larvae of invertebrates and of fish. The chemistry of the surface microlayer is extremely complex and poorly understood (see Brinckman et al., 1982 and 1987). Light impinging on the surface film may hasten the debutylation of tributyltin in the microlayer. Lee et al. (1986), found that under sunlight conditions that the half-lives of TBTR in the Elizabeth and James Rivers in June were 6 and 10 days respectively. They also found that for the Skidaway River during a year-long study that the half-lives varied from 4 to 13 days for individual data sets and that degradation was always higher in the light relative to dark treatments. The population of bacterio-neuston may also debutylate TBT into the less toxic and less bioavailable moieties, or they may serve principally as a food chain link passing the TBT to protozoans and subsequently to larval fish which are the most sensitive life stage for many species (Gucinski, 1986). Researchers at NBS have found that bacterial biofilm communities from paint panels did not degrade TBT but bioconcentrate it up to greater than 350 mg/l (Blair et al., 1987). Similar work in progress with algal biofilms has found that degradation does occur (Brinckman, personnel communication).

There are also no degradation rates estimated for butyltins in the surface microlayer. Each of these habitats has its own microbial communities with probably differing abilities to degrade tributyltin. Studies of the surface microlayer may have to wait for the development of better or at least standardized sampling procedures. There have been no studies investigating degradation rates within bottom sediments.

The marine diatom Skeletonema costatum has been identified as a primary agent for the debutylation of TBT at sublethal concentrations. Beaumont et al. (1987) give a 72 hour EC_{50} of 0.33 ug/l of TBT. They further state that Skeletonema virtually ceases to grow when subjected to 0.1 ug/l TBT and several other species of algae have similar significant depressions in their rate of growth at similar concentrations. The most effective debutylation of TBT has been found to occur at algal cell densities higher than those normally found in estuarine waters (Lee, 1986). It may well be that bloom conditions coupled with the cellular uptake of TBT will sequester enough TBT so that exposure concentration from the water stays below lethal levels.

Lee et al. (1987) suggest that hydroxybutyldibutyltin is formed by algae in the presence of light but not by bacteria under dark conditions. These results suggest a different metabolic pathway for the debutylation in algae and in bacteria. It may be possible to optimize the rate at which tributyltin is debutylated and thus reduced to a lower toxicity by carefully maintained populations of degrading organisms.

The metabolic pathways by which the debutylation occurs is poorly understood as are the limits to the process. It is possible that the presence of TBT in the water column may provide a selective advantage to bloom conditions, by being more toxic to specific species.

4.4.3 Adsorption to Sediments

Diverse results have been reported in studies to determine the persistence of tributyltin in bottom sediments. Table 4.16 summarizes the sorption and desorption coefficients for various sediment investigations conducted to date. Johnson et al. (1987) found that the concentration of TBT in sediment pore water, either decreased slightly or remained unchanged as the depth of sampling in the sediment increased from 10 cm to 20 cm. They reported a concentration of TBT in undisturbed sediment pore water of 40 ng/l. Bottom sediments which had been recently dredged were found to contain 10 ng/l of TBT in pore waters. This study was conducted in Back Creek in Annapolis, Maryland which has marinas lining the perimeter of the creek.

The ability of particulate and suspended matter to remove TBT from the water column varies with the distribution of turbidity within the estuary. In partially mixed estuaries, there can be well defined turbidity maximum where charge interactions with the saltwater interface increases flocculation and precipitation of suspended materials and solids. Harris and Cleary (1987) have found in the English river Tamar that the percent TBT adsorbed to particles exhibited a maximum which corresponded with the location of the turbidity maximum. The circulation patterns of the partially stratified estuary will tend to accumulate particulate bound TBT at the salinity interface, which may be well upstream from where concentrations of boats are moored. In this situation estuarine physical processes would act to transport TBT upstream to the turbidity maximum for deposition [see Figure 4.5 from Harris and Cleary (1987)]. In this case the sediment serves primarily as a sink and the TBT is removed and isolated from the water column by continued sedimentation.

Studies of Chesapeake Bay sediment sorption coefficents have been conducted by Unger et al. (1987). Table 4.16 summarizes the relationships that Unger et al. (1987) observed between sediment types and sorption coefficients for TBT. Table 4.17 summarizes partitioning coefficients of butyltin compounds between sediments and water reported by Stang and Seligman (1987). These studies have found that significant amounts of TBT may be associated with particulate material or sediments in coastal plain type estuaries. They have also observed that the sorption process is reversible suggesting that contaminated sediments may well act as sources for TBT to redissolve into the water column. Sorption to sediments decrease with increasing salinity (see Figure 4.5, from Harris and Cleary, 1987). Therefore, salinity changes and sediment types must be considered when estimating the effects of dredging of contaminated sediments or TBT transport and bioavailability.

Table 4.16

Sorption and Desorption Coefficients for Tributyltin in 1/kg for Chesapeake Bay Sediments.

Sediment Type	$K_{sorption}$	$K_{desorption}$	K_{oc}
Fine grained detritus, high in organics	8.2×10^3	7.8×10^3	2.0×10^5
Silt, high in organics	1.3×10^3	1.3×10^3	4.5×10^4
Sand, moderate organics	0.60×10^3	—	1.8×10^5
Coarse sand, low in organics	0.11×10^3	0.11×10^3	1.2×10^4

Source: Unger et al., 1987.

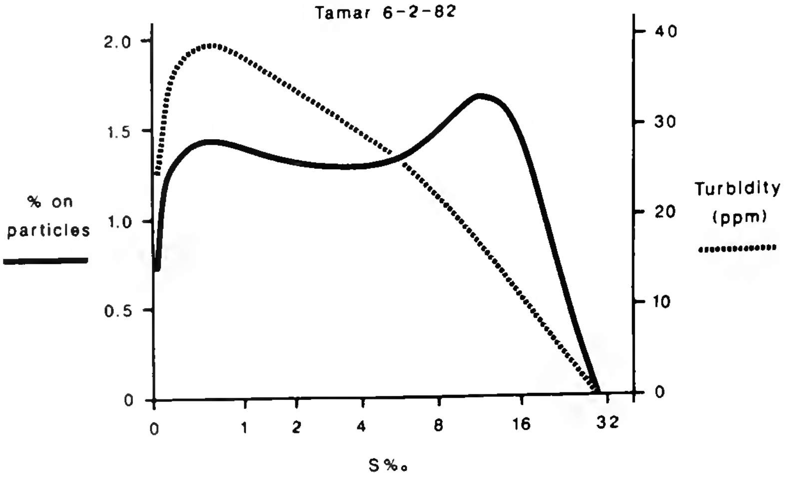
Table 4.17

Partitioning Coefficients (in ug/kg/ug/l) for Butyltin Compounds Between Sediments and Water.

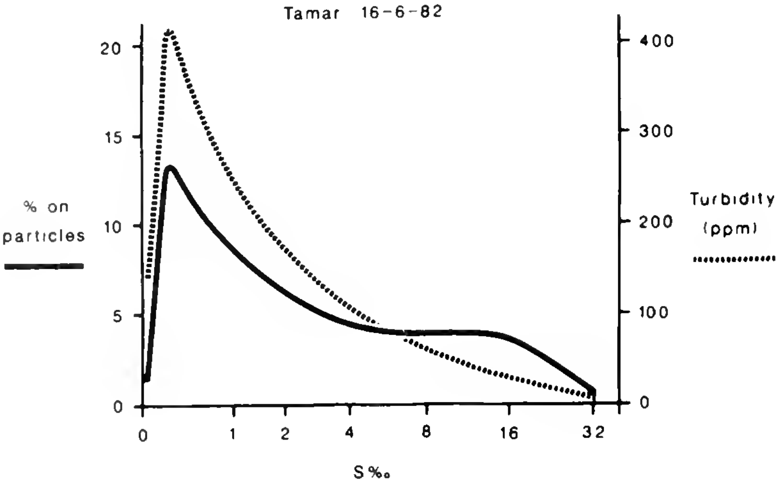
Station	Compound	Month	Kp	Month	Kp
1	TBT	February	24,706	May	55,439
	DBT		7,027		26,087
	MBT		28,750		11,346
2	TBT	February	14,821	May	6,250
	DBT		2,069		10,714
	MBT		1,758		3,878
MERL	TBT	July	4.0×10^4		
	DBT		4.5×10^2		

Source: Stang and Seligman, 1987.

Figure 4.5
Predicted Distribution of Tributyltin in Dissolved and Particulate Attached Phases for the Tamar Estuary for (A) Winter and (B) Summer Conditions.



(A) Winter Conditions.



(B) Summer Conditions. Turbidity profiles were produced by simulations using the model of Harris et al. (1987), and NERC (1988).

Results presented in Table 4.16 also suggest that butyltin species adsorb more strongly to sediment in warmer months, and that tributyltin generally adsorbs more strongly to sediment than dibutyltin, and that monobutyltin generally adsorbs more strongly than dibutyltin. Stang and Seligman (1986) have determined that butyltin concentrations in the sediments of Pearl Harbor appear to be at or near equilibrium with butyltin concentrations in the overlying bottom water and that the sediment there can potentially accommodate butyltin concentrations up to four orders of magnitude greater than the overlying bottom water without significant desorption of butyltin cations from the sediment.

4.5 BIOCONCENTRATION/BIOACCUMULATION/BIOMAGNIFICATION (FISH AND SHELLFISH)

Traditionally fish nets have been coated with tar or treated with tannic acid to prevent the settlement of bacteria and subsequent rotting of the net fibers. The effectiveness of tributyltin has led to its increasing use as an antifouling coating for fishnets, floating cages, livecars, traps and pots. This practice can subject the contained fisheries to a continuous dose of the tributyltin leaching from the antifouling coating. The growing practice of holding or raising young fish in pens or nets treated with TBT has been found to have increased the number of fish coming to market with a detectable load of tributyltin in the tissues (Davies, et al., 1987 in Scotland: Short and Thrower, 1986a in Alaska). This situation has been investigated in Atlantic salmon and the chinook salmon in the Pacific, due to public health concern related to human consumption of TBT contaminated fish. Davies et al. (1987) have found the occurrence of TBT at 0.5 to 1.0 mg/kg in the muscle tissue of Atlantic salmon farmed in cages treated with TBT. These results have contributed to the debate leading to new more stringent controls within the United Kingdom on the use of antifouling paints on boats and on fish farm structures. Similar concern has been voiced in Alaska and the West U.S. Coast where residues of TBT have been found in chinook salmon raised in TBT treated cages (Short and Thrower, 1986a) and due to TBT caused mortality in chinook salmon (Short and Thrower, 1986b). Tables 4.18 and 4.19 summarize the results of studies on the bioaccumulation of tributyltin in fish and molluscs. The concentration of TBT in muscle tissue of the chinook salmon (0.52 ppm) is similar to the 0.5 to 1.0 mg/kg found in the Atlantic salmon in fish farms in Scotland (Davies et al., 1987).

Table 4.18

Bioaccumulation Values for Tributyltin in Fish.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Cyprinodon variegatus (Sheepshead minnow)	^{14}C-TBTO	Residues in muscle and whole body after 58 days exposure were 2.91 and 4.19 ppm, respectively. Depuration was rapid within the first 7 days but slower for the remaining 21 days (74% muscle 80% head, 64% viscera). Total body burden of TBT not depurated of degraded.	LSC* measured concentrations	Exposed to TBTO for 58 days. Flow-through testing.	0.96 to 2.07 ppb	Ward *et al.* (1981)
Oncorhynchus tshawytscha (Chinook salmon)	TBT	96-hr exposure resulted in TBT concentrations in liver (7.0 ppm) brain (8.5 ppm) and muscle (0.52 ppm). This amounted to 4300, 1300, and 200 times the exposure concentration respectively.	Measured concentrations AAS** testing.	96-hr exposure Flow-through	1.49 ppb.	Short and Thrower (1986)

* LSC = Liquid Scintilation Counter

** AAS = Atomic Absorption Spectrophotometry

Source: EPA, 1987.

Table 4.19

Bioaccumulation Values for Tributyltin in Molluscs.

TEST ORGANISM	ORGANOTIN COMPOUND	EFFECT	ANALYTICAL METHODS	TYPE OF EXPOSURE	CONCENTRATION LEVELS	REFERENCE
Bivalves						
Mytilus edulis (Mussel larvae)	^{14}C-TBTO	Gills and viscera accumulated (80-100 ppb) more TBT than mantle and muscle tissue (0.03 ppb). TBT from food produced a higher tissue burden than TBT from water.	Liquid scintillation counting	Short term (24 hours) and long term (42 day) static renewal	5.0 ppb TBT dissolved in water Phytoplankton exposed for 2 hours to 5 ppb TBT in 2 liters of seawater.	Laughlin *et al.* (1986)
Crassostrea gigas (Pacific oyster larvae)	TBTO	Bioaccumulation of 2000- to 6000- fold after 22 days	FAAS* measured for the first 5 days of exposure.	Flow-through	0.15 and 1.25 ppb	Waldock, Thain, and Miller (1983)
Ostrea edulis (European oyster)	TBTO	Bioaccumulation of 1000- to 1500- fold after 22 days	FAAS* measured for the first 5 days of exposure and on alternate days until completion.	Flow-through	0.15 and 1.25 ppb	Waldock, Thain, and Miller (1983)

* FAAS = Flameless Atomic Absorption Spectrophotometry

Source: EPA, 1987.

Concern for bioaccumulation stems from two areas: (1) food chain accumulation (biomagnification) to higher levels, and (2) human public health risks from consumption. An acceptable daily intake [ADI] to quantify the maximum dose of Tributyltin considered safe for a human has yet to be established. However, Schweinfurth and Gunzel (1987) have estimated a provisional ADI derived from the available toxicological information based largely on rat and rabbit studies. Using the no observed effects level [NO-EL] of 0.32 mg/kg TBTO and a safety factor of 100 (which takes into account interspecies and intraspecies variation), an ADI of 3.2 ug/kg TBTO was estimated from calculations. Schweinfurth and Gunzel (1987) also reported a tentative ADI of 1.6 ug/kg has been estimated by the Japanese Ministry of Health and Welfare. Based on a provisional ADI of 3.2 ug/kg of TBTO, a person with a body weight of 60 kg could safely eat 192 micrograms of TBTO in food. Assuming that the average person eats 100 grams of seafood daily and has no other source of exposure to TBT, a concentration of 1.9 mg/kg TBTO in seafood appear to be acceptable. This is higher than the 0.5 to 1.0 mg/kg found in the salmon from TBT treated pens. (Schweinfurth and Gunzel, 1987). One concern raised by Frederick Brinckman at NBS was the use of TBTO as the organotin species by the authors in the above study presents a potential problem, because the weight of the TBT moiety effect could be wrong by a factor of two (e.g., TBTO = $Bu_3Sn-O-SnBu_3$ = 2 TBT molecules).

4.6 ENVIRONMENTAL CONCENTRATIONS OF ORGANOTIN IN COASTAL WATERS

4.6.1 Early Monitoring Studies

The first reports of shell thickening and deformation in the U.K. were published by Key in 1976. At that time, no means were available to measure organotins in water at the low concentrations which were then present. By 1982, the French government was sufficiently concerned to proceed to ban the use of TBT by recreational and smaller fishing vessels, even though very little actual measured butyltin concentration data were available. The British government issued their first regulations for TBT in 1985 which were intended to reduce environmental concentrations to less than 20 ng/l.

In the United States, the first published survey of TBT levels in coastal waters was by Valkirs et al. (1986). Since that time, environmental sampling has been conducted only in a few locations. The impetus for these studies initially was the U.S. Navy's Environmental Impact Assessment and their subsequent decision to apply TBT copolymer ablative paints to the entire fleet over a ten year span. The major studies of organotin concentrations in North American coastal waters, to date are:

Northern Chesapeake Bay - Hall, 1986
- EPA Gulf Breeze Lab, 1987
(Published by EPA, Chesapeake Bay
Program, CBP/TRS 14/87, 1987)

Southern Chesapeake Bay - Huggett, 1986
- Westbrook et al., 1986

California Coastal - Stallard et al., 1987

San Diego Bay - Seligman et al., 1986

Navy, Baseline - Valkirs et al., 1986
- Grovhoug et al., 1986

Canada, freshwaters - Maguire et al., 1982; 1985; 1986
- Maguire, 1984; 1987
- Maguire and Tkacz, 1987

These early efforts to determine the characteristic concentrations of TBT is selected coastal waters were also steps in methods development. These early studies uncovered several environmental variables which were affecting the measured concentrations of organotin.

4.6.2 Environmental Variables Affecting Organotin Levels

Mixing processes in an estuary, bay or river, are a major contributor to variation in the measured levels of TBT in the water column. Much of the mixing is tidal. Marinas and anchorage areas are located insofar as possible to minimize the effects of wind and wind waves on the boats and ships kept there. To provide protection from all points of the compass, the typical marina is constructed with a very narrow entrance relative to the volume of the enclosed body of water. This configuration has the poorest flushing characteristics and the greatest tendency to accumulate materials leaching or spilled from boats. The presence or absence of fresh water inflows and density gradients are also important in determining the mixing processes in any given body of water.

Sediment type and sediment water interactions also introduce variability to the measured concentrations of organotins in natural waters. Studying the relation of sediment loadings of butyltin and water column concentrations, Grovhoug et al. (1986) concluded that sediments accumulate butyltin to 3 orders of magnitude above the concentrations found in the adjacent water column. Most of the sampling of sediments has been single samples which provide no information on tidal or seasonal variations of TBT uptake or release. A question requiring further study is the effects of butyltin loadings (as paint chips, dissolved or bound to sediment or organic material) in bottom sediments on the benthic community. Goldberg (Scripps Institution of Oceanography) sampled surface waters and sediments in over eighty sites, primarily California coastal marinas and found that "in those marinas where the TBT concentrations were greater than about 100 ng/l, there was a conspicuous absence of native organisms, especially molluscs" (Stallard et al., 1986). Goldberg (1986) has also reported that Antioch Marina (Yacht Club) in San Francisco Bay had TBT concentrations over 500 ng/l and an absence of fauna (such as mussels and tunicates) on the submerged parts of docks and piers.

Salinity appears to have an effect on the rate at which TBT is debutylated to dibutyltin and monobutyltin. Most evidence points to the microalgae and bacteria as agents for debutylating TBT. Differences in species composition of the phytoplankton between fresh and salt water are sufficient to account for the difference in degradation rates observed by Maguire et al. (1986). The diatoms appear to be the principal marine/estuarine microphytes debutylating TBT in salt water.

Boating activity correlates with variations in the concentration of TBT observed in coastal waters (Hall et al., 1986; Grovhoug et al., 1986; Seligman et al., 1986). The Navy's baseline study demonstrated that recreational boat mooring facilities and also drydock and ship painting facilities were associated with higher water column concentrations of organotin (Grovhoug et al., 1986). Huggett (1986) observed high butyltin concentrations in the Elizabeth River shortly after the launching of a freshly painted commercial ship. The extreme variability in the Elizabeth River was found to be associated with intermittent discharges (Seligman et al., 1987). However, in Baltimore Harbor, which does not have major ship repair and painting facilities, TBT concentrations are more closely associated with recreational boating facilities than with commercial shipping (Hall et al., 1986). The EPA/Gulf Breeze Lab Study (1987) found a linear relationship between recreational boat density and mean TBT concentrations (Johnson et al, 1987). In addition to boat density, a strong seasonal effect has been observed with peak concentrations of TBT occurring in May and June in the Chesapeake Bay, during the peak period of launching newly painted recreational boats for the beginning of boating season.

4.6.3 Measured Environmental Concentrations of TBT

Concentrations of TBT have been measured in Chesapeake Bay by Huggett (1986), Hall et al. (1986), Grovhoug et al. (1986), Seligman et al. (1987), and the EPA Gulf Breeze Laboratory (Johnson et al., 1987). Huggett (1986) employed a Grignard reaction to derivatize the organotin, gas chromatography to separate the organotin into TBT and DBT species, and quantification by mass spectrometer. The level of detection is given as 1 part per trillion (see Unger et al., 1986 for protocols). Sampling was conducted once every two weeks from January 1986 through September 1986. Results are summarized in Table 4.20. The Hall et al. (1986) study was conducted at marina sites in the Severn River, West River, South River, Chester River, Patapsco, Choptank and Potomac Rivers and in the Chesapeake and Delaware Canals. Data was collected on the number of boats kept in marinas adjacent to sampling locations. The results permitted an estimation of the relationship between boat density and water quality with respect to tributyltin concentrations. The study used the borohydride derivatization method developed and in current use by the National Bureau of Standards. The NBS method uses GC for separation and quantification. Atomic Absorption Spectroscopy was used to quantify the chemical species. Only the TBT concentrations are given in Table 4.20. Each of the 8 stations was sampled once a month from July 1985 to June 1986. The limits of detection were given as 20 to 30 ng/l of TBT.

Table 4.20

Environmental Concentrations of Organotin Compounds in U.S. Waters.

Location	Sample Date	Environmental Concentrations Water	Sediment	Microlayer	Tin Species Measured	Measurement Technique	Citation/Reference
Detroit River	6/85	N.D.-0.17 ppb	5.0 - 180ppb	0.1-0.8 ppb	TBT, DBT	Hydride extract GC-FDP	Maguire et al., 1985 (in EPA, 1985)
Maryland							
Annapolis Harbor	6/86	736 ug/l to 20 ug/l			Butgltin ion [$BuSn^{+4}$]	Hydride extract GC-MS	Mathias et al., 1986
"	8/85	61 ug/l					Olson et al., 1986
Severn River	6/86	44 ug/l			TBT, DBT	Hydride extract AAD	Seligman et al., 1987
Back Creek Annapolis	6/86	283 ug/l to			TBT, DBT	Hydride extract AAD	" " "
" "	/86	0.34 ug/l to 0.071 ug/l		ug/l to N.D.	TBT, DBT		NOAA Status & Trends IN: (EPA, 1986)
West River, Hartges Marina	6/86	<20 ug/l		239 ug/l to N.D.		Hydride Extract	Mathias et al., 1986
Baltimore,	9,10/86	2.5 ug/l to			GC/MS		Olson & Brickmann, 1986
Patapsco River		3.6 ug/l		43 ug/l 41 ug/l			
Chesapeake Bay	6/86	587 ug/l to 471 ug/l		to N.D.			
Chesapeake Bay Surface	1986/87	2.3 ug/l to 9.1 ug/l		2 to 3 times Water content		AAS "	Hall (NOAA/NMPPO,1986)
" " "	"	464 ug/l			" "		AAS Hall (NOAA/NMPPO,1986)
Baltimore-marina	"	219 ug/l to 33 ug/l			" " " "		" " " " " "
Baltimore Harbor	"	24 ug/l to ND			TBT, DBT		Huggett (NOAA/NMPPO) 1986
Back Creek, Patuxent River	3/87	122 ug/l to 21 ug/l			TBT, DBT	Hydride extract	Johnson et al., 1987
" "	9/87	193 ug/l to 51 ug/l			TBT, DBT		" " " "

Table 4.20
(Continued)

Environmental Concentrations of Organotin Compounds in U.S. Waters.

Location	Sample Date	Environmental Concentrations Water	Sediment	Microlayer	Tin Species Measured	Measurement Technique	Citation/Reference
Elizabeth River	/85	66 ug/l to 16 ug/l	Several orders of magnitude higher than water content		TBT-DBT	GC/MS	Olson & Brickmann (1986)
"					" "		
"	9/85-5/87	87 ug/l to 2 ug/l			" "	AAS	Hall (Testimony-Hse MM & F Committee)
Hampton Roads	/87	231 ug/l to 7.0 ug/l				numerical computer model	Seligman et al. (1987)
Norfolk Navy Base	1/85	0.24 ug/l to 0.005 ug/l					Camp Dresser & McKee, Inc.
Norfolk	/86	0.06 ug/l to 0.006 ug/l					NOAA Status & Trends IN: (EPA, 1986)
Elizabeth River		160 ug/l to 5.0 ug/l				Hydride extract	Lee et al. (1987)
		5.0 ug/l				AAS	
James River		< 5ug/l				Hydride ext	"
California							
San Diego Bay	10/85	0.332ug/l to 0.017 ug/l			TBT	Hydride extract AAS	Calvell et al. (1986)
" " "	5,6/86	0.920 ug/l to 0.239 ug/l				" " "	Valkirs et al. (1986)
" " "	1/83	551 ug/kg to <2.0 ug/l				Hydride extract AAD	Stang & Seligman (1986)
" " "	1/83	467 ug/kg to				Hydride extract	Stang & Seligman (1986)
" " "	1/83	0.55 ug/l to ND			TBT/DBT/MBT	GC/MS	Valkirs et al. (1986)
San Diego-Comm. Basin	5,6/86	520 ug/l to 90 ug/l	22 ug/l to 7.5 ug/l		TBT/DBT/MBT	" " " "	" "
San Diego-Shelter	6/86	0.21 ug/l to 0.18 ug/l	228 ug/kg to				
Island Marina	/86	400 ug/l	445 ug/kg		TBT	Hydride extract	Goldberg (Unpublished Data)
Vallejo Yacht Club	4/84	0.046 ug/l to 0.034 ug/l					NOAA/NMPPO (1986)
Long Beach Harbor	6/85	0.027 ug/l to 0.019 ug/l					NOAA/NMPPO (1986)

Table 4.20
(Continued)

Environmental Concentrations of Organotin Compounds in U.S. Waters.

		Environmental Concentrations			Tin Species	Measurement	
Location	Sample Date	Water	Sediment	Microlayer	Measured	Technique	Citation/Reference
San Diego Bay		0.93 ug/l to 0.01 ug/l					Valkirs et al. (1986)
San Diego Navy Base	/85	0.24 ug/l to 0.01 ug/l			TBT	numerical computer model	Walton et al., 1986
Hawaii							
Pearl Harbor	4/84	<0.01 ug/l			TBT, DBT		Grovhoug et al. (1986)
Pearl Harbor	2/87	11.7 to 8.1 ug/l		252 ug/l		Hydride extract	NOAA/NMPPO (1986)
Dry dock #2	5/87	7.4 to 3.4 ug/l		316 ug/l		AAS	Stang et al. (1987)
Pier "B-16"	2/87	7.7 to 3.3 ug/l	83 ug/l				
	5/87	13.8 to 4.3 ug/l3		40 ug/l			
Honolulu	4/84	0.094 to					
			0.086 ug/l				NOA/NMPPO (1986)
Other States							
Charleston, SC	11/84	0.009 ug/l				Hydride extract	Lee et al. (1987)
Skidaway River		<5 ug/l				AAS	Lee
New London, CN	11/84	0.009 to 0.006 ug/l					NOAA/NMPPO (1986)
New Port Yacht Club, RI	10/85	0.010 to 0.008 ug/l					NOAA/NMPPO (1986)
Mayport, FL	6/85	<0.005 ug/l					NOAA/NMPPO (1986)
Port Townsend, WA	6/85	0.082 to 0.066 ug/l					NOAA/NMPPO (1986)

Source: Champ and Pugh, 1987.

The EPA laboratory in Gulf Breeze, Florida analyzed samples collected from 4 sites in the Chesapeake Bay once each week from May 1986 to September 1986. A tidal component to the variation in TBT concentrations was observed. The butyltin was derivatized with borohydride, separated to species by gas chromatography and quantified by mass spectrometry. The detection limits were given as 10 to 60 ng/l for TBT.

The only other region of the U.S. to be sampled in an comparable manner is San Diego Bay, California. The impetus for theses sampling programs was that both Chesapeake Bay and San Diego Bay have major U.S. Navy facilities. The Navy baseline study in San Diego Bay (Grovhoug et al., 1986) indicate that the highest environmental concentrations of TBT were associated with drydock facilities and recreational boating facilities. In Pearl Harbor, where the Navy drydock facilities are located, TBT was not detected. In Honolulu Harbor, where recreational vessels predominate, TBT concentrations in the water column were higher by an order of magnitude than concentrations of TBT measured around drydock areas.

Studies conducted by the U.S. Navy (NOSC) in San Diego Bay have reported concentrations in Commercial Basin to be <2.0 ng/l in 1983 (Stang and Seligman, 1986) . By 1986 the maximum measured concentration had become 520 ng/l (Valkirs et al., 1986). Monitoring studies conducted by Goldberg in the same area analyzed six surface water samples collected in January 1986, below the surface at an arms depth, from the Selter Island Marina Marlin Club Dock and found 4 above 400 ng/l (Stallard et al., 1987). Shelter Island is a very large recreational boating marina. The San Diego Bay Studies by NOSC utilized borohydride derivatization and gas chromatography to separate tributyltin and dibutyltin. Unspeciated total tin was measured from sediment samples collected at the same locations as the water samples. Sediment samples were collected by Stang and Seligman (1983) at the same time and were found to contain TBT concentrations of up to 551 ug/kg. The sediment samples collected by Valkirs et al. (1986) found concentrations up to 228 ug/kg. In general, the San Diego Bay studies found that sediment concentrations were three orders of magnitude higher than the concentrations in the overlying water.

4.7 LABORATORY ANALYTICAL METHODOLOGIES

As the nature and extent of TBT concentrations in the environment have become better understood as a result of monitoring studies, the focus of current research has shifted to study the speciation of butyltins and the relative partitioning of butyltins into the surface microlayer, the water column, and bottom sediments. The degradation pathway for tributyltin is progressive debutylation, to dibutyltin and then to monobutyltin. Each of these chemical species is less toxic than its predecessor.

With the ability to speciate organotins in the laboratory has come the discovery of tetrabutyltin in some locations (Olson et al., 1985; Matthias et al., 1986). Tetrabutyltin has not been identified as a degradation product of any known metabolic pathway. Tetrabutyltin has been observed only in locations close to where boats are being painted. Tetrabutyltin is even more hydrophobic and lipophilic than tributyltin and apparently does not disperse into the environment as TBT does. According to Ludgate (1987) [of International Paint, Incorporated], the TBTO purchased by paint manufacturers typically contains about 1% tetrabutyltin and 1% of other impurities from the manufacturing process. Tributylmethyltin and dibutyldimethyltin have been identified in sea water samples (Michel, 1987). The toxicological properties of these chemical species are unknown at present.

The ability to detect a single TBT molecule in 1 x 10^9 other molecules is a challenge to technology. Early work on methodology was developed independently by Hodge (1979) and Braman (1979) for methyltins. Currently the most sensitive procedure for detecting and measuring butyltin concentrations is the protocol developed by NOSC (Valkirs et al., 1985). This method represents a completely independent technique from Huggett at VIMS and the original method developed by NBS (Olson et al., 1985; Matthias et al., 1986). It employs an automated hydride generator to strip the butyltins from the seawater sample, a teflon chromatography column in the form of a U-shaped, partially filled with chromatographic packing and immersed in liquid nitrogen. The butyltin hydrides are trapped in the U column at low temperatures. Subsequently, liquid nitrogen is removed and the column is progressively heated by electric resistance wires to selectively evaporate the butyltin hydrides. Helium is used as a carrier gas. Hydrogen and oxygen are added downstream of the chromatography column to produce the flame for the flame photometric detector. Modifications have been made to this system to prevent deterioration of the column packing by adding monomethyl glycol to the samples and by using teflon lined glass to the column to prevent catalytic decomposition of the TBT hydride on the hot glass surface. The apparatus and technique appear to be suitable to test for the presence and concentrations of TBT in water. The NOSC method uses AA which is less sensitive than flame emission (which NBS uses) but is more specific. Each of the four butyltin chemical species can be determined by this method down to a detection limit of 5 ng/l. The differences of the two methods have been qualified by Valkirs (Analyst - January, 1987). The NOAA/NMPPO Workshop Proceedings (Landy et al., 1986) also have compared analytical methods for organotin. Further work is needed to develop a comparable technique for sediment and tissue. Interlaboratory comparability has been attempted, but examination of efficiency of recovery suffers from a lack of certified reference standards.

4.8 COMPARISON OF REPORTED UNITS IN THE LITERATURE

There is a lack of standardization of the units employed in reporting tributyltin concentrations in the literature. Table 4.21 presents the units which have appeared in the literature concerning butyltin in the environment and the interrelationships of these. In most of the papers published in the OCEANS '86 and '87 Organotin Symposium Proceedings, the initials PPT is used in the sense of parts per trillion in spite of the fact that the established usage of PPT is parts per thousand, a difference of 6 orders in magnitude. A better choice might be PPTr to indicate parts per trillion. The EPA has used standardizing reporting units as parts per billion (PPB).

Table 4.21

Comparison of Units Used in the Organotin Literature.

Parts per thousand [PPT]	grams/liter	10^{-0}	g/l
Parts per million [PPM]	milligrams/liter	10^{-3}	mg/l
Parts per billion [PPB]	micrograms/liter	10^{-6}	M/l or ug/l
Parts per trillion [PPTr]	nanograms/liter	10^{-9}	ng/l

4.9 NUMERICAL MODELING

The Dynamic Estuary Model was used to mathematically simulate the hydrodynamics of San Diego Bay to predict the increased TBT loadings that would be expected if the U.S. Navy implemented the plan to paint the entire 600-ship fleet with TBT antifouling paint (Waltin et al., 1986). The model was used to evaluate the environmental impact of continuous releases from docked ships and pulsed releases from drydock activities.

The simulated concentrations in San Diego Bay were derived in two steps. First the hydrodynamics of the Bay were modeled using a dynamic, pseudo two-dimensional link node model. The governing equations for the hydrodynamic model are the momentum equation, mass transport, dispersion and the continuity equations. Losses of organotin from the water column were estimated to occur as an exponential decay function. Simulated concentrations were generated using sets of assumptions of continuous releases, pulsed releases of different magnitudes and finally a set of decay rates derived from laboratory microcosm studies ranging from 4%/day to 11%/day. Values generated from the model have shown that pulse loadings are rapidly dispersed in the estuary, and that concentrations of TBT in the southern end of San Diego Bay where flushing is poorest are dependant on the assumptions of degradation rate used. Good correlation was obtained between the model and environmental concentrations where samples have been analyzed. The predictive ability of the model cannot be established until better information is available on the leach rates from underwater surfaces and the extent of underwater surfaces coated with TBT.

The EPA is also employing the Dynamic Estuarine Model in the Elizabeth River and Hampton Roads portion of Chesapeake Bay (EPA, 1987). The impacts of recreational boating activity, commercial shipping and military ship traffic are being simulated by assumptions regarding several loading levels caused by boating and shipping activity in the area. These estimated concentrations are expected to help EPA make its final regulatory decision regarding continued registration of TBT biocides in antifouling paint (EPA, 1987).

Seligman et al. (1987) have reported on the results of a series of Dynamic Estuarine modeling runs to investigate the environmental concentrations of TBT resulting from paint releases from drydocks in the Hampton Roads and Elizabeth River areas. The comparison of model estimates with observed concentrations in this area show generally good agreement except for intermittent higher measured concentrations than the model has predicted, suggesting that estimates of releases from drydock operations may be too low. The authors suggest that improved drydock cleanup procedures would reduce this discrepancy.

4.10 ALTERNATIVES TO ORGANOTIN ANTIFOULING PAINTS

There is not a product on the market which matches the performance of tributyltin as an antifoulant (Porter, 1980; Schatzberg, 1987). There are other antifouling chemicals. The primary alternative is copper, usually copper oxide. Research is being conducted on alternatives to organotin antifouling paints, however, useful results have not been clearly demonstrated. The three main areas being investigated are:
(1) alternative toxins, (2) non-toxic compounds, and (3) disruption of the successional stages of the development of the fouling communities. There are also specific, or selective biocides being investigated. These selective biocides are likely to be employed as an addition to rather than a replacement for either organotin or copper. Neither organotin nor copper controls all potential fouling organisms. Copper works well against calcarious fouling organisms such as barnacles but not well against algae, bacteria or some bryozoans. Organotin is repellant or toxic to a wider range of species but does not work as well against algae (Atherton et al., 1979; Callow et al., 1978).

The ideal antifouling material must be able to prevent the attachment of any members of the phylogenetic spectrum from bacteria to chordates (tunicates) without being toxic to any of them. The ideal antifouling material should adhere to all man made surfaces, be highly resistant to abrasion, non-soluble in sea water and not inactivated by contact with chemicals in aqueous solution, should remain effective indefinitely, be inexpensive, and easy to apply. In the absence of the ideal substance, research is progressing on the development of alternative toxins and non-toxic alternatives.

4.10.1 Alternative Toxins

Copper is the oldest and best-known biocide for antifouling use. Research is being directed to developing a controlled release structure by incorporating copper powder in a matrix of either epoxy resins or of polyester resins (Miller, 1985). These would provide essentially a hard finish paint which is not self polishing. Copper phosphate glass is also being investigated for antifouling use. By encapsulating the copper as much as possible the problems with galvanic corrosion are reduced (Rascio et al., 1978). Currently this is a major problem with the increasing use of aluminum in the marine environment (Mor et al., 1984). Aluminum is used for propellers, outboard motor and inboard/outboard lower units as well as entire hulls (Lennox et al., 1966). The Coast Guard, law enforcement agencies and the offshore oil industry are major users of aluminum hulled boats for their high speed capabilities and ability to take abuse.

Copper when alloyed with nickel is extremely resistant to corrosion and less galvanically active (Strange, 1986). The alloy also has antifouling properties. The use of a thin metallic cladding over steel hulls is being investigated by the Newport News Shipbuilding Company. The cladding will serve as a corrosion and antifouling barrier (Chenchrom, 1968; Czimmek, 1985). The Cu-Ni alloy has been added to chloroprene rubber to produce a resilient antifouling surface which has also good sound attenuating properties (Miller, 1985). At least one vessel has been built in England employing a 90/10 Copper-Nickel alloy to form the hull (Anon., 1979). Such a vessel may be able to avoid the use of antifouling paints altogether. However, periodic scrubbing of the hull to remove algae may be required (Griffith, 1985).

Other metal-based antifouling formulations include thin films of titanium-palladium alloy, fluorinated organolead compounds, a refinery waste containing a melange of Copper, Zinc, Lead, Antimony, Cadmium, Iron, Arsenic and Chlorine (Budon et al., 1985). In a variation of the same approach, the inclusion of a metals complexing agent, Chitosan, can be combined with cellulose triacetate to produce a membrane which over time accumulates naturally occurring metal ions from seawater to impart an increasing antifouling capability to the film.

Organic molecules which do not include a metal atom are also being tested for antifouling properties. These include Obtusaquinone, (Goodwin, 1974; Miller et al., 1980 and 1982) Sodiumpentachlorophenate (Anon, 1949) combined with chlorine, and chlorinated rubber coatings. The rubber based compounds offer abrasion resistance as well as good sound attenuation and are galvanically inert. A coating for aluminum hulls which claims both antifouling and anticorrosive properties has been developed from tar, chlorinated rubber, plasticizer and hydrocarbon resin.

4.10.2 Non-Toxic Alternatives

These materials either repel the fouling organisms or interfere with the attachment process (Ghanem et al., 1982). A repellant compound of cellulose acetate and metyl siloxane loaded with silica has been devised and is being tested. When an organic acid such as tannic acid or benzoic acid is combined with acrylamid polymers, a surface treating material is obtained which has the effect of repelling fouling bacteria, without being toxic to them.

During the recent period of extremely high world oil prices, the U.S. Navy experimented with underwater removal of fouling organisms using divers and motorized hull cleaning brushes on ships painted with conventional copper based antifouling paints, to extend antifoulant life (Cologer, 1984). A commercial towing firm in England is testing the use of a non-toxic low energy surface such as fluoropolymers (teflon) or silicon polymers which resist adhesion by fouling organisms and release the organisms readily when frequently (intervals as short or shorter than 6 months) scrubbed in the water using the divers and motorized in situ cleaning equipment. To date in the U.S., only the State of Maryland has indicated any concern over the ecological effects of the scrubbing of vessels in coastal waters. Recent TBT control legislation in Maryland also mandated a study of the environmental effects of under-water hull cleaning using motorized brushes (MD General Assembly, 1987).

When the surface being scrubbed is coated with conventional antifouling paints there exists the potential to remove a portion of the paint film by abrasion and introduce it directly into the water or sediments. Whether the introduction of fluoropolymers from a teflon coated surface will introduce new ecological problems remains to be investigated.

4.10.3 Disruption of Fouling Succession

The single most promising line of investigation to develop alternative antifouling materials, is the inquiry into the successional stages of biofouling. When a clean smooth surface is immersed in seawater the first organisms to settle are bacteria. The bacterial attachment to the surface is at first reversible by the bacterium but after a period of time the attachment becomes permanent. On surfaces where the bacterial film is periodically removed, further settlement by other organisms is strongly inhibited. This process is well known to sailboat racers who clean their antifouling paint with a sponge or brush, on weekly intervals during the racing season.

An undisturbed bacterial film soon embeds the bacterial cells in a matrix of polysaccharides secreted by the bacteria themselves (Madelyn Fletcher, personal communication). Current investigations by NBS and several researchers at U.S. universities are focusing on the roll of this polysaccharide as an attractant to further settlement by other organisms.

The next organisms to settle in this bacterial film are the single celled algae. Diatoms such as the chain forming diatom Skelotonema costatum, live on and in the polyscharide matrix. These algae have been shown to metabolize and degrade TBT into less toxic chemical species such as dibutyl- and monobutylin. This active component of the biofilm on the painted surface may be essential to the subsequent settlement of bryozoans (Stebbing, 1981; William Banta, personal communication) and barnacles by reducing the concentration of the antifouling agent at the surface of the biofilm. One source of the difference in release rates measured by the U.S. Navy's in-situ measurements of release rate and the EPA/ASTM release rate tests in the laboratory is the presence of the bacterial/algal biofilm on the TBT treated Navy Ships and its absence in the laboratory tests.

The next stage of succession is the attraction and attachment of the larval stages of multicellular plants (macrophytes) and animals producing hard or calcarious exteriors. This stage exhibits a marked increase in the surface roughness and drag on the painted hull. If the surface could be kept free of the bacterial/algal film, the subsequent settlement might be prevented by failure of the surface to attract the free swimming larvae of the next biofouling stages. Fundamental questions which need to be answered include the nature of the bacterial attachment and the mechanism involved in its irreversibly. What is the role of the polysaccharide slime as an attractant to subsequent settlement of other organisms? Is the presence of the film facultative or obligatory? What is the concentration gradient of TBT across the biofilm? What part of its success as an antifouling agent is due to its effectiveness in suppressing the initial biofilm and what part is due to direct toxicity to higher phylogenetic taxa? If the attachment of the bacteria could be prevented, would that be sufficient to prevent subsequent settlement of higher taxi?

New toxicants now being developed are targeted at the bacterial/algal biofilm. These include phenylmercuric oleate, barium metaborate, 2-4-isothiazolin-3-one and 4-5-dichloro-2-N-octyl-3(2H)-isothiazodone (Miller et al., 1980, 1982). The development of these new toxicants will require the usual period of testing to determine if they produce toxic effects on non-target species in the environment.

Mitsubishi Heavy Industries in Japan is developing a non-toxic mechanical removal system which operates continuously. In this system, electrolyzed sea water and compressed air are released from a series of nozzles along the ships bilges. The froth rises along the sides of the ship, potentially disrupting the permanent settlement of the microbiota on the surface of the hull.

Investigations are proceeding into the nature of the cement used by barnacles and by mussels to attach themselves to natural and man-made substrates. This cement is extremely strong and chemically quite inert. If a stable surface could be provided which chemically prevented the setting of the cement or which subsequently dissolved it, then no significant hard, calcarious fouling would be possible. These agents, to be effective, must be more general than specific.

CHAPTER V

RESEARCH NEEDS AND RECOMMENDATIONS

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RESEARCH NEEDS AND RECOMMENDATIONS

5.1 INFORMATION NEEDS AND LEVELS OF INFORMATION

Numerous meetings, workshops and symposia have been held over the past 3 years, all attempting to bring together researchers and policy and decision makers to identify, review and discuss information and research needs for understanding and regulating the use of organotin compounds in the environment. To date over 300 papers, reports or articles have been published related to some aspect of organotin compounds. However, most of these papers have not been prepared to advise Federal and/or State researchers, regulatory and/or policy and decision makers on research and information gaps. Degrees of scientific uncertainity have always reduced the confidence of Federal and State Agencies and have sensitized them to the use of safety factors in making regulatory or policy decisions in the absence of unrefutable scientific data. There are basically two levels of information needs:

(1) short-term data collection needs relative to immediate regulatory or policy and decision-making actions.

(2) long-term research as related to basic scientific understanding.

Short-term data collection needs are usually standardized laboratory studies, chemical analyses, monitoring efforts (field effects studies), etc. Long-term research projects are designed to test an hypothesis and are usually cause and effect relationship studies in the laboratory and/or the field. In Chapter II, we identified and discussed the short-term data collection activities that EPA has requested in its Data Call In Notices. These for the most part are standardized test response measurements (release rates, toxicity tests, etc.) except for the required monitoring studies. Therefore, this Chapter will identify and recommend the longer term research information needs.

5.2. RESEARCH NEEDS

For the International Organotin Symposium (OCEANS '87), a series of fundamental-basic research questions were posed and papers were presented to focus attention on understanding and predicting the implications of TBT in the marine environment (Champ and Pugh, 1987).

By the time the OCEANS '87 meeting was held in Halifax, Nova Scotia, a consensus on future research needs was developing among researchers. This consensus redirects research efforts away from delineating the degree of the effect to "why" and "how" to predict at what concentrations in given water bodies those effects would occur. There was no longer the need to demonstrate the case against TBT in coastal waters.

This rethinking has led to the development of this report. The areas of focus for future studies should be in quantification of the sources of TBT to the environment and determining the pathways of dispersion and transport, the fate and behavior and subsequent toxicity and results of the organotin species which have been introduced into the environment. Because, in order to predict the effects of exposure of marine organisms to tributyltin compounds in coastal waters, it will be necessary to understand the processes, mechanisms and rates that effect the distribution, transport, fate and behavior of tributyltin compounds in the environment and in living organisms. It will be also vital to understand the factors that influence the partitioning between the biotic and abiotic environments and the biological and chemical processes that degrade TBT to its metabolites.

5.2.1 Sources, Transport, and Fate

In order to predict the effects of the use of tributyltin compounds in antifoulant paints, it will be necessary to understand and quantify the inputs, rates of distribution and transport and subsequent fate and behavior of TBT in the environment. Input of TBT to the water column and the biota may continue long after regulatory actions, if the sediment serves as a temporary reservoir of the excess over the limits of solubility of TBT in water. To evaluate the probable consequences of a proposed regulatory strategy, the scientific community needs to be able to describe what occurs after TBT is introduced in the environment. Does it accumulate? Where does it accumulate and how much does accumulate? How fast is it converted to other products to which it is most probably converted? At least two degradation pathways have been identified each with a different sequence of intermediate chemical species. How many other degradation pathways are there for TBT within coastal waters?

5.2.1.1 Sources

Tributyltin enters the marine environment and becomes available to organisms in a variety of ways. Some of these pathways are not well understood or sufficiently quantified. There is very little information, for example, on the total contribution of nonpoint land sources (i.e. marinas), atmospheric inputs, and the quantities that become available to organisms from temporary reservoirs (i.e resuspension from sediments). Past studies have clearly shown that the major source of tributyltin to the marine environment is in the leachate from pleasure craft. For this reason, current and planned regulations and legislation is targeted at controlling this source. No legislation is being considered that will totally eliminate the use of organotin antifouling paints and, therefore some amounts of TBT will continue to enter the Nation's estuaries. Because of the serious concern about the toxicity of TBT to certain organisms, databases should be developed that will allow quantification of total loadings and identification of geographical areas of concern as well as providing direction for management decisions.

Currently, ambient concentrations of tributyltin are only being monitored in a few locations, particularly where there is a large U.S. Navy presence. The measurement of TBT should be included in ongoing routine watershed water quality monitoring programs. It is only in this manner that managers can evaluate the effectiveness of the reduction of inputs by legislation or regulation. Another area that is not well quantified is the contribution of TBT to receiving waters due to episodic events, such as heavy rainfall or flooding, that can deliver large amounts of TBT from nonpoint sources over very short periods of time. Frequently these episodic events occur in the spring when much of the boat bottom painting is done (at least for pleasure craft) and can coincide with spawning events in rivers and estuaries. The result is the intermittent exposure of sensitive live history stages (i.e. eggs and larvae) to toxic levels of TBT.

Studies are needed to provide information on:

- What are the quantities of atmospheric and other nonpoint source of TBT entering the marine environment.
- What monitoring of TBT is necessary to evaluate the effectiveness of the new legislation and regulation?
- What are the quantities of TBT delivered to receiving water during episodic or climatic events?
- What practices should be encouraged or required to ensure proper disposal by marinas of spilled paint, used brushes and rags, TBT contaminated sandpaper and grit, and empty paint cans?

5.2.1.2 Transport

To be able to predict downstream concentrations of tributyltin compounds, it is necessary to understand the patterns of tributyltin partitioning occurring in the environment. This means one has to be able to predict what proportion of the organotin, which is introduced into the environment, remains in solution in the water? What proportion resides in the surface microlayer and what portion is absorbed onto sediment? Within the sediments, how is the organotin species partitioned between the nephloid layer, the interstitial pore water and the subsurface layers? Can the behavior of organotin in different localities be described by similar partitioning coefficients?

Studies are needed to provide information on:

- What portion of TBT introduced into the environment from antifouling paint remains in solution in the water, in the surface microlayer and in the sediment?
- To what extent does TBT move with movement of bottom and suspended sediments, either by dredge spoil disposal or storm induced resuspension of sediments?
- What is the role of physical parameters on the distribution and concentration of TBT, including winds, waves, tidal cycles and turbidity maximums?
- Is there a biological component to TBT transport, is it being distributed as tissue burden or absorbed on external surfaces of planktonic or nektonic organisms?
- What are the effects of seasonal variations in temperature and salinity on leaching rates of TBT in antifouling paints?
- How rapidly does TBT and its degradation products accumulate or degrade in water, aerobic or anaerobic sediments from a seasonal perspective?
- Can the behavior of TBT in different localities be described with similar partitioning coefficients?

5.2.1.3 Bioavailability

Current research has focused on the filter feeding molluscs and the carnivorous gastropods. The deposit feeding molluscs and the polychaete/oligochaete worms are important components in the diet of many fish. These worms are feeding on material that has the strongest affinity for butyltins. These deposit feeders may be a significant pathway to the transfer of butyltin from the sediment into the food chain. An additional component in the consideration of bioavailability is the role played by the bacteria in sequestering, concentrating and metabolizing TBT. Bacteria are a food source for deposit feeding organisms. What is their role in the transfer of TBT from the water or from the sediment into the food chain?

Studies are needed to provide more information on:

- What are the roles of bacterial and other microorganisms in the availability of TBT to marine organisms?
- How available to the biota is tributyltin in the surface microlayer or the water column?

- How available to the biological community are organotins adsorbed on suspended or bottom sediments?

- Is the tributyltin in planktonic cells or on the surface membrane available to the consumer organisms or is it eliminated?

- Do pelagic birds feeding on neustonic organisms increase their risk of exposure to TBT? Some species of pelagic birds move into coastal waters seasonally. Does this seasonal migration provide a significant pathway to transport TBT beyond coastal waters?

- What is the relative bioavailability of butyltin compounds and metabolites from various sources such as spilled liquid paint, paint sanding dust, paint chips and scrapping, compared with leaching directly from the immersed cured paint film?

5.2.1.4 Bioaccumulation/Biomagnification

To date, the only documented path for butyltin loadings in vertebrates other than man is direct absorption from the water. No published studies are available concerning TBT levels in birds such as oyster-catchers or gulls which are known to feed on the type of invertebrates shown to accumulate TBT and its degradation products in their tissues.

Studies are needed to provide more information on:

- What are the key organisms in the bioaccumulation of TBT from the water and from the sediment?

- To what extent is biomagnification of TBT observed in the coastal food chain?

- What are the bioconcentration rates and feeding pathways from the lower trophic level organisms through sea birds and mammals?

5.2.1.5 Degradation

Identification of organisms and mechanisms responsible for degradation of organotins and the different metabolic results produced by different metabolic pathways (e.g., production of methylated butyltins vs. dibutyltins and monobutyltins) are critical. Studies should also focus more on the roles played by phytoplankton and bacteria.

Studies are needed to provide more information on:

- How do changes in salinity or temperature affect the biological and chemical degradation rates of TBT in marine or estuarine waters?

- Which is more important in the degradation of TBT in the surface microlayer, UV light or phytoplankton?

- What are the most important photosynthetic organisms for degrading TBT in the water column and under what environmental circumstances does degradation occur?

- What environmental conditions bring about maximum degradation rates?

5.2.1.6 Exposure Pathways

It is very probable that exposure pathways are one of the critical functions in relating the high toxicity of extremely low concentrations of TBT to certain organisms. Whereas the water column concentration may only be a few ng/l, the surface microlayer or suspended sediment levels can be 2 or 3 orders of magnitude higher. Therefore the actual dose level to the organism is not directly related to the water column concentration but to concentration mechanisms in specific critical pathways.

Studies are needed to provide more information on:

- What are the critical exposure pathways via the surface microlayer, suspended particulate material, sediments, pore water, water column, and/or food webs which affect specific organisms of concern?

- What are the effects of exposure to methylated butyltin vs. butyltin in the water and the sediment? This is important because bacterial products of metabolic debutylation of TBT include methyl-dibutyltin and methyl-monobutyltin, and algal metabolic debutylation products include dibutyl and monobutyltin.

5.2.2 Effects

The correlation of laboratory toxicity studies to effects found in the field will allow for field dose response estimates and cause and effect relationships. TBT and related organotins are toxic to certain organisms in trace quantities because of the characteristics of the physiology of these organisms and critical pathways as previously discussed. For example, the relative lack of mixed function oxidase systems in the bivalve molluscs does not permit them to purge themselves of TBT loadings as readily as other organisms. The mode of action of TBT is strongly membrane-oriented. To determine nonlethal but detrimental effects, toxicity testing in the field and laboratory will have to become more sophisticated and focused on physiological processes, in particular the reproductive processes. The case in point is the gastropod molluscs such as the dogwhelk, Nucella lapillus. Dogwhelk populations are in jeopardy due to reproductive failure even though the ambient concentrations are well below the lethal limit for individuals. A great deal of effort within the Chesapeake Bay has been expended to try to identify the cause or causes of seriously depressed recruitment of the oyster <u>Crassostrea virginica</u>. Individual oysters seem healthy enough but the reproduction has been so low over the past decade that the industry is in dire economic straits. The State of Maryland is funding an oyster relocation program. Oysters have been removed from oyster bars where reproduction is still occurring to supplement the populations of those oyster bars where only adults are found.

5.2.2.1 Public Health

The principal route of concern to public health for tributyltin is through contact with the paint as an aerosol or liquid during application or removal. Studies are needed to provide information on:

- o What are the most effective means to prevent dermal and respiratory exposure to TBT in paints during application or removal?
- o Is an acceptable daily intake (ADI) of 3200 ng/kg of body weight, adequate to protect the health of seafood-consuming public?
- o Are there individuals or specific conditions (e.g. pregnancy) which increase the risk of health effects from TBT in antifouling paint?

5.2.2.2 Toxicity Studies

The issues provoking most discussions regarding laboratory toxicity testing are: the need to know the actual butyltin species present and the actual amounts in exposure solutions, and the need to better understand the interactions of butyltins with sediment and the sediment dwelling biological community.

The EPA in its special review has accumulated a significant body of literature describing chronic toxic effects, lesions and tissue abnormalities as well as behavioral aberrations resulting from exposure to TBT in solution. As the ability to determine the actual flow through concentrations in the nanogram per liter range is improved, toxicity testing can be refined to the point where a true no effects level [NO-EL] can be determined for organotin compounds. Studies are also needed that focus on low-level physiological end-points determined by chronic exposure testing over the full life cycle of the organism. Testing for such effects as reproductive success, gametogenesis, imposex, calcification mechanism, and suppression of the immune response system.

TBT and related organotins have been found to be very toxic to molluscs in trace quantities because of the characteristics of the physiology of these organisms. To determine nonlethal but detrimental effects, toxicity testing must become more sophisticated and focused on physiological processes.

Studies are needed to provide more information on:

- How much of each butyltin species is actually present in the exposure solution at the time the bioassay is conducted?
- What concentrations of TBT elicit selected responses along the continuum from successfully counteracting the toxin to the complete overwhelming of homostatic mechanisms?
- What are the low level physiological effects on molluscs of chronic exposure to TBT extending over the full life cycle of the mollusc?
- What are the effects on gametogenesis and other aspects of reproductive success in molluscs during chronic exposure to TBT extending over the full life cycle of the mollusc?
- What are the effects on the calcification mechanism of molluscs during chronic exposure to TBT extending over the full life cycle of the mollusc?
- What are the mechanisms inducing imposex associated with chronic exposure to TBT extending over the full life cycle of the mollusc?
- What are the mechanisms inducing suppression of the immune response system due to chronic exposure to TBT over the full life cycle of the mollusc?
- What is the true no effects level (NO-EL) of TBT in coastal waters with respect to molluscs? With respect to fish?
- Can the coastal ecosystem response to the toxin (TBT) be adequately represented by toxicity tests on single species?
- Would mesocosm or microcosm community response to the toxin be representative of the response of the coastal ecosystem to TBT?

5.2.3 Measurement and Monitoring

More attention needs to be paid to developing rapid, sensitive and precise laboratory techniques involving measurement of substances at ng/l concentrations. This is the cornerstone upon which all the other research questions reset. Without the ability to accurately measure and speciate organotins, the research community will not be able to delineate exact cause and effect relationships in the laboratory or the field.

5.2.3.1 Analytical Methods

It is critical that rapid and inexpensive advanced analytical methodologies or protocols for the determination of ultratrace butyl- and mixed butylmethltin species at the ng/l level be developed for marine and estuarine waters and in tissues and sediments.

Studies are needed to provide more information on:

- What protocols are needed for the development of rapid, inexpensive and accurate analytical methodologies for organotins.
- What advanced analytical methodologies or protocols for determining butyl- and mixed butylmethyltin species at ng/l concentrations can be used in sediment?
- What analytical methodologies for determining butyl- or mixed butylmethyltin species at the ng/l concentrations can be used in tissue?

5.2.3.2 Standard Reference Materials (SRM's)

A very high priority should be given to the development and production of certified organotin reference standards or materials for calibration and intercalibration of analytical methods for water, sediment and tissue, as a mixed reference material for TBT and metabolites.

Studies are needed to provide more information on:

- What are the necessary standard reference materials necessary for calibration of laboratory instruments and methods to measure TBT at ng/l concentrations?
- In addition to standard reference materials for water, sediment, and tissue, what other SRM's are required to adequately monitor TBT in the environment?
- What additional mixtures of standard reference materials are needed in addition to mixtures of MBT, DBT, and TBT?

5.3 RECOMMENDATIONS FOR FUTURE RESEARCH

In order to develop sound policy and regulatory actions, policy and decision makers need clear statements of facts and problems. The scientific community cannot at the present time predict what the consequences to the environment would be for any given control strategy. The experience of regulatory actions in the United Kingdom is illustrative. The initial attempt was to reduce TBT loadings in the environment by a combination of public education and a limitation of the tin content of paints on a weight/percent basis. The result was a dramatic 50% reduction in the concentrations of TBT in the water column. However, that reduction was insufficient to bring the TBT loadings below the levels known to be harmful to the most sensitive species. Therefore, a second, more stringent round of legislation was required to protect the environment. The use of TBT in any paint applied to boats smaller than 25 meters length was prohibited (with the exception of aluminum-hulled vessels). The results of the second restriction on TBT paint use have not yet been determined.

At present, the U.S. Congress and many of the coastal states have adopted or are considering legislation and/or regulations that should reduce inputs of TBT to the marine environment. However, no legislation is being considered that will totally eliminate organotin paint usage. Owing to the serious public concern about the problem, TBT contamination in estuaries will continue to be a management and research issue, even after legislation is passed and strategies have been implemented to significantly reduce or eliminate certain organotin sources. Various aspects relating to the sources, fates, and effects of TBT in the marine environment are still not well understood or well documented. Therefore, research and monitoring activities to address these information gaps are necessary and should continue in the future.

A summary of the highest priority areas which continuing research, development, and monitoring should address is as follows:

- o Identify specific and critical exposure pathways of TBT to organisms at risk. In particular, the role of the surface microlayer, suspended and bottom sediments, pore water, and microorganisms.

- o Identify the mechanisms by which organisms concentrate TBT.

- o Identify and quantify key factors and mechanisms that control the degradation of TBT.

- o Improve detection and analysis methods to provide rapid and accurate measurements of butyltin species in ng/l concentrations.

- o Develop necessary Standard Reference Materials to allow intercalibration between laboratories and methods.

APPENDIX

International Organotin Bibliography

This bibliography has been prepared as a reference document for organotin compounds as related to the environmental scope of this NOAA Technical Report. It includes the papers cited in the body of the Report and additional references not cited. These references have been identified through Science Applications International Corporation's direct access to online computerized literature data bases, and with the assistance of David S. Moulder of the Marine Pollution Information Centre, of the Marine Biological Association of the United Kingdom, at Plymouth. An extensive list of references from the gray literature have also been included to make this bibliography as comprehensive as possible to enhance its value to future users. We appreciate notification of any corrections and/or additions.

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