

Human Exposure, Biomarkers, and Fate of Organotins in the Environment

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Contents

| | | |
|-----|---|----|
| 1 | Introduction | 28 |
| 2 | Routes of Human Exposure to the Organotins | 29 |
| 3 | Distribution of the Organotins in the Environment | 30 |
| 3.1 | Organotin in Aquatic Systems | 30 |
| 3.2 | Organotin in Sediments | 31 |
| 3.3 | Organotin in Organisms | 32 |
| 3.4 | Organotin in Soils | 33 |
| 3.5 | Effects of Organotins in the Environment | 34 |
| 4 | Fate of Organotins in the Environment | 34 |
| 4.1 | Degradation | 35 |
| 4.2 | Bioaccumulation | 36 |
| 4.3 | Sorption of the Organotins and Their Biological Effects | 37 |
| 4.4 | Biomethylation | 37 |
| 5 | Fate of Organotins in Marine Invertebrates | 38 |
| 5.1 | Bioaccumulation in Marine Invertebrates | 38 |
| 5.2 | Toxicity to Marine Invertebrates | 39 |
| 6 | The Role of Biomarkers | 40 |
| 6.1 | The Significance and Utility of Biomarkers | 41 |
| 6.2 | Biomarkers of TBT in Marine Invertebrates | 41 |
| 7 | The Regulation of Organotin Compounds | 44 |
| 8 | Conclusions | 47 |
| 9 | Summary | 48 |
| | References | 49 |

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1 Introduction

Organotin compounds (OTCs) are organic derivatives of tin (Sn^{4+}) and are characterized by the presence of covalent bonds between three carbon atoms and a tin atom. The organotins are designated as mono-, di-, tri-, or tetra-organotin compounds and have the general formula ($n\text{-C}_4\text{H}_9$), Sn-X , where X is an anion or a group linked covalently through a hetero-atom (Dubey and Roy 2003; Okoro et al. 2011). Organotin pollution in the aquatic environment is of global concern; two tri-organotin compound groups, the tributyltins and triphenyltins, are toxic to aquatic life (Fent 1996) and are used worldwide not only as biocides in antifouling paints but also as preserving agents for wood and timber, and as agricultural fungicides. These uses result in direct release to water, with consequential uptake and accumulation in aquatic fauna (Harino et al. 2000).

Because the organotins are used as antifouling agents in boat paints, they are common contaminants of marine and freshwater ecosystems. Fent and Muller (1991) detected concentrations of selected organotin species in a wastewater treatment plant in Zurich, Switzerland. It was discovered that municipal wastewater and sewage sludge contain considerable amounts of organotin species [tributyltin (TBT), butyltins (BTs), dibutyltins (DBTs), and monobutyltins (MBTs)]. MBT and DBT occurred as degradation products of TBT, and they are known to have entered the treatment plant as a contaminant of municipal wastewater. Moreover, the leaching and weathering of polyvinyl chloride (PVC) materials that contain OTCs may also result in their release on a large scale (Becker et al. 1997).

Organotin first became a topic of broad interest when it was discovered that antifouling paints were causing the decline of coastal marine mollusks. Such reports first surfaced in the 1970s when the phenomenon of imposex was reported for *Nucella lapillus* in the UK (Blanca 2008). As awareness of the effects of TBT has grown, global efforts to address the problem have increased, and measures have been taken by authorities to protect the aquatic environment from organotins. Hence, the use of TBT on small boats was prohibited by many countries beginning in the mid-1980s (Konstantious and Albanis 2004).

Because detection of environmental contaminants is so critical to their regulation, many methods have been developed to analyze for the OTCs in environmental media (Morabito and Quevauviller 2002). The most successful methods are those that involve separation of TBT and its degradation products by gas chromatography (GC); GC is sensitive and has both high resolving power and selective detection when coupled with mass spectrometry (Delucchi et al. 2007). Sentosa et al. (2009) used an ion-pair reversed-phase chromatography (IR-RP) technique to analyze for speciation of DBT, TBT, and triphenyltin (TPT). These three species were successfully resolved using an ion-pair reversed-phase chromatography column. The eluates were detected online by using a hydride generation-quartz furnace atomic absorption spectrometry (HG-QFAAS) method. The eluent consisted of a mixture of methanol, water, and acetic acid that had a composition of 80:19:1 and contained 1.0 mol L^{-1} of decane sulfonate acid as the ion pairing reagent. The pH of the eluent was adjusted to $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. All species were successfully resolved

under these conditions. The capacity factors (k^1) of DBT, TBT, and TPT were 0.27, 2.54, and 5.92, respectively. The resolution (R_s) values of DBT–TBT and TBT–TPT were 9.76 and 3.50, respectively. These values demonstrate the effectiveness of this chromatographic system to resolve the OTCs.

Aquatic organisms exposed to the OTCs have shown various effects. In many marine species, such effects include larval mortality (Bella et al. 2005a) and impairment in growth, development, reproduction, and survival (Haggera et al. 2005). Moreover, the results of several experiments have indicated that there is or may be a spectrum of potential adverse chronic systemic effects of organotin exposure in animals and humans. The type of damage that has been sustained by exposure to organotins in animal testing includes immunosuppression, endocrine effects, neurotoxic effects, and effects on enzymatic activity. In addition to being bioaccumulative, exposure to organotins may also produce the following types of damage: ocular, dermal, cardiovascular, pulmonary, gastrointestinal, blood dyscrasias, reproductive developmental, liver, kidney, and possibly carcinogenic effects (WHO-IPCS 1999; EU-SCOOP 2006; Nakanish 2007).

Although the fate and chemical characteristics of the organotin compounds have been much investigated in developed countries, only limited data are available from Africa. The aim of this chapter is to review the distribution, fate, and measurement of organotins in the environment.

2 Routes of Human Exposure to the Organotins

The OTCs constitute a large class of compounds that have widely varying properties and that have been used for many purposes. The global production, in 2003, was approximately 40,000 t (EVISA 2010). Annual production at such levels, the wide spread use of the OTCs, and their high stability in marine water have led to their presence as contaminants in various ecosystems.

Consumption of contaminated drinking water, beverages, and, in particular, marine food is an important route of human exposure to TBT (Forsyth and Jay 1997; Azuela and Vasconcelos 2002; Chieu et al. 2002). Marine fishery products have been reported to contain high concentrations of OTCs. Therefore, the human diet is expected to have some amounts of the OTCs that will result in human tissue and blood residues (Lo et al. 2003; EFSA 2004; ATSDR 2005; EU-SCOOP 2006). Recent results have shown that fish and fish products are generally the main source of OTCs in the diet; OTCs were detected in whole blood samples of fishermen and their family members, and an association existed of the levels found with age, gender, and level of fish consumption (Pann et al. 2008). These researchers concluded that their results give strong support to the hypothesis that fish constitute the main source of TPT for humans in Finland.

Sadiki and Williams (1999) analyzed Canadian drinking water samples that had been distributed through PVC (polyvinylchloride) pipes. These authors confirmed the presence of OTCs in some drinking water samples collected from residential

houses and commercial buildings that were supplied by recently installed PVC piping. The contamination levels detected ranged up to 291 ng (Sn) L⁻¹ MMT (monomethyltin trichloride), 49.1 ng (Sn) L⁻¹ DMT, 28.5 ng (Sn) L⁻¹ MBT, and 52.3 ng L⁻¹ (Sn) DBT (dimethyltin dichloride).

Takahashi et al. (1999) reported that several household commodities composed of polymethane, plastic polymers, and silicones, such as diaper covers, sanitary napkins, certain brands of gloves, cellophane wrap, sponges, and baking parchments, contained amounts (up to the $\mu\text{g g}^{-1}$ level) of several organotin compounds. DBT was detected in treated turkey livers at levels between <0.2 and 6 $\mu\text{g g}^{-1}$ when DBT derivatives were used as an anthelmintic and coccidiostat in poultry production (Tsuda et al. 1995).

In the UK, a survey showed that organotin levels were generally low in commercial species sampled from many locations throughout the country, and it was suggested that levels found did not present a health risk (FSA 2005). Lo et al. (2003) conducted a study in Germany using eight human volunteers (4 males and 4 females aged 18–54). The serum of the tested individuals exhibited levels of organotin that were below the limits of detection, and TBT and TPT were found at concentration ranges between 0.02–0.05 and 0.17–0.67 $\mu\text{g L}^{-1}$, respectively. Alzieu (2000) reported that contact exposure to TBT causes irritation of the eyes and skin, potentially leading to severe dermatitis. Because of these properties, it is difficult to guarantee a safe environmental level for TBT. Therefore, use of TBT as a biocide in aquatic systems may well be incompatible with the protection of the ecosystem and with certain marine activities such as oyster farming.

3 Distribution of the Organotins in the Environment

Because of the extensive use of organotins in numerous human activities, large amounts of the OTCs have been introduced to various ecosystems (Blunden and Evans 1990). Significant concentrations of the organotins and their metabolites have been detected in all phases of the aquatic environment: water, suspended matter, sediments, and biomass. The levels of organotins detected in the atmosphere are very low (Blunden and Evans 1990). Among the OTCs, even trace levels of TBT in the environment may be of concern, because it has been considered among the most hazardous compounds to marine organisms (Wagner 1993; Maguire 1996).

3.1 Organotin in Aquatic Systems

OTCs are of concern because of their high toxicity, widespread use, direct input into the environment, and their relatively high persistence. The OTCs enter the aquatic system by many routes. To date, organotin research has been restricted mainly to regions having high shipping volumes, harbors, and/or shipyards, because the primary way in which organotins reach the environment is through use as antifouling

agents. TBT in antifouling paints is directly emitted into water, resulting in contaminated water, marine sediments, lakes, and coastal areas (Hoch 2001). As expected, the butyltins have also been detected as residues in marine mammals.

The concentrations of hepatic butyltin reported in fireless porpoise, collected from the Seto Inland Sea, Japan, were as high as 10,000 ng g⁻¹ wet wt (wwt), whereas the levels in crustaceans taken from the Japanese coastline ranged from 110 to 5200 ng g⁻¹ wwt (Tanabe et al. 1998). Evidence exists to show that legislation introduced to govern the use of TBT in antifouling paints has reduced aquatic concentrations of this contaminant (Fent and Hunn 1995; Dowson et al. 1993).

3.2 Organotin in Sediments

Triorganotin compounds have low aqueous solubility and low mobility, and are easily adsorbed onto suspended particulate matter (SPM). The deposition of SPM leads to the accumulation of considerable amounts of trisubstituted organotins and their degradation products in sediment (Hoch 2001). Several studies have been conducted on organotin pollution of river-, lake-, and harbor-sediments. Brack (2002) investigated organotin compounds in sediments from the Goteborg harbor, Sweden, and reported that their levels ranged from 17 to 366 ng/g dwt for TBT and from 1.5 to 71 ng/g dwt for TPT. These results were similar to those recorded from other harbors and marinas, and from an earlier study in the Goteborg harbor, which is located in the estuary (Brack 2002). DBT, MBT, DPT (diphenyltin), and MPT (monophenyltin), which are the degradation products of TBT and TPT, were also found in this harbor. TBT concentrations are the highest in the inner harbor and in the upper ~10-cm sediment layer. This indicates that there is a risk of TBT mobilization from the sediment surface, which may be exacerbated by the frequently disturbed harbor environment.

Takashi et al. (1997) studied the chemical speciation of organotin compounds that exist in sediments at a marina in Tokyo, Japan. These authors reported that >20 organotin compounds, including biodegraded ones, existed at the sampled site, and their identity was confirmed against authentic standards using gas chromatography/mass spectrometry (GC-MS) and a GC/atomic emission detection (GC-AED) system. Eleven organotin compounds were found in the Technical TBTChloride. Among them were unexpected organotin compounds, such as di-*n*-butyl (2-methylhexyl)tin chloride and di-*n*-butyloctyltin chloride.

The half-life of TBT in sediments is in the range of years. The accumulation of organotin on suspended particulates or sediments makes them available to filter- or sediment-feeding organisms. Resuspension of contaminated sediment offers an additional risk to aquatic organisms (Hoch 2001). The accumulation in sediments of butyltin and phenyltin species constitutes an ongoing pollution source, because residues of these compounds are slowly released into aquatic systems (Chiron et al. 2000; Ceulemans and Adams 1995; Kuballa et al. 1996).

3.3 Organotin in Organisms

Previous studies have revealed that high concentrations of toxic organotin compounds exist in some fish and aquatic invertebrates, such as gastropods and filter-feeding organisms. The presence of high concentrations of the toxic organotin residues in invertebrates results in imposex. Little is known about the accumulation and toxic effects of organotin in high trophic-level vertebrate predators; hence, their ability to disrupt endocrines of organisms worldwide is of concern. Humans are also exposed to the OTCs. The major route of such exposure is through food ingestion or exposure to household materials containing or contaminated by the organotins.

Hu et al. (2006) studied trophic magnification of TPT in a marine food web of Bohai Bay, North China; five benthic invertebrate species and six fish species were investigated. The concentrations of TPT detected in marine fish were, as expected, higher than those of TBT. A positive relationship was also found between trophic level and the concentration of TPT, indicating trophic magnification (TMF) of TPT in this food web.

Analysis of organotin residues in water and surface sediment samples from the bay revealed low environmental inputs of TPT, which indicated that the high concentrations of TPT found in fish from Bohai Bay resulted from food web magnification. The species in the study were primary producers (phytoplankton/ seston and zooplankton) and comprised the following: five invertebrates: crab (*Portunus trituberculatus*), burrowing shrimp (*Upogebia* sp.), short-necked clam (*Ruditapes pluillippinarium*), veined rapa whelk (*Rapana venosa*), and bay scallop (*Argopecten irradians*). The other six species included the weever (*Lateolabrax japonicus*), catfish, (*Chateau - ichthys stigmatias*), bartail flathead (*Platycephalus indicus*), flower croakers (*Nibea albiflora*), wolfish (*Odontamblyopus rubicundus*), and mullet (*Lisa so-iuy*).

Zhang et al. (2003) worked on the butyltins in sediments and biota collected from the Pearl River Delta, South China. Both sediment and biota samples were collected and assessed using GC-AED analysis. The concentrations of TBT detected in the sediments ranged from 1.7 to 379.7 ng/g dwt. Shipping activities in the bay were thought to be responsible for the spatial distribution of the detected residues. A good linear relationship was observed between the residue ratios of DBT, TBT, and MBT samples taken from the Pearl River and associated estuary, and from the West River, suggesting a common source for the residues. All TBT concentrations in fish, mussel, and shrimp samples, which were collected in the study, retained residues that were below the seafood tolerable average residue level (TARL).

Meng-Pei et al. (2003) investigated the accumulation of OTCs in Pacific oysters (*Crassostrea gigas*), and both butyltin and phenyltin residues were quantified in this species. These oysters were collected during different seasons at several aquaculture sites, located along the west coast of Taiwan. Butyltin compounds were detected in oyster samples at all but one site. MPT and DPT compounds were not detected in any of the samples. The average concentration range of MBT, DBT, TBT, and tetrabutyltins (T₄BTs) in the sampled oysters was from non-detectable (n.d.) to 406 ± 12.7, n.d. to 280.9 ± 15.3, n.d. to 417.2 ± 11.2, and n.d. to 85.8 ± 8.3 ng g⁻¹

(wwt), respectively. The concentration of TBT compounds detected in the oysters varied both spatially and temporally.

Lisicio et al. (2009) used two different analytical methods to determine levels of organotin compounds in marine organisms. Both methods involved extraction by tropolone, derivatization, and purification on FlorisilTM, followed by analysis using GC-MS. The main difference between the two procedures used was in the derivatization step: one employed a Grignard reagent (*n*-pentylmagnesium bromide), whereas the other method used sodium tetraethylborate (STEB). All compounds analyzed showed lower detection limits with STEB derivatization, particularly with TBT. Lisicio et al. (2009) also performed an *in vivo* experiment on TBT. He exposed one mussel species (*Mytilus galloprovincialis*) to known amounts of TBT for several days; both control and contaminated tissues were then analyzed using the STEB derivatization method. Results indicated bioaccumulation of TBT, which accumulated especially in the gills.

Albalat et al. (2002) assessed the levels of organotin pollution along the Polish coast (Baltic Sea), using mussels and fish as sentinel organisms. TBT, MBT, and DBT and TPT were the target compounds for which monitoring was performed. The bioaccumulation patterns found for the butyltin and phenyltin compounds varied substantially. The butyltins were detected in mussels at all sampled stations. Mussels sampled in the Gulf of Gdansk had the highest residue levels (68 ng/g wwt, measured as Sn) and had elevated TBT/DBT ratios, which suggested that there had been recent inputs of TBT to the area. Additionally, flatfish were sampled in the Gulf of Gdansk, and several tissues (liver, digestive tube, and gills) were individually analyzed. Although TPT residues were not detected in mussels in the Gulf of Gdansk, they were present in fish tissues. The highest organotin concentrations were observed in the liver (69 ng/g wwt, measured as Sn) of fish caught near the port at Gdansk. Relatively high concentrations were observed in the digestive tube, suggesting that organotin-contaminated food had been ingested, and food sources comprised an important uptake route of those compounds by mussels. Cooke (2002) studied the effect of organotins on human aromatase activity *in vitro*. TBT, at concentrations of 12 and 59 μM , and DBT, at a concentration of 74 μM , inhibited aromatase activity *in vitro*. In contrast, other organotins, such as MBT and the tri-, di-, and mono-oxytins, were without effect.

3.4 Organotin in Soils

TPT acetate and TPT hydroxide have increasingly been used as soil treatment fungicides worldwide to treat a variety of crops. Such treatments have resulted in increasing levels of TPT acetate and TPT hydroxide in soils. Few studies have been conducted in which the abundance and persistence of TPT in soil has been measured. Kannan and Lee (1996) conducted a study on the foliage and soils of Pecan trees after application of TPT hydroxide. Their study results revealed that total phenyltin (MPT, DPT, and TPT) levels in foliage and soils ranged between

72 and 76 $\mu\text{g g}^{-1}$ (Sn) dwt. In addition, TPT residues were reported in fish (blue gill, largemouth bass, and channel catfish) taken from a pond near a recently treated Pecan orchard (Visoottiviseth et al. 1995). The vapor loss during field spraying of TPT hydroxide is negligible because of its low vapor pressure (1×10^{-7} mm Hg at 25°C). But TPT is photolytically degraded in soils only if it is near the soil surface, where light can penetrate (Visoottiviseth et al. 1995).

3.5 Effects of Organotins in the Environment

The European Food Safety Authority (EFSA 2004) has assessed the health risk to consumers associated with exposure to the OTCs. It was concluded that the critical toxicological endpoint is immunotoxicity. Because different OTCs are similar to one another, they are grouped for risk assessment purposes. The tolerable daily intake (TDI) for the group was established as 250 ng/kg body weight and applied to the sum of residues that contain TBT, DBT, TPT, and di-*n*-octyltin (DOT). Alzieu (2000) reported that contact exposure to TBT causes irritation of the eyes and skin, potentially leading to severe dermatitis. Because of these properties, it is difficult to guarantee a safe environmental level for TBT. This means that its use as a biocide in aquatic systems could be incompatible with protecting ecosystems, preventing damage to certain marine activities, such as oyster farming.

Organotin compounds produce various known effects on aquatic organisms when they are exposed to these substances. These effects include larval mortality (Bella et al. 2005a, b), growth impairment, developmental and reproductive effects, and survival reduction in many marine species (Haggera et al. 2005). In addition, the results of animal experiments have suggested what the spectrum of potential adverse chronic effects of the organotins on humans may be. Among effects that could be damaging to humans are primary immunosuppression, endocrinopathy, neurotoxicity, metabolic effects, and effects on enzymatic activity. OTC exposure may also induce adverse effects on the eyes, the skin, the blood (dyscrasias), liver, and kidney, and on the following organ systems: cardiovascular, upper respiratory, gastrointestinal, and reproductive/developmental. Moreover, there is a risk of bioaccumulation and possibly carcinogenicity from OTC exposure (WHO-IPCS 1999; EU-SCOOP 2006; Nakanish 2007).

4 Fate of Organotins in the Environment

There have been several investigations into how the OTC compounds are distributed and degraded in the natural environment, and such information is both useful and important (Hoch 2001).

The OTCs enter ecosystems after marine or agricultural applications or after industrial use and release. However, research to date has focused only on

tributyl- and triphenyl-tin pollution, because these compounds directly enter the environment through industrial use of organotin biocides. Recently, sewage sludge, municipal and industrial wastewater, and landfill leachates have also been discovered to constitute major sources of environmental organotins (Hoch 2001). Once these compounds become ecosystem pollutants, they may persist for long periods. How long they persist is a function of the status of various removal mechanisms. Removal mechanisms include physical ones (adsorption to suspended solids and sediments), chemical ones (i.e., chemical and photochemical degradation processes), and biological ones (i.e., uptake and biological degradation).

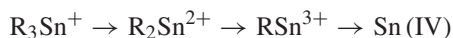
4.1 Degradation

The degradation of organotins in the environment occurs as a progressive elimination of organic groups from Sn cations. As successive organic groups are removed, toxicity is generally reduced. Degradation is achieved by both biotic and abiotic factors. Photodecomposition by ultraviolet (UV) light is the most important abiotic degradation process. In aquatic and terrestrial ecosystems, biological processes are the most important factor effecting degradation of the OTCs. Research has shown that organotin degradation is mediated by microorganisms; however, little information is available about the mechanism by which such degradation occurs. Also lacking is an understanding of the mechanism by which microbes are tolerant to the OTCs or the role played in degradation by anionic radicals (Dubey and Roy 2003). Biotic processes probably represent the most significant mechanisms by which TBT degradation occurs in soil, in freshwater, and in marine and estuarine environments (Dowson et al. 1993).

Research interest on the bioaccumulation and biodegradation of organotin in the water column, in sediments, and in marine organisms has been stimulated by the paucity of data available in these areas. Organotin compounds are known to be present in three main compartments of aquatic ecosystems: the surface microlayer, the water column, and at the surface layer of bottom sediments (Clark et al. 1988). TBT degrades rapidly to DBT and MBT, with half-lives of several days (Dubey and Roy 2003). The half-life value for the decline of TBT ($0.03 \mu\text{g}^{-1}$) from a clean water site was 9 and 19 days for light and dark treatments, respectively (Dubey and Roy 2003). A first-order multistep kinetic model was used to describe the sequential degradation rate and pattern of TBT to form DBT, MBT, and tin (IV). Using this model, the half-lives of TBT, DBT, and MBT were 2.1, 1.9, and 1.1 years, respectively (Sarradin et al. 1995).

Abiotic degradation processes constitute other potential pathways for the degradation of TBT from soil, sediments, and water columns. Such abiotic processes may attack the Sn–C bonds by several different processes. Examples are UV irradiation-facilitated breakdown, chemical cleavage, gamma irradiation, and thermal cleavage. Only UV radiation (300–350 nm), in which the energy level corresponds to about 300 kJ mol^{-1} , is likely to cause direct photolysis of TBT. Because UV light does not

penetrate deeply, photolysis is expected to occur only in the upper few centimeters of the water column (Clark et al. 1988). Maureen and Willingham (1996) reported that the TBT degradation process may be explained as a sequential loss of an alkyl groups from TBT to form toxic inorganic tin, as depicted immediately below:



TPT has low mobility, low solubility, and a strong ability to bind to soil and sediment in the aquatic environment (Blunden et al. 1986). For unbound organotins that can be reached by chemical action, chemical cleavage may be mediated by mineral acids, carboxylic acids, and alkali metals. These agents are capable of heterolytically cleaving Sn–C bonds, through both nucleophilic and electrophilic reactions (Blunden and Evans 1990). Albalat et al. (2002) have studied the biodegradation of the organotins. They monitored levels of TBT, MBT, and DBT at 10 stations along the Polish coast (Baltic Sea). One mussel (*Mytilus edulis*) and one fish species (*Platichthys flesus*) were used as sentinel organisms. The bioaccumulation patterns of butyltin and phenyltin compounds varied substantially. Butyltin compounds were detected in mussels from all sampled stations. TPT was not detected in mussel but was found in fish, which indicated that ingesting organotin-contaminated food was an important uptake route of those compounds in *P. flesus*. Paton et al. (2006) investigated the microbial and chemical degradation and toxicity of phenyltin compounds in soil. These authors discovered that the degradation of organotins was significantly slower in sterile soils vs. nonsterile soils. In nonsterilized soils, the half-life of TPT was 27 and 33 days at amendment levels of 10 and 20 mg kg⁻¹ Sn, respectively. There was an increase in observed toxicity as the degradation of triphenyltin proceeded. This phenomenon proved that the metabolite formed is either more bioavailable or more toxic than is the parent compound, or both.

4.2 Bioaccumulation

Lipophilicity is a criterion for the environmental persistence of organotins. Among the organotins, TBT is considered to be an important pollutant because of its extreme toxicity to several organisms and because of its tendency to bioaccumulate. Bacteria have been reported to display a remarkable ability to accumulate TBT. Marine bivalves are also able to accumulate significant amounts of TBT (up to 5 µg g⁻¹). But fish and crustaceans accumulate much lower amounts, owing to their possession of efficient enzymatic mechanisms to degrade TBT (Laughlin 1996). Absorption in mice is also low, and TBT is mainly excreted unchanged via the feces. Mammals and birds accumulate high levels of the butyltins in their organs and tissues (Iwata et al. 1995). In mammalian species, TBT compounds may be metabolized to DBT and related metabolites. An undetermined amount of this compound is known to remain in fat, liver, and kidney (Adeeko et al. 2003). Other researchers have undertaken studies to evaluate the bioaccumulation of organotins (Harino et al. 2005; Strand

et al. 2005; Azumi et al. 2007). Similar results to those of Adeeko et al. (2003) were recorded in these other studies.

4.3 Sorption of the Organotins and Their Biological Effects

In recent years, restrictions have been placed on the use of TBT on pleasure boats in Europe. Although considerable progress has been made in reducing TBT effects, they still continue to be observed in marine ecosystems. An essential source of contamination of TBT along the German North Sea and the Baltic Coast has been remobilization (by desorption) of the high TBT concentrations present in sediments (Langston and Popoe 1995).

A comparison of the burden of TBT in sediments to which snails and mussels are exposed gives rise to concern for conducting any future dredging and disposal of TBT-contaminated sediments (WWF 1995). Because suspended matter has a high affinity for organotin compounds, any perturbation of sediments by dredging may remobilize TBT and thereby substantively increase TBT residue levels in the water column. Presently, desorbed or actively remobilized TBT-contaminated sediment, in harbors and in some coastal areas, constitutes the main source of biologically available TBT (Langston and Popoe 1995).

Hongwen et al. (1996) investigated the adsorption behavior of eight organotin species and Sn^{4+} (SnCl_4) on estuarine sediments. They found that adsorption of the organotins varies greatly and depends on molecular structure. The order of adsorption coefficient for tin compounds in the studied sediment samples was as follows: tetra \rightarrow mono \rightarrow di \rightarrow triorganotins. Correlations of the log K values (using eight different structural parameters) showed that the electronic properties of the Sn atom constitute the principal factor controlling their adsorption behavior.

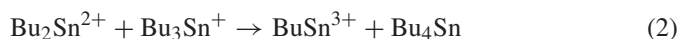
The mechanism by which the organotins are adsorbed is mainly through an ion exchange process and involves little lipophilic partitioning (Hongwen et al. 1996). Hermosin et al. (1993) reported the adsorption mechanisms of MBT to various clay minerals and found that its adsorption capacity for all clays was higher than the corresponding cation exchange capacity (CEC value).

Adsorption onto clay is important to the environmental distribution and fate of organotins, because research has shown that large proportions of organotin contaminants are associated with the clay fraction of particulate matter. Thus, soils and sediments may serve as traps for these toxic contaminants. Unfortunately, the number of studies conducted on the remobilization of adsorbed organotin from environmental media is still few (Hoch 2001).

4.4 Biomethylation

Methyltin compounds can be formed by processes that involve biomethylation. Several biotic and abiotic methylation agents exist. Methylcobalamin (CH_3B_{12}), the

methyl co-enzyme of vitamin B₁₂, is a carbanion donor that is able to convert inorganic Sn (IV) to several methyltin species (Hoch 2001). Methylcobalamin has been demethylated by SnCl₂ in aqueous HCl solution, in the presence of an oxidizing agent (Fe³⁺ or Co³⁺), to form a monomethyltin species. Methyl iodide (CH₃I) can also methylate tin species, whereas tin (IV) compounds do not so react. Chemical or biological processes are capable of methylating inorganic tin (II), Sn (IV), and methyltin derivatives under stimulated environmental conditions. Recently, methylation of butyltin species in sediments has been reported (Hoch 2001) and may arise from biological methylation of anthropogenic butyltins in the aquatic environment. Selected possible reactions of Sn–C include the following:



Biomethylation processes are of great ecological relevance, because some methylated metals have higher toxicity to aquatic organisms than does the inorganic metal (Hoch 2001).

5 Fate of Organotins in Marine Invertebrates

5.1 Bioaccumulation in Marine Invertebrates

Most research on TBT accumulation by marine invertebrates was concentrated on mollusks (bivalves) and crustaceans (decapods), because these groups dominate the ecological habitat and serve as important seafood resources (Laughlin 1996). Research conducted on TBT accumulation by marine invertebrates revealed that marine bivalves are able to accumulate significant amounts of TBT (up to > 5 μg g⁻¹) (Laughlin 1996). Azumi et al. (2007) studied the accumulation of organotin compounds at aquaculture sites in Korea. High concentrations of butyltin compounds (mono-, di-, and tri-butyltins) were detected, especially in the gills, hepatopancreas, and digestive tracts of sea squirt (*Halocynthia roretzi*).

Meng-Pei and Shin-Mei (2003) investigated levels of OTCs in Pacific oysters (*Crassostrea gigas*) collected from aquaculture sites. Butyltin compounds were detected in most samples, whereas no MPT and DPT compounds were detected. The average concentrations of monobutyl-, tributyl-, triphenyl-, and tetraphenyltins ranged from detectable (n.d.) to 406.6 ± 12.7, n.d. to 28.09 ± 15.3, n.d. to 417.2 ± 11.2, and n.d. to 85.8 ± 8.3 ng g⁻¹ (wwt), respectively.

The accumulation of OTCs also occurred in deep-sea organisms, namely gastropods (*Colliloconcha nankaiensis*), sea cucumbers (*Psychropotes verrucosa*),

galatheid crabs (*Munidopsis albatrossae* and *Munidopsis subsquamosa*), and bivalves (*Calyptogena tsubasa* and *Calyptogena nautilei*). High concentrations of BT and PT (phenyltin) compounds were observed in gastropods and sea cucumbers. The composition of BT in deep-sea organisms was calculated, and an increase in the MBT proportion was recorded, while a decline in DBT proportion was observed at higher trophic levels (Harino et al. 2005). Accumulation of organotins in marine invertebrates has also been reported by Harino et al. (2008). The concentration of OTC in seven species of dolphin (bottlenose, finless porpoise, Indo-Pacific hump-backed, long-backed common, Pantropical spotted, spinner and striped), which were stranded on the coast of Thailand, was measured. The ratio of the average of BT and PT compounds in tissues and organs was 16:1; average residue levels in tissues and organs for the dolphins were 152 and 62 $\mu\text{g kg}^{-1}$, respectively. The highest concentration of TBT was generally observed in the liver. No significant difference in the concentration of OTC between genders was observed. The concentrations of BTs in all organisms were high and of following order: whales > dugongs > dolphins. The concentrations of PTs in whales were higher than those in dolphins and dugongs. In general, it has been observed that species with a high rate of uptake or a low rate of metabolic conversion and elimination display relatively high bioaccumulation ratios (Meador and Rice 2001).

5.2 Toxicity to Marine Invertebrates

TBT causes impairments in growth and development, and induces reproductive failures, shell anomalies, and gel formation. It also causes chambering and high mortality, disturbs the energy metabolism of bivalves, and inhibits the activity of many enzymes; these effects reduce the survival of many species (Beaumont and Budd 1984; Haggera et al. 2005). TBT, as early as the 1970s, was known to be very toxic to many aquatic organisms (Blabber 1970; Smith 1981). The high toxicity of TBT is attributed to its effects on mitochondrial function (Blabber 1970; Smith 1981). The embryonic and larval stages of marine invertebrates are less tolerant to toxicants than are adults, and this difference has been used to assess the biological quality of marine water and sediments (Fent and Muller 1991).

TBT is known to have other toxic endpoints (Horiguchi et al. 1998), e.g., acute lethal toxicity in rock shell larvae (*Thais clavigera*). However, growth impairment is a much more sensitive endpoint for measuring exposure to TBT than is mortality (Meador and Rice 2001). TBT is known to inhibit oxidative phosphorylation, which affects cell metabolism by stimulating the production of adenosine diphosphate, and results in mitochondrial membrane malformation.

TBT affected larval development of bivalves (*C. tsubasa*) and caused sexual disturbances in gastropods (*C. nankaiensis*) at nanogram per liter levels in seawater. At a level of 1.0 ng L⁻¹, TBT caused masculinization in many female gastropods (*C. nankaiensis*), a phenomenon known as imposex. It also limits cell division in

phytoplankton and reproduction of zooplankton. TBT has been reported to induce shell calcification anomalies in the oyster *Crassostrea gigas* at a level of 2 ng L^{-1} and to disturb the reproduction of bivalve mollusks at 20 ng L^{-1} (Bella et al. 2005a). Ruiz et al. (1995) investigated the effect of TBT exposure on veliger larval development of the bivalve (*C. tsubasa*). They found that TBT contributed to the demise of clam populations by preventing successful and timely development of veliger larvae. TBT also affects the abundance and relative growth rates of male and female whelks around marinas (Gil et al. 2000).

6 The Role of Biomarkers

Pollution of the marine environment is a global concern because of the adverse effects caused by various contaminants, whose levels are growing at an alarming rate. Residues of many contaminants, such as the OTCs, continue to enter the natural environment and continue to accumulate in many organisms. Therefore, it is crucial that means to track both the presence and effects of such contaminants be developed. Biomarkers offer one important way in which environmental contaminate effects can be monitored.

The idea behind biomarkers is not a new concept but is a new name for a preexisting monitoring principle (Adams 1990). Biomarkers are defined as the measurements of body fluids, cells, or tissues that indicate, in biochemical or cellular terms, the presence of contaminants or the magnitude of the host response (Bodin et al. 2004). According to Van Gestel and Van Brummelen (1996), “biomarkers” are any biological response to an environmental chemical that is measured inside an organism or its products (urine, feces, hairs, feathers, etc.), and indicates a departure from the normal status. A response may result from a biochemical, a physiological, a histological, and/or a morphological (including appearance, pigmentation, and surface deformation) measurement of health, although behavioral effects are excluded. Hence, biomarkers cannot be used to measure effects in intact organisms or cause affected organisms to deviate from their normal status (Van Gestel and Van Brummelen 1996). Therefore, one can discern that biomarkers are potentially sensitive tools of immense importance for measuring biological effects that affect environmental quality (Sarkar et al. 2006).

Some authors claim that biomarkers may also be accommodated into whole animal studies (Ross et al. 2002; Magni et al. 2006) and may be specific to one pollutant or may be altered in response to either pollutant effects or the presence of natural stressors (Pfeifer et al. 2005). What is certain is that they are potentially very useful as prognostic and diagnostic early warning tests and offer the potential of specificity, sensitivity, and application to a wide range of organisms (Sarkar et al. 2006). The use of properly researched biomarkers is not limited to laboratory use but may be applied to field studies too. However, the initial development of biomarkers usually involves laboratory experimentation to first identify potential responses, and to establish causal mechanisms, before application to field use (Sarkar et al. 2006).

6.1 The Significance and Utility of Biomarkers

Biomarkers are used to evaluate the exposure effects of many different contaminants (i.e., metals, organic xenobiotics, and organometallic compounds) (Ross et al. 2002; Depledge and Fossil 1994). The most significant features of the use of biomarkers are summarized below:

1. They offer means to achieve sensitive detection of selected chemical stresses within organisms.
2. They generate insights on possible harmful effects that cannot be obtained from chemical analysis alone (Depledge and Fossil 1994).
3. They may be used to predict effects on invertebrate populations and communities (Largardic et al. 1994), and may help assess types or degree of environmental damage, or formulation of regulations to control such damage (Sarkar et al. 2006).
4. They offer means to identify interactions between contaminants and organisms, and measure sublethal effects (Sarkar et al. 2006).
5. They offer alternative ways of detecting the presence of both known and unknown contaminants (Sarkar et al. 2006).
6. They constitute a temporally and spatially integrated measure of the degree to which pollutants are bioavailable (Sarkar et al. 2006).
7. They may be used to establish important routes of exposure by application to species from different trophic levels and aid in designing strategies for intervention and remediation (Sarkar et al. 2006).

6.2 Biomarkers of TBT in Marine Invertebrates

Useful biomarkers have been developed to help monitor the effects of contaminants in marine invertebrates. Among these are the following biomarkers that have been used to assess the toxicity of TBT: metallothionein induction, acetyl cholinesterase inhibition, imposex, lysosomal enlargement, lysosomal membrane destabilization, peroxisome proliferation, lysosomal activity, genetic or molecular biomarkers, TBT-sensitive immunological biomarkers, apoptosis induction, phagocytic index, and amoebocytic index.

Some of these biomarkers are more useful than others. Below, we provide greater detail on prominent types of these.

6.2.1 Metallothionein (MT) Induction

MTs are cysteine-rich peptides that exist in the cytosol and the nucleus and in lysosomes. They are non-enzymatic proteins that have low molecular weight, no aromatic amino acids, and are heat stable (Olsson et al. 1998; Roeva et al. 1999). MT-like proteins have been reported in many aquatic invertebrates but occur mainly

in mollusks (Isani et al. 2000). Mussels, used worldwide in environmental pollution assessment, are good candidates for monitoring MT for assessment of metal contamination (Leinio and Lehtonen 2005; Raspor et al. 2004; Mourgand et al. 2002; Petrovic et al. 2001). The use of MT as a biomarker has been validated in many in situ studies (Lionetto et al. 2001; Petrovic et al. 2001; Rodriguez-Ortega et al. 2002; Ross et al. 2002; Mourgand et al. 2002). Such studies have generally found MT to work well for the purpose intended. Fafandel et al. (2003) investigated molecular response to TBT stress in marine sponges (*Suberites domuncula*). Proteolytic cleavage and phosphorylation of stress response KRS-SD protein kinase in control and TBT-treated sponges were investigated. Exposure of sponges to TBT resulted in alteration of KRS-SD1 and KRS-SD2 expression levels and their phosphorylation state. KRS-SD induction, its phosphorylation, and proteolytic cleavage during TBT stress suggest that in sponge cells, mechanisms exist similar to ones present in human cells in which KRS/MST protein kinase is involved in promotion of apoptosis following oxidative stress.

6.2.2 Acetyl Cholinesterase (AChE) Inhibition

AChE enzymes are responsible for hydrolyzing the neurotransmitter acetylcholine into choline and acetic acid. AChE is usually located in the membranes of erythrocytes of both vertebrates and invertebrates. AChE controls ionic current in excitable membranes and plays an essential role in nerve conduction at the neuromuscular junction (Pfeifer et al. 2005; Magni et al. 2006). AChE biomarkers may be less useful in fish, because fish have higher levels of tolerance to AChE inhibition. Measurements of AChE inhibition are most frequently used where a biomarker for organophosphate insecticide exposure is required (Matozzo et al. 2005).

However, AChE biomarkers have also been used with the OTCs. Rebeiro et al. (2002) evaluated TBT subchronic effects in tropical freshwater fish (Linnaeus *Astyanax bimaculatus*). Linnaeus *A. bimaculatus* adult fish were acclimatized in a laboratory and isolated into groups of eight individuals. Two groups were used as controls and one group was exposed to TBT chloride, dissolved in corn oil ($0.0688 \pm 0.0031 \mu\text{g TBT g}^{-1}$), every 6 days for 32 days. A muscle fragment was excised for the determination of the acetylcholinesterase activity and blood smears were obtained for differential white cell counts. The results indicated nuclear irregular shapes, chromatin condensation, presence of intranuclear lipid bodies, and degenerative nuclei. AChE activity was not affected by TBT exposure. The increasing number of metaphils may represent cytotoxic and stress conditions facilitating the invasion of the opportunist.

6.2.3 TBT-Sensitive Immunological Biomarkers

Several xenobiotics alter immune function and the immune system. TBT has been observed to have adverse effects on cellular immune functions of hemocytes. The three indices established as TBT pollution biomarkers are amoebocytic index, phagocytic index, and lysosomal activity index (Chima et al. 1999).

6.2.4 Lysosomal Biomarkers

Matozzo et al. (2002) studied the effects of TBT on circulating cells from the clam *Tapes philippinarum*. They found that exposure of hemocytes to 0.05 μm TBT caused a significant increase ($p < 0.05$) in neutral red dye uptake into the lysosomes, compared with controls, whereas exposure to TBT caused no differences. Enlarged lysosomes were observed in hemocytes exposed to TBT. Moreover, in hemocytes treated with 0.05 μm and 0.1 μm of TBT, superoxide chromatase activity significantly decreased ($p < 0.05$ and $p < 0.1$, with respect to that of the control). A significant decrease in lysozyme activity was also observed in hemocytes exposed to 0.05 and 0.1 μm TBT. Lysozyme is a lysosomal enzyme that may be secreted by hemocytes in the hemolymph during phagocytosis. Reduced lysozyme activity suggests immunosuppression, resulting in lowered resistant bacteria challenge (Matozzo et al. 2002).

6.2.5 Molecular (genetic) Biomarkers

Because pollutants interact with the receptors of organisms at the molecular level to cause their effects, the measurement of certain molecular biomarkers may have obvious advantages for detecting early chemical effects (Nicholson and Lam 2005).

Schroth et al. (2005) utilized a strategy that identified molecular biomarkers and linked the study of abiotic stress to evolutionary history. These authors used the Moon jellyfish, *Aurelia* spp., as a model species. The authors used complementary DNA subtraction analysis to identify genes that were differentially regulated after exposure to the chemical stressor TBT. They also identified differential expression patterns following exposure to TBT at different temperatures. Results suggested that the identified genes were involved in response to the chemical, as well as to heat-induced stress.

6.2.6 Apoptosis

This is a form of genetically programmed cell death, which can be initiated by an internal clock or by exposure to extracellular agents such as hormones, cytokines, killer cells, and a variety of chemical and viral agents. These methods that are applied when using apoptosis as a biomarker are normally characterized by morphological and biochemical criteria (Micic et al. 2001).

Micic et al. (2001) investigated the induction of apoptosis by tri-nTBT in gill tissue of the mussel *M. galloprovincialis*. These authors used the terminal dUTP nick-labeling technology (TUNEL) to detect cells displaying DNA fragmentation within gill structures. Genomic DNA fragmentation was detected as characteristically ladder-like patterns of DNA fragments that were induced by a single injection directly into the pallial fluid of different doses of TBT below the mantle, after 1 day of incubation.

After 1.5 h of TBT incubation, DNA degradation of a higher order DNA structure and a reduced G₀/G₁ cell cycle region were detected. The effect of TBT on the cell

cycle in the mussel (*M. galloprovincialis*) gill was dose related and exposure time dependant. In this study, three types of investigation were performed: (a) detection of internucleosomal fragmentation by conventional gel electrophoresis, (b) identification of DNA fragments of higher chromatin organization by pulsed-field gel electrophoresis, and (c) the detection of apurinic sites in gill sections of TBT-treated mussel (*M. galloprovincialis*) using TUNEL. The process of apoptosis in vivo induction in the blue mussels (*Mytilus galloprovincialis*) was described for the first time (Micic et al. 2001).

6.2.7 Imposex

Imposex is characterized by the development of morphological features (i.e., penis and vas deferens) in female gastropod mollusks or superimposition of male morphological features onto females. Imposex results from exposure of certain invertebrates to organotin antifouling paints (Marshall and Rajkumar 2003). Imposex serves as a useful morphological biomarker for measuring organotin contamination of marine ecosystems. High incidences of imposex were characterized by lower female to male ratios, suggesting that sterility and female mortality were TBT related (Marshall and Rajkumar 2003). In other studies, organotins were found to accumulate in the tissue of marine invertebrates. TBT generally shows the greatest accumulation among the butyltin compounds and is the primary cause of imposex (Bryan et al. 1988; Barreiro et al. 2001). The induction of imposex by TBT may account for a sizable portion of the decline of certain coastal marine mollusks (Gibbs and Bryan 1996).

Pessoa et al. (2001) studied the occurrence of organotin compounds in Portuguese coastal waters and found that acute effects from TBT were induced at concentrations as low as 1 µg/L in aquatic organisms; moreover, imposex was induced at levels below 0.5 ng/L of TBT (as Sn). TBT at 20 ng/L (as Sn) caused sterility, and this was followed by the disappearance of the most sensitive neogastropods on a given shore. The authors concluded that the use of imposex was the most sensitive indicator of exposure to TBT of all known non-target pathological conditions.

7 The Regulation of Organotin Compounds

The presence of tributyltin in the environment has attracted the most regulatory attention because of the volume of its use in antifouling paints to coat boat hulls or harbor edifices. When biocides are released from paint over time, it forms a thin layer of concentrated TBT in the vicinity of its immediate use area. This contaminated area repels or kills organisms such as barnacles (Huggett et al. 1992). Moreover, TBT diffuses from the application area to contaminate adjacent water, sediments, and non-target organisms. As previously mentioned, TBT contamination causes morphological aberrations in oysters and mussels (Wadlock and Thain

1983). These effects and other associated environmental impacts of TBT had led the authorities of many countries to target TBT for regulation (Abbott et al. 2000).

According to the USEPA (United States Environmental Protection Agency) (2001), TBT restrictions apply in many countries around the world. For example, the European Union, Canada, Scandinavia, and South Africa have banned the use of TBT on vessels that are less than 25 m in length. As a result of increasing awareness of the undesired effects of TBT, global efforts have been made to solve this problem, and increasingly, legal requirements have been enforced to protect the aquatic environment from TBT (Konstantinon and Albanis 2004).

France, in 1982, was the first country to ban the use of organotin in antifouling paints for application to boats of less than 25 m in length (Alzieu et al. 1986). This ban was sequel to the collapse of the oyster industry in France' Archon Bay in the late 1970s and early 1980s (Alizieu et al. 1989, 1991). The enhanced TBT concentrations in seawater and the frequency of oyster shell anomalies were the cause of the collapse. Subsequently, comparable regulations as those imposed in France were also passed, after 1988, in North America, UK, Australia, New Zealand, Hong Kong, and most European countries (Alzieu et al. 1989; Champ 2000, 2003; De Mora et al. 1995).

The International Maritime Organization (IMO) campaigned for a global treaty to ban the application of TBT-based paints starting 1 January 2003; as a result, a total prohibition took place by January 2008 (IMO 2001). In Europe, the current Water Framework Directive is the major community instrument for controlling port and diffused discharges of dangerous substances. Decision no. 2455/ 2001/EC (20 November 2001) of the European Commission Parliament amended the water policy directive 2000/ 60/EC and defined 11 priority hazardous substances, including TBT compounds, that were subject to cessation of emission, discharge, and lose to water.

In addition, regulation No. 782 /2003 of the European Parliament and of the council of 14 April 2003 was aimed at prohibiting organotin compounds on all ships entering European seaports. TBT monitoring was also mandated by legislation from several European Commissions, including the council decisions 75/437/EC (marine pollution from land-based sources), 77/585/EC (Mediterranean Sea), and 77/586/EC (River Rhine), and the council directive 80/68 EC (groundwater) (Champ 2000).

In 1985, the government of the United Kingdom (UK) prohibited the application of TBT-based antifouling paints to small vessels. In 1986, an Environmental Quality Target Concentration (EQTC) was set for TBT at a level of 20 ng L⁻¹. This value was based on the lethal concentrations that were effective for control of selected commercially important mollusks. Because of the high toxicity value of the TBT, this value was reduced by a factor of ten 1 year later to achieve improved environmental protection (Takahashi et al. 1997). In Spain, a Royal Decree (995/2000) established the concentration limit of organotin species in waste discharges to continental surface waters. The value selected was less than 20 ng L⁻¹. Legislation that addresses concentrations in seawater samples has yet to be approved.

The United States enacted the Organotin Antifouling Paint Control Act in 1988; a leaching rate of organotins from the application sites was limited

to $4 \mu\text{g cm}^{-2} \text{d}^{-1}$ (USA 1988). Moreover, the Occupational Safety and Health Administration (OSHA), the American Federal Agency, and the National Institute for Occupational Safety and Health (NIOSH) have established workplace exposure limits of 0.1 mg m^{-3} . The Food and Drug Administration (FDA) has also set a limit for the use of tin as a food additive (ATSDR 2005). In addition, the water quality criterion of the USEPA is that aquatic life and the uses to which aquatic life are put should not be unacceptably affected.

In 1989, the Canadian government regulated TBT (under the Canadian Pest Control Products Act) by stipulating a maximum daily release rate for antifouling paints of $4 \mu\text{g TBT per cm}^3$ of boat–ship hull surface. In Australia, the evidence for establishment of a relationship between deformities in oysters and the presence of TBT in oyster tissue led to the banning of TBT-based paints (Takahashi et al. 1997). Japan also restricted TBT usage on antifouling coatings of boats and aquaculture nets by implementing limits in 1990. But TBT is still used as an antifouling agent for ocean liners and deep-sea fishing boats (Takahashi et al. 1997).

Similar actions on the usage of TBT in paints were taken by Switzerland, the Netherlands, Sweden, New Zealand, South Africa, and most European countries (Sergi et al. 2005). However, the legislative restrictions on the use of TBT-based marine paints in Tanzania are less clearly defined. As a result of legislation restricting the use of TBT-based antifouling paints, some reduction in the levels of TBT has been reported, particularly in areas proximate to recreational shipping activities (Rees et al. 2001; Hawkins et al. 2000). However, in areas near industrial shipping activities (e.g., ports), TBT levels remain high (Valkirs et al. 2003; Peachery 2003; Horiguchi et al. 2004; Harino et al. 2006).

South Africa is positioned along a primary shipping route between Europe, the Americas, and Asia. South African harbors provide infrastructural support to the global shipping industry, with some of the largest and busiest African harbors being located on the eastern seaboard of South Africa. The Constitution of the Republic of South Africa (Act 108 of 1996) and the Bill of Rights enshrine basic human rights, such as having access to sufficient water and a safe and healthy environment. The two Acts that enable the South African government to fulfill these rights (through the Department of Water affairs) are the Water Services Act (Act 108 of 1997) and the National Water Act (1998). In South Africa, the Maritime International organization (IMO) held an international convention on the control of harmful antifouling systems in 1990. The convention was adopted in 2001, and South Africa was a signatory. The convention required prohibition or restriction of the application of antifouling systems and they listed the substances to be controlled. The convention also required signatory states to ensure that controlled substance application or removal was done appropriately and required such states to perform surveys of their own ships. The regulations required that any ships in violation of the convention standard were subject to being warned, detained, dismissed, or excluded from a country's port (IMO 2001).

This convention required the South African government to develop new legislation to effect provisions of the convention. The Annex 1 of the convention included a list of organotin compounds. The waste resulting from the removal of these toxins,

as stated in Article 5 of the convention, should be disposed of in accordance with permits from the Department of Water affairs (DWA) and Environmental Affairs (DEA). The South African Maritime Safety Authority (SAMSA) became responsible for enforcing and implementing the legislation; the provision of waste disposal was taken over by the National Port Authority (NPA) (IMO 2001).

The Facilitation of International Maritime Traffic (FAL) 1991 amendments to the convention were passed to prevent unnecessary delays in maritime traffic. This required the port authority to inspect foreign ships to verify that their condition, manning, and operation were in compliance with international rules and the regulating act of the South African Maritime Authority. Several other conventions for protection of coastal and marine ecosystems are in force, and are indirectly related to organotin contamination. For example, the Ballast Water Convention requires that pollution checks be made of the maritime environment resulting from discharges of oil and other hazardous waste generated outside Africa into African countries. The Lome IV Convention also bans the export of hazardous waste from European countries to Africa (EC report 2007).

In general, despite the ban on, or regulation of, TBT usage in some countries, TBT contamination continues in the aquatic environment; therefore, environmental concerns for this contaminant remain high and warrant continued assessment and monitoring. Continued diligence is needed, particularly in countries that do not restrict the use of TBT-containing antifouling paints; moreover, further research is necessary on elucidating the pathways, kinetics, and persistence of organotin compounds.

8 Conclusions

In this chapter, we have reviewed the fate and distribution of, and the human exposure to, organotin compounds in the environment. The organotins, some of which are very toxic, have been confirmed as predominant pollutants of freshwater and marine ecosystems. The presence of these organotin residues in the environment is clearly undesirable. Researchers have defined the toxicity of many organotin compounds and have reported organotin residue to exist in both aquatic and terrestrial ecosystems. Although a considerable amount of research has been conducted on the response of marine species to organotins in water, only limited data are available on the deposition of butyltin in humans. This is disturbing, because there is evidence of human exposure to OTCs. Therefore, we conclude that additional research is needed in the following areas:

- the absorption kinetics in humans, mechanisms of action, and human exposure levels, along with body burdens of the organotins;
- additional studies of the toxicity of organotin compounds in water;
- investigations designed to better understand the effects of sediments on organotin exposure in aquatic organisms;

- further definition of the use of biomarkers that can delineate organotin toxicity in mussels;
- studies to define levels of organotin compounds that exist in foodstuffs;
- studies to better define the toxic responses of marine species to TBT residues; and
- an evaluation of the extent to which human exposure exist to organotins in the atmospheric environment.

9 Summary

Organotin compounds result from the addition of organic moieties to inorganic tin. Thus, one or more tin–carbon bonds exist in each organotin molecule. The organotin compounds are ubiquitous in the environment. Organotin compounds have many uses, including those as fungicides and stabilizers in plastics, among others in industry. The widespread use of organotins as antifouling agents in boat paints has resulted in pollution of freshwater and marine ecosystems. The presence of organotin compounds in freshwater and marine ecosystems is now understood to be a threat, because of the amounts found in water and the toxicity of some organotin compounds to aquatic organisms, and perhaps to humans as well. Organotin compounds are regarded by many to be global pollutants of a stature similar to biphenyl, mercury, and the polychlorinated dibenzodioxins. This stature results from the high toxicity, persistence, bioaccumulation, and endocrine disruptive features of even very low levels of selected organotin compounds.

Efforts by selected governmental agencies and others have been undertaken to find a global solution to organotin pollution. France was the first country to ban the use of the organotins in 1980. This occurred before the international maritime organization (IMO) called for a global treaty to ban the application of tributyltin (TBT)-based paints. In this chapter, we review the organotin compounds with emphasis on the human exposure, fate, and distribution of them in the environment. The widespread use of the organotins and their high stability have led to contamination of some aquatic ecosystems. As a result, residues of the organotins may reach humans via food consumption. Notwithstanding the risk of human exposure, only limited data are available on the levels at which the organotins exist in foodstuffs consumed by humans. Moreover, the response of marine species to the organotins, such as TBT, has not been thoroughly investigated. Therefore, more data on the organotins and the consequences of exposure to them are needed. In particular, we believe the following areas need attention: expanded toxicity testing in aquatic species, human exposure, human body burdens, and the research to identify biomarkers for testing the toxicity of the organotins to marine invertebrates.

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