

The Environmental Persistence of Organotin Compounds

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ARTICLE INFO

Article history:

Received: 26 April 2017;

Received in revised form:

16 May 2017;

Accepted: 30 May 2017;

Keywords

Organotin,
Environmental,
Persistence,
Degradation,
Bioaccumulation.

ABSTRACT

The wide application of organotin compounds have caused considerable amounts of these compounds to enter the different ecosystems. Organotins have been of environmental concerns due to their direct introduction into the environment, bioaccumulation, and toxicities even to non-target organisms both aquatic and terrestrial. They are notable sources of pollution and may be of ecotoxicological effects on the various ecosystems. It is not only the particular organisms that may be affected but the whole ecosystems. They are very persistent and bioavailable to biota even after a long time. The persistence of organotins in polluted ecosystem is a function of adsorption and degradation processes. Hence, this review which aim at providing an overview of the environmental persistence of organotin compounds.

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Introduction

Organotin compounds (OTCs) are compounds that have at least one covalent bond between carbon-tin bond [1, 2]. They belong to an organometallic class of pollutants [2]. They have been known since 1853, but did not become important for industrial use until 1940s. Since then, they have been used extensively in industrial sectors. Organotins (OTs) have been used in many industrial and agricultural applications such as polyvinyl chloride and heat stabilizers, catalysts, industrial and agricultural biocides, wood preserving and antifouling agents [1, 3-12]. The various commercial applications of OTCs led to a drastic increase in their worldwide production and thereby considerable amounts of OTs have entered different ecosystems [13].

Organotins as antifouling agents help prevent the settlement and growth of aquatic organisms (such as barnacles, algae, mussels and other marine invertebrates) on ship hulls, fishing nets or cages, oil rig supports and different tools used in sea water [14-16]. For this reasons, these compounds are often found in seawater, sediments and biota. Antifoulants contain two main triorganotins that are the most toxic OTs: Tributyltin (TBT) and triphenyltin (TPT) [2, 10, 17, 18].

Triorganotins have been categorized as persistent organic pollutants. An enormous amount of these toxic substance has been introduced into the environment (terrestrial and aquatic), resulting in bioaccumulation in the food chain [2, 19-22]. It has been reported that the coastal waters of most Asian countries are badly affected by persistent organic pollutants due to extensive use of these chemicals in paints and agrochemicals [22-24]. High level of TBT chloride (TBTCl) have been reported in estuarine, marine and freshwater, harbours and areas that are primarily associated with boating [21-24]. TBT and TPT are recognized as one of the most hazardous substances that have been released into the environment deliberately. The persistence of TBT in the estuarine environment is reported to have immunological,

carcinogenic and teratogenic effects on non-target organisms [17, 22, 25].

Lately, studies have shown that municipal and industrial wastewater, sewage sludge and landfill leachates are also important sources of OTs [26, 27]. The collection of municipal waste on landfill sites is one of the most commonly employed waste management system worldwide. Thus, a landfill can be considered to be an important pool of OTCs as a result of their presence in plastic materials, manufactured household products and cans for food packing. Both OTCs and inorganic tin can be mobilized and likely released to the environment by percolation of water through the waste pile. The environment in landfills generate conditions for the chemical and biological modification of OTCs and inorganic tin, which can be transformed by hydration, methylation, ethylation, dealkylation or transalkylation reactions. This lead to the formation of new tin compounds in landfill leachates and biogases [12]. Organotin usually degrade in the environment. The degradation of OTCs in the environment occurs as a progressive elimination of organic groups from tin cations. For example, TBT breakdown to dibutyltin (DBT) and monobutyltin (MBT) while TPT breakdown to diphenyltin (DPT) and monophenyltin (MPT). The final degradation product is inorganic tin. As successive organic groups are removed, it is generally believed that toxicity is reduced. On the other hand, the inverse process can occur through the bioalkylation of inorganic tin, leading to the formation of unsymmetrical OTCs. Also, inorganic tin can undergo methylation thereby producing other OTCs that were not previously introduced to the area.

Although, there are different legislative restrictions on the use of some OTs, but only developed countries have taken steps in enforcing them. There is still lack of enforcement on their control in Africa.

Therefore, there is need to know the environmental impact of these compounds in Africa in order to draw the attention of the government and different individuals on their

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environmental implications. There are empowerment schemes in some African countries currently in which people are being trained how to make insecticides, pesticides, rodent repellants, and disinfectants among other chemical products. Some of the starting materials of these products are OTs, for example, trimethyltin is used for insecticides and disinfectants. There is a need for public awareness. The populace have to be informed on the environmental persistence and toxic effects of these compounds. Therefore, this review which is aimed at providing an overview on the environmental persistence of OTCs.

Removal mechanisms of organotins in the environment

The persistence and fate of OTCs in the environment is a function of the different removal mechanisms (fig. 1). The removal mechanisms include physical (adsorption to suspended solids and sediments), chemical (chemical and photochemical degradation processes), and biological mechanisms (uptake and biological degradation) [5].

Degradation

The degradation of OTCs in the environment may be defined as the sequential removal of the alkyl or aryl groups (organic groups) attached to the tin atom. It can be depicted as below:



The cleavage is initiated by hydro attack (Eqn. 1). It involves the stepwise loss of the organic groups from the metal which leads to the breaking of carbon-tin bond and also, accompany by a progressive lowering of the biological activity, since the biological activity depends on both the nature and number of the organic group. Studies have revealed the degradation of TBT as a sequential loss of alkyl groups from TBT to form toxic inorganic tin Sn^{4+} [26]. This is because the methylation of the tin(IV) which is the end product in the environment can produce mono-, di-, tri- and tetramethyltin compounds that were not previously introduced in the area. Researches revealed that both Sn^{2+} and Sn^{4+} undergo microbial transformation to methyltin compounds in water. Volatilization of mono-, di-, and triorganotins is likely negligible because of the tendency of these compounds to strongly adsorb to suspended solids and sediments [28].

Degradation of OTCs can be achieved by both abiotic and biotic mechanisms. Abiotic mechanisms include: ultraviolet (UV) irradiation, gamma (γ) irradiation, thermal cleavage, and chemical cleavage while biotic mechanism involves the biological cleavage which can be aerobic or anaerobic [3, 29]. Among these processes, thermal cleavage has no significance under environmental conditions because OTs are reported to be stable at temperature up to 200°C. Likewise, the γ - irradiation will have little effect because of its negligible intensity on the earth's surface, although, researches have shown that γ -irradiation will degrade TBT compounds [30].

Ultraviolet irradiation

Ultraviolet light (UV) is the aspect of electromagnetic spectrum that has the wavelength in the range 10nm-400nm, it is adjacent to visible light. However, the light below 200nm is absorbed by air and so can only be transmitted in a vacuum. Emission reaching the surface of the earth from the sun contain mostly light of wavelengths above 290nm.

Ultraviolet light of 290nm equals an energy of about 300KJ/mol which is above the mean bond dissociation energies for Sn-C bond. Therefore, this amount of energy is sufficient to cause Sn-C bond cleavage, provided there is

absorption of light. Sunlight photolysis seems to be the fastest way of degradation in water. Although, photolysis is probably not important at greater depths in water because of the attenuation of sunlight with the depth in water column likewise, in sediment [31-33]. But, irradiation by UV rapidly dealkylates TPT and tricyclohexyltin (TCHT) species while lower rates of degradation is observed with TBT derivatives [3, 26, 29, 34, 35]. Zhai and coworkers studied the ultraviolet degradation of methyltins; elucidating the mechanism by identification of a detected new intermediary product and investigating the kinetics at various environmental conditions. The results of the research suggested that monomethyltin (TMT), dimethyltin (DMT) and trimethyltin (TMT) can be degraded under UV irradiation rapidly at different pH, with a degradation rate sequence of TMT < DMT < MMT. Increasing salinity and humic acid concentration were shown to decrease the UV degradation rates of methyltins remarkably under laboratory conditions [36].

Chemical cleavage

Chemical cleavage can break Sn-C bond in unbound OTs that can be reached by chemical action. The Sn-C bond can be broken by reaction with electrophiles and nucleophiles. Since the Sn-C bond is capable of polarization in either direction, ($Sn^{\delta+}-C^{\delta-}$) or ($Sn^{\delta-}-C^{\delta+}$). Examples of reagents that can heterolytically cleave Sn-C bond are mineral acid, carboxylic acid, halogens, alkali and alkali metals etc. Free radicals (succinimidyl, t-butoxyl) processes can cause homolytic Sn-C bond cleavage. Fragmentation can also be induced through the radical cations which are formed by electron transfer [37].

Recently, some researchers synthesized a nine amino acid-peptide with CXC motif corresponding to the putative TMT binding site of the membrane protein stantin. Studies revealed the strong dealkylating property of the peptide for trisubstituted OTs having 1-3 carbons in the organic groups [38]. Paton, Cheewasedtham and Dawson [39] investigated the chemical and microbial degradation and toxicity of phenyltins (PTs) in soil. These authors discovered that the degradation of OTs was significant slower in sterile soils. In nonsterile soils, the half-life of TPT was 27 and 33 days at amendment levels of 10 and 20mg/kg (Sn) respectively. There was an increase in the observed toxicity as the degradation of TPT proceeded. This phenomenon proved that the metabolite formed is either more bioavailable or more toxic than the parent compound or both [26].

Biological degradation

Biological processes are the most important factor effecting degradation of OTCs in aquatic and terrestrial ecosystems. Studies have shown that OT degradation is mediated by microorganisms. Degradation of OTCs has been shown for a wide range of microorganisms, including algae, fungi and bacteria [40]. Biodegradation of OTCs is particularly essential in situations where, for example, the compounds are not directly exposed to light such as in the soil or on the sea bed. Microbial degradation of OTCs may be the most relevant pathway of OT dealkylation in soil. In some cases, environmental conditions (e.g. pH and redox potential) established by microbial activity strongly influence the extent of abiotic degradation of OTCs [40, 41]

Microorganism-organotin interactions are influenced by environmental conditions (e.g. turbidity, light, Oxygen and temperature etc.). In aquatic systems, both pH and salinity can determine organotin speciation and therefore reactivity. These environmental factors may also alter selectivity for

resistant microorganisms in polluted systems. Tin-resistant microorganisms have been identified, and resistance can be either plasmid or chromosomally mediated. In one TBT-resistant organism, an *Altermonas* sp., an efflux system was suggested as the resistance mechanism [42-52]. Many investigations have shown that aerobic biodegradation is faster than the anaerobic biodegradation [16, 34, 40]. The rate of degradation of OTCs depend not only on the type of sediment and chemical species (such as chlorides, oxides, hydroxides), but also on the concentration of the OTCs as the biodegradation rate of TBT may be inhibited if OTCs are present in concentrations that are toxic to bacteria [37, 53-55].

Peeters, Zuliani, Scancar and Milacic [10] investigated the use of isotopically enriched tin tracers to follow the transformation of OTCs in landfill leachate, in the course of the experiment, the microbial degradation of TBT was clearly manifested in Sn-enriched spiked leachate samples, while abiotic pathway of degradation was observed for DBT.

There is variation in the half-life of TBT in marine environment. It is estimated to be between 1-5 years in sediments while it ranges between a few days – few weeks in sea water [13, 16, 29]. The degradation rate of OTCs in sediments is considerably low [29, 37]. Therefore, the capability of sediments to act as sinks for OTCs poses a permanent risk of OT for water contamination by these contaminant due to desorption processes and for bivalves via ingestion of particles. Also, the slow degradation of OTC in soils [13]. The half-lives of OTC documented are often related to laboratory experimental conditions and so are not directly comparable with natural circumstances under which the actual rate of breakdown depends.

Tributyltin naphthenate (TBTN) and Tributyltin oxide (TBTO) have been shown to be degraded by fungal action to di-, and monobutyltins. The green alga *Ankistrodemum falcatus* and some gram-negative bacteria have been reported to dealkylate TBT to DBT, MBT and inorganic tin. The alga was able to metabolize around 50% of the accumulated TBT over a four week period. Studies showed that the action of some microorganisms on ^{14}C -labelled TPT acetate also produced diphenyl-, monophenyl and inorganic tin products [3]. Furthermore, several researches have shown that some microorganisms: bacteria (e.g. *Pseudomonads*, *Alcaligenes faecalis*, *Shewanella putrefaciens* and *Phytoplankton* (e.g. *Skeletonema costatum*, *Chlorella vulgaris*, *Scenedesmus dimorphus*), can degrade OTCs ([16, 48, 49].

Bacteria play an important role in biogeochemical cycling along with organic matter degradation and recycling of toxic compounds, including OTs in the environment [21, 48]. Studies revealed that the degradation by bacteria, marine *Pseudomonads* (*Pseudomonas pseudoalcaligenes*, *Pseudomonas stutzeri*, *Pseudomonas mendocina*, *Pseudomonas putida* and *Pseudomonas bacteria*) is a two-step process: dispersion of TBT in aqueous phase and tin-carbon bond cleavage by siderophores affecting debutylation of TBT. TBTCl-resistant bacteria are able to resist very high levels of TBTCl by employing a number of mechanism: biotransformation into less toxic di- and mono-BTs by dealkylation; efflux of TBTCl outside the bacteria cell mediated by efflux pumps; degradation/metabolic utilization of TBTCl as sole carbon source mediated by enzymes; intracellular sequential and bioaccumulation mediated by metallothionein-like proteins; siderophore production and alteration in cell morphology. [40, 42, 43, 49-51, 56-59].

The bacteria decomposition of TPT acetate to di and monophenyltin and inorganic tin was observed in a soil sample with a half-life of about 140 days, nevertheless, decomposition did not occur in soil. These data are strongly dependent on conditions like soil type (which affect the adsorption and the bioavailability), moisture content, sunlight and the actual microbial activity. Also, structural complexity and low water solubility limit TPT's availability to microorganisms, resulting in its persistence in a natural environment [37].

TBT is much more persistent than TPT, its degradation products: DBT and MBT are also persistent [13, 60, 61]. The persistence of TBT increases when it is associated with paint particles [16, 53].

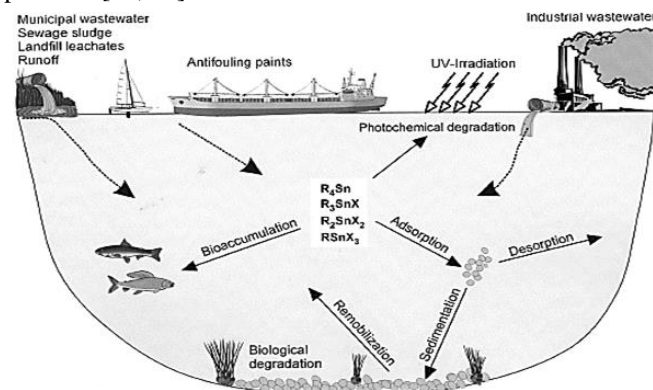


Figure 1. Distribution and fate of OTC and their general routes into the aquatic environment [3].

Bioaccumulation

Bioaccumulation is the process by which toxic substances (e.g. heavy metals, pesticides and other chemicals) are taken up by an organism either directly by exposure to a contaminated medium or by consumption of food containing the toxic substances [62]. It occurs when an organism absorbs a toxic substance at a rate faster than that at which the substance is lost by catabolism and excretion. Many toxic substances attain concentrations in biota in several orders of magnitude greater than their aqueous concentrations, and therefore, bioaccumulation poses a serious threat to both the biota and humans that feed on them (It poses a threat to health, life and the environment) [63, 64]. The bioaccumulation of a compound depends on its hydrophobicity and some physicochemical parameters such as salinity, humic acid and pH that can alter speciation, thereby affecting the bioavailability of the compound. For instance, bioconcentration factors (BCFs) of both TBT and TPT for fresh guppy (*Lebistes reticulatus*) are approximately twice as great as those for marine fishes which is indicative of a negative effect of salinity on accumulation of TBT and TPT. Bioaccumulation of TBT by marine mussels is inversely proportional to the concentration of humic materials in the water. In contrast, accumulation of OTs by aquatic organisms is directly proportional to pH. The bioaccumulation of both TBT and TPT was greater for both invertebrates and fishes at pH 7.8 than at pH 6.8 or 6.0. Apart from these abiotic factors, biotic factors, such as life stage of the organism and species-specific characteristics, can potentially affect the bioaccumulation of TPTs [65].

Organotin compounds have high bioaccumulation potential. They are accumulated significantly by aquatic species while some species degrade or eliminate the effects of bioaccumulation because of having an efficient enzymatic mechanism [66-68]. Organotin polluted sites pose remarkable

environmental hazards for aquatic and terrestrial ecosystems. They are significant sources of pollution and may result in ecotoxicological effects on aquatic, groundwater and terrestrial ecosystems. At acutely polluted sites, acute effects occur, but the basic problem lies in long-term chronic effects. Ecotoxicological effects occur at all levels of biological organization, from the molecular to the ecosystem level. It is not only the particular organisms that may be affected, but the whole ecosystems, both terrestrial and aquatic, in its function and structure. Pollutants at large polluted sites often share critical properties such as high acute and/or chronic toxicity, high environmental persistence, often high mobility leading to contamination of groundwater, and high lipophilicity leading to bioaccumulation in food webs [69, 70]. Pollutants present at polluted sites occur as mixtures, therefore interactions between individual compounds are of importance. The bioavailability is a key factor for ecotoxicological effects of pollutants.

Organotin compounds in the environment (especially aquatic) are available for uptake for organism at various levels of the food web. The uptake of OTs is influenced by the lipophilic character of the compounds. The uptake from the water or sediment phase via the body surface is called bioconcentration whereas uptake via the food chain is referred to as biomagnification [69]. Accumulation, the result of both pathways, is often proportional to the concentration of the compound in the environment. The extent of bioaccumulation is further influenced by biodegradation/excretion mechanisms of the respective organism. [37, 65, 69, 71].

The potential for aquatic biota to concentrate OTs from the environment depends on the specific number and types of organic moieties attached to the tin atom. The greater the number and molecular weight of the organic groups bound to the tin atom, the more lipophilic the compound and the greater the potential for bioconcentration. Most OTs have a moderate octanol-water partition coefficient (K_{ow}), indicating that these compounds have the potential to bioaccumulate in biota (Canadian Water Quality Guidelines, 1999).

Bioaccumulation of OTs has been reported in a wide range of organisms. The microbial uptake is generally considered to be a biphasic process. The first step is biosorption when metal ions can bind to the predominantly anionic cell surfaces by various interactions (to hydroxyl, phosphate or carboxylate functions of the cell wall polymers) and the second step is a metabolism-dependent transport of the metal across the membrane [37].

The bacterium *Pseudomonas* sp was shown to accumulate a very high amount of TBT, up to 2% of its cellular dry weight without any significant biotransformation. Researches showed that the uptake of tri-substituted OTCs increase with increasing molecular mass of the OTCs (TPT > TBT > Tripropyltin \geq TMT \geq Triethyltin) [37]. The bioconcentration factors (BCFs) for OTCs vary considerably, most likely as a result of different environmental conditions and different taxonomic groups. According to [72], the BCFs for TBT range from < 1 -152,000. The highest BCFs were observed when low concentration of TBT were applied in the test systems.

Dibutyltin and MBT showed a lower tendency to bioaccumulate. Avery, Codd and Gadd [73] observed a weak effect of pH, a strong inhibitory effect of salinity on TBT uptake and a TBT-concentration dependence. The bioaccumulation of various OTs was investigated in algae and

in some cases, significant bioconcentration factors (BCF) were determined for *Scenedesmus obliquus*, BCF > 3.32×10^5 TBT and 1.4×10^5 TPT. Some of the studied algae showed toxicity resistance for TBT and they metabolized TBT to the less toxic DBT [74]. Marine bivalves are able to accumulate significant amounts of TBT while Crustaceans and fish accumulate much lower amounts of these contaminants because of their possession of efficient enzymatic mechanisms that degrade TBT in the body. Uptake of uncharged TBT across epithelia or membranes is one possible mechanism [3]. The absorption of TBT in mice is low, it is mainly excreted unchanged via their feces. Organotin contaminants can get into animals being at higher levels of the food chain, e.g. vertebrates [75-77] and humans [37, 78]. The accumulation of OT by higher trophic organisms proceeds through either uptake from solution alone or of a combination with diet ingestion. Studies have shown that marine mammals and birds can accumulate high levels of OTs in various tissues and organs [3]. TBT may be metabolize to DBT and related metabolites in mammals [26, 79-83].

Marine invertebrates can accumulate OTs quickly and the BCFs for accumulation of TPT by marine mussels *Mytilus graynus* and *M. edulis* were 4.3×10^4 and 3.6×10^4 , respectively. The bioconcentration of TPT has been determined for several fishes, including the guppy (*Poecilia reticulata*), rainbow trout (*Salmo gairdneri*), common carp (*Cyprinus carpio*), red sea bream (*Pagrus major*), mullet (*Mugil cephalus*), filefish (*Rudarius ercodes*) and minnow (*Phoxinus phoxinu*); among which the greatest BCF was 4.1×10^3 , which was observed for *R.ercodes* [65, 84-87].

Significant amounts of BTs and PTs (up to ≈ 90 and 210ng/g dry weight, respectively) were found in sediment samples and deep sea organisms (gastropods, sea cucumbers, galatheid crabs and bivalves) taken from the Nankai Trough, Japan (≈ 3000 m water depth). Analysis of BT residues in the sediment and some vertebrates at Polish Coast revealed high concentration of BTs in some fishes (14 -455 ng/g wet weight) and birds (35-870 ng/g wet weight) and a very high level was found in the liver of a long-tailed duck (4600 ng/g wet weight). These suggest the trophic transfer of the studied compounds through the aquatic food chains [88]. Butyltin levels in human liver in the range of 2.4 – 11ng/g (wet weight) was reported by Kannan and Falandysz [88] and in the range 0.8 – 28.3 ng/g (wet weight) by Nielson and Strand [89]. Accumulation of TBT was shown in the roots of willow trees. Although, OTs are less critical in plants because they do not act as systemic biocides in crop protection [37]. Generally, species with a high rate of uptake or low rate of metabolic conversion and elimination display relatively high bioaccumulation ratios [26, 90, 91]. The higher the trophic levels of the organisms, the more OTs are accumulated in their tissues. Some predatory fishes, such as salmon, mackerel and cod, are regularly consumed by humans and contribute to nearly 38% of our total OT exposure [92, 93].

Adsorption

Adsorption is the adhesion of a chemical species onto the surface of particles (e.g. sediment). Hydrophobic compounds in water tend to adsorb to particulate inorganic and organic matter, dissolved organic matter, or sediment. A great proportion of OTCs are found to be associated with the clay fraction of particulate matter. The adsorption and desorption of OTs to solid particles is an important factor that determine the distribution and fate of OTCs in the environment.

Triorganotin cation acts as a 'hard' cation and undergoes cation exchange at low pH with clay minerals and metal oxides bearing a net negative charge. Generally, the adsorption behaviour of OT contaminants can be characterized by the cation exchange process on the negatively charged metal oxide or clay mineral surfaces and deprotonated surface hydroxyl groups. However, beside the sediment composition, there are many factors, including the molecular structure of the OTs, complexation processes with negatively charged ligands, salinity and pH, which influence substantially the adsorption and desorption processes [71, 94-96]. Organotins form surface complexes with oxide surfaces in the pH range of natural waters [55, 69]. Tributyltin has a low aqueous solubility and relatively high affinity for particulate matter, providing a direct and potentially persistent route of its entry into benthic sediment.

Experimental studies on the adsorption mechanisms of MBT to various clay minerals showed that the MBT adsorption capacity for all clays was higher than the corresponding cation exchange capacity [3]. Berg, Arnold, Muller, Muhlemann and Schwarzenbach [97] investigated the adsorption and desorption behaviour of TBT and TPT in sediments. Their experiments showed that the sorption is a fast and reversible process involving mainly the particulate organic matter as sorbent. They concluded that any resuspension of the contaminated sediment will enhance OT concentrations in the overlying water phase. Also, the adsorbed material is potentially bioavailable for filtrators and benthic organisms [69, 98]. Furthermore, Bueno, Astruc, Astruc and Behra [99] reported the sorptive behaviour of TBT on natural quartz. They showed that the sorption mechanism is reversible in natural quartz sand. Although, the adsorption and desorption of OTs is considered to be reversible, yet, TBT and TPT derivatives were shown to remain in harbour sediments for a long time [37, 100]. Consequently, their slow release process may have long-time ecotoxicological consequences by influencing the bioavailability of OTCs [69]. Laboratory investigation under simulated estuarine conditions showed that the adsorption behaviour of various OTC also depends on their molecular structure. For example, the sequence of adsorption affinity of BT compounds on hydrous iron oxide (MBT > TBT > DBT) suggests that MBT is most likely to remain in an estuary, while DBT preferentially remains in solution and the strongly toxic TBT is likely to be present in the water column as well as in the sediment phase and thus, it might be available to both pelagic and benthic organisms [3].

Owing to OTs high sediment/water partition coefficients (e.g. TBT $K_{oc} = 3370$), their adsorption to suspended solids and sediments is potentially an important mechanism for their removal from water. However, caution is warranted in viewing adsorption to suspended solids and sediments as the ultimate fate of OTs in aquatic environments, as toxic residues may be remobilized through desorption, sediment resuspension, or uptake by benthic biota [28].

Tributyltin and TPT are very persistent and bioavailable to biota in lake sediments even after a long time. Remobilization of accumulated organotins in sediments occurs when contaminated sediments are being disturbed and dredged [100, 101]. Consequently, despite the restriction on the application of TBT and TPT in antifouling agents, the question still remains as to what extent these contaminants have accumulated in the sediments over the past decades. In the sea, TBT and TPT tend to adsorb onto particulate matter

and accumulate in sediments due to their hydrophobic properties. Their rate of degradation in the particulate matter and sediments depend on environmental conditions. Organotins deposited in sediments may undergo various processes such as resuspension, diffusion into the water column, biotic and abiotic transformations. Filipkowska, Kowalewska and Pavoni [16] studied OTCs in the surface sediments of the Southern Baltic coastal zone. Their results confirmed that since the IMO ban came into force, the main source of OTCs for aquatic life is the release from sediments settled in ports, harbours, and shipyards rather than vessels. Dredging worsens the risk for OT remobilization from sediments to the water phase and poses a threat to marine environment especially to benthos and bottom fishes [102, 103]. This is because more contaminated sediments (deposited many years ago) can be exposed during dredging [16, 31, 102-104]. Hence, OTs in the most contaminated sediments will persist for years, and the risk of OT remobilization contaminated sediments at sea.

Biomethylation

Biomethylation is the process whereby living organisms produce a direct linkage of a methyl group to metal or metalloid, thus forming metal-carbon bonds. Biomethylation activity has been found in soil, but mainly occurs in sediments (e.g. in estuaries, harbours, rivers, lakes and oceans). The addition of a methyl group to a metal or metalloid changes the chemical and physical properties of the element, and influences its toxicity. The organisms responsible for biomethylation of metals/metalloids are nearly all microorganisms. Several biotic and abiotic methylation agents are known. Anaerobic bacteria are believed to be the main agents of biomethylation in sediments and other anoxic environments. Some aerobic and facultatively anaerobic bacteria, as well as certain fungi and lower algae, may also methylate metals [105].

Biomethylation influences the available forms of OTs in the environment. It is the main process of biotransformation of OTCs, whereas chemical agents such as methylcobalamin, methyl iodide, humic and fulvic acid (produced due to decomposition of vegetation) and other methylmetals can transmethylate OTs. Biomethylation of tin compounds occurs in both aerobic and anaerobic conditions by means of bacterial substrates [22, 98, 105, 106]. Methylcobalamin (CH_3B_{12} , the methyl co-enzyme of vitamin B_{12}) is believed to be the main methylating agent for tin compounds. Methylcobalamin is a carbanion donor and is able to convert inorganic Sn(IV) to several methyltin species. It has been demethylated by SnCl_2 in aqueous HCl solution, in the presence of an oxidizing agent (Fe^{3+} or Co^{3+}), to form monomethyltin species [3, 66]. Di and monobutyltin species have been detected as breakdown products of bis(tributyltin) oxide. Methyltin derivatives may be formed by biomethylation processes representing the only non-anthropogenic origin of OT in the environment [29, 40, 105]. Methyltin formation in anaerobic sediments has been associated with sulfate-reducing bacteria, e.g. *Desulfovibrio* sp [40, 105]. Sulphate-reducing bacteria form mono and dimethyltin from inorganic tin(IV). Some *Pseudomonas* bacteria are able to form various methyltin compounds.

Other methyl donors, e.g. methyl iodide, produced by certain algae and sea weeds can also be involved in the methylation of inorganic tin(II) salts in aqueous medium [3, 66, 105, 106]. Methyl iodide methylates inorganic Sn(II) salts in an aqueous medium to produce monomethyltin species.

The abiotic methylation of tin(IV) is favoured by low pH values and low ionic strengths of the aquatic environment. Both Sn(II) and Sn(IV) compounds and methyltin derivatives can be methylated by chemical or biological processes under simulated environmental conditions.

Although, methylation or biomethylation can engage sediment or estuary-containing microorganisms, sulphate-reducing bacteria and yeast are mainly involved in methylating OTs [66-68, 105-107]. Biomethylation is of great ecological relevance because methylated metals have a higher toxicity to aquatic organisms than inorganic metal. Transmethylation of methyltins by other heavy metals is also important [3, 73, 107, 108].

Biotransformation of organotin compounds

Biotransformation is the chemical change(s) made by an organism on a chemical compound. The metabolism of OTs influences their environmental fate and tissue retention. Although, OTCs biodegrade in both aerobic and anaerobic conditions but the addition of organic nutrients in the soil can slow down the process of degradation [109-111]. The exposure of *Chlorella vulgaris* to TBT results in the rapid biosorption with sequential degradation to DBT and MBT. The reaction rates for the cleavage of carbon bonds are greater for TBT to DBT than that for DBT to MBT or MBT to inorganic tin. Butyltins are metabolized by the microsomal cytochrome P450 enzyme hydroxylation system. However, debutylation of DBT to MBT by microsomal monooxygenase system is considerably slower than that of TBT to DBT. Isolated rat liver microsomes metabolize TBT to hydroxybutyldibutyltin derivatives with further oxidation to 1-butanol, 1-butane and ketones. Tributyltin is metabolized more rapidly than TBT. Phenyltins biodegrade via sequential dephenylation with cleavage of the tin-carbon bond by biological, UV, chemical or thermal mechanisms [109-111]. Triphenyltin is metabolized by the cytochrome P450 enzyme system, but it can convert cytochrome P450 into cytochrome P420 and thereby affect the function of the monooxygenase system. The metabolic products are less toxic than parental compounds. In humans, the cytochrome P450 system enzymes are not involved in dealkylation and dearylation of OTCs [109-111].

Organotin an endocrine disruptor

Organotins are well-known endocrine disruptors particularly TBT and TPT. Endocrine disruptors (ECDs) are chemicals, or chemical mixtures, that interfere with normal hormone function. They are agents that interfere with the synthesis, secretion, transport, binding, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development and/or behaviour [92, 112]. They are heterogeneous and can be classified into two categories: Natural and synthetic.

Natural ECDs are the natural chemicals found in human and animal food while synthetic ones are human synthesized. Example of these compounds are pesticides, fungicides, plasticizers, plastics and synthetic chemicals used as industrial solvents or lubricants and their byproducts.

Pesticides are usually made in a way that they are highly sensitive towards the neural and reproductive systems of the organisms. The likeness of these processes with human physiological system shows that these chemicals can also affect humans. Some of these chemicals can impede the neuroendocrine systems which directly influence the cardiovascular and metabolic, reproductive systems in humans [92, 112, 113].

Apart from the biochemical methylation of tin, OTCs are not synthesized through natural processes. Hence, they are under the synthetic ECDs. Endocrine disrupting compounds are present in our day to day products, starting from children's products, electronics, textile/clothing, personal care products, and antimicrobial agents to building materials. Although, humans are not aware of these facts in most cases since it is not always written in the materials' chemical list. This call for concerns because these chemicals can be released into the environment and come in contact with humans.

Endocrine disruptors act by altering the hormonal and homeostatic systems that enable the organism to communicate with and respond to the environment. These systems are involved in the regulation of various important processes in humans like metabolism, sexual development, insulin production and utilization, growth, stress response, gender behaviour, reproduction and utilization, growth, stress response, gender behaviour, reproduction and fetal development of living body. Several studies conducted on animal bodies, clinical observations and epidemiological studies have revealed the possible roles of ECDs in affecting reproductive systems, prostate, breast, lung, liver, thyroid, metabolism and causing obesity. Epidemiological data showed evidences that increase in the incidences and prevalence of some diseases such as cancer, diabetes, obesity, and decreased fertility which had been observed for over the last 50 years are associated with ECD chemicals [112, 114].

Conclusion

Organotins have been shown to have adverse effects on the environment at reasonably low concentrations, and bioaccumulation can occur in real samples. As a result, it is necessary to monitor the environment for these compounds and appropriate actions such as legislation and restriction of the use of OTs in some products like biocides should be taken by the government, especially in Africa, with a view to controlling their use and release. Thus safeguarding the marine ecosystem and human health.

Acknowledgement

The authors thank Organization of Women in Science for the research fellowship granted to A.I. Demehin, to study in University of Malaya. Also, they acknowledge the management of Adeyemi College of Education, Ondo, Nigeria for granting A.I. Demehin, a study leave.

References

- [1] A.I. Oloyede-Akinsulere, J.O. Babajide, S.O. Salihu, Organotin applications and environmental toxicity, Elixir Appl. Chem., 90 (2016) 37738-37753.
- [2] J.B. Graceli, G.C. Sena, P.F. Lopes, G.C. Zamprogno, M.B. da Costa, A.F. Godoi, D.M. Dos Santos, M.R. de Marchi, M.A. Dos Santos Fernandez, Organotins: a review of their reproductive toxicity, biochemistry, and environmental fate, Reprod Toxicol., 36 (2013) 40-52.
- [3] M. Hoch, Organotin Compounds in the Environment- An Overview, Appl. Geochem, 16 (2001) 719-734.
- [4] R. Oliveira, R.E. Santeli, Occurrence and Chemical Speciation Analysis of Organotin Compounds in the Environment: A Review, Talanta, 82 (2010) 9-24.
- [5] H.K. Okoro, O.S. Fatoki, F.A. Adekola, B.J. Ximba, R.G. Snyman, Sources, Environmental Levels and Toxicity of Organotin in Marine Environment-A Review, Asian Journal of Chemistry, 23 (2011) 473-482.
- [6] T. Zuliani, G. Lespes, R. Milacic, J. Scancar, M.J. Potin-Gautier, Influence of the soil matrices on the analytical

performance of headspace solid-phase microextraction for organotin analysis by gas chromatography-pulsed flame photometric detection, *J. Chromatogr A*, 1132 (2006) 234-240.

[7]T.Zuliani, G.Lespes, R.Milacic, J.Scancar, M.J.Potin-Gautier, Comprehensive study of the parameters influencing the detection of organotin compounds by pulsed flame photometric detector in sewage sludge, *J. Chromatogr* 1188 (2008) 281-285.

[8]T.Zuliani, G.Lespes, R.Milacic, J.Scancar, M.J.Potin-Gautier, Preparation of a sewage sludge laboratory quality control material for butyltin compounds and their determination by isotope-dilution mass spectrometry, *Anal. Bioanal. Chem.*, 403 (2012) 857-865.

[9]J.Scancar, T.Zuliani, T.Turk, R.Milacic, Organotin compounds and selected metals in the marine environment of Northern Adriatic Sea, *Environ. Monit. Assess*, 127 (2007) 271-282.

[10]K.Peeters, T Zuliani, J.Scancar, R.Milacic, The use of isotropically enriched tin tracers to follow the transformation of organotin compounds in landfill leachate, *Water Research*, 53 (2014) 297-309.

[11]M.Long, J.Strand, P.Lassen, T.Krüger, I.Dahllöf, R.Bossi, M.M.Larsen, P.Wiberg-Larsen, E.C.Bonefeld-Jørgensen, Endocrine-disrupting effects of compounds in Danish streams, *Archives of environmental contamination and toxicology* 66 (2014) 1-18.

[12]M.Furdek, M.Vahčić, J.Scancar, R.Milacic, G.Kniewald, N. Mikac, Organotin compounds in seawater and *Miltilus galloprovincialis* mussels along the Croatian Adriatic Coast *Mar. Pollut. Bull*, 64 (2012) 189-199.

[13]J.-H.Huang, E.Matzner, Degradation of organotin compounds in organic and mineral forest soils, *J. Plant Nutr. Soil Sci.*, 167 (2004) 33-38.

[14]M.Choi, H.Moon, J.Yu, J.Eom, H.Choi, Butyltin contamination in industrialized bays associated with intensive marine activities in Korea, *Arch Environ Contam Toxicol*, 57 (2009) 77-85.

[15]M.A.Champ, A Review of Organotin Regulatory Strategies, Pending Actions, Related Costs and Benefits, *Science of the Total Environment*, 258 (2000) 21-71.

[16]A. Filipkowska, G. Kowalewska, B. Pavoni, Organotin compounds in surface sediments of the Southern Baltic coastal zone: a study on the main factors for their accumulation and degradation, *Environ Sci Pollut Res Int.*, 21 (2014) 2077-2087.

[17]M.F.L.Lesmos, A.C.Esteves, J.L.T.Pestana, Fungicides as Endocrine Disrupters in Non-target Organisms, in: N. Thajuddin (Ed.) *Fungicides- Beneficial and Harmful Aspects*, InTech, Rijeka, Croatia, 2011, pp. 179-196.

[18]C.Gumy, C.Chandsawangbhuwana, A.A.Dzyakanchuk, D.V.Kratschmar, M.E.Baker, A.Odermatt, Dibutyltin disrupts glucocorticoid receptor function and impairs glucocorticoid-induced suppression of cytokine production, *PLoS ONE*, 3 (2008) e3545.

[19]S.A.Mendo, P.R.Nogueira, S.C.N.Ferreira, R.G.Silva, Tributyltin and triphenyltin toxicity on benthic estuarine bacteria, *Fresenius Environ. Bull*, 12 (2003) 1361-1367.

[20]S.Bangedphol, H.E.Keenan, C.Davidson, A.Sakultanti metha, A.Songsasen, The partition behavior of tributyltin and prediction of environmental fate, persistence and toxicity in aquatic environments, *Chemosphere*, 77 (2009) 1326-1332.

[21]O.S.Ayanda, O.S.Fatoki, F.A.Adekola, B.J.Ximba, Fate and Remediation of Organotin Compounds in Seawaters and Soils, *Chem. Sci. Trans.*, 1 (2012) 470-481.

[22]D.S.Khanolkar, S.K.Dubey, M.M.Naik, Bio transformation of tributyltin chloride to less toxic dibutyltin dichloride and monobutyltin trichloride by *Klebsiella pneumoniae*, *International Biodeterioration & Biodegradation*, 104 (2015) 212-218.

[23]A.Garg, R.M.Meena, N.B.Bhosle, Distribution of butyltins in water and sediments of the Mandovi and Zuari estuaries, west coast of India, *Environ. Monit. Assess*, 165 (2010) 643-651.

[24]S.Jadhav, N.B.Bhosle, P.Massanisso, R.Morabito, Organotins in the sediments of the Zuari estuary, west coast of India, *Environ. Manag*, 90 (2009) 4-7.

[25]A.C.A.Sousa, C.M.Barroso, S.Tanabe, T.Horiguchi, Involvement of Retinoid X receptor in imposex Development in *Nucella lapillus* and *Nassarius reticulatus*- Preliminary Results, in: N. Hamamura, S. Suzuki, S. Mendo, C.M. Barroso, H. Iwata, S. Tanabe (Eds.) *Interdisciplinary Studies on Environmental Chemistry-Biological Responses to Contaminants*, TERRAPUB, 2010, pp. 189-196.

[26]H.K. Okoro, O.S. Fatoki, F.A. Adekola, B.J. Ximba, R.G. Snyman, B. Opeolu, Human exposure, biomarkers, and fate of organotins in the environment, *Rev Environ Contam Toxicol.*, 213 (2011) 27-54.

[27]R.F.Cole, G.A.Mills, R.Parker, T.Bolam, A.Birchough, S.Kröger, G.R. Fones, Trends in the analysis and monitoring of organotins in the aquatic environment, *Trends in Environmental Analytical Chemistry*, 8 (2015) 1-11.

[28]CCME (Canadian Council of Ministers of the Environment), Canadian water quality guidelines for the protection of agricultural water uses: Organotin-Tributyltin, triphenyltin, and tricyclohexyltin. In: *Canadian water quality guidelines*, 1999, Canadian Council of Ministers of the Environment, Winnipeg., (1999).

[29]F.Cima, P.J.Craig, C.Harrington, *Organometallic compounds in the Environment*, 2nd ed., John Wiley and Sons, Ltd, Chichester, UK, 2003.

[30]S.J.Blunden, A.Chapman, *Organotin Compounds in the Environment*, in: P.J. Craig (Ed.) *Organometallic Compounds in the Environment*, Longman, London, 1986, pp. 111-159.

[31]S. Brosillon, C.Bancon-Montigny, J.Mendret, Study of photocatalytic degradation of tributyltin, dibutyltin and monobutyltin in water and marine sediments, *Chemosphere*, 109 (2014) 173-179.

[32]S.Brosillon, L.Lhomme, D.Wolbert, Modelling of a falling thin film deposited photocatalytic step reactor for water purification: pesticide treatment, *Chem. Eng. J.*, 169 (2011) 216-225.

[33]G.Plantard, T.Janin, V.Goetz, S.Brosillon, Solar photocatalysis treatment of phytosanitary refuses: efficiency of industrial photocatalysts, *Appl. Catal. B: Environ.*, (2012) 115-116, 138..

[34]B. Antizar-Ladislao, Environmental Levels, Toxicity and Human Exposure to Tributyl (TBT) Contaminated Marine Environment- A review, *Environ Int*, 34 (2008) 292-308.

[35]R.J. Maguire, Review of the persistence, bioaccumulation and toxicity of tributyltin in aquatic environments in relation to Canada's Toxic Substances Management Policy, *Water Qual. Res. J. Canada* 35 (2000) 633-679.

[36]G.S. Zhai, J.F. Liu, B. He, J.B. Zhang, Q.F. Zhou, G.B. Jiang, Ultraviolet degradation of methyltins: elucidating the

mechanism by identification of a detected new intermediary product and investigating the kinetics at various environmental conditions, *Chemosphere*, 72 (2008) 389-399.

[37]T.Gajda,A.Jancsó, Organotins. formation, use, speciation, and toxicology, *Met Ions Life Sci.*, 7 (2010) 111-151.

[38]B.A.Buck-Koehntop, F.Porcelli, J.L. Lewin, C.J.Cramer, G. Veglia, Biological Chemistry of Organotin Compounds: Interactions and Dealkylation by Dithiols, *J. Organomet. Chem.*, 691 (2006) 1748-1755.

[39]G.I.Paton, I.L. Cheewasedtham, M. Dawson, Degradation and toxicity of phenyltin compounds in soil, *Environ Pollut* 144 (2006) 746-751.

[40]G.M.Gadd, Microbial Interactions with Tributyltin Compounds, Detoxification, Accumulation, and Environmental Fate., *Sci Tot Environ*, 258 (2000) 119-127.

[41]A.Sakultantimetha, H.E. Keenan, T.K. Beattie, T.J. Aspray, S. Bangkedphol, A. Songsasen, Acceleration of tributyltin biodegradation by sediment microorganisms under optimized environmental conditions, *Int. Biodeterior. Biodegrad*, 64 (2010) 467-473.

[42]S.K.Dubey, U.Roy, Biodegradation of tributyltins (organotins) by marine bacteria, *Appl. Organomet. Chem*, 17 (2003) 3e8.

[43]A.Cruz, T.Caetano, S.Suzuki, S.Mendo, *Aeromonas veronii*, a tributyltin (TBT) degrading bacterium isolated from an estuarine environment, Ria de Aveiro in Portugal, *Mar. Environ. Research*, 64 (2007) 639e650.

[44]A.Cruz, I.Henriques, A.Correia, S.Suzuki, S.Mendo, *Aeromonas molluscorum* Av27: a Potential Natural Tool for TBT Decontamination, in: Y. Obayashi, Isobekama, T., Subramanian, A., Suzuki, S., Tanabe, S. (Ed.) *Interdisciplinary Studies on Environmental Chemistry-Biological Response to Contaminants*, TERRAPUB, Japan, 2010, pp. 37e46.

[45]A.Cruz, R.Moreira, S.Mendo, An easy, rapid and inexpensive method to monitor tributyltin (TBT) toxicity in the laboratory, *Folia Microbiol*, 59 (2010) 203e207.

[46]A.Cruz, V.Oliveira, I.Baptista, A.Almeida, A. Cunha, S. Suzuki, S. Mendo, Effect of tributyltin (TBT) in the metabolic activity of TBT-resistant and sensitive estuarine bacteria, *Environ. Toxicol. Chem*, 27 (2012) 11e17.

[47]A.Cruz, I.Henriques, A.C.A.Sousa, I.Baptista, A. Almeida, S.Takahashi, S.Tanabe, A.Correia, S.Suzuki, A.M. Anselmo, S. Mendo, A microcosm approach to evaluate the degradation of tributyltin (TBT) by *Aeromonas molluscorum* Av27 in estuarine sediments, *Environ. Res*, 132 (2014) 430e437.

[48]S.E.Lee, J.W.Chung, H.S.Won, D.C.Lee, Lee, Y.W, Removal of methylmercury and tributyltin (TBT) using marine microorganisms, *Bull. Environ. Contamin. Toxicol.*, 88 (2012) 239-244.

[49]R. Sampath, H. Venkatakrishnan, V. Ravichandran, R.R. Chaudhury, Biochemistry of TBT-degrading marine Pseudomonads isolated from Indian coastal waters, *Water Air Soil Pollut*, 223 (2012) 99e106.

[50]K.Shamim, M.M Naik, A.Pandey, S.K.Dubey, Isolation and identification of *Aeromonas caviae* strain KS-1 as TBTC and Lead resistant estuarine bacteria, *Environ. Monit. Assess*, 185 (2013) 5243e5249.

[51]V.Ramachandran, S.K Dubey, Expression of TBTCI-induced periplasmic proteins in a tributyltin chloride resistant marine sediment bacterium *Alcaligenes* sp, *Curr. Sci*, 97 (2009) 1717e1718.

[52]K.Fukushima, S.K.Dubey, S.Suzuki, YgiW homologous gene from *Pseudomonas aeruginosa* 25W is responsible for tributyltin resistance, *J. General Appl. Microbiol*, 58 (2012) 283e289.

[53]K.V.Thomas, S.J.Blake, M.J.Waldock, Antifouling paint booster biocide contamination in UK marine sediments, *Mar Pollut Bull*, 40 (2000) 739-745.

[54]A.Filipkowska, G.Kowalewska, B.Pavoni, L.Łęczyński, Organotin in surface sediments from seaports on the Gulf of Gdańsk (southern Baltic coast), *Environ Monit Assess*, 182 (2011) 455-466.

[55]M.Furdek, N.Mikac, M.Bueno, E.Tessier, J.Cavalheiro, M. Monperrus, Organotin persistence in contaminated marine sediments and porewaters: In situ degradation study using species-specific stable isotopic tracers, *Journal of Hazardous Materials*, 307 (2016) 263-227.

[56]H.Inoue, O.Takimura, K. Kawaguchi, T. Nitoda, H. Fuse, K. Murakami, Y. Yamaoka, Tin-carbon cleavage of organotin compounds by pyoverdine from *Pseudomonas chlororaphis*, *Appl. Environ. Microbiol.*, 69 (2003) 878e883.

[57]F.Jude, C. Arpin, C. Castang, M. Capdepuy, P. Caumette, C. Quentin, btABM, a multidrug efflux pump associated with tributyltin resistance in *Pseudomonas stutzeri*, *T. FEMS Microbiol. Lett.*, 232 (2004) 7e14.

[58]R.Krishnamurthy, L.Cabral, R.Vidya, S.K.Dubey, Isolation and biological characterization of a TBTCI degrading marine bacterium, *Vibrio* sp. from Bombay high oil field, India., *Curr. Sci.*, 93 (2007) 1073e1074.

[59]G.X.Sun, W.Q.Zhou, J.J.Zhong, Organotin decomposition by pyochelin, secreted by *Pseudomonas aeruginosa* even in an iron e sufficient environment, *Appl. Environ. Microbiol.*, 72 (2006) 6411e6413.

[60]S.Dubascoux, G.Lespes, L. enaix, M.P.Gautier, Kinetic monitoring of trisubstituted organotins in soil after sewage sludge application, *Applied Organometallic Chemistry*, 22 (2008) 481-487.

[61]J.Heroult, Y.Nia, L.Denaix, M.Bueno, G.Lespes, Kinetic degradation processes of butyl- and phenyltins in soils, *Chemosphere*, 72 (2008) 940-946.

[62]U.S. Environmental Protection Agency, Solid waste and emergency response glossary--Bioaccumulation: U.S. Environmental Protection Agency, access date March 18, 2016, (2010).

[63]U.S. Environmental Protection Agency, Bioaccumulation testing and interpretation for the purpose of sediment quality assesment: U.S. Environmental Protection Agency, access date March 18, 2016, (2000).

[64]C.T. Chiou, Bioconcentration of organic contaminants, in *Partition and Adsorption of Organic Contaminants in Environmental Systems*, John Wiley & Sons, Inc., 2002.

[65]A.X. Yi, K.M.Y. Leung, M.H.W. Lam, J.-S. Lee, J.P. Giesy, Review of measured concentrations of triphenyltin compounds in marine ecosystems and meta-analysis of their risks to humans and the environment, *Chemosphere*, 89 (2012) 1015-1025.

[66]C. Bini, J. Bech, PHEs, Environment and Human Health: Potentially harmful elements in the environment and the impact on human health, Springer, 2014.

[67]M.Gielen, Tin-Based Antitumour Drugs., Springer Science and Business Media, 2013.

[68]H.Schumann, I.Schumann, Sn Organotin Compounds: Part 14: Dimethylation-, Diethylation-, and Dipropyltin-oxygen compounds, Springer Science and Business Media, 2013.

- [69]H.Rudel, Case study: bioavailability of tin and tin compounds, *Ecotoxicology and Environmental Safety*, 56 (2003) 180-189.
- [70] M.A. Champ, Economic and environmental impacts on ports and harbours from the convention to ban harmful marine anti-fouling systems *Mar Pollut Bull*, 46 (2003) 935-940.
- [71]H. Rudel, J. Muller, J. Steinhanses, C. Schroter-Kermani, Retrospective Monitoring of Organotin Compounds in Freshwater Fish from 1988 to 2003: Results from the German Environmental Specimen Bank, *Chemosphere*, 66 (2007) 1884-1894
- [72]H.Rudel, W.Bohmer, H.J.Bruckert, P.Lepper, H.Sohn, J.Steinhanses, A.Wenzel, Organische Zinnverbindungen, Alkylphenole und Bisphenol A in marinen und limnischen Biota der Umweltprobenbank, UBA-Texte 06/2001, Umweltbundesamt, Berlin, 1999.
- [73]S.V.Avery, G.A.Codd, G.M.Gadd, Biosorption of tributyltin and other organotin compounds by cyanobacteria and microalgae *Appl Microbiol Biotechnol*, 39 (1993) 812-817.
- [74]I.P.o.C.S. WHO-IPCS. World Health Organisation, Tributyl compounds, Environmental health criteria, in, 1999.
- [75]U.Schulte-Oehlmann, T.Albanis, A.Allera, J. Bachmann, P.Berntsson, N.Beresford, et al., Compendo: focus and approach, *EHP* 114 (2006) 8-100.
- [76] S.Ohhira, M.Enomoto, H.Matsui, In vitro metabolism of tributyltin and triphenyltin by human cytochrome P-450 isoforms, *Toxicology*, 228 (2006) 171-177.
- [77] M. Ohji, T. Arai, S. Midorikawa, H. Harino, R. Masuda, N. Miyazaki, Distribution and fate of organotin compounds in Japanese coastal waters, *Water Air Soil Pollut.*, 178 (2007) 255-265.
- [78]M.Azenha, R.Evangelista, F.Martel, M.T. Vasconcelos, Estimation of the human intestinal permeability of butyltin species using the Caco-2 cell line model, *Food Chem Toxicol*, 42 (2004) 1431-1442.
- [79]H.Harino, N.Iwasaku, T.Arai, M.Ohji, N.Miyazaki, Accumulation of organotin compounds in the deep-sea environment of Nankai Trough, Japan, *Arch Environ Contam Toxicol*, 49 (2005) 497-503.
- [80]H.Harino, O.Madoka, G.Wattayakorn, K. Adulyanukosol, T.Arai, N.Miyazaki, Accumulation of organotin compounds in tissues and organs of dolphins from the coasts of Thailand, *Archi Environ Contam Toxicol*, 54 (2008) 146-153.
- [81]J.Strand, M.M.Larsen, C.Lockyer, Accumulation of organotin compounds and mercury in harbour porpoises (*Phocoena phocoena*) from the danish waters and West Greenland, *Sci Total Environ* 350 (2005) 59-71.
- [82]K.Azumi, S.Nakamura, S.Kitamura, S.Jung, K. Kanehira, H.Iwata, S.Tanabe, S.Suzuki, Accumulation of organotin compounds and marine birnavirus detection in korean ascidians, *Fish Sci* 73 (2007) 263-269.
- [83]M.A.Wetzel, A.Winterscheid, D.S. Wahrendorf, Baseline of the butyltin distribution in surface sediments (0-20 cm) of the Elbe estuary (Germany, 2011), *Mar. Pollut. Bull.* , 77 (2013) 418-423.
- [84]P.L.Podratz, E.Merlo, G.C.Sena, M.Morozesk, M.M. Bonomo, S.T. Matsumoto, M.B.d. Costa, G.C. Zamprogno, P.A.A. Brandão, M.T.W.D. Carneiro, E.d.C. Miguel, L. Miranda-Alves, I.V. Silva, J.B. Graceli, Accumulation of organotins in seafood leads to reproductive tract abnormalities in female rats, *Reproductive Toxicology*, 57 (2015) 29-42.
- [85]M.B.Costa, G.C. Zamprogno, F.C. Pedruzzi, L.d. Morais, M.M.P. Tognella, A.F.L. Godoid, D.M. Santos, M.R.R.d. Marchi, M.A. Fernandez, Differential organotin sensitivity in two *Leucozonia* species from a ship traffic area in southeastern, Brazil. *Mar Biol Res* 10 (2014) 712-724.
- [86]M.B.Costa, B.S.Mardegan, G.C.Zamprogno, F.C. Pedruzzi, L.d. Morais, G.B. Dalbem, D.A.d. Silva, J.B. Graceli, Penis malformations in *Leucozonia nassa* (Gmelin, 1792) and *Leucozoniacellata* (Gmelin, 1791) in a TBT contaminated region from Brazil, *Aquat Sci Tech*, 2 (2014) 52-66.
- [87]M.Furdek, M.Vahčić, J.Šćancar, R.Milacić, G.Kniewald, N.Mikac, Organotin compounds in seawater and *Mytilus galloprovincialis* mussels along the Croatian Adriatic Coast, *Marine Pollution Bulletin* 64 (2012) 189-199.
- [88]G.M.Cooke, Toxicology of tributyltin in mammalian animal models, *Immunol Endoc Metabol Agents Med Chem* 6(2006) 63-71.
- [89]J.B.Nielsen, J.Strand, Butyltin compounds in human liver, *Environmental Research*, 88 (2002) 129-133.
- [90]J.P.Meador, C.A.Rice, Impaired growth in the polychaete *Armandia brevis* exposed to TBT in sediments, *Mar Environ Res* 51 (2001) 43-29.
- [91]H.Meng-Pei, L.Shin-Mei, Accumulation of organotin compounds in Pacific oysters, *Crassostrea gigas*, collected from aquaculture sites in Taiwan, *Sci Total Environ* 313 (2003) 41-48.
- [92]K.Y. Kevin, M.Y.L. Kenneth, Organotin contamination in seafood and its implication for human risk in Hong Kong, *Marine Pollut. Bull*, 85 (2014) 634-640.
- [93]T.Guerin, V.Sirot, J.L.Volatier, J.C.Leb Blanc, Organotin levels in seafood and its implications for health risk in high-seafood consumers, *Sci Tot Environ*, 388 (2007) 66-77.
- [94]H.Rudel, J.Muller, H.Jurling, C.Schroter-Kermani, Retrospective Monitoring of Perfluorinated Compounds in Archived Herring Gull Eggs, in: T. Isobe, K. Nomiyama, A. Subramanian, S. Tanabe (Eds.) *Interdisciplinary Studies on Environmental Chemistry — Environmental Specimen Bank, TERRAPUB Japan*, 2010, pp. 81-86.
- [95]H.Rüdel, W.Böhmer, C. Schröter-Kermani, Retrospective monitoring of synthetic musk compounds in aquatic biota from German rivers and coastal areas, *J. Environ. Monit.*, 8 (2006) 812-823.
- [96]A.Fliedner, H.Rüdel, H.Jürling, J.Müller, F. Neugebauer, C.Schröter-Kermani, Levels and trends of industrial chemicals (PCBs, PFCs, PBDEs) in archived herring gull eggs from German coastal regions. , *Environmental Sciences Europe*, (2012) 24-27.
- [97]M.Berg, C.G.Arnold, S.R.Muller, J.Muhlemann, R.P. Schwarzenbach, Sorption and desorption behavior of organotin compounds in sediment-pore water systems, *Environ. Sci. Technol.* , 35 (2001) 3151-3157.
- [98]D.M.Whitacre, *Reviews of Environmental Contamination and Toxicology*, Springer Science & Business Media, 2011.
- [99]M.Bueno, A.Astruc, M.Astruc, P.Behra, Dynamic sorptive behaviour of tributyltin on quartz sand at low concentration levels: effect of pH, flow rate, and monovalent cations., *Environ. Sci. Technol*, 32 (1998) 3919-3925.
- [100]K. Fent, Ecotoxicological effects at contaminated sites, *Toxicology*, 205 (2004) 223-240.
- [102]Y.Mamindy-Pajany, F.Geret, M.Roméo, C.Hurel, N.Marmier, Ex situ remediation of contaminated sediments using mineral additives: assessment of pollutant

bioavailability with the Microtox solid phase test, *Chemosphere*, 86 (2012) 1112-1116.

[103] M.M.Larsen, J.Strand, J.H.Christensen, K.Vorkamp, A.B.Hansen, O.Andersen, Metals and organotins in multiple bivalve species in a one-off global survey, *J. Environ. Monit.*, 13 (2011) 1793-1802.

[104]Í.B.Castro, M.Rossato, G.Fillmann, Imposed reduction and residual butyltin contamination in southern Brazilian harbours, *Environ. Toxicol. Chem.*, 31 (2012) 947-954.

[105]A.Gianguzza, E.Pelizzetti, S.Sammartano, *Chemical Processes in Marine Environments*, Springer Science & Business Media, 2013.

[106]J.Xu, D.L.Sparks, *Molecular Environmental Soil Science*, Springer Science & Business Media, 2014.

[107]E.Marlon, M.Flores, *Microwave-Assisted Sample Preparation for Trace Element Determination*, Newnes, 2014.

[108]V.Minganti, R.Capelli, G.Drava, R.De Pellegrini, Solubilization and methylation of HgS, PbS, and SnS by iodomethane, a model experiment for the aquatic environment, *Chemosphere*, 67 (2007) 1018-1024

[109]M.Nordberg, G.F.Nordberg, B.A.Fowler, L.Friberg, *Handbook on the Toxicology of metals*, in, Springer Science and Business Media, 2011, pp. 1024.

[110]P.L.Chamber, W.Klinger, Further studies in the assessment of Toxic Actions, in: *European Society of Toxicology Meeting*, Springer Science and Business Media, Dresden, 2012, pp. 510.

[111]T.Arai, H.Harino, M.Ohji, W.Langston, *Ecotoxicology of Antifouling Biocides*, in, Springer Science and Business Media, 2009.

[112]E.R.Kabir, M.S.Rahman, I.Rahman, A review on the endocrine disruptors and their possible impacts on human health, *Environmental Toxicology and Pharmacology*, 40 (2015) 241-258.

[113]A.C.Gore, Neuroendocrine targets of endocrine disruptors. *Hormones*, Athens, 9 (2010) 16-27.

[114]K.A. Kidd, G.Becher, A.Bergman, D.C.G.Muir, T.J. Woodruff, *Human and Wildlife exposures to EDC's*. Chapter 3. State of the science of endocrine disrupting chemicals, UNEP, (2012) 189-250.