Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268
e-ISSN: 2395-3454

Vol. 18 | No. 1 | pp. 217-224 | 2019

Review Research Paper | Open Access

Aquatic Ecotoxicology and Water Quality Criteria of Three Organotin Compounds: A Review

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 08-06-2018
Accepted: 02-08-2018

Key Words:
Organotin compounds
Toxicology
Environmental behavior
Water quality criteria
Pollution control

ABSTRACT

Organotin compounds (OTCs) are metal-organic compounds, such as triphenyltin (TPT), tributyltin (TBT) and trimethyltin (TMT), containing at least one Sn-C covalent bond. They can be used as polyvinyl chloride (PVC) stabilizers, wood preservatives, pesticides, anti-corrosion coatings, and molluscicide agents. OTCs are frequently detected in water bodies and have a long half-life. Their ecotoxicological behaviour in the aquatic environment has long been a cause of concern. In this paper, we briefly summarize the physicochemical characteristics, fate in the aquatic environment, biodegradation/bioconcentration, metabolism, and toxicity for aquatic organisms of three organotin compounds. Furthermore, we discuss the water quality criteria of the three compounds for aquatic ecosystems, which could provide important indications for future application, management, risk assessment, as well as pollution control associated with OTCs.

INTRODUCTION

Organotin compounds (OTCs) are metal-organic compounds containing at least one Sn-C covalent bond. They are widely used as pesticides, bactericides, polyvinyl chloride (PVC) stabilizers, as well as wood preservatives, anti-corrosion coatings, and molluscicide agents (Fang et al. 2017, Sousa et al. 2014). However, they have high toxicity and can cause serious damage to the environment. As the only metallic compounds among the known endocrine disruptors, OTCs can lead to developmental malformations in oyster shells (*Crassostrea gigas*), death of shellfish larvae, and deformation of gastropods in ng/L concentrations. In addition, various organisms (especially fish and shellfish) are strong OTC accumulators that has indirect adverse effects on human health (Pagliarani et al. 2013, Anastasiou et al. 2016, Ho et al. 2014). Therefore, the toxicity of OTCs including triphenyltin (TPT), tributyltin (TBT), and trimethyltin (TMT) has become a hotspot of current research.

Many studies of the sources, distribution, environmental fate, and toxicity mechanism of OTCs have been published (Laranjeiro et al. 2018). In this paper, we review the aquatic ecotoxicological behaviour and data of the three OTCs mentioned above, to systematically understand their aquatic ecotoxicology and quality criteria, and provide a key reference for future water ecotoxicology studies.

SOURCE AND FATE OF OTCS IN AQUATIC ENVIRONMENTS

Aquatic OTCs mainly originate from PVC plastics, anti-fouling coatings, and pesticides. In particular, TPT and TBT are used in marine anti-fouling coatings, bactericides, pesticides, and plastic stabilizers, which can directly release them into the aquatic environment. They are detected in high levels, especially in harbour and wharf environments (Laranjeiro et al. 2018, Okoro et al. 2016). TPT and TBT have been found even in Antarctic waters (He et al. 2018). Wastewater and waste gas produced during the synthesis of plastic stabilizers contain TMT, which reaches the water environment through wastewater, surface runoff and other channels (Ashraf et al. 2017). In addition to artificial introduction, the biomethylation process can also form OTCs in aqueous environments. For instance, Chen et al. (2007) reported that some *Pseudomonas* bacteria can form various methylated OTCs; moreover, methylated iodide produced by some seaweed species can methylate inorganic Sn(II) salts, and diosmin can convert inorganic Sn(IV) salts into methylated Sn compounds in the presence of trivalent iron.

The migration mechanism of OTCs in aquatic environments (Fig. 1) is mainly controlled by adsorption processes. The water solubility and migration rate of aquatic OTCs are generally low, especially in the case of TPT and TBT, which

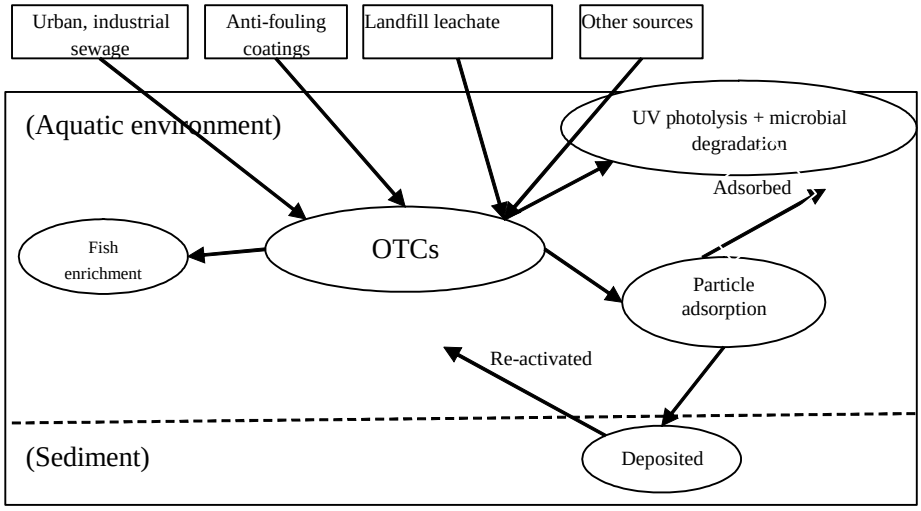

Fig. 1: Fate of organotin compounds in aquatic environments.

are easily adsorbed on suspended particles in water. TBT fractions between 57% and 95% exist in adsorbed form under simulated estuarine conditions (Laranjeiro et al. 2018). Chen et al. (2001) found that, upon entering the water environment, TBT is distributed between microlayers, water bodies, sediments, algae, and other suspended matter, as well as fish. The system reaches a steady state at certain time after TBT has entered the aqueous environment. TBT is strongly adsorbed on suspended matter (such as algae and organic compounds) and sediments, whereas the surface of microlayers is less enriched in TBT. This adsorption behaviour plays a key role in the migration process of OTCs and in their bioavailability. Dissolved OTCs are prone to enter the sea or the food chain through bioaccumulation. However, TMT has strong hydrophilic and lipophilic groups that mainly exist in ionic form in water, and is easily accumulated in aquatic organisms (Wei et al. 2013). In addition to adsorption, the interaction of OTCs with dissolved organic matter also depends on the pH value and the nature of the organic species in the water environment. The maximum adsorption of organic matter to TBT is observed at pH 8.0 (Fang et al. 2017).

OTCs are widely found in aquatic environments (including drinking water), sediments, soil, and organisms. At present, the areas contaminated with OTCs are mainly found in ports, wharfs and berths. For example, the average TBT concentrations in waters and sediments around the Cape Town harbour in South Africa, are 0.067-111.290 and 0.010-0.829 µg/L, respectively, whereas those of TPT are 0-23008.0 and 0-0.691 µg/L, respectively (Okoro et al. 2016). The TBT and TPT concentrations in the Saudi coastal water are 0.14-1.9 and 0.12-0.70 µg/L, respectively (Al-Shatri et al. 2015). The net weight of TBT per gram sediment reaches 10000 ng in many sites, such as Port Camargue in France (Briant et al. 2013) and the Elbe river in Germany (Becker et al. 1992). TPT has also been detected in aquatic animals, sediments, soils and water (Shim et al. 2005, Harino et al. 2000). The concentration of TMT in the North Sea and in the Elbe River in Germany reaches 2-11 ng/L (Shawky et al. 1998).

Similar to other countries, studies of OTCs in China also focus on ports, wharves, and related areas. Jiang et al. (2001) measured the OTCs concentration in ports located in Dalian, Tianjin, Qingdao, Beihai, Jinan, Peking, Qinghuangdao, Yantai, the Yangtze, the Yellow River, Baiyangdian and Taihu. Every tested sample presented organotin pollution, without exception. In particular, the average concentration of TBT was 93.8 ng/L, which is much higher than the accepted limits of the Western countries. Huang et al. (2005) detected OTCs in water, sediments, and animals around the ports of Xiamen, Shantou, and Huiyang, in the southeastern coast of China. Liu et al. (2003) measured TMT concentrations of up to 360 ng/L in the Beijing Guanting reservoir and Yongding River. Qiu et al. (2008) analysed the subterranean water resources of industrial areas in Zhujiang and found TMT contents of up to 1.07×10^5 ng/L. These data highlight the presence of different degrees of organotin pollution in different countries; however, there are some similarities in the distributions of OTCs. Although the concentration levels of different areas show large variations, the contribution focus on the crowded water. Moreover, even though different locations have been studied, the maximum concentrations are found within 2 cm from the surface of

sediments; the concentrations decrease with increasing depth (Briant et al. 2013, Anna et al. 2014).

The degradation of OTCs in the aquatic environment involves the continuous removal of the organic groups bonded to the tin atom. In nature, this process is often the overall result of photodegradation, biodegradation and chemical degradation. Photodegradation in water is the fastest degradation route. Since the light intensity decreases with increasing water depth, the OTCs degrade slowly in deep-water sediments and soils.

The half-life of the OTCs show significant variations with the environmental conditions. Various studies indicated that the half-life of TBT in water ranges from days to months, whereas that in sediments is longer. Briant et al. (2016) measured the half-life of TBT in sediments as 360-775 days.

Turning to the biodegradation route, not many microorganisms able to induce degradation of organotin compounds have been identified. Bacteria (pseudomonads, *Alcaligenes faecalis, Shewanella putrefaciens*) and phytoplankton (*Skeletonema costatum, Chlorella vulgaris, Scenedesmus dimorphus*) degrade OTCs in aquatic systems (Briant et al. 2013). Ultraviolet light can promote TPT degradation (Hoch 2001), the photodegradation rate can reach 89.4% after exposure to ultraviolet light for 75 min (He et al. 2008). On the other hand, biodegradation of TPT in soil and sediments proceeds slowly, with only 5% degradation in 14 days (Kannan & Richard 1996). Our present understanding of the photodegradation and biodegradation processes of TMT is still limited, and further studies are needed.

QUANTITATIVE STRUCTURE-ACTIVITY-PROPERTY RELATIONSHIPS

The physicochemical properties of TPT, TBT and TMT are given in Table 1. The three OTCs contain one chlorine atom and different alkyl groups. Their molecular structure (type of substituents and positions of functional groups), average molecular polarizability, molecular weight and electron distribution directly affect the octanol-water partition coefficient (K_{ow}), solubility and biological activity (Eng 2017). OTCs are highly toxic to aquatic organisms including molluscs, fish and algae, and their toxicity is related to electronic effects. Liu et al. (2008) studied the quantitative structure-activity relationship (QSAR) of 13 OTCs based on their highest occupied orbital energy (E_H) and molecular hydration energy (E_W), and developed an effective model to predict the acute toxicity of these compounds. It shows that there is an electron supply and accepts the relationship between organic tin molecules and large target molecules *in vivo*. In addition, both E_H and E_W are positively correlated with the biological toxicity.

The K_{ow} of organic pollutants is considered an important parameter for predicting the migration rate of these compounds in various phases of the environment, but it does not exactly match the ionic organic pollutants and metal-organic compounds. Li et al. (2002) explored the accumulation and distribution of TBT in tilapia. Their results show that a more accurate prediction of the concentration and distribution of OTCs can be obtained using an artificial biofilm-water system instead of K_{ow}. This may be due to the ionic character of the OTCs, which host the tin atom inside the molecule; therefore, their accumulation is controlled not only by the lipophilic partitioning of their simple nonpolar components, but also by the bioenrichment mechanisms that rule the heavy metal ions.

BIOACCUMULATION AND METABOLISM OF OTCS

The OTCs, and especially TBT, TMT and TPT are liposoluble and easily bind to glutathione and α-keratin in organisms, which leads to their accumulation. In addition to accumulation, OTCs can also lead to food chain amplification. OTC accumulation has been detected in marine organisms ranging from lower plants, to plankton, to endothermic vertebrates and birds (Laranjeiro et al. 2018, Nsengimana et al. 2015). In addition, they have long lifetimes in organisms, after four years of restricted use of OTCs as anti-fouling coatings in Italy, TBT was still detected in 46% of fish (Amodio-Cocchieri et al. 2000).

The extent of bioenrichment of OTCs is generally measured by the bioconcentration factor (BCF). Many studies have shown that organotin compounds are easily accumulated in molluscs and fish. The bioenriched concentration of TBT in conchs is 1000 times higher than that of the surrounding water environment (Gibbs & Bryan 1986), whereas the BCF of TBT in oyster tissue in water is as high as 50000. Mussels exhibit the highest accumulation rate of OTCs from water and planktons (Zhou et al. 1994). Quintas et al. (2017) found that the concentration of TBT in mussels from different water bodies worldwide was in the range of 1-6434 ng/g; for example, the concentration of TBT in mussels from the northern Adriatic Sea was up to 6434 ng/g. Yamada et al. (1997) measured the OTC concentration in the liver of eels from the Sea of Japan and Hokkaido, and found that the BCF of TPT reached 500000, much higher than that of TBT. Organotin compounds are also easily accumulated in fish. Marine environmental surveys showed high OTC concentrations in marine fish populations worldwide. For example, the TBT and TPT concentrations in fish from the Arabian Gulf were 126.4-228.4 ng/g (dry weight) and 64.9-281.7 ng/g (Ashraf et al. 2017), respectively. The TMT ac-

Table 1: Physico-chemical properties of the three organotin compounds investigated in this study.

Indicators	TPT	TBT	TMT
International designation	66183	3535715	71166
CAS No.	639-58-7	1461-22-9	1066-45-1
Name	Triphenyltin chloride	Tributyltin chloride	Trimethyltin chloride
Chemical formula	$(C_6H_5)_3SnCl$	$C_{12}H_{27}ClSn$	C_3H_9ClSn
State	White powder	Colorless or yellowish oily liquid	White crystal
Relative molecular weight	385.5	325.5	199
Fusion point (101.3kPa)	103-109°C	-9°C	37-39°C
Boiling point (101.3kPa)	240°C	171-173°C	148°C
Density (g/cm^3)	1.49	1.2	0.988
Flashing point	70°C	>112°C	97°C
pka	5.2	6.99	6.6
$logK_{ow}$ (Eng, 2017)	2.65	2.6	2.3
Hazard level*	T, N, C	T,N	T+, N
Solubility in various solvents	Insoluble in water, soluble in organic solvents. Colorless after dissolution. Stable at room temperature.	Soluble in ethanol, heptane, benzene and toluene. Insoluble in cold water. Soluble in hot water.	Soluble in water, Volatile.
Applications	Anti-fouling coating of marine boats, bactericides.	Wood antisepsis, varnishes of boats.	Plastics processing, insecticides, bactericides.

*T = poisonous, N = harmful to the environment, C = corrosive

cumulation is significantly lower than that of TPT and TBT. Hadjispyrou et al. (2001) reported that the TMT content in *Artemia* was 75 times higher than that in the aquatic environment. Moreover, Nsengimana et al. (2015) found efficient accumulation of OTCs in phytoplankton algae.

The accumulation of OTCs in aquatic organisms varies with the type of organism, survival environment, size and organs. TPT and TBT accumulation is obviously lower in fish muscle than in molluscs such as oysters. Morcillo et al. (1997) also found that the TBT concentration in molluscs was higher than in other aquatic animals, and reached a maximum of 514 µg Sn/g in shellfish. This result may be related to the enzymatic metabolism, as fish can degrade TBT *in vivo*, its corresponding accumulated content is relatively low. TBT and its metabolites exhibit a heterogeneous distribution in different tissues and organs. The content of TBT in metabolic active sites such as liver, kidney, spleen, and bladder is low, which may be due to the presence of cytochrome P450 reductase that degrades TBT into dibutyltin and monobutyltin (Briant et al. 2013).

TOXICITY OF OTCs TO AQUATIC ORGANISMS

When the concentration of organotin compounds in the water environment reaches nanogram per litre levels, toxic effects can be produced on oysters, shellfish and gastropods (Sousa et al. 2014). Numerous studies have focused on the acute aquatic toxicity of common OTCs, especially of TBT and TPT on different aquatic organisms. The acute toxicity value (LC_{50}) of TBT is in the range of 0.14-282.20 µg/L, with a median value of about 4.0 µg/L; TBT has acute toxicity to some algae, copepods and shellfish, as well as aquatic crustaceans. The LC_{50}/EC_{50} values of TBT to *S. costatum* (Walsh et al. 1985), *Platymonas* sp. (Huang et al. 1996), as well as *U. Intestinalis* and *F. spiralis* germlings (Girling et al. 2015) at 96 h are 0.36, 0.31, 0.007 and 0.0045 µg/L, respectively. On the other hand, the LC_{50}/EC_{50} values of TBT to *E. affinis* (Bushong et al. 1988) and *A. tonsa* (Kusk & Petersen 1997) are 1.98 and 0.87 µg/L, respectively, whereas the corresponding values for *M. edulis* (Thain 1983), *R. abronius* and *H. nudus* are 2.38, 108.00 and 83.28 µg/L, respectively (Bushong et al. 1988). According to previous studies, TPT is more toxic to aquatic plants, with LC_{50} to *N. closterium*, *Platymonas* sp., *P. tricornutum* and *I. galbana* of 6.21, 4.55, 0.93 and 1.32 µg/L, respectively (Li et al. 1996, Zhao et al 1990). However, TPT shows low acute toxicity to fish, for example, the LC_{50} to carp at 96 h is 134.46 µg/L (Han et al. 2008).

Studies on the chronic toxicity of the three OTCs considered in this review have focused on reproductive toxicity and chronic death. TBT has a chronic toxicity (LD_{50}) in the range of 0.01-1.50 µg/L, with a median value of approximately 0.11 µg/L (Mu et al. 2010), the LD_{50} of TBT against *D. magna*, *B. calyciflorus* and *S. macrocephalus* are 0.14, 0.31 and 0.54 µg/L, respectively (Zhu et al. 2009, Mu et al. 2010). Alfred et al. (1988) studied the 30-day LD_{50} of TPT hydride against fathead minnows and found a significantly decreased survival rate at 2 µg/L. This result demonstrated that TPT in concentrations higher than 1 µg/L has

some inhibitory effects on the survival and reproduction of *Daphnia magna*. A TPT concentration of 2 µg/L prolongs the culture cycle of *N. awatschensis*, increases the mortality rate of broodstock in the incubation period, and decreases the production of shrimp, leading to the conclusion that breeding water containing 1 µg/L TPT can suppress the reproduction of *N. awatschensis*. The results of chronic toxicity tests of TMT are not clear at present, and further studies are needed.

OTCs are the only metal compounds with endocrine disrupting effects. The main manifestations of their toxicity are abnormal embryonic development, increased testosterone levels, malformations and loss of immune function in aquatic organisms. Anastasiou et al. (2016) found that TBT concentrations below 1 ng/L can cause malformations in *H. trunculus*, a biologically sensitive species. Mcallister et al. (2003) found higher male numbers of newborn zebrafish upon exposure to 0.1 µg/L TBT for 70 days, and all sperm lacked flagella upon exposure to 10 µg/L TMT. When the mass concentration of TBT and TPT reaches 1 µg/L, they cause sexual alterations in gastropods, leading to increased male characteristics and decreased fertility (Abidli et al. 2013, Anastasiou et al. 2016). Laranjeiro et al. (2016) reported that TPT can cause *Nucella lapillus* distortion through a phallic route. TBT has an inhibitory effect on the immune system of fishes and mammals. The accumulation of OTCs in the animals affects the activity of phagocytic cells and suppresses the immune system of animals. TBT can inhibit the Na^+/H^- exchange pump, which induces unfavourable stress conditions in fish, especially hypoxic stress. TBT and TPT have highly toxic effects on algae, which can destroy the reticular structure of chloroplast photosynthetic sheets and hinder the growth of sensitive sea algae and plankton. When heavily concentrated in animal brains, TBT and TPT disrupt the normal activity of the neuroendocrine system and inhibit the release of neuroendocrine factors from the thoracic ganglion (Lu et al. 2017). The effect of endocrine-disrupting chemicals is often not isolated, and can often affect the endocrine function of the body through multiple pathways involving the neurological, immune, and endocrine systems (Lu et al. 2017).

HEALTH EFFECTS OF OTCs

A limited number of experimental studies showed that the three OTCs may be human carcinogens (B2 grade), with clear animal carcinogenicity. However, it is hard to assess the human health risks associated with exposure to low concentrations of OTCs (Gueguen et al. 2011), despite the continuous occurrence of human poisoning cases under different work environments (Lee et al. 2016). The main OTC intake channel for humans is through ingestion of polluted marine fish, especially the blood of contaminated fish, which has the highest levels of OTCs (Ho et al. 2014). Although OTCs exhibit genetic toxicity, causing gene mutations, chromosome aberrations and DNA damage, their toxicity to humans has not been extensively investigated. In bacterial susceptibility experiments, Paredescervantes et al. (2017) used 28 bacterial strains to test their sensitivity to TBT and TPT without being metabolically activated. They found that only 12 of the 28 tested strains were inhibited at TBT or TPT concentrations of 1 mM, and the bacteria were essentially not affected by TBT or TPT during 48 h of *in vitro* culture growth. In SOS colour tests, we found that all dibutyltin compounds have genetic toxicity. TBT concentrations of 20-90 µg/L were found to produce genetic toxicity. Comet assays showed that TBT can induce oxidative and DNA damage in rats (Liu et al. 2006) and also cause nuclear DNA damage in nucleated red blood cells of rainbow trout (Luca et al. 2001). TPT can cause micronuclei and sister-chromatid exchange in Chinese hamster cells (Chao et al. 1999). *In vitro* assays showed that TMT increases the chromosomal aberration rate in human peripheral blood lymphocytes, and the sister chromatid exchange and positive micronucleus test. *In vivo* tests revealed that TMT causes malformations in chromosomes of rat bone marrow cells (Tang & Li 1999).

ECOLOGICAL EFFECTS OF OTCs

The water quality criteria indicate the maximum dose or concentration of pollutants in aquatic ecosystems that do not adversely affect humans or other organisms. The purpose of establishing these criteria is to prevent unacceptable long- and short-term effects of pollutants on commercial and recreational aquatic organisms, as well as other species such as fish, benthic invertebrates, and plankton in rivers and lakes. Statistical extrapolation methods based on risk statistics are generally used in the international derivation of pollutant reference values; among these, two methods are the most widely used. The first is the toxicity percentile rank method based on acute/chronic toxicity ratios, developed by the United States Environmental Protection Agency (EPA) (Stephan 1985); this method is also used in South Africa. The other one is the species sensitivity distribution (SSD) method, also known as A&S method, by Aldenberg & Slob (1993). It is based on Monte Carlo simulations and adopted by the OECD, the Netherlands, Australia and New Zealand.

At present, the development of water quality criteria for organotin compounds is still in its infancy, and the relevant data are limited, as only the TBT criteria have been published. In particular, the U.S. EPA published the TBT

water quality criteria in 2003. Based on these criteria, and taking Monte Carlo data into account, the SSD curve was established to predict the maximum concentration (CMC) and final chronic value (FCV) of TBT compounds to aquatic organisms in fresh and marine water. Based on the EPA standard method and acute/chronic toxicity ratios, the CMC values of TBT in freshwater and seawater are 0.4589 and 0.4175 μg/L, respectively, while the corresponding FCV values are 0.0723 and 0.0658 μg/L, respectively. Based on the water quality criteria adopted in European Union countries, Mu et al. (2010) introduced some improvements to the setting method of datum value, the application of the model, and the determination of the evaluation factor. They proposed to establish the datum of seawater quality of our country by using the data requirement method of "the value of double value datum". They used TBT as an example to develop China's high value water quality criteria (HSWC) and to determine the upper and lower TBT concentration limits in seawater as 0.43 and 0.002 μg/L, respectively. Although the criteria for TBT have been established, they only apply to a specific ecosystem, and do not take geographical and human health effects into account.

At present, large amounts of data on the acute and chronic toxicity of TPT are available. Related toxicity studies have been carried out for zooplankton, plants, arthropods and vertebrates; however, the data on the acute and chronic toxicity of TPT are incomplete. In particular, no specific data on its chronic toxicity are available (Alfred et al. 1988, Sun et al. 2000), and the corresponding water quality criteria has not been reported. Only acute toxicity data to *Chlorella pyrenoidesa*, *Daphnia magna*, *Oryzias latipes*, *Artemia* and zebrafish were reported (Nagase et al. 2010, Hadjispyrou et al. 2001, Li et al. 2011). In addition, there are insufficient data to complete the development of water quality criteria for TMT.

PERSPECTIVES

Organotin compounds, as typical representatives of environmental endocrine disruptors, cause global pollution of the water environment, posing a direct threat to aquatic organisms and human health. This reflects the current interest in the transfer processes of OTCs into water and in the environmental effects of their toxicity. Many systematic studies have focused on the presence of OTCs in the water environment, their transfer and deposition in water, as well as their adsorption characteristics, ecological toxicity and toxicity mechanism in sediments. However, these investigations are mainly focused on dibutyltin and phenyltin compounds and are limited to individual and population levels, whereas studies on other OTCs are still scarce. In addition, our understanding of the mechanisms of organotin toxicity and detoxification is only superficial, and most studies are still at a speculative level. Therefore, we need to improve our understanding of the toxicity and detoxification mechanisms of OTCs and their influence on the biological and marine ecosystems.

The similarities in the migration mechanisms of different OTCs highlight the important role of their deposition in the sediment; the sediment microorganisms are not only the main disintegrators, but also the producers of some substances with a very important role in the biological chain. However, the effect of the OTCs on the microbial population of the sediment is still unclear, while at the same time the fraction of bacteria that can be separated and culture directly from the sediment is only 1% of the total bacteria in the bottom sediments. The study of the relationship between OTCs and microorganisms in sediment, as well as the degradation of OTCs by sediment microorganisms, are still the limitation of organotin in aquatic ecological cycling.

In terms of management and monitoring of OTC pollution, only the water quality criteria for TBT are currently available; therefore, it is essential to complete the development of water quality criteria for OTCs, especially in freshwater, in order to deal with serious water pollution issues worldwide.

ACKNOWLEDGEMENTS

This work was supported by the Modern Agro-industry Technology Research System (grant number CARS-45-21).

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