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REVIEW

Interaction of triorganotin compounds with Chesapeake Bay sediments and benthos

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Triorganotin compounds can interact with various segments of natural water systems. In sediments, for example, these compounds can undergo speciation, and can also become injurious to benthos. The interactions of tributyltin (TBT) and triphenyltin (TPT) compounds with sediments have been studied using extraction techniques in addition to directly observing these compounds in sediments using Mössbauer spectroscopy. The effect of these compounds on benthos has also been examined. The results of these studies are reviewed with particular regard to studies on sediments from the Chesapeake Bay, USA.

Keywords: Triorganotin, triphenyltin, tributyltin, sediments, Mössbauer spectroscopy, speciation, benthos, Chesapeake Bay

INTRODUCTION

Organotin compounds are used as PVC stabilizers and catalysts, fungicides and biocides, and as the active agent in some antifouling paints.[1,2] The increasing use of organotin compounds, such as tributyltin (TBT) and triphenyltin (TPT) compounds, in antifouling marine paints generated great concern and interest in regard to their fate in the environment and their toxic effects on marine organisms.[3,4] this has led to the restriction of the use of these compounds in paints in several countries.[5]

Although the use of triorganotin compounds has been restricted by government regulations, these compounds may have entered the water system during their previously unrestricted use in antifouling paints. In the aquatic environment, triorganotin compounds have low aqueous solubility and low mobility, and exhibit strong binding to sediments.[6] These compounds are easily absorbed by particulate matter in the water, which, upon settling to the bottom, can be incorporated into the sediment. This permits the direct and continuous introduction of these toxicants into the aquatic ecosystem, which may have adverse effects on non-targeted species such as crustaceans and fish.[7] Thus, it is important to determine the fate and speciation of these triorganotins in the water environment, particularly in sediments.

The speciation of organotin compounds in sediments has usually been studied by extraction and/or derivatization procedures.[8] However, Mössbauer spectroscopy affords an opportunity to observe directly the speciation of organotin compounds in sediments.[9]

This review summarizes the studies of the fate, speciation, and effect on benthos of these triorganotin compounds (TBT and TPT) in the sediments of the Chesapeake Bay.

MODE OF ENTRY

One mode of entry of triorganotin compounds into the Chesapeake Bay is through their release from vessels and underwater structures, such as piers, that have been treated with antifoulant paints. The evidence indicates that the leaching of these compounds from marine paints results in higher concentrations in static environments, such as harbors, estuaries, marinas and bays, than in open waters. Recent studies have shown that the level of TBT observed is directly related to the amount of boating activity. For example, Seligman *et al.*[10] observed that the level of TBT was highest in the vicinity of a commercial shipyard along the Elizabeth River with the concentrations decreasing as the distance from the shipyard increased. Similar findings were

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reported by Matthias *et al.*,[11,12] who found low levels of TBT compounds in the open waters of the Chesapeake Bay, whilst elevated levels were detected in the Annapolis marina areas. In addition, the presence of trimethyltin was also reported in the waters of Baltimore harbor by Brinckman and co-workers.[13,14]

FATE IN SEDIMENTS

Matthias *et al.*[12] measured the concentration of TBT in sediments from seven northern Chesapeake Bay sites. The concentrations ranged from <0.05 to 1.4 $\mu g\, g^{-1}$ (dry weight) of sediment. Furthermore, the study showed that there was an enhancement by a factor of approximately 1000 of TBT in the sediments, compared with the concentrations found in the water column or microlayer. Similar findings from other authors have indicated that concentrations of butyltin compounds in sediments were one to three orders of magnitude larger than in water columns.[15–18]

In order to understand the transport and fate of TBT in the estuarine environment, Unger *et al.*[19,20] determined the adsorption behavior of TBT in Chesapeake Bay sites. On the basis of 24 h desorption isotherms, these investigators concluded that the adsorption of TBT in Chesapeake Bay sediments is reversible and that there is a decrease in adsorption with an increase in salinity. They attributed this to charge–charge and charge–dipole interactions between the TBT species in solution and the various sediment components. It has also been shown that the adsorption of TBT to sediments decreases with increasing water movement.[21] These findings suggest that the sediment can no longer be considered the terminal TBT sink.

The degradation of TBT and/or TPT compounds to inorganic tin in the marine environment is widely accepted as proceeding through a series of debutylation or dephenylation steps. The degradation of the TBT species in sediments has been found to proceed at a much slower rate than in water. A study by Seligman *et al.*[22] showed that the half-lives for the degradation of TBT species in sediments were an order of magnitude longer than in water. Similar results have been reported by other investigators. For example, a half-life of 162 days was reported by Stang and Seligman[23] for the degradation of the TBT species in San Diego Bay sediments and a half-life of 60 days (by extrapolation) was found in seawater.[24]

Maguire *et al.*[25] reported that the degradation process in anaerobic sediment was significantly shorter than under aerobic conditions. However, a more recent study by Waldock *et al.*[26] found half-lives of less than one year for TBT in aerobic sediment, whilst half-lives of approximately two years were found in anaerobic sediment. These conflicting results suggest that the degradation of the TBT species in various types of sediments may be a function of the characteristics of the sediment.

SPECIATION

One of the earliest speciation studies was reported by Guard *et al.*,[27] who measured the ^{119}Sn NMR spectra of chloroform extracts of sediments spiked with TBT acetate, chloride and oxide. The extracts of aerobic sediments contained TBT chloride, carbonate, and hydroxide, whereas TBT carbonates and sulfides were found in the extracts of the spiked anaerobic sediments. Using tin Mösbauer spectroscopy, Eng *et al.*[9] observed the major TBT species directly in sediments spiked with TBT acetate, chloride and oxide. Their results differed from those reported by Guard *et al.*[27] In samples of aerobic sediment from Baltimore Harbor, the TBT acetate and chloride were unchanged, but the oxide was converted to the hydroxide.[9] However, the TBT acetate and chloride were found to be converted to the hydroxide in spiked anaerobic sediments, and the oxide interacted with the sediment to form an unidentified product.

A possible explanation for the observed differences in speciation may be the different characteristics of the sediments used. To test this hypothesis, the Mössbauer spectra of sediments from different sites of the Chesapeake Bay spiked with TBT acetate, chloride, fluoride (TBTF), and oxide were examined.[28] It was found that with the exception of TBTF, which retained its polymeric form in all sediments, the speciation of the TBT differed in the different sediments, confirming this hypothesis.

Another Mössbauer study[29] using Chesapeake Bay sediments spiked with TPT hydroxide, acetate, chloride and fluoride indicated that TPT hydroxide and acetate were converted to TPT^{+}, which then interacted directly with the sediment.

TPT chloride and fluoride were reported to remain in their molecular forms when they interacted with the sediments. A later study reported that the speciation of the TPT in aerobic and anaerobic estuarine sediments from the same site was unaffected by pH or salinity.[30]

Sediments from different sites spiked with the same TPT gave similar Mössbauer spectra.[29] This indicates that the speciation of the TPT does not depend upon the characteristics of the sediment as was observed with TBT.[28] The influence of the sediment on the degradation processes with TBT was also observed.[25,26] This indicates that the two triorganotins, except the fluorides, interact differently with the sediments.

EFFECT ON BENTHOS

Trace quantities of organotin compounds have been found to be detrimental to untargeted benthos at various sites in the Chesapeake Bay. Evidence indicates that TBT can adversely effect marine and estuarine organisms at aqueous concentrations of less than 1 $\mu g\,dm^{-3}$, and there is increasing evidence that concentrations of less than 100 $ng\,dm^{-3}$ are harmful to some species.[31] Concentrations near these levels have been detected in the Chesapeake Bay and have been found to vary considerably over both location and time.[32] Triorganotins in the water column have been found to associate with suspended and bottom sediments. The sediment can then become toxic to benthic organisms.[33] Rice *et al.*[33] have found TBT concentrations as high as 290 $\mu g\,kg^{-1}$ (dry weight) in Chesapeake Bay sediment.

The toxicity of organotins towards benthos depends upon several factors. Some studies have suggested possible correlations between organotin toxicity and the number and/or types of organic groups attached to the tin,[34,35] the total surface area of the compound,[36] and the molecular mass[37] of the compound. The toxicity of a compound has also been estimated using its lipid solubility.[38] Lipid solubility is determined using octanol and water partition coefficient (K_{ow}) values.

Characteristics of the biota and of the marine environment can affect the uptake and toxicity of the organotin compound. Different organotin compounds may affect organisms at one taxonomic level and not affect organisms in another level. Barron[39] points out that body size, metabolism and environment (temperature, concentration of particulates and the presence of surfactants) play a large role in the uptake and retention of toxic chemicals. He also stresses that physical structures, e.g. gills, can facilitate the uptake of toxic compounds into an organism.[39] The toxicity of the organotin compound to a particular species may also depend upon the developmental stage of that organism. The larval stage of a species may find trace quantities of organotins lethal, whereas adult members of the same species may experience deformities or no apparent effects. For example, Hall[40] found that some levels of TBT were toxic to early-life stages of bivalves but not adults. Hall[41] emphasizes that, in order to assess the chronic effects of TBT on a particular species, the full life cycle must be evaluated.

Trace levels of organotins have been found to be toxic to microorganisms in the Chesapeake Bay. Hallas and Cooney[34] determined minimum inhibitory concentrations (MIC) of several organotin compounds on microbial isolates from estuaries of the Chesapeake Bay. Results from their study led to the conclusion that many microorganisms show sensitivity to organotin compounds, and that organotin pollution can alter the microbial flora of an estuary. Some microorganisms examined were found to be resistant to high concentrations of some organotins. Hallas and Cooney[34] suggested that because sensitivity patterns to individual organotins varied, more than one mechanism may be involved in microbial resistance to organotins. Blair *et al.*[42] found a number of bacterial isolates to be resistant to TBTs in sediments. It was speculated that these isolates accumulate the TBT through passive absorption, but do not metabolize TBT. Avery *et al.*[35] found that organotins could inhibit cyanobacterial metabolism in aquatic systems. Olson and Brinckman[43] speculated that photosynthetic microorganisms in some areas of the Chesapeake Bay were responsible for the degradation of tributyltin to dibutyltin and monobutyltin species.

Various other toxicity studies have been performed on marine biota. Hall[40,44] reported toxicity studies for various invertebrates and fish in the Chesapeake Bay, including amphipods, copepods and larval bivalves, which he found to be highly sensitive. Hall[45] also reviewed toxicity data on early-life stages of striped bass, *Morone saxatilis*. It was noted that amongst a multitude of marine contaminants, TBT was one of the most toxic pollutants to striped bass larvae.

Extensive research has been undertaken on the

interactions of triorganotins and bialves, an important product of the Chesapeake Bay. Existing data indicate that triorganotins can be concentrated by bivalves.[33] Rice *et al.*[33] reported that oysters have been shown to have a limited ability to metabolize TBT compared with other organisms and have the potential to accumulate TBT to levels that may prove harmful to both themselves and their predators.[33] In addition, they found that analyses of samples collected from contaminated and unpolluted sites indicated that the TBT is present in sediment and oysters at levels consistent with the boating activity.[33]

TBT concentrations were measured in soft-shell clam (*Mya arenaria*) and American oyster (*Crassostrea virginica*) tissues from ten Maryland sites of the Chesapeake Bay by Unger *et al.*[46] This study showed that the TBT concentrations in soft-shell clam tissues were related to seasonal climate changes. The lower concentration levels in the soft-shell clam tissue found during the winter months were attributed to a decrease in clam activity in low water temperatures, as well as to a decrease of TBTs in the water column, which coincided with a decrease in boating activity. In addition, TBT concentrations in clam tissues varied between individual clams. The authors suggested that the possible factors contributing to this variability were lipid content and clam weight. Levels of TBT concentrations between the soft-shell clams and oysters were compared and found to be less in oysters than in soft-shell clams at the same site. The general trends of TBT concentration levels, however, were similar in both species at all sites, and the amount of TBT in the tissues of the organisms was related to the TBT concentrations in the water.

American oysters were also examined by Espourteille[47] at Virginia sites of the Chesapeake Bay and were found to have a range of TBT concentrations that fell within the range found by Unger *et al.*[46] The evidence in these studies supported the hypothesis of Unger *et al.*[46] that environmental factors control the TBT concentrations in bivalve tissue. Unger *et al.*[46] speculated that the differences in habitat and feeding behavior between the two species may be responsible for the differences in uptake of the TBTs.

Further research is necessary before the fate and interactions of triorganotins in the sediments of the Chesapeake Bay can be fully understood. In a review of the ecotoxicity of TBT, Rexrode[48] emphasized that although a general database for the toxicity of TBTs is not complete, the existence of concentration-dependent modes of TBT toxicity has been demonstrated with many organisms. Rexrode[48] suggested that tests be designed to evaluate the toxicity of TBTs, with special attention being paid to the cellular, physiological and behavioral effects of long-term low-level exposure to TBTs. A more complete database for organotin toxicity studies on Chesapeake Bay benthos would assist in measures aimed at ensuring the protection of the benthos.

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