

**Report for 2003DC42B: Speciation of Triorganotins in  
Sediments of the Anacostia and Potomac River Sediments as the  
Result of their Interaction with Bacteria**

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**Speciation of Triorganotins in Sediments of the Anacostia and Potomac River**  
**As the Result of Their Interactions with Bacteria**

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## **Speciation of Triorganotins in Sediments of the Anacostia and Potomac River as the Result of Their Interactions with Bacteria**

### **Introduction**

The Anacostia and Potomac rivers are two major waterways located in the District of Columbia. Each year these rivers play host to extensive recreational activities for the residents of the metropolitan area. The majority of these activities involve boating and fishing. Optimally, these rivers should be free of hazardous chemicals and/or agents that can be detrimental to the aquatic biota. If this is not possible, then it is imperative to know what hazardous species are present and their interactions and/or relationships with the aquatic biota. Armed with this type of knowledge beforehand, potential problems such as the recent *Pfiesteria piscicida* outbreak can be avoided. Two classes of pollutants that find their way into the Anacostia and Potomac rivers, as well as other waterways that have high boat traffic, are tributyltins (TBTs) and triphenyltins (TPTs) since they are the toxic additives added to antifoulant marine paints. Marine paints are used to inhibit the attachment of barnacles, sea grass, hydroids and other marine organisms to the bottom of ships and other submerged marine structures. Organotin marine paints contain as much as 20% by weight of the antifoulant (1). One mode of entry of these triorganotins into the various waterways is through their release from vessels and underwater structures, such as piers and docks that have been treated with antifoulant paints. The leaching of these compounds from marine paints results in higher concentrations of these chemicals in static environments, such as harbors, estuaries, marinas and bays, than in open waters. Studies have shown that the level of TBT observed is directly related to the amount of boating activity (2). For example, Seligman *et al.* (2) 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 reported by Matthias *et al.*(3,4) who found low levels of TBT compounds in the open waters of the Chesapeake Bay, while elevated levels were detected in the Annapolis marina areas. The use of triorganotin compounds in the United States has been restricted by the Organotin Act (5), which prohibits the use of organotin-based paints on vessels smaller than 25 meters. However, vessels larger than 25 meters may still use marine

paints containing organotin and a number of these larger vessels still travel these rivers, particularly the Anacostia river, where a naval shipyard is located. Even with the restricted use of these antifouling marine paints, these compounds have already entered various water systems during their previously unrestricted use. In the aquatic environment, triorganotin compounds are known to have low aqueous solubility and mobility, and exhibit strong binding to sediments (6). Therefore, particulate matter in the water, which upon settling to the bottom, can be incorporated into the sediment, easily absorbs these compounds. Any disturbance of the sediment will permit the direct and continuous re-introduction of the triorganotins back into the water column, where they can have adverse effects on non-targeted species such as crustaceans and fish (7). Furthermore, these compounds still possess a major threat to the aquatic environment even after government regulations have restricted their use. For example, a recent study of Canadian water and sediment samples (8) done after the banning of TBTs indicated that while there has been a reduction of TBT concentrations in fresh waters, such a reduction was not evident in sea water. The study also revealed that at many sites, the TBT concentrations were still high enough to cause acute and chronic toxicity to aquatic and benthic organisms. Another recent study from Canada (9) indicated that since 1989, when the use of TBTs was banned, there was an actual increase in the TBTs contained in sediments from large vessel harbor sites.

Several countries (8) have made attempts to assess the effectiveness of their TBT regulations. In general, it was found that with restricted usage, there was a reduction of the TBT contamination of water and some organisms. Some recovery of the populations of some organisms has been observed, particularly those close to marinas (8). However, this reduction was not observed in areas where the boat traffic involved vessels larger than 25 meters since the ban of TBT does not apply to them. Reductions of TBT concentrations in water systems have been observed in France (10), the United Kingdom (11 - 14), Ireland (15, 16) and Switzerland (17, 18). However, the concentrations of TBT in water still exceeded the guidelines for a particular jurisdiction in some of these countries (12). Furthermore, in some sampling sites in the United Kingdom (19) and the Netherlands (20), there was little or no decrease in TBT concentrations in the water at the time of sampling. In addition, many workers have reported that little or no reduction in

TBT concentrations was observed in sediments several years after the enactment of the TBT regulations (13, 14, 17, 18, 21 - 23). This non-reduction was attributed to the appreciable persistence of TBT in sediments, most probably due to their strong binding to the sediments. Thus, TBT contaminated sediments may continue to pose a hazard to benthic organisms and other organisms in the water column, either through sediment re-suspension directly or indirectly through benthic eating organisms.

While there have been numerous speciation studies of organotin compounds in various bodies of water around the world, there have been no similar extensive studies in DC waterways. While most investigators have focused on the determination of organotin species and their concentrations in the environment, only a few studies have been initiated to study triorganotins in sediments as a result of their interactions with bacteria. Thus, a study of the speciation of triorganotins in sediments of the Anacostia and Potomac rivers, as a result of their interaction with bacteria, would be essential for a more complete understanding of the effects of triorganotins on the aquatic environment. The results from this study will alert those responsible for water quality to the long term impact of these hazardous chemicals and, therefore, allow them to plan accordingly.

## **Experimental**

### **Chemicals.**

Tributyltin chloride (TBTCI) was obtained from Gelest, Inc., Tullytown, PA, USA. Triphenyltin chloride (TPTCI) was obtained from Aldrich Chemical Co., Inc., Milwaukee, WI, USA. The compounds contained the normal abundance of  $^{119}\text{Sn}$  and were used as received without further purification to spike the sediment samples.

### **Sediment Samples.**

Sediment samples were obtained as grab samples from the Potomac River in the DC metropolitan area. The samples were kept frozen until they were ready to be spiked. The locations of the various sites are given in Table 1.

### **Bacterium**

The *E. coli* was obtained from the Biology Department at the University of the District of Columbia, Washington, DC, 20008. The concentration of the *E. coli* was determined by measuring its absorbance at 540 nm.

### **Preparation of Sediment Samples.**

Five grams of sediment, 0.1 grams of the triorganotin,  $10^6$  cells of *E. coli* were added to 100 mL of nutrient agar broth since the *E. coli* did not survive in deionized water alone. The mixture containing the sediment, triorganotin, *E. coli*, and nutrient agar broth was then mechanically shaken in the dark for a period of two weeks at ambient temperature. The samples were kept in the dark for an additional week. Samples were shaken in the dark to simulate the natural environment of the sediment. Also some triorganotins are known to degrade to other species when exposed to sunlight or UV light in a laboratory photo reactor (24). After three weeks, the sediment samples were filtered and frozen until the Mössbauer spectra were recorded. To identify the organotin species present, the experimental spectra were compared to spectra of known triorganotin compounds. Controls consisting of sediment, triorganotin and nutrient agar broth were also prepared and their Mössbauer were also used for comparison.

### **Mössbauer Spectral Studies.**

The Mössbauer spectra were recorded using a Model MS-900 (Ranger Scientific Co., Burleson, TX) spectrometer in the acceleration mode with a moving source geometry. A 5 mCi  $\text{Ca}^{119\text{m}}\text{SnO}_3$  source was used, and counts of 30,000 or more were accumulated for each spectrum. The spectra were measured at 80K using a liquid-nitrogen cryostat (CRYO Industries of America, Inc., Salem, NH). The velocity was calibrated at ambient temperature using a composition of  $\text{BaSnO}_3$  and tin foil (splitting  $2.52 \text{ mm s}^{-1}$ ). The resultant spectra were analyzed by a least-square fit to Lorentzian shaped lines.

### **Results and Discussion**

Determination of structures of triorganotin compounds using various spectroscopic techniques is well documented in the literature. Mössbauer spectroscopy has proven very useful for determining the coordination and bonding in organotin compounds (1). Mössbauer spectroscopy yields two parameters, the isomer shift (IS) and quadrupole splitting (QS) values. The former is primarily sensitive to changes in *s*-electron density at the tin nucleus and the latter to the stereochemistry about the tin atom. The ratio of the quadrupole splitting to isomer shift values ( $\rho = \text{QS/IS}$ ) has been used to determine the coordination number of the central tin atom. Tin compounds which are

four coordinated have  $\rho$  values smaller than 1.8 while  $\rho$  values larger than 2.1 are indicative of compounds with greater than four coordination.<sup>21</sup>

A comparison of the QS and IS values of the pure compounds and the spiked compounds (control and bacterial) at the various sites indicate that the sediments affect the speciation of the compounds. This conclusion is based on the observation of the differences in the QS and IS Mössbauer parameters.

While the sediments affect the speciation of the compounds, the characteristics of the sediments at the different sites do not appear to affect the speciation. For example, the QS values in Table 2 for the TBTCI control samples ( $3.14 - 3.34 \text{ mm s}^{-1}$ ) in sites I, II, IV and V are within experimental error of each other. This is also true for the TBTCI samples containing bacteria whose QS values ranged from  $3.14$  to  $3.41 \text{ mm s}^{-1}$ . These findings, with the exception of site III, would suggest that, in general, the speciation of the TBTCI is independent of the characteristics of the sediments at these sites.

Similarly, the speciation of the TPTCI was independent of the sediment characteristics in sites I, II and IV. The QS values for the controls ranged from  $2.77$  to  $2.86 \text{ mm s}^{-1}$  while the bacterial samples ranged from  $2.77$  to  $2.96 \text{ mm s}^{-1}$ .

The stereochemistry of the tin atom can be deduced from the  $\rho$  values. As can be seen in Table 2, all the TBTCI spiked anaerobic samples have  $\rho$  values in the range 2.08 to 2.46, indicative of triorganotin compounds that are five coordinated. This is also true for the TPTCI spiked anaerobic samples (Table 3) with the exception of samples from sites III and V. The tin atoms in these samples are four coordinated.

It is also observed that the QS values for TPTCI spiked samples are lower than for the TBTCI spiked samples, which indicate that the geometry of the tin atoms in these samples are more symmetrical. This is not surprising since the phenyl groups are more symmetrical as compared to the butyl groups and thus, expected to lead to a more symmetrical species.

The higher observed IS values for the TBTCI can be rationalized by its electron donating abilities. It has been reported that an increase in electron density at the tin atom will increase the IS value (1). The data in tables 2 and 3 support this conclusion. In

addition, the lower observed IS values for the TPTCl spiked samples indicate that there is less *s*-character in the tin atoms for these species.

The average QS and IS values for both TBTCI and TPTCl in the control and bacterial samples (Tables 2 and 3) are within experimental error, suggesting that the bacteria had no effect on the speciation of either compound. However, on closer examination, the data in Tables 2 and 3 indicate that there is a difference, beyond experimental error, in the QS values of the sediments with and without the bacteria, *E. coli*, for several sites. This would suggest that the *E. coli* is affecting the speciation of the triorganotins, however, the mechanism is not clear at present.

This study clearly indicates that the speciation of the triorganotins as well as the bacterial effects on the speciation is a function of several factors. These factors would include variation in the components of the sediments and the heterogeneous nature of the sediments. A fuller understanding of these variations awaits analyses of the structure of the sediments.

**Table 1. Location of Potomac River Sediment Samples.**

Site	Latitude	Longitude
1	38.89997 N	77.07510 W
2	38.89464 N	77.06253 W
3	38.88553 N	77.05939 W
4	38.85290 N	77.03464 W
5	38.82120 N	77.03790 W

**Table 2.** Mössbauer spectral parameters ( $\text{mm s}^{-1}$ ) of anaerobic Potomac River Sediments spiked with tributyltin chlorides in the presence and absence of *E. coli*.

Site	TBTCI					
	Control			Bacteria		
	QS	IS	$\rho$	QS	IS	$\rho$
<b>I</b>	3.20	1.36	2.35	3.22	1.33	2.42
<b>II</b>	3.14	1.44	2.18	3.41	1.45	2.35
<b>III</b>	3.09	1.41	2.19	2.87	1.38	2.08
<b>IV</b>	3.34	1.34	2.54	3.14	1.43	2.20
<b>V</b>	3.27	1.42	2.37	3.34	1.36	2.46
<b>Average</b>	3.21	1.39	2.33	3.20	1.39	2.30
<b>Pure Compound</b>	3.38	1.54	2.19	---	---	---

**Table 3.** Mössbauer spectral parameters ( $\text{mm s}^{-1}$ ) of anaerobic Potomac River Sediments spiked with triphenyltin chlorides in the presence and absence of *E. coli*.

Site	TPTCI					
	Control			Bacteria		
	QS	IS	$\rho$	QS	IS	$\rho$
<b>I</b>	2.86	1.21	2.36	2.77	1.16	2.39
<b>II</b>	2.85	1.19	2.39	2.96	1.18	2.51
<b>III</b>	2.38	1.12	1.92	2.08	1.17	1.78
<b>IV</b>	2.77	1.21	2.30	2.91	1.20	2.42
<b>V</b>	2.13	1.05	2.03	2.40	1.12	1.97
<b>Average</b>	2.60	1.16	2.20	2.62	1.17	2.21
<b>Pure Compound</b>	2.53	1.31	1.93	---	---	---

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