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Speciation of some triorganotin compounds in sediments from the Anacostia and Potomac Rivers, Washington, DC, using Mössbauer spectroscopy

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Triorganotin compounds, namely the tributyltin (TBT) and triphenyltin (TPT) moieties, have been used as the active components in antifoulant marine paints. Mössbauer spectroscopy was used in this work to identify the products of speciation of these triorganotin compounds in various types of sediment from rivers around the Washington, DC, USA, area. Aerobic and anaerobic sediments from several sites in the Anacostia and Potomac Rivers were spiked with tributyl- and triphenyl-tin chloride, *bis*-(tri-*n*-butyltin) oxide and triphenyltin hydroxide. Mössbauer spectra were recorded for the resultant interactions of the species produced with the various sediments. The Mössbauer spectra of both types of sediment, aerobic and anaerobic, spiked with tributyltin chloride and *bis*-(tri-*n*-butyltin) oxide were the same, suggesting that these compounds were converted to the same species, mostly likely the hydrated tributyltin cation, TBT^+. The spectra of all triphenyltin chloride and triphenyltin hydroxide spiked sediment samples were the same, indicating again that these compounds were converted to the same species, in this case the hydrated triphenyltin cation, TPT^+. Thus the species that interacts with the various sediments are the respective hydrated cations. The results also support the previous conclusion obtained with Chesapeake Bay sediments, that the product of triorganotin speciation depends on the nature of sediment. Copyright © 2001 John Wiley & Sons, Ltd.

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The use of tributyltin (TBT) and triphenyltin (TPT) compounds in antifouling marine paints has generated great concerns and interest in their fate in the environment because they are known to have toxic effects on non-targeted marine organisms.[1–4] The use of triorganotin compounds in the USA has been restricted by the Organotin Act,[5] which prohibits the use of organotin-based paints on vessels smaller than 25 m. However, the hulls of older pleasure crafts may still contain these toxicants, which may leach into waterways and become potential environmental problems. Hence, it is important to study the fate and chemical speciation of these compounds in sediments when they enter the water system.

In general, speciation of organotin compounds has been determined by extraction and/or derivatization procedures.[6–8] However, tin Mössbauer spectroscopy offers an advantage in that it permits the direct observation of the triorganotin species in the sediments. Mössbauer spectroscopy yields information about the structure, bonding and oxidation states in organotin compounds by providing a probe of the tin atom. The two parameters obtained from the Mössbauer spectrum are the isomer shift δ and the quadrupole splitting Δ. The isomer shift is related to the *s*-electron density at the tin nucleus, which can provide information as to its oxidation states and the bonding of the tin atom. The quadrupole splitting reflects the electronic environment around the tin nucleus, and its magnitude gives information concerning the symmetry of the ligands

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about the tin atom. Hence, this form of spectroscopy can give information pertaining to the tin atom directly in the sediments. Previously, our laboratories have use this approach to study the speciation of TBT and TPT compounds in various waterways around the District of Columbia (DC), such as the Anacostia River,[9] Baltimore Harbor[10] and Chesapeake Bay.[11–14]

The results of the Mössbauer studies from the spiking of aerobic and anaerobic sediments obtained from these rivers with TPT and TBT compounds are reported here. Both rivers play host to extensive recreational activities for the residents of the DC metropolitan area. Understanding the long-term environmental effects of these compounds would alert those responsible for water quality to the long-term impact of these chemicals and, therefore, allow them to plan accordingly. These include triphenyltin chloride (TPTCl), triphenyltin hydroxide (TPTOH), tributyltin chloride (TBTCl), and *bis*-(tri-*n*-butyltin) oxide (TBTO).

MATERIALS AND METHODS

Chemicals

TPTCl, TBTCl, and TBTO were obtained from M & T Chemicals, Inc., Rahway, NJ and TPTOH was obtained from Alpha Products, Danvers, MA. All the compounds contained the normal abundance of ^{119}Sn and were used as received without further purification to spike the sediment samples.

Samples

Sediment samples were obtained as grab samples from the Anacostia and Potomac Rivers in the DC metropolitan area. The samples were kept frozen until they were ready to be spiked. Aerobic sediments were prepared by allowing the anaerobic sediments to dry in air. The color of the sediments changed from black–greenish black to brown. The locations of the various sites are given in Table 1.

Preparation of sediment samples

The anaerobic sediments were thawed in water to prevent oxidation. The following procedure was used in all experiments. 5 g of aerobic or anaerobic sediment was spiked with 0.1 g of the triorganotin compound. The mixture was then covered with 100 ml of deionized water. The mixture was shaken mechanically in a closed vessel in the dark for 2 weeks at room temperature and then remained in darkness at room temperature for an additional week. The sediment samples were then removed by gravity filtration and kept frozen until the Mössbauer spectra were recorded.

Table 1. Location of sediment sample sites

Site	Latitude (N)	Longitude (W)
Anacostia River		
AR-1	38° 52′ 35″	76° 58′ 51″
AR-2	38° 52′ 15″	76° 59′ 49″
AR-4	38° 52′ 13″	77° 00′ 20″
AR-6	38° 52′ 41″	77° 00′ 52″
Potomac River		
PR-4	38° 51′ 11″	77° 02′ 17″
PR-7	38° 40′ 15″	77° 11′ 00″
PR-9	38° 40′ 00″	77° 09′ 15″
PR-10	38° 40′ 30″	77° 12′ 00″

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 $Ca^{119m}SnO_3$ source was used, and counts of 30 000 or more were accumulated for each spectrum. The spectra were measured at 80 K using a liquid-nitrogen cryostat (CRYO Industries of America, Inc., Salem, NH). The velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and tin foil (splitting 2.52 mm s^{-1}). The resultant spectra were analyzed by a least-squares fit to Lorenzian-shaped lines.[15]

RESULTS AND DISCUSSION

Comparison of Mössbauer spectra of anaerobic and aerobic sediments

Typical Mössbauer spectra for TBTCl-spiked aerobic and anaerobic sediments are shown in Fig. 1. As seen in this figure, the intensities of the Mössbauer spectra of aerobic sediments are less than the intensities of anaerobic sediments, indicating that the Mössbauer effect is less in the aerobic than the anaerobic sediments. With a few exceptions, the average intensities for the aerobic sediments are about 0.76 of the intensities for the anaerobic sediments (Tables 2 and 3). These exceptions may occur because there is no way to ensure that all the sediment samples retain identical amounts of the tin compounds. Previously, we had suggested that this difference is due to the different amounts of tin compound that were absorbed by the sediments.[10] An alternate explanation may be related to the amount of water associated with the sediments. The spectral area is proportional to the Mössbauer effect *f*, which is defined as $\exp(-kx^2)$, where x^2 is the mean square vibrational amplitude of the absorbing tin nucleus.[16] The general decrease in spectral areas in the aerobic sediments can be attributed to the fact that there is less water surrounding the tin nuclei, thus allowing the tin atom more movement than in the anaerobic sediment. More movement of the tin nucleus or larger x^2 values will result in less intense spectra than when the value of x^2 is smaller. Similar findings were observed for spiked aerobic and anaerobic sediments from the Chesapeake Bay.[12,14]

TPT compounds

The Mössbauer parameters, Δ and δ, for the aerobic and anaerobic sediments from the Anacostia and Potomac Rivers spiked with TPTCl and TPTOH are given in Tables 2 and 3 respectively. The Δ and δ values for TPTCl- and TPTOH-spiked samples from both rivers are the same, within experimental error, in both aerobic and anaerobic sediments. This suggests that both of these compounds are converted to the same species, most likely the hydrated TPT cation, TPT^+. The Mössbauer parameters of the spectra of the spiked sediments are very similar to the parameters for pure TPTOH ($\Delta = 2.95$ mm s^{-1} and $\delta = 1.23$ mm s^{-1}),[12] suggesting that the environment of the tin atom is similar in both the sediments and the pure compound. The smaller Δ values observed indicate that the environment around the tin atom in the sediments is more symmetrical. This observation is consistent with the hypothesis that there is an interaction between the TPT cation and the sediments. Strong binding between organotins and sediments has been reported in the literature.[17]

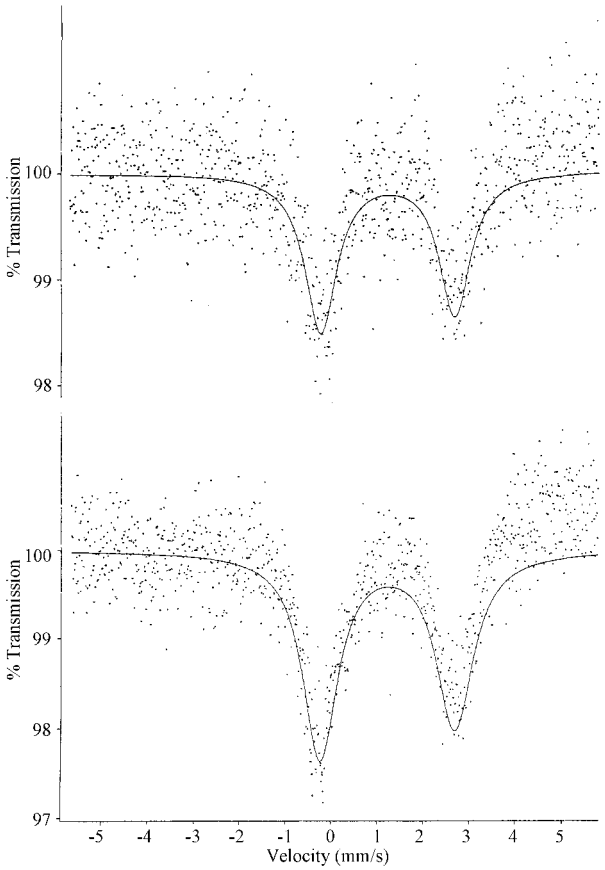

Figure 1. Mössbauer spectra of TPTCl in aerobic (top) and anaerobic (bottom) sediments from site PR-10 in the Potomac River.

TBT compounds

As was found with the TPT compounds, the the Δ and δ values of TBTCl and TBTO (Tables 2 and 3) in both aerobic and anaerobic sediments were the same within experimental error. This would again suggest that the products of the interaction with the sediments from both rivers involved the same species, most likely the hydrated TBT cation, TBT^+. The δ parameters for the TBT-spiked sediments are larger than those observed for the TPT-spiked sediments, indicating that the interactions of the hydrated TBT^+ cation with the sediment are not as strong as in the case for the TPT, because δ values vary with the bonding of the tin atom. This may be due to the more flexible *n*-butyl group, which prevents the cation from having strong contacts with the sediments.

Interaction between the triorganotin compounds and the sediments

The interactions between TPTCl, TPTOH and TBTCl and the sediments can be represented by Equations (1) and (2), and the interaction between TBTO and the sediments can be shown by Equations ((3)–(5)).

$$R_3SnX \rightleftarrows R_3Sn^+ + X^- \quad (1)$$

$$R_3Sn^+ + \text{Sediment} + xH_2O \rightleftarrows R_3Sn^+(H_2O)_x\text{–Sediment} \quad (2)$$

where R = Ph or Bu and X = Cl or OH.

$$(Bu_3Sn)_2O + H_2O \rightleftarrows 2Bu_3SnOH \quad (3)$$

$$Bu_3SnOH \rightleftarrows Bu_3Sn^+ + OH^- \quad (4)$$

$$Bu_3Sn^+ + xH_2O + \text{Sediment} \rightleftarrows Bu_3Sn^+(H_2O)_x\text{–Sediment} \quad (5)$$

Though the organotin species most likely to interact with the sediments are hydrated, as shown in the above scheme, Mössbauer spectroscopy, however, cannot distinguish whether the species is monohydrated $[R_3Sn(H_2O)X]$ or dihydrated $[R_3Sn(H_2O)_2^+]$. The binding of the organotin species to the Anacostia and Potomac sediments is most likely to be between the partial positive charge of the organotin species and the anionic centers found in the humic acid or clay that exist in these freshwater sediments.[18]

Comparison with sediments from Chesapeake Bay

It has been previously reported that Chesapeake Bay[12] aerobic and anaerobic sediments spiked with TPTCl and TPTOH resulted in the speciation of these compounds into the TPT cation, as was observed for the aerobic and anaerobic sediments from the Anacostia and Potomac Rivers. However, results for the TBTCl- and TBTO-spiked sediments from the Anacostia and Potomac Rivers differ from those obtained with spiked Chesapeake Bay sediments. In the earlier study, it was found that the TBTCl did not change when it interacted with aerobic Chesapeake Bay sediments, whereas a variety of products were formed in the spiked anaerobic sediments depending upon the location of the sample. TBTO was converted to the hydroxide and chloride compounds in anaerobic and aerobic sediments

Table 2. Mössbauer spectroscopy of triorganotin-spiked sediments of the Anacostia River[a]

		Aerobic		Anaerobic		
Compound	Site	Δ (mm s^{-1})	δ (mm s^{-1})	Δ (mm s^{-1})	δ (mm s^{-1})	Aerobic area/anaerobic area
TPTCl	AR-1	2.81(5)	1.20(1)	2.83(3)	1.13(1)	0.58
	AR-2	2.80(7)	1.30(2)	2.82(3)	1.23(1)	0.55
	AR-4	2.6(3)	1.28(7)	2.83(3)	1.22(1)	0.68
	AR-6	2.74(5)	1.17(1)	2.79(3)	1.21(1)	0.50
TPTOH	AR-1	2.76(3)	1.18(1)	2.76(3)	1.16(1)	1.66
	AR-2	2.91(4)	1.21(1)	2.74(2)	1.18(1)	0.44
	AR-4	2.75(3)	1.17(1)	2.77(3)	1.19(1)	1.26
	AR-6	2.74(5)	1.18(1)	2.76(2)	1.21(1)	0.60
TBTCl	AR-1	3.42(4)	1.53(1)	3.25(2)	1.43(6)	0.41
	AR-2	3.23(8)	1.39(2)	3.32(2)	1.45(1)	0.64
	AR-4	3.30(5)	1.39(1)	3.23(3)	1.39(1)	0.49
	AR-6	2.91(5)	1.25(1)	3.32(4)	1.43(1)	1.62
TBTO	AR-1	3.27(4)	1.39(1)	3.21(5)	1.39(1)	0.89
	AR-2	3.30(6)	1.47(1)	3.32(5)	1.47(1)	0.54
	AR-4	3.16(6)	1.38(2)	3.19(4)	1.44(1)	0.55
	AR-6	3.25(6)	1.46(1)	3.23(5)	1.41(1)	0.64

[a] The numbers in parentheses are the errors in the last figures. All values relative to $BaSnO_3$ at 80 K.

respectively.[14] It was further concluded from the Chesapeake Bay study that the speciation of TBT compounds depends upon the nature of the sediment. This conclusion is further supported by the results of the current study, because the speciations of both TBTCl and TBTO in aerobic and anaerobic sediments from the Anacostia and Potomac Rivers differ from those obtained for the spiked Chesapeake Bay sediments.

Table 3. Mössbauer spectroscopy of triorganotin-spiked sediments of the Potomac River[a]

		Aerobic		Anaerobic		
Compound	Site	Δ (mm s^{-1})	δ (mm s^{-1})	Δ (mm s^{-1})	δ (mm s^{-1})	Aerobic area/anaerobic area
TPTCl	PR-4	2.75(3)	1.17(1)	2.74(2)	1.17(1)	0.44
	PR-7	2.85(7)	1.20(2)	2.79(3)	1.22(1)	0.94
	PR-9	2.83(3)	1.19(1)	2.85(2)	1.20(1)	0.51
	PR-10	2.88(3)	1.21(1)	2.84(2)	1.20(1)	0.67
TPTOH	PR-4	2.76(3)	1.20(1)	2.78(2)	1.18(1)	0.68
	PR-7	2.76(5)	1.18(1)	2.73(3)	1.19(1)	0.80
	PR-9	2.83(4)	1.23(1)	2.72(3)	1.14(1)	0.89
	PR-10	2.75(3)	1.18(1)	2.79(4)	1.22(1)	0.74
TBTCl	PR-4	3.19(5)	1.43(1)	3.06(7)	1.37(1)	0.80
	PR-7	3.24(8)	1.33(2)	3.38(7)	1.45(2)	0.94
	PR-9	3.29(4)	1.41(1)	3.40(7)	1.51(2)	1.21
	PR-10	3.76(6)	1.62(2)	3.35(3)	1.44(1)	0.91
TBTO	PR-4	3.41(7)	1.34(2)	3.13(5)	1.43(1)	4.03
	PR-7	3.21(6)	1.44(3)	3.17(4)	1.41(1)	0.82
	PR-9	3.10(8)	1.47(2)	3.07(3)	1.36(1)	0.50
	PR-10	2.97(5)	1.44(1)	3.10(3)	1.43(1)	0.70

[a] The numbers in parentheses are the errors in the last figures. All values relative to $BaSnO_3$ at 80 K.

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