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Speciation of Tributyltin and Triphenyltin Compounds in Clays from Sediments Including the Effect of Microorganisms Using Mõssbauer Spectroscopy

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Introduction

Previously, we had examined the speciation of tributyltin(TBT) and triphenyltin (TPT) compounds directly in sediments from the Chesapeake Bay (1-3) and waterways in the Chesapeake Bay watershed: Anacostia River (4), Baltimore Harbor (5), and Potomac River (4). To determine the nature of the tin compounds directly in the sediments, tin Mössbauer spectroscopy was used. It was found that the speciation of triorganotin compounds varies with the nature of the sediment. It is important to determine which component or components of the sediment are involved in the speciation of the tin compound. The Anacostia and Potomac Rivers are in the Washington Quadrangle of which one-fourth is in the Piedmont Plateau and the remainder in the Coastal plain (6). Clays and sand are important components of these formations. For example, it was reported that kaolin is one of the clays that have been found in the sediment of the Anacostia River (6, p. 27). In 1992, we observed that TPTCl spiked anaerobic and aerobic sediments from the Chesapeake Bay contained microorganisms by streaking agar plates with these sediments. In anaerobic sediments the microorganisms are both facultative and anaerobic, but in aerobic sediments, only facultative microorganisms are found (1). Experiments were performed to determine the speciation of tributyltin and triphenyltin compounds in components of sediments, such as different clays and sand. The effect of microorganisms on the fate of tributyltin and triphenyltin compounds in components of sediments was also examined by including *E. coli* in the mixtures.

X-Ray Diffraction of Sediments

To determine if clays other than kaolin were in the sediments of the Anacostia and Potomac Rivers, the x-ray diffraction patterns of dried sediments from the Anacostia (AR-1) and Potomac Rivers (PR10) were measured using the LabX, XRD-6000 (Shimadzu, Co.). For comparison, the pattern for a sample from Colgate Creek (25 cm below sea level), a tributary of Chesapeake Bay was also measured. The x-ray results are given in Table 1. The samples contained as a major constituent, α-quartz (sand), and clays plus other constituents such as goethite. The clays included chlorite, illite, kaolinite, montmorillonite, and nontronite or smectite (7).

pH of Clay-Water Mixtures

To assist in the interpretation of the speciation experiments with spiked clays, the pH of the various clays in distilled water were measured using a glass pH electrode and the Vernier LabPro. The clay and distilled water were mixed thoroughly and the clay allowed to separate from the solution before the pH was read. The results are given in Table 2. The pH of the water suspensions of clay and sand varies in some cases from the pH of the distilled water alone (pH = 5.7) although with most of the clays, the suspensions have about the same pH as the distilled water. With kaolinite, the pH is much lower at 2.7 and higher in sand at 7.0. The pH also varies with the tin compound added with the highest pH found with TBTO and the lowest with TPTCl. Thus, some component or components of the clay and the tin compound contribute to the acidity of the suspensions.

Spiking of Tin Compounds in Clays and Sand using Mössbauer Spectroscopy

The following procedure was used in all experiments: Mixtures of 5 g of the clay sample and 5 mL or 100 mL of solution containing the organotin compound amounting to 3.3 % of the weight of the clay were shaken mechanically in closed test tubes or Erlenmeyer flasks for two weeks at room temperature. To determine the effect of bacteria on the speciation, E.coli and broth was added. After remaining at room temperature for two additional weeks, the clay was removed by gravity filtration and kept frozen until the Mössbauer spectrum is measured. The Mössbauer spectra were measured at 80K on a Mössbauer spectrometer model MS-900 (Ranger Scientific Co.) in the acceleration mode with moving source geometry. 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-square fit to Lorentzian shaped lines.

Mössbauer Spectroscopic Results with Spiked Clays and Sand

The Mõssbauer spectral parameters, quadrupole splitting, Δ, and isomer shift, δ, found with the spiked clays, spiked sand, and spiked sediments from the Anacostia River are given in Tables 3 and 4. In Table 5, the results found with spiked clays mixed in the presence of the microorganism, *E. colil*, are recorded. Duplicate spectra of the clay spiked with a particular TBTCl or TPT compound do not always give reproducible

values. The results will be considered based upon those values that are duplicated within experimental error.

The Δs in the spectra of TBTCl in spiked Illite and kaolinite are close to the Δ in the spectrum of the pure compound, but the δ is lower in most spectra. For comparison, the average of the parameters in spiked sediments from the Anacostia River is lower than the parameters of the spectra of the pure TBTCl or in the clays.

The situation is different in the case of the TBTO spiked samples where the Δ in the spectrum of the pure compound is the lower than in any sample. The δs are about the same except for the spectra of the spiked Illite where both parameters are larger than in the other spectra. The TBTO exists as TBT-O-TBT in the solid and dissociates into TBT^+ when dissolved in water. The cation then interacts with the clay and sediments resulting in Mössbauer spectra with parameters different from those in the pure compound. The average Δ in the spectra of the spiked sediments from the Anacostia River is greater than in the pure compound or spiked clay and sand samples. However, the average δ is intermediate between values found in the pure compound, sands and some clays and Illite.

The Δs in the spectra of the kaolinite and sand, spiked with TBTAc are larger than the Δ in the spectrum of the pure TBTAc. The δs for most of the spiked samples and the pure compound are about 1.4 mm/s. The TBTAc in water undergoes the following reactions:

$$TBTAc + H_2O \leftrightarrow TBT(H_2O)^+ + Ac^-$$

$$Ac^- + H_2O \leftrightarrow HAc + OH^-$$

The amount of the TBTAc that will exist as the cation or the molecule will depend upon the pH. As can be seen from Table 2, the pH varies with the clay so the Mössbauer parameters will reflect this.

The Mössbauer parameters are different in the spectra of TPTCl spiked clays and sand. In spiked sand and kaolinite, the Δs are greater than the Δ in the spectrum of the pure compound, but the δs are the same. However, in spiked montmorillonite and nontronite, the parameters are less than the parameters in the pure compound. For

illite, the Δs are the same but the δ in spectrum of the spiked sample is less than the pure compound. The average Mössbauer parameters in the spectra of the spiked sediments from the Anacostia River is different from those in the spectra of the spiked clays and sand and the pure compound.

In TPTOH spiked clays and sand, the Δs are lower than in the pure compound whereas the δs are about the same. This is also true for the average of the values in TPTOH spiked sediments from the Anacostia River (5).

With TPTAc spiked clays, the Δs are less than the value in the pure compound. The δs of all spectra were about the same. This suggests that the TPT species are different in the spiked samples from the pure compound. The reactions of the TPTAc are similar to those of the TBTAc so we find differences in the spectra in the different clays and sand.

The variation in the Mössbauer parameters would reflect the variation in the clays and sand whose chemical nature changes differently with the pH. The TBT or TPT structure that interacts with the clay or sand will also vary with the pH. The possible heterogeneity of the clays and sand seems to partly explain the poor reproducibility of some combinations. Additional mixtures are being run to resolve this problem.

Effect of Microorganisms on the Speciation of the Organotin Compounds

The preliminary results of mixing *E. coli* with nontronite and the triorganotin compounds are given in Table 4. There are changes in both Δ and δ which suggests that the microorganism is affecting some change in the structure of the tin compound. These mixtures included the broth used for growing the *E. coli,* and the chemicals included in the broth may have interacted with the tin compound and/or the clay. Additional studies are needed to confirm this.

Literature Cited

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Table 1. Prominent Lines in the X-ray Diffraction of Sediments from the Anacostia and Potomac Rivers and Chesapeake Bay, 2Θ[a].

Component	Anacostia River	Potomac River	Chesapeake Bay
Quartz	20.9, 26.7, 50.2	20.9, 26.7, 50.2	20.9, 26.7, 50.2
Illite	8.9	61.9	8.9
Kaolinite	45.6		23.1, 45.6
Chlorite	60.0	60.0	60.0
Nontronite		5.8	6.2
Montmorillonite			61.8
Goethite	17.8	17.9	17.8
Calcite	45.5		

[a]Sediment from Chesapeake Bay was sampled 25 cm below sea level at Colgate Creek.

Table 2. pH Measurements of Tributyltin (TBT) and Triphenyltin (TPT) Compounds in Aqueous Suspensions of Clays and Sand.

Compound	pH	Compound	pH
		Illite	
Water	5.7	TBTCl	6.0
TPTCl	6.4	TBTO	7.9
TPTAc	7.3	TBTAc	6.0
		Sand	
Water	7.0	TBTCl	6.0
TPTCl	3.0	TBTO	8.0
TPTOH	.5.8	TBTAc	4.9
TPTAc	4.1		
		Kaolinite	
Water	2.7	TPTCl	2.9
		Nontronite	
Water	5.4	TPTAc	4.8
		Montmorillonite	
Water	5.7		

[a]Water is distilled water.

Table 3. Mössbauer Spectra of Tributyltin (TBT) Compounds in Sediments and Components[a]

Compd	Clay	Δ	δ
TBTCl	Neat	3.43(4)	1.56(1)
	Kaolinite	3.43(3)	1.47(7)
	Kaolinite	2.64(3)	1.29(1)
	Kaolinite	3.45(3)	1.48(1)
	Sand	2.60(3)	1.30(1)
	Sand	3.63(4)	1.43(1)
	Nontronite	4.03(4)	1.58(1)
	Nontronite	3.75(6)	1.48(1)
	Illite	3.19(5)	1.34(1)
	Illite	3.47(1)	1.497(3)
	Illite	3.41(3)	1.48(2)
	Montmorillonite	3.03(7)	1.51(5)
	Montmorillonite	4.12(2)	1.65(1)
	AR- Average	3.22(22)	1.39(11)
TBTO	Neat	1.55(5)	1.11(1)
	Kaolinite	3.84(3)	1.49(1)
	Kaolinite	2.16(3)	1.03(1)
	Kaolinite	2.13(3)	0.98(1)
	Kaolinite	2.61(2)	1.09(1)
	Sand	2.96(5)	1.42(1)
	Sand	2.11(3)	1.05(1)
	Sand	2.06(2)	0.96(1)
	Nontronite	2.16(3)	1.01(1)
	Illite	2.62(5)	1.25(1)
	Illite	3.176(4)	1.482(2)
	Illite	3.354(8)	1.523(5)
	Illite	3.14(7)	1.63(5)
	Sand	2.56(5)	1.34(1)
	Sand	3.92(5)	2.62(1)
	Montmorillonite	2.37(8)	1.49(6)
	Montmorillonite	2.45(4)	1.24(2)
	Montmorillonite	2.86(5)	1.22(1)
		4.12(3)	1.85(1)
	AR-Average	3.25(6)	1.43(5)

Table 3. (Continued). Mössbauer Spectra of Tributyltin (TBT) Compounds in Sediments and Components[a]

Compd	Clay	Δ	δ
TBTAc	Neat	3.52(4)	1.46(1)
	Kaolinite	3.70(2)	1.46(4)
	Kaolinite	3.77(3)	1.47(1)
	Kaolinite	3.85(7)	1.58(4)
	Sand	3.45(6)	1.47(2)
	Sand	2.79(6)	1.40(2)
	Sand	3.729(5)	1.486(3)
	Illite	3.09(5)	1.42(1)
	Illite	3.35(3)	1.51(2)
	Montmorillonite	2.96(6)	1.48(3)
	Montmorillonite	4.03(2)	1.67(1)

[a]Compd = Compound. All values are relative to $BaSnO_3$ at 80K in mm/s.

Table 4. Mössbauer Spectra of Triphenyltin (TPT) Compounds in Sediments and Components

Compd	Clay	□	□
TPTCl	Neat	2.52(7)	1.35(2)
	Kaolinite	2.70(3)	1.34(1)
	Kaolinite	2.61(5)	1.26(1)
	Kaolinite	3.042(4)	1.455(1)
	Sand	2.56(5)	1.34(1)
	Sand	3.92(5)	2.62(1)
	Sand	2.75(1)	1.39(1)
	Montmorillonite	2.45(4)	1.24(2)
	Montmorillonite	2.23(4)	1.15(2)
	Nontronite	2.46(7)	1.27(3)
	Illite	2.58(3)	1.29(1)
	AR- Average	2.74(10)	1.24(6)
TPTOH	Neat	2.95(7)	1.23(7)
	Kaolinite	2.73(2)	1.14(1)
	Kaolinite	2.94(4)	1.26(2)
	Sand	2.78(5)	1.20(1)
	Sand	2.979(3)	1.241(2)
	Sand	2.80(2)	1.27(1)
	Nontronite	1.84(7)	1.10(2)
	Illite	2.76(2)	1.23(1)
	Illite	3.16(4)	1.37(1)
	Montmorillonite	2.65(3)	1.22(2)
	AR-Average	2.79(8)	1.19(2)
TPTAc	Neat	3.31(7)	1.29(2)
	Illite	2.31(4)	1.11(1)
	Illite	4.67(5)	1.95(3)
	Illite	2.37(5)	1.15(3)
	Sand	3.14(1)	1.22(1)
	Sand	3.07(3)	1.27(1)
	Nontronite	2.13(2)	1.10(1)
	Montmorillonite	2.01(6)	1.20(4)
	Montmorillonite	2.16(3)	1.04(1)
	Kaolinite	3.12(4)	1.25(2)

Table 5. Mössbauer Spectra of Tributyl (TBT) and Triphenyltin (TPT) Compounds in Clays in the presence of *E. coli*.

Clay	Compound	No *E. coli*		In presence of *E. coli*	
		Δ	δ	Δ	δ
Nontronite	TBTO	3.50(2)	1.48(12)	2.16(3)	1.01(1)
Nontronite	TBTCl	3.66(1)	1.57(1)	3.75(6)	1.48(1)
Nontronite	TPTAc	2.44(2)	1.19(1)	2.13(2)	1.10(1)

[a]All values are relative to $BaSnO_3$ at 80K in mm/s.