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SHORT PAPER

The effects of salinity and pH on the speciation of some triphenyltin compounds in estuarine sediments using Mössbauer spectroscopy

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The speciation of some triphenyltin compounds i.e. triphenyltin hydroxide, triphenyltin chloride, triphenyltin fluoride, under varying salinity and pH conditions, was studied by Mössbauer spectroscopy in both anoxic and oxic estuarine sediments. The results indicate that altering the pH or salinity of the sediment environment does not apparently affect the speciation of these compounds.

Keywords: Anoxic sediments, oxic sediments, Mössbauer spectroscopy, pH, salinity, speciation, triphenyltin compounds, triphenyltin hydroxide, triphenyltin chloride, triphenyltin fluoride

INTRODUCTION

The use of organotin compounds as antifouling agents has caused concern regarding their toxicity to untargeted marine biota in aquatic environments.[1–3] The primary organotin compounds used as biofoulants are tributyltin (TBT) and triphenyltin (TPT) compounds.[4,5] Earlier studies from our laboratories on the speciation of TPT in both oxic and anoxic estuarine sediment indicated that triphenyltin chloride (TPTCl) and triphenyltin fluoride (TPTF) remain in the molecular form in their interactions with the sediments.[6] Triphenyltin acetate (TPTOAc) and triphenyltin hydroxide (TPTOH), however, formed the TPT^+ cation, which is the species that reacts with the sediment.[6] Because marine estuaries consist of areas with varying salinity and pH, it is important to determine whether or not these parameters influence the speciation of TPT compounds. Furthermore, the evaluation of the speciation of these compounds as a function of pH would give an insight into how these compounds might interact with sediments in waters where industrial chemical run-offs affect the pH of the estuarine environment. As in earlier studies, Mössbauer spectroscopy was used to study the speciation of the TPT compound directly in the sediment.[6,7] This paper reports the results of investigations of the effect of salinity and pH on several TPT compounds in estuarine sediment samples using Mössbauer spectroscopy.

EXPERIMENTAL

Chemicals

Triphenyltin hydroxide was purchased from Alfa Products (Danvers, MA, USA), triphenyltin chloride from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA), and triphenyltin fluoride from Organometallics, Inc., (E. Hampstead, NH, USA). All the compounds were used as received to spike the estuarine sediment samples, without further purification.

Seawater solutions

The salinity of the anoxic and oxic sediment was adjusted so that the resulting salinities of the samples were 20%, 40%, 60%, and 80% of that of synthetic seawater, which is taken as 100%. Tap-water was used for 0% salinity solutions.

The pH of the synthetic seawater was adjusted to the desired values with HCl and NaOH solutions prior to the addition of either the organotin compound or sediment.

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Table 1 Mössbauer spectral parameters of spiked 3801 Midbay anoxic sediments with varying salinity

	TPTOH		TPTCl		TPTF	
Salinity (%)	QS	IS	QS	IS	QS	IS
0	2.75 ± 0.07	1.14 ± 0.02	2.78 ± 0.07	1.17 ± 0.02	—[b]	
20	—[b]		2.77 ± 0.07	1.16 ± 0.02	2.99 ± 0.20	1.30 ± 0.05
40	2.74 ± 0.07	1.15 ± 0.02	2.68 ± 0.07	1.14 ± 0.02	3.09 ± 0.10	1.36 ± 0.03
60	2.79 ± 0.07	1.18 ± 0.02	2.70 ± 0.07	1.18 ± 0.02	3.40 ± 0.08	1.30 ± 0.02
80	2.71 ± 0.07	1.12 ± 0.02	2.71 ± 0.07	1.20 ± 0.02	—[b]	
100	2.75 ± 0.07	1.15 ± 0.02	2.64 ± 0.07	1.22 ± 0.02	3.54 ± 0.07	1.22 ± 0.02
Mean[a]	2.77 ± 0.02	1.14 ± 0.01	2.69 ± 0.07	1.22 ± 0.02	3.57 ± 0.02	1.27 ± 0.02

[a] Ref. 6. [b] —, Not determined.

Sediment collection

Sediment samples were collected aboard the *Ridgely Warfield* research vessel from selected sites in the Chesapeake Bay as grab samples. The location of the two sites are as follows: 3801 Midbay, 39° 01′ 05″ N latitude, 76° 21′ 57″ W longitude; Mellon Point, 39° 08′ 14″ N latitude, 76° 04′ 31″ W longitude. The oxic sediment samples were prepared by air-drying the anoxic sediment and then grinding it with a mortar and pestle. The anoxic sediments were thawed in synthetic seawater to prevent oxidation.

Sediment spiking

Dry oxic or wet anoxic sediment (5 g) was spiked to 3.3% (w/w) of the solid TPT compound of interest and covered with 100 cm^3 of the seawater solution. The sediments were mechanically shaken in closed vessels in the absence of light for one week at room temperature. The samples remained in the dark without disturbance for another two weeks. As in previous studies, samples were kept in the dark in order to minimize the conversion of the TPT compounds to their degradation products. Oxic sediment samples were filtered; anoxic sediment samples were isolated by simply decanting the seawater. Samples were immediately frozen and kept for spectral analysis.

Mössbauer spectroscopy

The Mössbauer spectra were measured at 80 K on a Mössbauer spectrometer model MS-900 (Ranger Scientific Co., Burleson, TX, USA) in the acceleration mode with a moving-source geometry using a liquid-nitrogen cryostat (CYRO Industries of America, Inc., Salem, NH, USA). The samples were mounted in Teflon holders. The source was 15 mCi Ca^{119m}SnO$_3$, and 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.[7]

Table 2 Mössbauer spectral parameters of spiked 3801 Midbay oxic sediments with varying salinity

	TPTOH		TPTCl		TPTF	
Salinity (%)	QS	IS	QS	IS	QS	IS
0	2.75 ± 0.07	1.14 ± 0.02	2.76 ± 0.07	1.14 ± 0.02	3.50 ± 0.07	1.25 ± 0.02
20	2.77 ± 0.07	1.17 ± 0.02	2.77 ± 0.07	1.13 ± 0.02	3.44 ± 0.07	1.26 ± 0.02
40	2.72 ± 0.07	1.16 ± 0.02	2.77 ± 0.07	1.16 ± 0.02	3.55 ± 0.08	1.27 ± 0.02
60	2.71 ± 0.07	1.10 ± 0.02	2.74 ± 0.07	1.16 ± 0.02	3.60 ± 0.08	1.23 ± 0.02
80	2.76 ± 0.07	1.14 ± 0.02	2.75 ± 0.07	1.16 ± 0.02	3.56 ± 0.08	1.26 ± 0.02
100	2.80 ± 0.07	1.13 ± 0.02	2.72 ± 0.07	1.19 ± 0.02	3.57 ± 0.08	1.25 ± 0.02
Mean[a]	2.76 ± 0.02	1.14 ± 0.02	2.64 ± 0.05	1.22 ± 0.02	3.50 ± 0.15	1.25 ± 0.02

[a] Ref. 6.

Table 3 Mössbauer spectral parameters of spiked 3801 Midbay anoxic sediments with varying pH

	TPTOH		TPTCl		TPTF	
pH	QS	IS	QS	IS	QS	IS
3	2.66 ± 0.06	1.13 ± 0.01	2.43 ± 0.03	1.23 ± 0.01	3.43 ± 0.04	1.32 ± 0.01
5	2.71 ± 0.03	1.19 ± 0.01	2.59 ± 0.04	1.22 ± 0.01	3.43 ± 0.03	1.30 ± 0.01
7	2.70 ± 0.06	1.22 ± 0.04	2.47 ± 0.06	1.20 ± 0.01	3.36 ± 0.05	1.33 ± 0.01
9	2.68 ± 0.03	1.18 ± 0.01	2.44 ± 0.02	1.28 ± 0.02	3.45 ± 0.05	1.30 ± 0.01
Mean[a]	2.77 ± 0.02	1.14 ± 0.01	2.69 ± 0.07	1.22 ± 0.02	3.57 ± 0.02	1.27 ± 0.02

[a] Ref. 6.

RESULTS AND DISCUSSION

The Mössbauer parameters, i.e. the quadrupole splitting (QS) and the isomer shift (IS) for the salinity studies, are listed in Table 1 for the anoxic sediment and the parameters for the oxic sediment are given in Table 2. The results indicated that these parameters are the same within experimental error under the various salinity concentrations, in both anoxic and oxic sediments. Thus, salinity does not appear to be a major factor influencing the speciation of these TPT compounds. A second salinity study using sediment from a different site (Mellon Point) gave similar results, thus confirming these observations.

Listed in Tables 3 and 4 are the results of the pH studies for each compound in anoxic and oxic sediments, respectively. Similar to the salinity results, changing the pH from 3 to 9 did not seem to affect the speciation of these compounds in either type of sediment. The pH results for the TPT compounds are different from those observed for tributyltin compounds extracted from seawater by Guard *et al.*,[8] where the speciation of TBT compounds was found to be a function of pH changes.

The Mössbauer parameters found in the present study under varying salinity and pH conditions are consistent with those found previously using a variety of sediments where the salinity and pH were not altered. The average values for anoxic and oxic sediments obtained from the previous study are given as 'mean' values in the tables.[6] Therefore, the results indicate that TPTF exists in both types of sediments in its polymeric form. The TPTCl exists in the molecular form, even at the lowest salinity concentration, in the sediment as a consequence of the following reaction:

$$\mathrm{TPTCl} \rightleftharpoons \mathrm{TPT}^+ + \mathrm{Cl}^-$$

The above equilibrium is shifted to the left as a result of the excess Cl^- ion concentration contained within the sediment. Thus, the species that interacts with the sediment is molecular TPTCl. The Mössbauer parameters observed for the TPTOH compounds are similar to those observed in our earlier studies.[6] This would then indicate that the TPTOH interacts with the sediment as the TPT^+ cation.

In summary, salinity or pH changes do not appear to affect the speciation of the triphenyltin compounds examined. This is in contrast to the speciation of TBT compounds extracted from seawater, in which pH plays a major role.[8]

Table 4 Mössbauer spectral parameters of spiked oxic 3801 Midbay sediments with varying pH

	TPTOH		TPTCl		TPTF	
pH	QS	IS	QS	IS	QS	IS
3	2.78 ± 0.07	1.15 ± 0.02	2.61 ± 0.07	1.24 ± 0.02	3.53 ± 0.07	1.27 ± 0.02
5	2.75 ± 0.07	1.16 ± 0.02	2.64 ± 0.04	1.21 ± 0.01	3.54 ± 0.08	1.29 ± 0.02
7	2.73 ± 0.07	1.16 ± 0.02	2.77 ± 0.08	1.17 ± 0.02	3.57 ± 0.07	1.28 ± 0.02
9	2.76 ± 0.08	1.12 ± 0.02	2.50 ± 0.05	1.22 ± 0.01	3.58 ± 0.07	1.28 ± 0.02
Mean[a]	2.76 ± 0.02	1.14 ± 0.02	2.64 ± 0.05	1.22 ± 0.02	3.50 ± 0.15	1.25 ± 0.02

[a] Ref. 6.

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