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Speciation of some triphenyltin compounds in estuarine sediments using Mössbauer spectroscopy

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The speciation of several triphenyltin compounds, i.e. triphenyltin hydroxide, acetate, chloride and fluoride, was studied by Mössbauer spectroscopy in both anaerobic and aerobic estuarine sediments. The results indicated that triphenyltin hydroxide and acetate were converted to the triphenyltin cation, the species that interacts with the sediments. However, both triphenyltin fluoride and chloride remained in their molecular form in their interaction with the sediments.

Keywords: Triphenyltin compounds, sediments, Mössbauer spectroscopy, speciation, triphenyltin hydroxide, triphenyltin acetate, triphenyltin chloride, triphenyltin fluoride

INTRODUCTION

Organotin compounds are widely used as poly(vinyl chloride) stabilizers and catalysts, fungicides and biocides, and as the active agent in some antifouling paints.[1,2] The increasing use of organotin compounds in marine paints has generated great concern in regard to their fate and toxic effects on marine organisms.[3-5] This has led to legislation that limits the use of antifouling paints containing organotin compounds on vessels in the United States which are smaller than 25 m in length.[6]

Triphenyltin compounds (TPTs) are one class or organotins that are used as the active biocide in antifoulant paints.[4,7,8] These toxic TPT additives have been found, in general, to be effective against marine organisms.[9]

Although the use of TPT compounds as antifoulants prevents biofouling, it permits the direct introduction of these toxicants into the aquatic ecosystem.[7] This may have adverse effects on non-targeted species.[10] Thus, it is of interest to determine the fate of TPT compounds that may be entering the marine hydrosphere and their conversion to other species as a result of their leaching from marine paints. In the aquatic environment, TPTs have been shown to have low mobility in environmental media, low aqueous solubility, and strong binding to soil and organic sediments.[7] 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 in sediments by extraction and/or derivatization procedures.[11] However, tin Mössbauer spectroscopy permits the direct observation of the TPT 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 (IS) and the quadrupole splitting (QS). The isomer shift is related to the *s*-electron density at the tin nucleus. This can provide information as to the 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 about the tin atom. Hence, this form of spectroscopy can give information pertaining to the tin atom directly in the sediments.

This paper reports the results of Mössbauer studies from the spiking of aerobic and anaerobic marine sediments with triphenyltin compounds that are commonly incorporated into marine paints[9] such as triphenyltin hydroxide (TPTOH), triphenyltin acetate (TPTOAc), triphenyltin chloride (TPTCl), and triphenyltin fluoride (TPTF).

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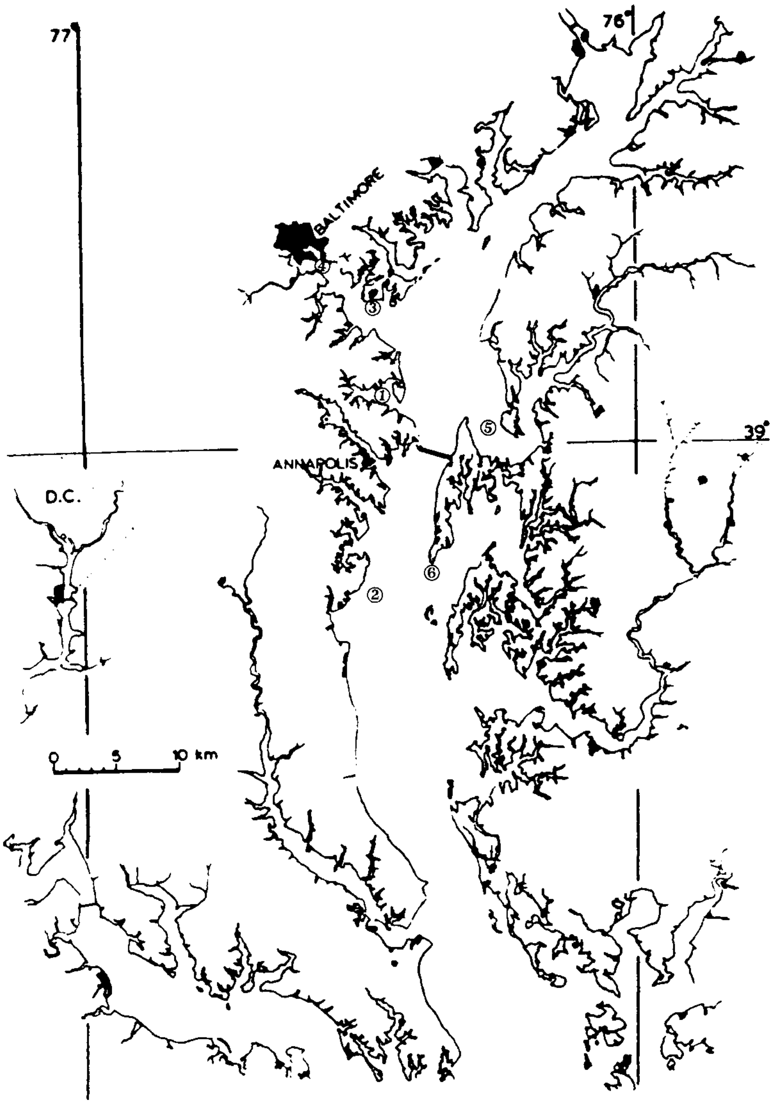

Figure 1 Location of the sampling sites in the Chesapake Bay, USA (see Table 1).

EXPERIMENTAL

Chemicals

Triphenyltin acetate and triphenyltin hydroxide were 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 without further purification to spike the estuarine sediment samples.

Sediment collection

Sediment samples were collected aboard the *Ridgely Warfield* research vessel from selected sites in the Chesapeake Bay, USA, as grab samples. The samples were split into two parts for aerobic and anaerobic studies and kept frozen until spiked. The aerobic sediment samples were prepared by air-drying the anaerobic sediment and then grinding it with a mortar and pestle. The anaerobic sediments were thawed in synthetic seawater to prevent oxidation. The locations of the various sites are given in Fig. 1 and Table 1.

Sediment spiking

Either dry aerobic or wet anaerobic sediments (5 g) were spiked with 3.3% (w/w) of the triphenyltin compound of interest and covered with 100 cm^3 of synthetic seawater. The sediments were shaken in the dark mechanically in closed vessels for approximately one week at room temperature and remained in the dark for an additional two weeks. The mixture was kept in the dark to minimize conversion of the TPTs to their degradation products. Soderquist and Crosby[12] have shown that there is no degradation of the TPT$^+$ cation kept in the dark up to 17 days. The sediment samples were then filtered and the solids kept frozen prior to 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 sediment samples were mounted in polyethylene or 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.[13] All isomer shifts (IS) were calculated relative to BaSnO$_3$.

Detection of Microbial presence

Samples of spiked sediments were streaked on potato dextrose agar plates. The plates were left at room temperature or incubated at 37 °C. The detection of micro-organisms was indicated by the presence of the growth of colonies.

Table 1 Location of sediment sample sites[a]

	Site	Latitude	Longitude
1	Magothy River	39°02'42"N	76°24'05"W
2	848E	38°47'59"N	76°24'30"W
3	Sparrows Point	39°11'30"N	76°28'30"W
4	Jones Fall	39°16'56"N	76°36'12"W
5	Chester River	39°04'23"N	76°19'08"W
6	Kent Point	38°48'30"N	76°23'30"W
7	South River	38°53'11"N	76°38'10"W

[a] Number refers to the numbers of the Chesapeake Bay map (Fig. 1).

RESULTS AND DISCUSSION

The Mössbauer parameters, QS and IS, of the spectra of the triphenyltin compounds studied in anaerobic and aerobic sediments are listed in Tables 2 and 3. The parameters of the spectra for the pure compounds are listed as well. Typical spectra are shown in Fig. 2. As seen in this figure, the intensities of the Mössbauer spectra of aerobic sediments were less than the intensities of anaerobic sediments. This indicates that less TPT compounds are absorbed by the aerobic sediments than by the anaerobic sediments. The aerobic sediments are prepared by drying the anaerobic sediments. During the drying, the lattice contracts as the water leaves, giving a more compact structure than in the anaerobic sediment. Thus, fewer groups are available in the aerobic sediment than in the anaerobic sediment to interact with the TPT compound, resulting in less intense spectra for the aerobic sediment samples.

As indicated in Tables 2 and 3, the average Mössbauer parameters of the triphenyltin compounds in both anaerobic and aerobic sediments show a change from the value for the parameters of the original compound. The average values for the parameters for the anaerobic and aerobic sediment samples are the same within experimental error but different from the values found with the original compound. This suggests that the TPT compounds are altered biologically and/or chemically in the same manner in both types of sediments. This is in contrast to the tributyltin compounds in which the changes were different with the different types of sediments.[13]

The average QS and IS values of TPTOH and TPTOAc in both types of sediments, whilst different from their original compounds, are the same within experimental error. This implies that both compounds are being converted in solution to the same species as indicated by Eqns [1] and [2]:

$$\mathrm{TPTX} \rightleftharpoons \mathrm{TPT}^+ + \mathrm{X}^- \qquad [1]$$

$$\mathrm{TPT}^+ + 2\mathrm{H_2O} \rightleftharpoons \mathrm{TPT(H_2O)}_2^+ \qquad [2]$$

where X = OH$^-$ or OAc$^-$. Therefore, it is the TPT$^+$ species that interacts with the sediment. These results are similar to the findings of May, Eng and co-workers[14,15] in their investigation of triphenyltin compounds in the inhibition of *Ceratocystis ulmi*.

However, the results with TPTCl show an increase in the average QS and a decrease in the

Table 2 Mössbauer spectral parameters of various triphenyltin compounds in estuarine anaerobic sediments[a]

	TPTOH		TPTOAc		TPTCl		TPTF	
Site	QS	IS	QS	IS	QS	IS	QS	IS
1 Magothy River	2.79 ± 0.07	1.16 ± 0.02	2.69 ± 0.07	1.13 ± 0.02	2.69 ± 0.07	1.22 ± 0.02	3.55 ± 0.08	1.26 ± 0.02
2 *848E*	2.76 ± 0.07	1.14 ± 0.02	2.73 ± 0.07	1.18 ± 0.02	2.79 ± 0.07	1.21 ± 0.02	3.62 ± 0.08	1.36 ± 0.02
3 Sparrows Pt	2.74 ± 0.07	1.15 ± 0.02	2.72 ± 0.07	1.14 ± 0.02	2.73 ± 0.07	1.28 ± 0.02	3.56 ± 0.08	1.28 ± 0.02
4 Jones Fall	2.76 ± 0.07	1.12 ± 0.02	2.69 ± 0.07	1.12 ± 0.02	2.72 ± 0.07	1.21 ± 0.02	3.56 ± 0.08	1.25 ± 0.02
5 Chester River								
0–25 cm	2.77 ± 0.07	1.13 ± 0.02	2.76 ± 0.07	1.21 ± 0.02	2.69 ± 0.07	1.21 ± 0.02	—[c]	—[c]
25–50 cm	2.78 ± 0.07	1.14 ± 0.02	2.76 ± 0.07	1.14 ± 0.02	2.67 ± 0.07	1.19 ± 0.02	3.58 ± 0.08	1.27 ± 0.02
50–75 cm	2.81 ± 0.07	1.17 ± 0.02	2.71 ± 0.07	1.16 ± 0.02	2.77 ± 0.07	1.22 ± 0.02	3.53 ± 0.08	1.25 ± 0.02
6 Kent Point	2.77 ± 0.07	1.14 ± 0.02	2.63 ± 0.07	1.21 ± 0.02	2.54 ± 0.07	1.23 ± 0.02	3.60 ± 0.09	1.25 ± 0.02
7 South River	2.77 ± 0.07	1.13 ± 0.02	2.73 ± 0.07	1.13 ± 0.02	2.64 ± 0.07	1.24 ± 0.02	3.59 ± 0.08	1.25 ± 0.02
Mean value[b]	2.77 ± 0.02	1.14 ± 0.01	2.71 ± 0.04	1.16 ± 0.03	2.69 ± 0.07	1.22 ± 0.02	3.57 ± 0.02	1.27 ± 0.01
Parent compound	2.95 ± 0.07	1.23 ± 0.02	3.31 ± 0.07	1.29 ± 0.02	2.52 ± 0.07	1.35 ± 0.02	3.62 ± 0.07	1.36 ± 0.02

[a] All values in mm s^{-1} relative to $BaSnO_3$ at 80 K.

[b] The errors in the mean values are ±standard deviation of the mean.

[c] —, Not determined.

average IS values in the spiked samples in both types of sediments. The increase in the QS suggests that the environment of the tin nucleus becomes more asymmetric, and the decrease in the IS indicates that the *s*-electron density around the tin atom decreases. The average QS and IS for the TPTCl samples are different from those observed for the TPTOH and TPTOAc, indicating that the TPTCl compounds do not dissociate into the triphenyltin cation within the sediments as is the case with the other two compounds. The TPTCl remains in its molecular form, probably due to the presence of excess Cl^- ions in the seawater, which would shift the equilibrium towards its molecular form, as follows (Eqn [3]):

$$\mathrm{TPTCl} \rightleftharpoons \mathrm{TPT}^+ + \mathrm{Cl}^- \qquad [3]$$

These observations suggest strongly that there is binding between TPTCl and the sediments. This binding could occur through the chlorine atom, which has a partial negative charge, to cationic centers in the sediments, or five-coordination at tin could be involved.

The average QS for TPTF was the same in the sediment and the original compound, whilst the

Table 3 Mössbauer spectral parameters of various triphenyltin compounds in estuarine aerobic sediments[a]

	TPTOH		TPTOAc		TPTCl		TPTF	
Site	QS	IS	QS	IS	QS	IS	QS	IS
1 Magothy River	2.74 ± 0.07	1.15 ± 0.02	2.66 ± 0.07	1.11 ± 0.02	2.65 ± 0.07	1.20 ± 0.02	3.63 ± 0.10	1.30 ± 0.03
2 848E	2.76 ± 0.07	1.13 ± 0.02	2.51 ± 0.07	1.04 ± 0.02	2.58 ± 0.07	1.23 ± 0.02	3.57 ± 0.08	1.28 ± 0.02
3 Sparrows Pt	2.80 ± 0.11	1.17 ± 0.03	2.75 ± 0.07	1.15 ± 0.02	2.62 ± 0.07	1.24 ± 0.02	3.54 ± 0.08	1.24 ± 0.02
4 Jones Fall	2.75 ± 0.07	1.15 ± 0.02	2.70 ± 0.07	1.17 ± 0.02	2.61 ± 0.07	1.25 ± 0.02	3.51 ± 0.08	1.24 ± 0.02
5 Chester River								
0–25 cm	2.75 ± 0.07	1.14 ± 0.02	2.52 ± 0.07	1.09 ± 0.02	2.71 ± 0.07	1.20 ± 0.02	3.54 ± 0.09	1.24 ± 0.02
25–50 cm	2.76 ± 0.07	1.16 ± 0.02	2.73 ± 0.07	1.14 ± 0.02	2.69 ± 0.07	1.22 ± 0.02	3.63 ± 0.08	1.26 ± 0.02
50–75 cm	2.76 ± 0.07	1.15 ± 0.02	2.76 ± 0.07	1.15 ± 0.02	2.66 ± 0.07	1.21 ± 0.02	3.51 ± 0.09	1.24 ± 0.02
6 Kent Point	2.72 ± 0.07	1.13 ± 0.02	2.76 ± 0.10	1.13 ± 0.03	2.66 ± 0.07	1.22 ± 0.02	3.09 ± 0.10	1.24 ± 0.03
7 South River	2.79 ± 0.08	1.11 ± 0.02	2.74 ± 0.07	1.13 ± 0.02	2.55 ± 0.07	1.21 ± 0.02	3.49 ± 0.09	1.21 ± 0.02
Mean values[b]	2.76 ± 0.02	1.14 ± 0.02	2.68 ± 0.09	1.12 ± 0.04	2.64 ± 0.05	1.22 ± 0.02	3.50 ± 0.15	1.25 ± 0.02
Parent compound	2.95 ± 0.07	1.23 ± 0.02	3.31 ± 0.07	1.29 ± 0.02	2.52 ± 0.07	1.35 ± 0.02	3.62 ± 0.07	1.36 ± 0.02

[a] All values in mm s^{-1} relative to $BaSnO_3$ at 80 K.

[b] The errors in the mean values are ±standard deviation of the mean.

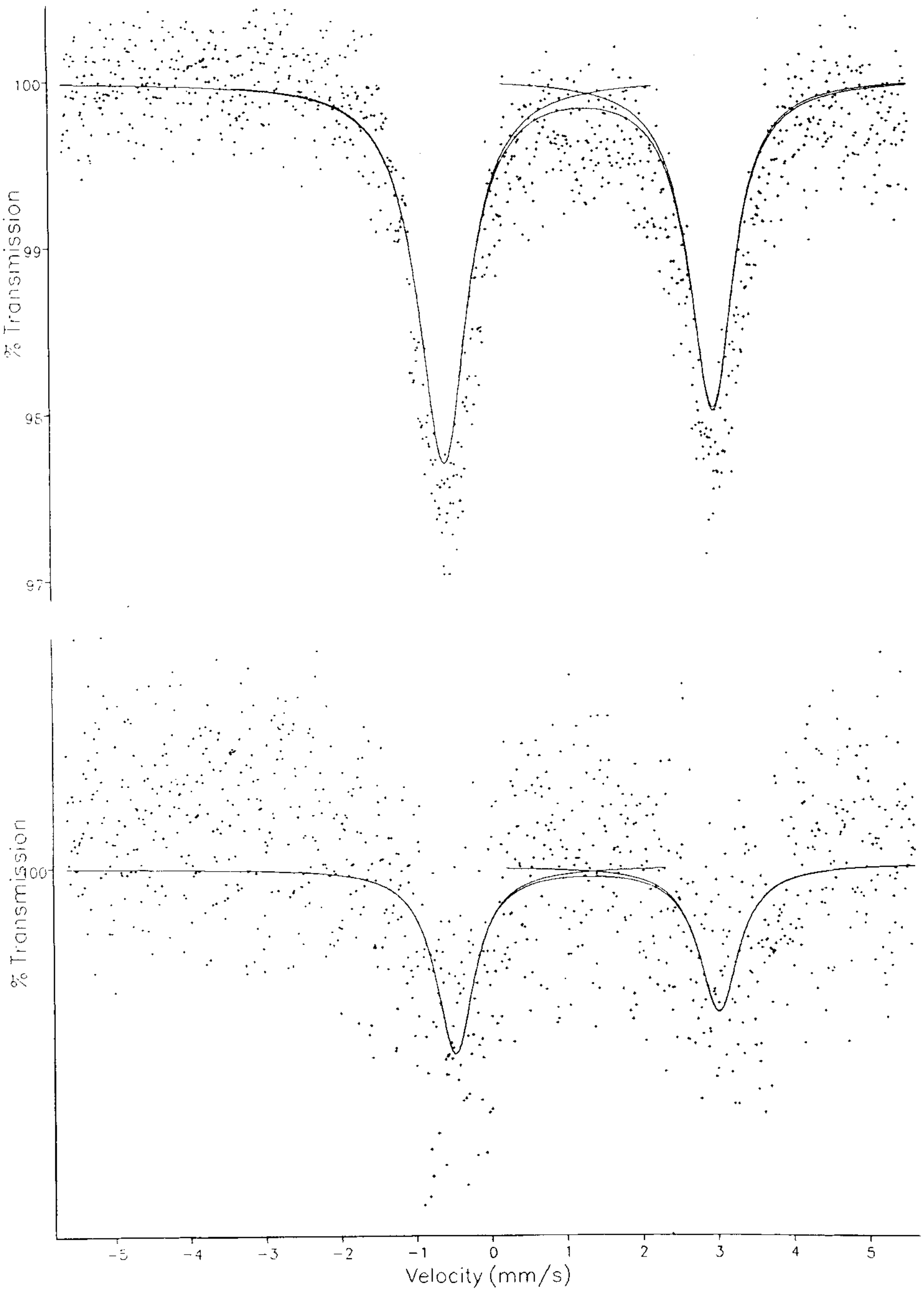

Figure 2 Mössbauer spectra of triphenyltin fluoride in anaerobic (top) and aerobic (bottom) sediments (848E).

average IS decreased in comparison with the original compound in both types of sediments studied. The observation that there is not a significant change in the QS indicates that the TPTF does not change its symmetry in the various sediments. this would be consistent with the fact that TPTF is polymeric in nature[16] and dissociation in the sediments would be unlikely. The observed decrease in the IS, however, as compared with the original compound, indicates that there is some interaction between the TPTF and the sediments. This interaction could be as a result of hydrogen bonding between the TPTF and (for example) the hydroxide groups found in the sediments, or by direct donations of sediment ligands to tin atoms.

The observation of colony growth on the agar plates that were streaked with the TPTCl spiked in both types of sediments indicates that micro-organisms (e.g. bacteria) are still present. Thus, it is possible that these micro-organisms, still present in both types of sediments, might interact with the TPT compounds. In anaerobic sediments there are two types of bacteria, anaerobic and facultative, whereas in aerobic sediments only facultative bacteria exist. Because the average QS and IS values are equal within experimental error for the same TPT compound in both types of sediments, the same conversion must have taken place in both types of sediments. This observation suggests that only the facultative bacteria is involved. If the bacterial action controlled the interaction of the TPT compounds within the sediments, then all TPT compounds might be expected to be converted to the same species in both types of sediments from the same sites. The conversion would then depend upon the nature of the bacteria at the sites and could be different for the various sites because the bacterial content might be different. Our evidence (Tables 2 and 3) shows that the same products are obtained with sediments from all sites. Thus, the more plausible explanation is that the interaction between the TPT compounds and the sediments is due to the formation of the TPT^+ or the hydrated cation from TPTOH and TPTOAc, whilst TPTCl and TPTF remain in the molecular form in the sediments.

SUMMARY

The study showed that there is interaction between the triphenyltin compounds and the aerobic and anaerobic sediments. This observation is based on the changes in the Mössbauer spectral parameters of the compounds in the sediments as compared with the parameters for the original compounds. In both types of sediments, TPTOH and TPTOAc are probably converted to TPT^+, which is the species that interacts with the sediment. Because of the presence of Cl^- ions in seawater, the triphenyltin chloride remains in its molecular form whilst TPTF is found to remain in its polymeric form in their interaction with the sediments.

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