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SPECIATION OF TRIPHENYLTIN COMPOUNDS USING MÖSSBAUER SPECTROSCOPY

Final Report

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Introduction

Organotin compounds have been used widely in industry and agriculture as poly(vinyl chloride) stabilizers and catalysts, fungicides, biocides, and as the active agent in antifouling marine paints.^{1,2} The increased use of organotin compounds as the active ingredient in antifouling marine paints has generated great concern regarding their fate in the aquatic environment. Organotin compounds, i.e., tributyltin compounds (TBTs) and triphenyltin compounds (TPTs) have been found to be effective in preventing the unwanted attachment and development of aquatic organisms such as barnacles, sea grass and hydroids on ships, hulls and underwater surfaces. However, these organotin compounds have been found to be toxic to non-targeted marine species as well.^{3,4} Consequently, several countries, including the United States, have enacted legislation limiting the use of marine paints containing organotin compounds.⁵ Although government regulations have led to an overall decrease in the presence of these compounds in the water systems, they are nonetheless present, and often in quantities that are harmful. Areas in which increased boating activity is present, such as marinas and harbors, may contain organotin compounds which have entered the water system during their previously unrestricted use. In the aquatic environment, triorganotin compounds have low aqueous solubility, low mobility, and exhibit strong binding to sediments.⁶ These compounds are easily absorbed by particulate matter in the water, which, after settling to the bottom, can be incorporated into the sediment. This permits the direct and continuous introduction of these toxicants into the aquatic ecosystem, which may have adverse effects on non-targeted species such as fish,^{7,8} oysters,^{7,8} benthic organisms,⁹ and clams.¹⁰

While speciation of tributyltins in environmental water systems has received much attention in the literature, little information concerning the speciation of triphenyltins is found. Therefore, it would be important to study the fate of TPTs in the aquatic environment, particularly in sediments, both oxic and anoxic, in order to obtain speciation data. This data would assist in assessing the

potential impact of these compounds on the environment and may assist in the regulation of their usage. In addition, it may lead to a better understanding of their mechanism of action in the various types of sediments. Since marine estuaries consist of areas with varying salinity and pH, it is important to investigate the speciation of these compounds under varying salinity conditions. In addition, 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 can affect the pH of the estuarine environment. Finally, since organotins are present in both salt and fresh water environments, the speciation of the organotins in seawater and distilled water should also be studied.

The speciation of organotin compounds in sediments usually has been studied by extraction and/or derivatization procedures.¹¹ It would be more advantageous to examine the original organotin species than to study their derivatized analogs since derivatization may lead to the masking of the species.¹² A method that would eliminate the derivatization problem is Mössbauer spectroscopy, since this method would allow direct examination of the samples.¹³ The use of Mössbauer spectroscopy for the elucidation of molecular structure of organotin compounds is well documented in the literature. Mössbauer spectroscopy provides a probe of the tin atom that is sensitive to oxidation states and the ligands around the tin atom¹³. The chemical information from the Mössbauer spectrum is mainly contained in the isomer shift (IS) and quadrupole splitting (QS) values. The isomer shift is related to the *s*-electron density at the tin nucleus which varies with the oxidation state and/or the bonding of the tin atom. It has been established that a decrease in the *s*-electron density at the tin atom will result in a decrease in the IS value.¹⁴ The quadrupole splitting value is influenced by the configuration of the electronic environment around the tin nucleus. Its magnitude yields information concerning the bonding of the tin atom. It has also been observed that the definite ranges of QS values are associated with a particular tin atom geometry. For example, R_3SnX and R_2SnX_2

compounds usually fall within $1.00 - 2.40 \text{ mm s}^{-1}$,¹⁵⁻¹⁷ while five coordinated triorganotin species may vary from $1.70 - 2.40 \text{ mm s}^{-1}$ for the *cis*- R_3SnX_2 compounds to $3.00 - 4.00 \text{ mm s}^{-1}$ for the *trans*- R_3SnX_2 compounds.¹⁷⁻²⁰

Although Mössbauer spectroscopy is indeed a powerful tool for identifying organotin species, it has not found its way into routine environmental studies. There are only limited references cited in the literature involving environmental investigations using Mössbauer spectroscopy.^{13,21} Eng *et al.*¹³ used Mössbauer spectroscopy to study the speciation of tributyltin compounds in seawater and sediment samples. The compounds studied included: *bis*-(tributyltin) oxide, tributyltin acetate, and tributyltin chloride. They were able to detect and identify various butyltin species in the sediment samples as well as in the water samples.

Thus, Mössbauer spectroscopy would provide a preferred method to study the speciation of triphenyltins as they leach from marine paints into the aquatic environment. Compounds used in this study are those triphenyltin compounds that are commonly incorporated into marine paints²² such as triphenyltin fluoride (TPTF), triphenyltin acetate (TPTOAc), triphenyltin chloride (TPTCl) and triphenyltin hydroxide (TPTOH).

OBJECTIVES

The overall objective is to investigate the speciation and environmental fate of triphenyltin compounds that are leached from marine antifouling paints. A second objective of this project is to provide training to students at the University of the District of Columbia in typical research that is being undertaken at university and government laboratories as well as in industry, with the aim of increasing the number of students from under-represented groups in the field of science.

EXPERIMENTAL

Chemicals

Triphenyltin acetate and triphenyltin hydroxide were purchased from Alfa Products (Danvers, MA), triphenyltin chloride from Aldrich Chemical Company, Inc. (Milwaukee, WI), and triphenyltin fluoride from Organometallics, Inc., (E. Hampstead, NH). All the compounds were used as received, without further purification, to spike the estuarine sediment samples. The salt mixture used to prepare the synthetic seawater was purchased commercially and diluted according to the directions.

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 oxic and anoxic studies and kept frozen until spiked. 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. The locations of the various sites are given in Fig. 1 and Table 1.

Sediment Spiking

Dry oxic or wet anoxic sediment (5g) was spiked to 3.3% (w/w) with the solid TPT compound of interest and covered with 100 cm³ of artificial seawater. The sediments were mechanically shaken in closed vessels in the absence of light for one week at room temperature and then kept in the dark without disturbance for another two weeks. Samples were kept in the dark in order to minimize the conversion of the TPT compounds to their degradation products.²³ Oxic sediment samples were then filtered, while anoxic sediment samples were isolated by simply decanting the seawater. Samples were then kept frozen for spectral analysis.

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 microorganisms was indicated by the presence of colonies.

Seawater Solutions

The salinity of the anoxic and oxic sediments 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%. 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.

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 (CRYO industries of America, Inc., Salem, NH, USA). The samples were mounted in Teflon holders. The source was 15 mCi Ca $^{119m}\text{SnO}_3$, and the velocity was calibrated at ambient temperature using a composition of BaSnO_3 and tin foil (splitting 2.52 mm s^{-1}). The spectra obtained were analyzed by a least-squares fit to Lorentzian-shaped lines. All isomer shifts were calculated relative to BaSnO_3 .

RESULTS AND DISCUSSION

Speciation Studies

The Mössbauer parameters, QS and IS, of the spectra of the anoxic and oxic sediments spiked with triphenyltin compounds 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 Figure 2. As seen in Figure 2, the intensities of the Mössbauer spectra of oxic sediments were less than the intensities of anoxic

sediments. This indicates that less TPT compounds are absorbed by the oxic sediments than by the anoxic sediments. During the drying process, the lattice in oxic sediments may contract as the water leaves, giving a more compact structure than in anoxic sediments. Thus, fewer groups are available in the oxic sediments than in the anoxic sediments to interact with the TPT compound resulting in less intense spectra for the oxic sediment samples.

As indicated in Tables 2 and 3, the average Mössbauer parameters of the triphenyltin compounds in both anoxic and oxic sediments show a change from the value for the parameters of the original parent compound. The average values for the parameters for the anoxic and oxic 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 Mössbauer parameters varied with the different types of spiked sediments.¹³

The average QS and IS values of TPTOH and TPTOAc in both types of sediments, while different from their original compounds, are the same within experimental error. This implies that both compounds are being converted to the same species as indicated by the following equations:

where $\text{X} = \text{OH}^-$ or OAc^- . Therefore, it is the TPT^+ species or the hydrated cation that interacts with the sediment. These results are similar to the findings of May and Eng^{24,25} in their investigation of triphenyltin compounds in the inhibition of *Ceratocystis ulmi*.

However, the studies with TPTCl show an increase in the average QS and a decrease in the average IS values in the spiked samples in both types of sediments. The increase in the QS value suggests that the environment of the tin nucleus becomes more asymmetric, and

the decrease in the IS value indicates that the *s*-electron density around the tin atom decreases. The average QS and IS values 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:

These observations strongly suggest that there is some type of binding between TPTCl and the sediments. This binding most likely will occur through the Cl atom, which has a partial negative charge, to cationic centers in the sediments.

The average QS value for TPTF is the same both in the sediment and the original compound, while the average IS value 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 value 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 nature²⁶ and dissociation in the sediments would be unlikely. The observed decrease in the IS, however, as compared to the original compound, indicates that there is some interaction between the TPTF and the sediments. This interaction could be a result of hydrogen bonding between the TPTF and, for example, the hydroxide groups found in the sediments.

The observation of colony growth on agar plates that were streaked with oxic and anoxic sediments spiked with TPTCl indicates that microorganisms such as bacteria are still present. Thus, it is possible that these microorganisms, still present in both types of

sediments, might interact with the TPT compounds. In anoxic sediments there are two types of bacteria, anaerobic and facultative, whereas in oxic sediments only facultative bacteria exist. Because the average QS and IS values are 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 indicates 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 should 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 would be different for the various sites because the bacterial content would 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 while TPTCl and TPTF remain in the molecular form in their interaction with the sediments.

Salinity and pH Studies

The Mössbauer parameters for the salinity studies are listed in Table 4 for the anoxic sediment and the parameters for the oxic sediment are given in Table 5. The results indicated that these parameters are the same within experimental error under the various salinity concentrations, in both anoxic and oxic sediments. Thus, it appears that 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 confirming these observations.

Listed in Tables 6 and 7 are the results of the pH studies for each compound in anoxic and oxic sediments, respectively. Similar to the salinity results, the changing of 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 sea water by Guard *et al.*,²⁷ 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.²⁸ The average values for anoxic and oxic sediments obtained from the previous study are given as "Mean" values in the tables.²⁸ 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 excess Cl⁻ ion concentration contained within the sediment [Equation 3]. Thus, the molecular form of TPTCl is the species that interacts with the sediment. The Mössbauer parameters observed for the TPTOH compounds are similar to those observed in our earlier studies.²⁸ This would then indicate that the TPTOH interacts with the sediment as the TPT⁺ or its hydrated cation.

Solution Studies

The isomer shifts and the quadrupole splitting values for the TPTs extracted from seawater are given in Table 8. As evident from the table, all the QS values, with the exception of TPTCl, are the same within experimental error. This suggests that the compounds (TPTOH, TPTOAc, TPTF) are converted to the same species upon extraction

from the seawater, probably the TPT^+ cation. The QS value for the extracted TPTCl (2.50 mm s^{-1}) is the same as the parent compound, TPTCl (2.52 mm s^{-1}). This is not surprising, since in excess Cl^- ion concentration, the equilibrium for the dissociation of TPTCl should lie in favor of the undissociated form.

The QS values for the extracts from distilled water for TPTOAc , TPTOH and TPTCl are all the same within experimental error. This suggests that these compounds form the same species upon extraction. These values obtained are within the range ($2.51 - 2.81 \text{ mm s}^{-1}$) for those that were previously assigned to the TPT^+ cation in the speciation studies,²⁸ again suggesting that the extracted species is the TPT^+ cation. The TPTF extracted from distilled water is converted to another species as evident from the change of both its QS and IS values, however, these parameters do not correspond to either the cation or molecular form of triphenyltin. Thus, this species remains unidentified at present.

Summary

In summary, the study showed that there is interaction between the triphenyltin compounds and the oxic and anoxic sediments. This observation is based on the changes in the Mössbauer spectral parameters of the compounds in the sediments as compared to the parameters for the original compounds. In both types of sediments, (anoxic/oxic) TPTOH and TPTOAc are converted to the TPT^+ or $\text{TPT}(\text{H}_2\text{O})_2^+$, 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, while TPTF is found to remain in its polymeric form in its interaction with the sediments.

Solution studies suggest that the TPTOAc, TPTOH and TPTF compounds extracted from seawater are converted to their cation while TPTCl remains in its molecular form. Distilled water extracts of TPTOAc, TPTOH and TPTCl suggest that they are converted to the TPT^+ cation, while TPTF is changed to an as yet unidentifiable species.

In addition, 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 in their speciation.²⁷

STUDENT TRAINEES

A second objective of the project was to provide training to UDC students in current research techniques and to encourage them to pursue careers in the field of science. To this end, the project has fulfilled its objective since all student trainees have continued with graduate studies or are employed in the field of science. Five students have been supported by this project. Mr. Peter Jamison is currently pursuing graduate studies at the University of California, Ms. Monicah Otieno is finishing her third year of graduate work at the University of Rochester, Ms. Rosemarie Lucero is completing her second year at Georgetown University School of Medicine, Ms. Deborah Whalen is employed full time as a Research Assistant, and Ms. Elizabeth Luedke is currently teaching chemistry at the secondary level in the state of Virginia.

PUBLICATIONS

Review: Interaction of Triorganotin Compounds with Chesapeake Bay Sediments and Benthos. L. May, D. Whalen and G. Eng, *Appl. Organometal. Chem.*, In press.

The Effects of Salinity and pH on the Speciation of Some Triphenyltin Compounds in Estuarine Sediments Using Mössbauer Spectroscopy. D. Whalen, R. Lucero, L. May and G. Eng, *Appl. Organometal. Chem.*, 7, 219 (1993).

Speciation of Some Triphenyltin Compounds in Estuarine Sediments Using Mössbauer Spectroscopy. R. Lucero, M. Otieno, G. Eng and L. May, *Appl. Organometal. Chem.*, 6, 273 (1992)

PRESENTATIONS

204th National Meeting of the American Chemical Society, Washington, DC, August 1992:

Effect of pH and Salinity on the Speciation of Triphenyltin Compounds in Estuarine Sediments Using Mössbauer Spectroscopy. D. Whalen, G. Eng and L. May.

Fourth Asian Chemical Congress, Beijing, China, August 1991:

The Use of Mössbauer Spectroscopy to Investigate the Speciation of Triphenyltin Compounds in Sediments. G. Eng, R. Lucero and L. May.

25th Middle Atlantic Regional Meeting of the American Chemical Society, Newark, DE,
May 1991:

**Effect of Concentration on the Speciation of Triphenyltin Compounds in Marine
Sediments Using Mössbauer Spectroscopy.** R. Lucero, M. Otieno, G. Eng and L.
May.

200th National Meeting of the American Chemical Society, Washington, DC. August 1990:

**The Study of the Speciation of Triphenyltin Compounds in Chesapeake Bay
Sediments.** M. Otieno, R. Lucero and G. Eng.

24th Middle Atlantic Regional Meeting of the American Chemical Society, Florham
Park/Madison, NJ, May 1990:

Mössbauer Studies of the Speciation of Triphenyltins in the Chesapeake Bay. R.
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The 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Decem-
ber 1989:

**Mössbauer Studies of the Speciation of Triorganotin Compounds in the Aquatic
Environment.** G. Eng, L. May and B. Reed.

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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
8	3801 Midbay	39°01'05"N	76°21'57"W

^aNumber refers to the numbers of the Chesapeake Bay Map (Figure 1).

Table 2 Mössbauer Spectral Parameters of Various Triphenyltin Compounds in Estuarine Anoxic Sediments

		TPTOH		TPTOAc		TPTCl		TPTF	
		QS	IS	QS	IS	QS	IS	QS	IS
1.	Magothy River	2.79 ± .07	1.16 ± .02	2.69 ± .07	1.13 ± .02	2.69 ± .07	1.22 ± .02	3.55 ± .08	1.26 ± .02
2.	848E	2.76 ± .07	1.14 ± .02	2.73 ± .07	1.18 ± .02	2.79 ± .07	1.21 ± .02	3.62 ± .08	1.36 ± .02
3.	Sparrows Pt	2.74 ± .07	1.15 ± .02	2.72 ± .07	1.14 ± .02	2.73 ± .07	1.28 ± .02	3.56 ± .08	1.28 ± .02
4.	Jones Fall	2.76 ± .07	1.12 ± .02	2.69 ± .07	1.12 ± .02	2.72 ± .07	1.21 ± .02	3.56 ± .08	1.25 ± .02
5.	Chester River								
	0-25cm	2.77 ± .07	1.13 ± .02	2.76 ± .07	1.21 ± .02	2.69 ± .07	1.21 ± .02	————	————
	25-50cm	2.78 ± .07	1.14 ± .02	2.76 ± .07	1.14 ± .02	2.67 ± .07	1.19 ± .02	3.58 ± .08	1.27 ± .02
	50-75cm	2.81 ± .07	1.17 ± .02	2.71 ± .07	1.16 ± .02	2.77 ± .07	1.22 ± .02	3.53 ± .08	1.25 ± .02
6.	Kent Point	2.77 ± .07	1.14 ± .02	2.63 ± .07	1.21 ± .02	2.54 ± .07	1.23 ± .02	3.60 ± .09	1.25 ± .02
7.	South River	2.77 ± .07	1.13 ± .02	2.73 ± .07	1.13 ± .02	2.64 ± .07	1.24 ± .02	3.59 ± .08	1.25 ± .02
	Mean Values ^a	2.77 ± .02	1.14 ± .01	2.71 ± .04	1.16 ± .03	2.69 ± .07	1.22 ± .02	3.57 ± .02	1.27 ± .01
	Parent Compound	2.95 ± .07	1.23 ± .02	3.31 ± .07	1.29 ± .02	2.52 ± .07	1.35 ± .02	3.62 ± .07	1.36 ± .02

^aThe errors in the mean values are ± standard deviation of the mean.

Table 3 Mössbauer Spectral Parameters of Various Triphenyltin Compounds in Estuarine Oxidic Sediments

	TPTOH		TPTOAc		TPTCl		TPTF	
	QS	IS	QS	IS	QS	IS	QS	I.S.
1. Magothy River	2.74 ± .07	1.15 ± .02	2.66 ± .07	1.11 ± .02	2.65 ± .07	1.20 ± .02	3.63 ± .10	1.30 ± .03
2. 848E	2.76 ± .07	1.13 ± .02	2.51 ± .07	1.04 ± .02	2.58 ± .07	1.23 ± .02	3.57 ± .08	1.28 ± .02
3. Sparrows Pt	2.80 ± .11	1.17 ± .03	2.75 ± .07	1.15 ± .02	2.62 ± .07	1.24 ± .02	3.54 ± .08	1.24 ± .02
4. Jones Fall	2.75 ± .07	1.15 ± .02	2.70 ± .07	1.17 ± .02	2.61 ± .07	1.25 ± .02	3.51 ± .08	1.24 ± .02
5. Chester River								
0-25cm	2.75 ± .07	1.14 ± .02	2.52 ± .07	1.09 ± .02	2.71 ± .07	1.20 ± .02	3.54 ± .09	1.24 ± .02
25-50cm	2.76 ± .07	1.16 ± .02	2.73 ± .07	1.14 ± .02	2.69 ± .07	1.22 ± .02	3.63 ± .08	1.26 ± .02
50-75cm	2.76 ± .07	1.15 ± .02	2.76 ± .07	1.15 ± .02	2.66 ± .07	1.21 ± .02	3.51 ± .09	1.24 ± .02
6. Kent Point	2.72 ± .07	1.13 ± .02	2.76 ± .10	1.13 ± .03	2.66 ± .07	1.22 ± .02	3.09 ± .10	1.24 ± .03
7. South River	2.79 ± .08	1.11 ± .02	2.74 ± .07	1.13 ± .02	2.55 ± .07	1.21 ± .02	3.49 ± .09	1.21 ± .02
Mean Values*	2.76 ± .02	1.14 ± .02	2.68 ± .09	1.12 ± .04	2.64 ± .05	1.22 ± .02	3.50 ± .15	1.25 ± .02
Parent Compound	2.95 ± .07	1.23 ± .02	3.31 ± .07	1.29 ± .02	2.52 ± .07	1.35 ± .02	3.62 ± .07	1.36 ± .02

*The errors in the mean values are ± standard deviation of the mean.

Table 4 Mössbauer Spectral Parameters of Spiked 3801 Midbay Anoxic Sediments With Varying Salinity

Salinity	TPTOH		TPTCI		TPTF	
	QS	IS	QS	IS	QS	IS
0%	2.75 ± .07	1.14 ± .02	2.78 ± .07	1.17 ± .02	----- ^b	
20%	----- ^b		2.77 ± .07	1.16 ± .02	2.99 ± .20	1.30 ± .05
40%	2.74 ± .07	1.15 ± .02	2.68 ± .07	1.14 ± .02	3.09 ± .10	1.36 ± .03
60%	2.79 ± .07	1.18 ± .02	2.70 ± .07	1.18 ± .02	3.40 ± .08	1.30 ± .02
80%	2.71 ± .07	1.12 ± .02	2.71 ± .07	1.20 ± .02	----- ^b	
100%	2.75 ± .07	1.15 ± .02	2.64 ± .07	1.22 ± .02	3.54 ± .07	1.22 ± .02
Mean ^a	2.77 ± .02	1.14 ± .01	2.69 ± .07	1.22 ± .02	3.57 ± .02	1.27 ± .02

^a Reference 28

^b —, Not determined

Table 5 Mössbauer Spectral Parameters of Spiked 3801 Midbay Oxidic Sediments With Varying Salinity

Salinity	TPTOH		TPTCI		TPTF	
	QS	IS	QS	IS	QS	IS
0%	2.75 ± .07	1.14 ± .02	2.76 ± .07	1.14 ± .02	3.50 ± .07	1.25 ± .02
20%	2.77 ± .07	1.17 ± .02	2.77 ± .07	1.13 ± .02	3.44 ± .07	1.26 ± .02
40%	2.72 ± .07	1.16 ± .02	2.77 ± .07	1.16 ± .02	3.55 ± .08	1.27 ± .02
60%	2.71 ± .07	1.10 ± .02	2.74 ± .07	1.16 ± .02	3.60 ± .08	1.23 ± .02
80%	2.76 ± .07	1.14 ± .02	2.75 ± .07	1.16 ± .02	3.56 ± .08	1.26 ± .02
100%	2.80 ± .07	1.13 ± .02	2.72 ± .07	1.19 ± .02	3.57 ± .08	1.25 ± .02
Mean ^a	2.76 ± .02	1.14 ± .02	2.64 ± .05	1.22 ± .02	3.50 ± .15	1.25 ± .02

^a Reference 28

Table 6 Mössbauer Spectral Parameters of Spiked 3801 Midbay Anoxic Sediments With Varying pH

pH	TPTOH		TPTCl		TPTF	
	QS	IS	QS	IS	QS	IS
pH=3	2.66 ± .06	1.13 ± .01	2.43 ± .03	1.23 ± .01	3.43 ± .04	1.32 ± .01
pH=5	2.71 ± .03	1.19 ± .01	2.59 ± .04	1.22 ± .01	3.43 ± .03	1.30 ± .01
pH=7	2.70 ± .06	1.22 ± .04	2.47 ± .06	1.20 ± .01	3.36 ± .05	1.33 ± .01
pH=9	2.68 ± .03	1.18 ± .01	2.44 ± .02	1.28 ± .02	3.45 ± .05	1.30 ± .01
Mean ^a	2.77 ± .02	1.14 ± .01	2.69 ± .07	1.22 ± .02	3.57 ± .02	1.27 ± .02

^a Reference 28**Table 7** Mössbauer Spectral Parameters of Spiked Oxidic 3801 Midbay Sediments With Varying pH.

pH	TPTOH		TPTCl		TPTF	
	QS	IS	QS	IS	QS	IS
pH=3	2.78 ± .07	1.15 ± .02	2.61 ± .07	1.24 ± .02	3.53 ± .07	1.27 ± .02
pH=5	2.75 ± .07	1.16 ± .02	2.64 ± .04	1.21 ± .01	3.54 ± .08	1.29 ± .02
pH=7	2.73 ± .07	1.16 ± .02	2.77 ± .08	1.17 ± .02	3.57 ± .07	1.28 ± .02
pH=9	2.76 ± .08	1.12 ± .02	2.50 ± .05	1.22 ± .01	3.58 ± .07	1.28 ± .02
Mean ^a	2.76 ± .02	1.14 ± .02	2.64 ± .05	1.22 ± .02	3.50 ± .15	1.25 ± .02

^a Reference 28

Table 8 Mössbauer Spectral Parameters of Various Triphenyltin Compounds Extracted From Seawater and Distilled Waters.

	TPTOH		TPTOAc		TPTCl		TPTF	
	QS	IS	QS	IS	QS	IS	QS	IS
Seawater	$2.83 \pm .06$	$1.25 \pm .02$	$2.83 \pm .04$	$1.29 \pm .01$	$2.50 \pm .07$	$1.32 \pm .02$	$2.80 \pm .07$	$1.22 \pm .02$
Distilled Water	$2.72 \pm .05$	$1.27 \pm .01$	$2.70 \pm .04$	$1.18 \pm .01$	$2.60 \pm .08$	$1.12 \pm .02$	$2.43 \pm .08$	$1.22 \pm .02$

Figure 1: Location of the Sampling Sites in the Chesapeake Bay, U.S.A.

Figure 2. Mossbauer Spectra of TPTF in Anoxic (top) and Oxic (bottom) Sediments.

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