Final Report on: Speciation of some tributyltin compounds in Anacostia and Potomac River sediments using ^{119}SnNMR spectroscopy

Abstract: The speciation of Three tributyltin compounds (TBTs), tributyltin chloride (TBTCl), Bis(tributyltin) Oxide (TBTO) and tributyltin acetate (TBTOAc) under varying pH conditions (5, 7 and 9) was studied by NMR spectroscopy in both anaerobic and aerobic Anacostia River sediments. All TBT were found to first convert to a hydrated TBT species and then further decomposition depends on the speciation time and the nature of the sediments. The ^{119}Sn NMR chemical shifts of the spiked sediments indicated that changes in the pH did not affect the speciation of the tin compounds in either aerobic or anaerobic sediments. Dealkylation to mono/dibutyltin specicies was obserserved when speciation time is 4 weeks or longer. This dealkylation is very limited as the signal around -341 ppm is very weak for all sediment samples. This would suggest that the decomposition of toxic TBTs to low toxic DBT or MBT should take more than 8 weeks in sediment. A Comparison of the strength of signal of dealkylation species and undecompose TBT species revealed that only less than 5% was decomposed to less toxic DBT or MBT.

Key words: antifoulant . NMR spectroscopy . speciation . Anacostia River . sediments . tributyltins .

Objectives

The overall objective of this research project was to investigate the environmental speciation of tributyltin compounds that are leached from antifouling paints into DC waterways, such as the Anacostia and Potomac Rivers, as a function of pH and to determine the transformation through interaction with the river sediments. Speciation of triorganotins is of major concern due to their species-specific toxicity. Tributyltins were used in antifouling paints on ship hulls because of its strong biocidal effect. These applications are inevitably associated with triorganotin releases into the surrounding water, where it accumulates in suspended matter and in sediments. These compounds have been found to be toxic to other non-targeted marine organism, such as oysters and fish. The species that were produced as a result of these interactions were determined using NMR spectroscopy. Compared with other analytical methods, such as derivatization, pressurized liquid extraction, liquid chromatography –inductively coupled plasma mass spectroscopy, and Mossbauer spectroscopy, NMR spectroscopy offers an advantage in that it permits direct observation of the interaction between the triorganotins and the sediments.

Introduction

The Anacostia River and Potomac River are two major waterways located in the District of Columbia. Each year these rivers play host to extensive recreational activities for the residents of the metropolitan area. Two classes of pollutants that find their way into Anacostia and Potomac rivers, as well as other waterways that have high boat traffic, are tributyltins(TBTs) and triphenyltins(TPTs) since they are the toxic additives added to antifoulant marine paints. [1] Marine paints are used to inhibit the attachment of barnacles, sea grass, hydroids and other marine organisms to the bottom of ships and other submerged marine structures. Organotin marine paints contain as much as 20% by

weight of antifoulant.[1] One mode of entry these triorganotins into the various waterways is through their release from vessels and underwater structures, such as harbors, estuaries, marinas and bays, than in open waters. The use of triorganotin compounds in the United States has been restricted by the Organotin Act which prohibits the use of organotin-based paints on vessels smaller than 25 meters.[2] However, vessels larger than 25 meters may still use marine paints containing organotins and a number of these larger vessels still travel these rivers, particularly, the Anacostia River where a naval shipyard is located.

Studies have shown that these organotin compounds still possess a major threat to the aquatic environment even after government regulations have restricted their use.[3,4] In the aquatic environment, triorganotin compounds are known to have low aqueous solubility and mobility, and exhibit strong binding to sediments. These compounds are therefore easily absorbed by particular matter in water, which upon settling to he bottom, can be incorporated into the sediment.[5] Any disturbance of the sediment will permit the direct and continuous re-introduction of the organotins back into the water column, where they can have adverse effect on non-targeted species such as crustaceans and fish.[6]

The presence of triorganotin in sediments has been regarded as long-term threat to marine and estuarine environments due to its persistence. Understanding its fate in the environment is therefore of primary importance to prevent its migration. TBT and TPT sorption were found to be reversible, indicating that contaminated sediment may release triorganotins to overlying waters following sediment disturbance.[7] Hence the approach to understand the conditions affect the mobility of tin becomes a significant. While there have been numerous speciation studies of organotin compounds in various bodies of water around the world, there have been no similar extensive studies in DC waterways. While most investigators have focused on the determination of organotin species and their concentration in the environment, only a few studies has been initiated to study the interactions of the organotins with sediments. Thus, a study of the speciation of triorganotins in the sediments of Anacostia and Potomac rivers as a function of pH to evaluate their interaction with sediments would be essential for the understanding of the effects of triorganotins on the aquatic environment. The results from this study will alert those responsible for water quality to the long term impact of these hazardous chemicals and, therefore, allow them to plan accordingly. The results from this study will provide individuals and/or government agencies interested in water quality and planning of Anacostia and Potomac rivers with knowledge of the fate of these triorganotins once they are leached into these rivers. This information will enable those making decisions about the water quality to better assess the long term impact of these chemicals on the aquatic environment. In addition, understanding the long term environment effects of these compounds, particularly on the fish population in the Anacostia and Potomac rivers, is critical since many of the fish taken from these rivers are consumed. Consuming large amounts of these fish could have an adverse impact on the health of individuals since triorganotin are known to have mammalian toxicities.

There are numerous analytical procedures in the literature for the determination of organotin compounds. Two recent reviews[8,9] have indicated that the method most employed for the quantitative determination of organotin species in sediments involves some types of derivatization of the organotin species followed by species detection. For example, the determination of organotin by gas chromatography (GC) involves four steps: (1) extraction/concentration; (2) derivatization (hydridization or alkylation); (3)

separation; and (4) detection. [8] However, strong interaction between triorganotins and sediments can bias the results.[9] Furthermore, the accuracy of butyl- and phenyltin determination is hampered by the lack of certified reference materials.[9] It would be more advantageous to examine the original organotin species than to study their derivatized analogs, since metals and any organic species contained in the sediment can interfere with the derivatization of the organotin species.[10-12] Mossbauer spectroscopy has been used in this lab to directly examine the original species in sediments.[13-15] However, two unsolved problems in the speciation of organotin using Mossbauer spectroscopy make it difficult to get accurate information on the structure of the organotin species in sediments. First, due to low resolution of the Mossbauer spectrometer towards tin, to get a perfect Mossbauer spectrum, enough triorganotin compounds (0.1 g) have to be spiked with the sediment (100 g). In order to get a sediment sample close to nature, it usually will take at least 1 month to prepare a sample. The interaction between the unknown organic species contained in the sediments and the triorganotins will normally result in more than more organotin species in the sediments, it is not possible to differentiate these similar organotin species by using Mossbauer spectroscopy only.

A method that would eliminate this problem is NMR spectroscopy, since this method would allow direct examination of the organotin species in the sediments at a very low concentration. Lower concentration of tin in sediments would be environmentally closer to the natural sediment samples. The use of NMR spectroscopy for the elucidation of the molecular structure of the organotin compound is well documented in the literature.[16] Specially, $^{117/119}$Sn NMR provides a probe of the tin atom that is sensitive to oxidation number and the ligands around the tin atom. It has been established that the coordination number of the tin atom is related to the ^{119}Sn Chemical shift. For trialkyltin complexes, four coordinate tin has 119Sn chemical shift ranging from about +200 ppm to -60 ppm, five coordinate tin from -90 to -190 ppm, and six coordinate tin from -200 to -400 ppm. [16] For butyltin complexes, tributyltins with a coordination number 4 or 5 around tin atoms has ^{119}Sn chemical shift in the rang 200ppm to 60 ppm, di butyl tin with a coordination number of 6 or even higher has ^{119}Sn chemical shift in the rang -80ppm to -400 ppm, Small change of the coordinate environment to the tin atom will sensitively be reflected on the ^{119}Sn NMR. Therefore, ^{119}Sn NMR is an ideal analytical tool to record the complicate interaction between the triorganotin complexes and the sediments.

Experimental

Triorganotin Compounds

Tributyltin chloride (TBTCl) and *bis*-tributyltin oxide (TBTO) were obtained from M & T Chemicals, Inc., Rahway, NJ, USA. Tributyltin acetate (TBTOAc) were purchased from Gelest, Inc., Tullytown, PA. All the compounds contained the normal abundance of ^{119}Sn and were used as received without further purification to spike the sediment samples.

Collection of Sediments

Sediment samples were obtained as grab samples from the Anacostia River (Latitude: 38^{o} 52' 17" N; Longitude: 77^{o} 00'18''W) 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 to black to brown.

Speciation Studies

The pH of the deionized water was adjusted to the desired values with either HCl or NaOH solutions prior to the addition of the triorganotin compounds and sediments. The anaerobic sediments were thawed in water to prevent oxidation. The following procedure was used in all experiments. Five g of aerobic or anaerobic sediment were spiked with 50 mg of the tributyltin 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 two weeks at room temperature and remained in the dark at room temperature for an additional week. The sediment samples will then be collected by gravity filtration and extracted with three portions of 15 mL of dichloromethane. The combined dichloromethane layer will be concentrated to about 5 mL using rotary evaporator and then sent for ^{119}Sn NMR analysis.

^{119}Sn NMR Analysis

All NMR measurements were made on a Varian Unity Inova 500 MHz spectrometer. Sample and instrument temperatures were controlled at 298 K. Proton-decoupled ^{13}C and ^{119}Sn spectra were acquired with WALTZ decoupling. ^{119}Sn chemical shifts were referenced to tetramethyltin externally. To identify the organotin species present, the experimental spectra were compared to spectra of known organotin compounds. Spectra of the pure compounds were recorded and used for comparison.

Results and Discussions

For preliminary studies, 8 sediment samples spiked with TBTs were prepared. The chemical shifts (δ) for the sediments spiked with TBT compounds at different pH are listed in Table 1. Typical spectra for the spiked aerobic and anaerobic sediments are shown in Fig. 1-8.

The preliminary data also indicated that changes in the pH values did not affect the decomposition of the tributyltin compounds in the same sediments. For example, TBTCl spiked with same Sediments at pH 5 (Fig 1) and 7 (Fig 2) shows very similar pattern in NMR spectra. However, different patterns were observed in NMR spectra for TBTs in anaerobic and aerobic sediments samples. Compared with Fig 31 (aerobic sample at pH 7), anaerobic TBTOAc sample was decomposed more at same speciation time (2 weeks) Except the major signal from un-decomposed hydrated TBT, two signals at 105 (medium) and -341 (weak) ppm were also observed as shown in Fig 4. This would suggest that the organisms in the sediments are responsible for the decomposition of the TBTs. Since anaerobic and aerobic sediments have different organism composition, different pattern of decomposition are observed. This decomposition was also clearly shown in the ^{1}H NMR of TBTOAC samples. The typical acetate CH_3 proton with chemical shift around 2.1 ppm is missing in the ^{1}HNMR spectrum (Fig 5). The multiplets from 0.8-1.7-ppm are ascribed for butyl group in the sample. There are no other protons in the sample except typical protons from water around1.6 ppm. Only very weak signals in the range of 0-400

ppm were observed which are ascribed to decomposition of the TBTs in sediments. This indicated that two weeks duration was not long enough to decompose TBTs in sediment.

For these reason, further studies have focused on the anaerobic and aerobic samples spiked in 2 weeks and 8 weeks at pH 7. Total 12 sediment samples spiked with TBTs were prepared. The chemical shifts (δ) for the sediments spiked with TBT compounds at different pH are listed in Table 2 for TBTCl, TBTO and TBTOAC.

The ^{119}Sn NMR parameters indicated that all TBTs, TBTOAc(δ: 118 ppm), TBTCl(δ: 141 ppm) and TBTO(δ: 89 ppm) were easily converted to other butyltin species in sediments. When compare with pure TBTs, no sediments samples have chemical shifts same as the pure one. This may be due to the formation of hydrated tributyltin complexes in sediment samples. Most of the hydrated TBT remained unchanged during the two weeks speciation. This is based on the observation that the major peaks around 158 ppm remain as medium to strong in the ^{119}Sn NMR spectra. This hydrated tributyltin species could be $Bu_3Sn(OH_2)_n^+$.

The equations shown in scheme 1 account for the possible mechanism of the formation of the hydrated tributyltin species.

$$Bu_3SnOAc + H_2O \rightleftharpoons Bu_3SnOH + HOAc$$

$$Bu_3SnOSnBu_3 + H_2O \rightleftharpoons 2Bu_3SnOH$$

$$Bu_3SnOH + H^+ \rightleftharpoons Bu_3SnOH_2^+$$

$$Bu_3SnOH_2^+ + £¨n\text{-}1)H_2O \rightleftharpoons Bu_3Sn(OH_2)_n^+$$

Scheme 1

It was also found that the tributyl hydroxide (TBTOH) and hydrated tributyltin species $Bu_3Sn(OH_2)_n^+$ in sediments will further decompose to more unknown tributyltin species if enough time is given for the speciation. As shown in Fig 6 and 7, TBTOAC was converted to hydrated TBTs, then this hydrated TBT was converted to two major unknown species with chemical shift around -11ppm and-109 ppm. Possible structures for these two unknown species could be $Bu_3Sn(OH_2)2^+$ (-11ppm) and $Bu_3Sn(OH_2)_3^+$ (-109 ppm) .

$$Bu_3SnOH_2^+ \rightleftharpoons Bu_3Sn^+ + H_2O$$

$$Bu_3Sn^+ + CO_3^{2-} \rightleftharpoons (Bu_3Sn)_2CO_3$$

$$Bu_3Sn^+ + HS^- \rightleftharpoons Bu_3SnSH$$

$$Bu_3Sn^+ + S^{2-} \rightleftharpoons Bu_3SnSSnBu_3$$

Scheme 2

Chemical shifts in 60ppm to 200 ppm are typical for four coordinated tributyl tin. Most of the samples have several minor peaks other the major peak around 157 ppm. This is indication of the formation of the Bu_3Sn^+ cation in the decomposition process, minor species could be formed with different anions such as carbonate, sulfide and hydrogen sulfide. The peaks from 70-90 ppm could be assigned to tributyltin sulfides while the peaks around 110ppm could be assigned to tributyltin carbonate (Scheme 2).

Chemical shifts around -340.9 ppm is an indication of dealkylation to di or monobutylatin species, though the amount of decomposition is low as the signals around -341 ppm are all very weak (Fig. 7). This would suggest that dealkylation of TBT takes a longer time than 8 weeks in sediment samples. A Comparison of the strength of signal of dealkylation species and undecomposed TBT species revealed that only less than 5% was decomposed to less toxic DBT or MBT. This is different from the conclusion we made in the studies on the speciation of triorganotins using Mossbauer Spectrometry when all the TBT were shown in Mossbauer spectra to convert to other hydrated TBT species. This would suggest that NMR spectroscopy is more sensitive spectrometer for detection of organotin species than Mossbauer spectrometer.

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Table 1. ^{119}Sn NMR chemical shifts for TBTs spiked with sediment samples from the Anacostia River.

TBTs	pH	Speciation Duration	Sample type	Chemical shifts	
				200 to 60 ppm	0 to -400 ppm
TBTCl	7	2 weeks	Anaerobic	157.0 (medium) 109.9 (medium) 107.3 (strong) 95.1 (weak) 76.9 (medium) 76.6 (medium) 64.3 (medium)	-11.4 (weak) -109.1(weak)
TBTCl	5	2 weeks	Anaerobic	158.0 (strong) 107.8 (medium) 110.7 (weak) 77.1 (weak)	
TBTCl	Pure			85	
TBTO	7	2 weeks	Anaerobic	156.0 (medium) 105.2 (strong)	-109.1(weak) -340.9 (weak)
TBTO	Pure			141	
TBTOAc	7	2 weeks	Aerobic	157.1 (strong)	
TBTOAc	7	2 weeks	Anaerobic	156.0 (medium) 105.2 (strong)	-340.9 (weak)
TBTOAc	7	4 weeks	Anaerobic	157.5 (strong)	-340.9 (weak)
TBTOAc	7	8 weeks	Anaerobic	156.1 (medium) 109.6 (medium) 106.8 (strong) 76.3 (medium) 63.8 (medium)	-11.4 (weak) -340.9 (weak)
TBTOAc	Pure			118	

Table 2. ^{119}Sn NMR chemical shifts for TBTOAc spiked with Anaerobic and Aerobic sediment samples from the Anacostia River at pH 7.

Sample type	Speciation Duration	Chemical shifts	
		200 to 60 ppm	0 to -400 ppm
TBTCl (Aerobic)	2 weeks	158.0 (strong) 107.8 (medium) 110.7 (weak) 77.1 (weak)	
	8 weeks	158.0 (medium) 107.8 (medium) 110.7 (weak) 77.1 (weak)	-11.4 (weak) -109.1(weak)
TBTCl (Anaerobic)	2 weeks	157.0 (medium) 109.9 (medium) 107.3 (strong) 95.1 (weak) 76.9 (medium) 64.3 (medium)	-11.4 (weak)
	8 weeks	157.2 (weak) 109.5 (medium) 108.1 (medium) 95.7 (weak) 77.5 (medium)	-11.4 (medium) -109.0(weak)
TBTCl		85	
TBTO (Aerobic)	2 weeks	156.4 (medium) 105.3 (strong)	-340.9 (weak)
	8 weeks	156.2 (medium) 105.6 (strong)	-11.5 (minor) -340.9 (weak)
TBTO (Anaerobic)	2 weeks	156.0 (medium) 105.2 (strong)	-109.1(weak) -340.9 (weak)
	8 weeks	156.7 (medium) 105.4 (medium)	-109.1(weak) -340.9 (weak)
TBTO		141	
TBTOAc (Aerobic)	2 weeks	157.1 (strong)	
	8 weeks	157.5 (strong) 109.6 (medium) 106.8 (strong) 76.3 (medium)	-11.5 (weak) -340.9 (weak)
TBTOAC (Anaerobic)	2 weeks	156.0 (medium) 105.2 (strong)	-340.9 (weak)
	8 weeks	156.1(medium) 109.6(medium) 106.8 (strong) 76.3 (medium) 63.8 (medium)	-11.4 (weak) -340.9 (weak)
TBTOAc		118	

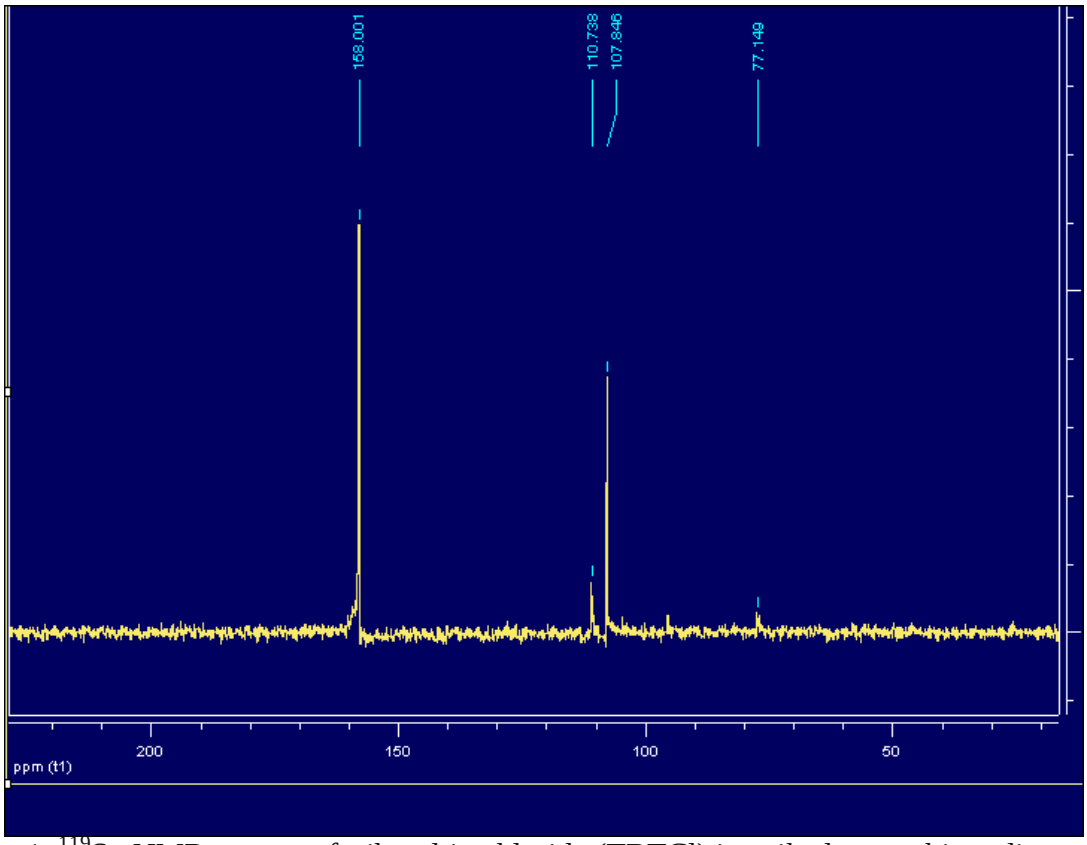

Fig. 1. ^{119}Sn NMR spectra of tributyltin chloride (TBTCl) in spiked anaerobic sediments from Anacostia River at pH 5. (Speciation time 2 weeks)

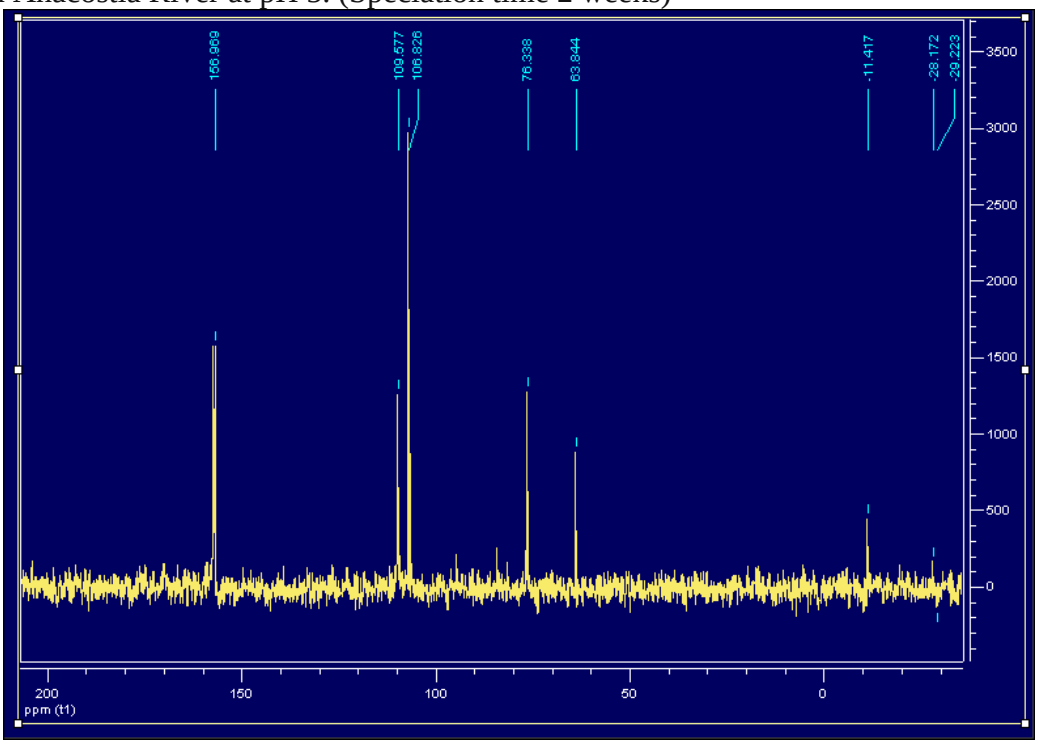

Fig. 2. ^{119}Sn NMR spectra of tributyltin chloride (TBTCl) in spiked anaerobic sediments from Anacostia River at pH 7. (Speciation time 2 weeks)

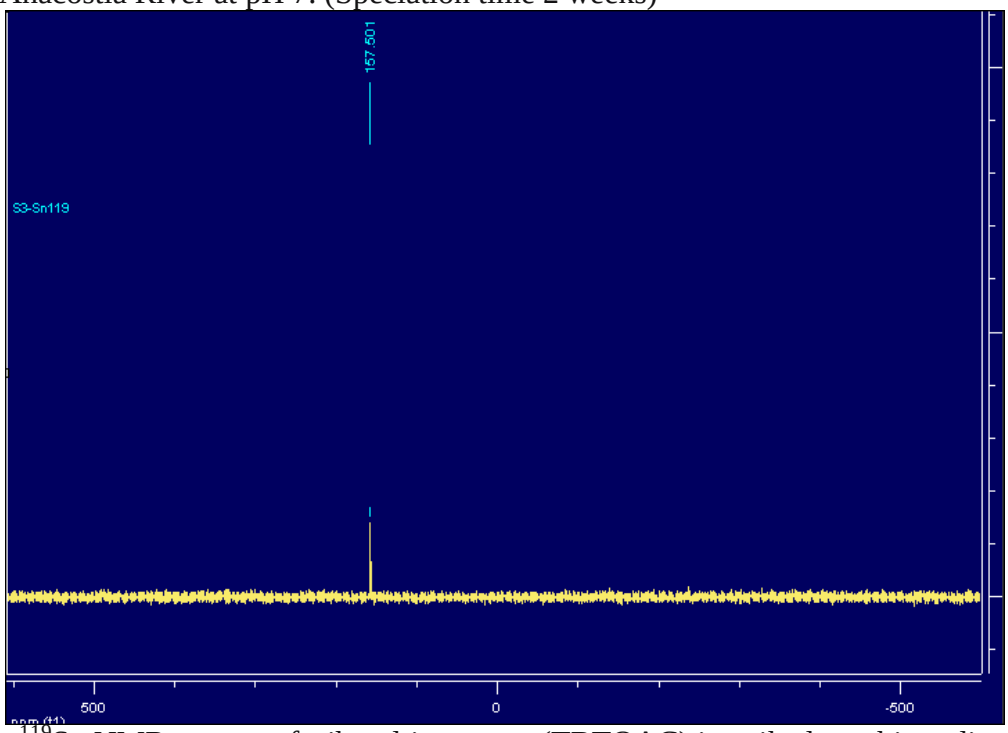

Fig. 3. ^{119}Sn NMR spectra of tributyltin acetate (TBTOAC) in spiked aerobic sediments from Anacostia River at pH 7 (speciation time 2 weeks).

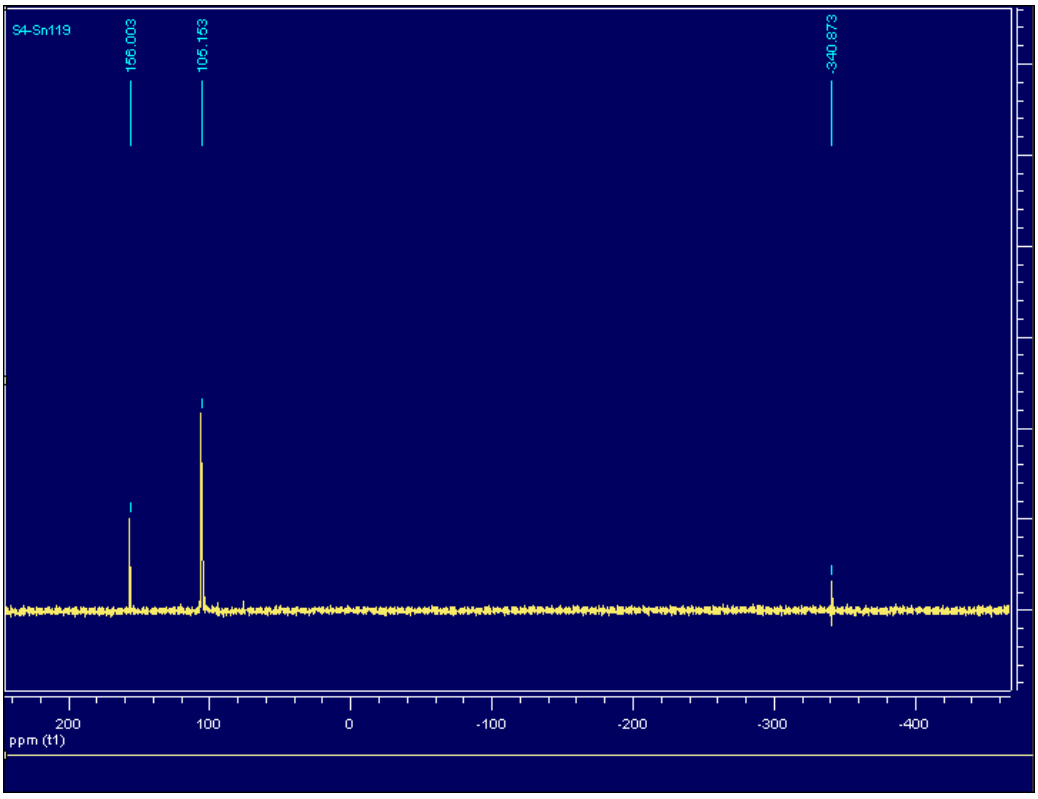

Fig. 4. ^{119}Sn NMR spectra of tributyltin actate(TBTOAc) in spiked anaerobic sediments from Anacostia River at pH 7. (Speciation time 2 weeks)

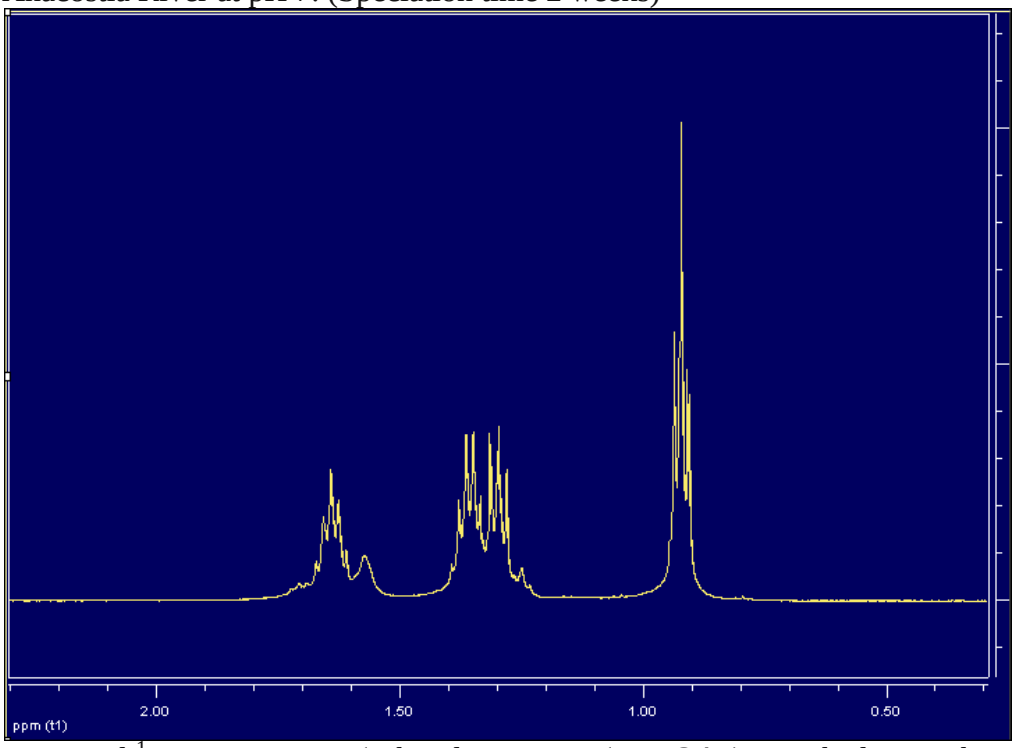

Fig. 5. Typical ^{1}H NMR spectra (tributyltin acetate (TBTOAc) in spiked anaerobic sediments from Anacostia River at pH 7).

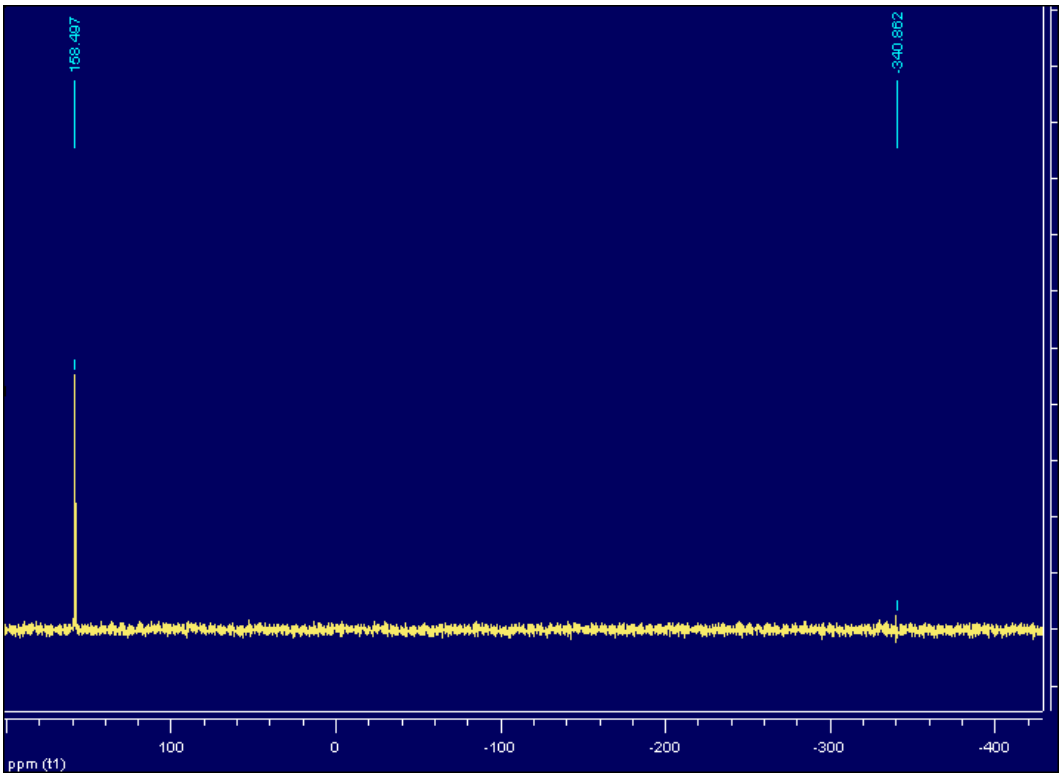

Fig. 6. ^{119}Sn NMR spectra of tributyltin actate(TBTOAc) in spiked anaerobic sediments from Anacostia River at pH 7. (Speciation time: 4 weeks)

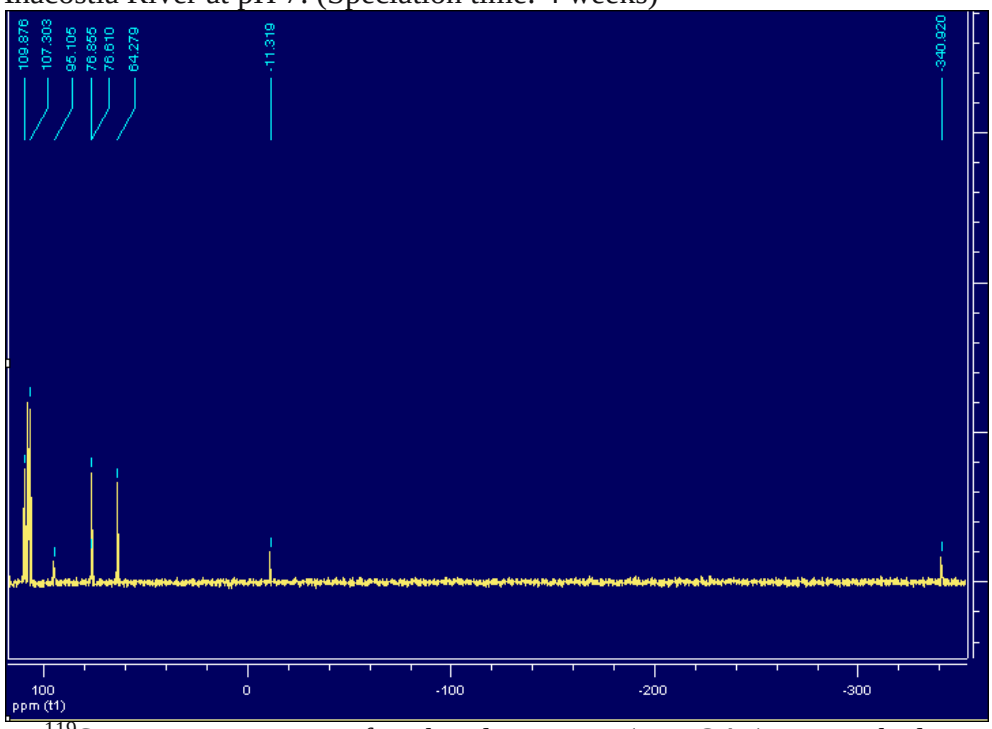

Fig. 7. ^{119}Sn NMR spectra of tributyltin actate(TBTOAc) in spiked anaerobic sedimentsfrom Anacostia River at pH 7. (Speciation time: 8 weeks)

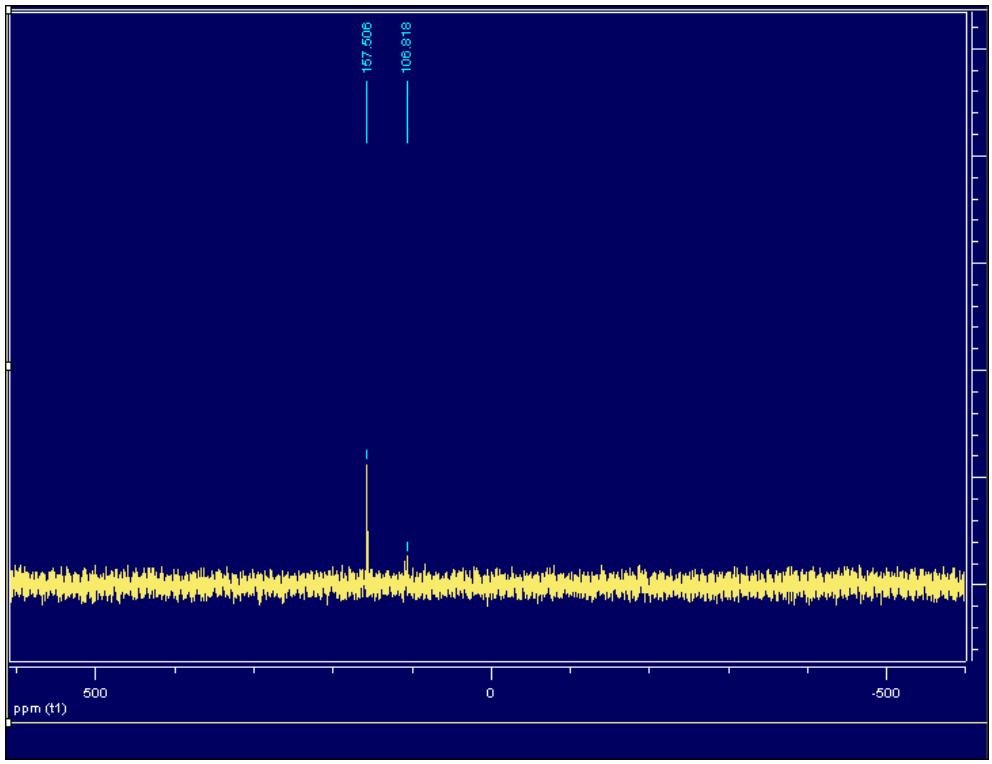

Fig. 8. ^{119}Sn NMR spectra of bistributyltin oxide (TBTO) in spiked anaerobic sediments from Anacostia River at pH 7. (Speciation time 2 weeks)