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Methylation of tin(II) by methyl iodide in porewater

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The methylation of tin(II) chloride by methyl iodide in porewater and formation of monomethyltin as the only methyltin product are described. A factorial experiment tested the effects of concentrations of tin(II), methyl iodide, and oxygen on monomethyltin yields. The experiments gave 0.18 to 12.8 % yield. Analysis of variance (ANOVA) calculations showed that all three variables were significant at the 95 % level. Comparison of yields in aqueous 23 g kg^{-1} sodium chloride solutions to those in porewater and to those containing fulvic acid, salicylic acid, and EDTA showed that only fulvic acid significantly reduced yields. Reasons for this observation are discussed and the findings in the model system are related to methylation of tin compounds in sediments.

Keywords: Methylation, tin, methyl iodide, porewater, methyltin, salicylic acid, fulvic acid, sediments

INTRODUCTION

Methyltin compounds are very common in natural waters,[1–5], sediments,[1,4,5] and aquatic plant life.[6] Their concentrations in sediments and plant life are 1000 or more times those in surrounding water. Methyltin compounds are not nearly as toxic as butyltin ones, but trimethyltin has considerable toxicity.[7]

Methyltin compounds in the aquatic environment are very likely to originate from natural methylation processes rather than from man-caused pollution. There are several reasons for the above statement. First, Maguire *et al.*[4] observed mixed butylmethyltin compounds that have no industrial origin. Second, these compounds often occur in unpolluted waters,[1–5] and in plants[6] and oysters[8] living in them.

Aquatic methyltin compounds are probably the result of methylation of inorganic tin. For example, Gilmour *et al.*[9,10] clearly demonstrated that sulfate-reducing micro-organisms in anaerobic sediments produce monomethyltin as major product and dimethyltin as minor product. In addition Donard *et al.*[6] showed that macroalgae mediate formation of methyltin compounds.

It is very likely that micro-organisms cause biological methylation of tin within the cell or mediate methylation outside the cell by released chemicals. Methylating agents are common in the aquatic environment, especially near plant life. They include 3-(dimethylsulfonio)propionate[11] and methyl iodide (MeI).[12,13] Both chemicals, which transfer methyl as a carbocation, can methylate tin(II), but not tin(IV). The process is called oxidative addition and results in a two-electron oxidation of tin(II) to tin(IV).

Because the methylation process is so little understood, researchers often study model systems. For example, Weber and co-workers have shown that MeI can methylate tin(II) to monomethyltin in aqueous solutions[14] and under simulated environmental conditions.[15] In addition Craig and co-workers observed that MeI in distilled water[16] and fungal species[17] methylate Sn(II).

The goal of this study is to study methylation of tin(II) by MeI in porewater. We tested several conditions such as the presence or absence of oxygen, the presence of potential ligands, tin(II) and MeI concentrations, pH, and reaction time. Major findings were that monomethyltin is the only methyltin product and that yields were significantly higher under anaerobic than aerobic conditions. This result rationalizes the observation that monomethyltin forms in anaerobic sediments. Reasons are that tin(II) is needed for oxidative addition processes and that tin(II), but not tin(IV), is soluble in porewater.

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EXPERIMENTAL

Materials and reagents

Most materials and reagents were previously described.[15] All water was doubly de-ionized and then distilled.

The 0.01 mol dm^{-3} tin(II) chloride ($SnCl_2$) stock solution in 0.1 mol dm^{-3} hydrochloric acid was prepared by dissolving 0.59 g tin metal (Alfa Products, 20 mesh) in 60 cm^3 concentrated hydrochloric acid, adding water, adjusting to pH 1.54 with NaOH, and adding water to a 500 cm^3 final volume. Oxidation of the $SnCl_2$ solution was prevented by adding tin powder (20 mesh) to the flask and sealing it under nitrogen. The 0.01 mol dm^{-3} solution of $SnCl_4.5H_2O$ (Fisher Scientific Co.) was prepared by dissolving 0.35 g in 100 cm^3 of 0.1 mol dm^{-3} hydrochloric acid solution.

Sediment samples were collected in December during middle-to-high tide at the Jackson Estuarine Laboratory (JEL) site in the Great Bay Estuary, New Hampshire, USA. In a shallow water location, about 2 cm of the upper oxidized layer of sediment were packed into polystyrene centrifuge bottles. After centrifugation at 5000 rpm for 45 min at 10 °C (Sorvall Superspeed RC2-B), the supernatant was filtered using 0.45 μm Nuclepore filters. Filtered porewater samples were collected in glass vials and stored in the dark at 4 °C.

Dissolved organic carbon (DOC) in porewater was measured by a Dohrmann DC-80 Carbon Analyzer. Porewater salinity was measured by a Model 10419 Salinity Meter (American Optical Corp.).

Based on the salinity results for the porewater, a 23 g kg^{-1} saline solution was prepared by dissolving sodium chloride in water. Several model organic substances were dissolved in this solution: salicylic acid (172 mg dm^{-3}) the disodium salt of EDTA (326 mg dm^{-3}), and soil fulvic acid[18,19] (19.8 mg per 100 cm^{-3}). Each solution contained 105 mg dm^{-3} DOC.

Calibration curves

Calibration curves (Table 1) were drawn for mono-, di-, and tri-methyltin chlorides using the methyltin concentration range of 1.13–28 μmol dm^{-3} after diluting 1000 mg dm^{-3} stock solutions to 100 mg dm^{-3}. All methyltin concentrations are *as tin*. Methyltin chloride samples were prepared by adding the desired volume of diluted standard solutions to 15 cm^3 of 23 g kg^{-1} sodium chloride solution or to porewater. The pH of all solutions was adjusted to pH 3. Hydride derivatization and gas-chromatographic determinations of methyltin hydrides were as previously discussed.[15] Retention times were: $MeSnH_3$, 1.19 min; Me_2SnH_2, 2.10 min; and Me_3SnH, 3.79 min.

Table 1 Calibration data and limits of detection for determination of methyltin compounds[a,b]

Medium	Compound	Slope ($\times 10^{-6}$)	Intercept ($\times 10^{-6}$)	LOD (μmol)
NaCl	$MeSnCl_3$	8.50	0.0202	0.016
NaCl	Me_2SnCl_2	15.6	0.0597	0.011
NaCl	Me_3SnCl	20.5	0.0499	0.010
PW	$MeSnCl_3$	8.04	0.0272	0.012
PW	Me_2SnCl_2	15.1	0.0092	0.0087
PW	Me_3SnCl	19.6	0.0407	0.015

Abbreviations used: LOD, limit of detection (3σ), PW, porewater.
[a] (i) In aqueous NaCl (23 g kg^{-1}) solution and (ii) in porewater.
[b] Calibration range is 0.0169–0.422 μmol.
Detection was by GC FID (Ref. 15).

Instrumentation

Use of the gas chromatograph was identical to a previous report[15] except that the detector was at 200 °C.

Reactions

Reactions were carried out in 160-cm^3 vials sealed with 'crimp on' Teflon-lined silicone septa (Supelco Inc.) in the dark at room temperature for 17 h. Reaction solutions were 5 cm^3 filtered porewater plus 10 cm^3 aqueous 23 g kg^{-1} sodium chloride. The inorganic tin source was 0.06 cm^3 or 0.3 cm^3 of 0.01 mol dm^{-3} $SnCl_2$ stock solution resulting in a total tin concentration of 40–200 μmol dm^{-3}. Variables and variable values for factorial experiments are shown in Table 2. Samples were prepared in random order. The pH was determined with the Orion 701A pH-meter and Corning Combination X-EL pH electrode. Adjustments of pH were done by micropipettes using 0.1 mol dm^{-3} sodium hydroxide or 0.1 mol dm^{-3} hydrochloric acid. The pH of the samples before and after the reactions were within 0.3 pH units. The samples were shaken for 17 h using a shaker (Eberbach Corp., Ann Arbor, Michigan).

Table 2 Factorial experiment: percentage monomethyltin yield on the methylation of tin(II) by methyl iodide in porewater

Variable	Levels	
	+ (high level)	- (lower level)
S, μmol tin(II)	3	0.6
M, μmol methyl iodide	100	20
A, anaerobic/aerobic[a]	Anaerobic	Aerobic

	Variable levels			Yield $MeSn^{3+}$ (%)		
Expt no.	S	M	A	Expt A	Expt B	Average
1	+	+	+	14.0	11.6	12.8
2	-	+	+	2.52	4.13	3.33
3	+	-	+	5.43	5.57	5.50
4	-	-	+	1.28	1.51	1.40
5	+	+	-	4.27	4.13	4.20
6	-	+	-	0.63	0.65	0.64
7	+	-	-	1.66	1.54	1.60
8	-	-	-	0.14	0.22	0.18

[a] Anerobic conditions mean carefully kept under nitrogen (see Experimental section); aerobic conditions mean stirred in air for 30 min.

Air was carefully excluded from anaerobic experiments. The tin(II) stock solution was kept under nitrogen in a round-bottomed flask with a three-way stopcock. A reaction flask containing sample and enough NaOH to neutralize the tin(II) to be added was flushed with nitrogen and capped with a serum cap. Aliquots were taken from the flask containing tin(II) under a nitrogen stream and injected directly into the capped vial.

Several other experiments were done with porewater samples. One proved that 7 h and 17 h reaction times gave similar yields. Another measured possible formation of methyltin compounds from the reaction of tin(IV) and methyl iodide. Decomposition experiments were carried out to determine the stability of mono-, di-, and tri-methyltin chlorides in the presence of porewater.

Measurement of percentage yield in the presence of various ligands

Yields of methylation products of reactions between tin(II) and methyl iodide in 23 g kg^{-1} aqueous sodium chloride were compared in the presence of several ligands. Ligands included salicylic acid, EDTA, and fulvic acid at concentrations of 105 mg dm^{-3} dissolved organic carbon. These experiments were performed under anaerobic and aerobic conditions.

RESULTS

Calibration curves of standards

Table 1 contains slopes, intercepts, and limits of detection for $MeSn^{3+}$, Me_2Sn^{2+}, and Me_3Sn^+ in 23 g kg^{-1} aqueous sodium chloride solution and in porewater. Slopes in saline water increase from $MeSn^{3+}$ to Me_3Sn^+ with a $Me_3Sn^+/MeSn^{3+}$ slope ratio of 2.41. The slopes are approximately proportional to carbon content of methyltin compounds because of the GC flame ionization detector. The slope of each methyltin compound is nearly the same in saline solution and porewater, showing that matrix effects are unimportant for determinations of methyltin compounds. Furthermore, the $Me_3Sn^+/MeSn^{3+}$ ratio of 2.43 in porewater is nearly identical to the value in saline water. This agreement ensures that use of Me_3Sn^+ as an internal standard is valid for determination of $MeSn^{3+}$.

Methylation of tin(II) in porewater

A duplicate 2^3 set of factorial experiments (Table 2) on methylation of $SnCl_2$ by methyl iodide in porewater included varying amounts of tin(II) (S),

Table 3 Statistical significance of parameters for methylation of tin(II) by methyl iodide in porewater

Effect	*F*-values[a]
S	162.77
M	71.37
A	127.09
SM	26.65
SA	34.95
MA	17.99
SMA	4.93

Abbreviations used: S, μmol tin(II); M, μmol MeI; A, anaerobic/aerobic.

[a] Underlined values indicate significance at the 95% confidence level. The literature *F*-value at the 95% confidence level is 5.32.

Table 4 Percentage monomethyltin yield from methylation of tin(II) by methyl iodide under aerobic and anaerobic conditions in saline water containing various ligands[a]

	Yield (%)		
Medium	Anaerobic	Aerobic	Anaerobic/ Aerobic ratio
Sodium chloride only	17.8	11.6	1.5
Porewater	12.8	4.23	3.0
Salicylic acid	15.0	13.3	1.1
EDTA[b]	6.70	3.93	1.7
Fulvic acid	0.038	0.019	2.0

[a] Experimental conditions: 3 μmol tin(II); 100 μmol methyl iodide; 105 mg dm^{-3} dissolved organic carbon in 23 g kg^{-1} aqueous NaCl at pH 7. [b] Disodium salt of EDTA.

methyl iodide (M), and oxygen (A). Average percentage yields of monomethyltin, the only methyltin product, ranged from 0.18 (Expt 8) to 12.80 (Expt 1). Average RSD for the eight pairs of experiments was 9.0 %.

Analysis of variance (ANOVA) calculations (Table 3) for methylation of tin(II) in porewater show whether S, M, and/or A and their interactions are significant at the 95% level for production of monomethyltin. The *F*-test showed that all three variables and their pair interactions are significant.

Increased tin(II) and methyl iodide concentrations result in increased monomethyltin yield (Table 2). For example, the average yield with high tin(II) concentration is 6.0 %, whilst that for low tin(II) concentration is 1.4 %. A similar effect result occurs for monomethyltin yields in the absence (5.8 %) and presence (1.7 %), of oxygen to give an anaerobic/aerobic yield ratio of 3.4.

Methylation experiments in the presence of various ligands

We tested tin(II) methylation by methyl iodide in the presence of various ligands in saline aqueous solution under anaerobic and aerobic conditions (Table 4). In all experiments the media contained 23 g kg^{-1} sodium chloride and 105 mg dm^{-3} DOC to simulate the porewater. Yields are always higher in the absence of oxygen than in its presence. The anaerobic percentage yield order is: sodium chloride > salicylic acid > porewater > EDTA > fulvic acid; and the aerobic order is identical except for the reversal of sodium chloride and salicylic acid. The anaerobic/aerobic ratio of percentage yields shows that methylation in porewater, but not in salicylic acid solution, is very sensitive to oxygen.

DISCUSSION

Methylation of tin(II) in porewater

Tin(II) compounds react with the methyl donor methyl iodide (CH_3I) in water,[14–16] mimicking methylation observed for sediments[9,10] and fungal species.[17] Methylation of tin(II) by methyl iodide in aqueous 0.1 mol dm^{-3} potassium chloride yields predominantly monomethyltin in a yield of 7 % in the presence of manganese dioxide and 11 % in its absence.[14] Ring and Weber[15] studied the methylation of tin(II) to the sole methyltin product monomethyltin by methyl iodide under simulated estuarine solutions in the absence and presence of fulvic acid. They observed a maximum yield of 10 % in the absence of fulvic acid and of 3.0 % in its presence. This analogous study of methylation in porewater resulted in a maximum monomethyltin average yield of 13 % (Table 2). This study demonstrates that yield is enhanced by increased tin(II) and methyl iodide concentrations, and especially by strictly anaerobic conditions.

The reasons for monomethyltin being the sole methyltin product are quite clear. First, the absence of di- and tri-methyltin products demonstrates that the initial monomethyltin product does not undergo re-

arrangement to form, for example, dimethyltin and inorganic tin(IV). In addition, none of the three methyltin compounds decomposes under reaction conditions in porewater. Second, the oxidative addition mechanism, which requires oxidation of tin(II) to the maximum oxidation state of tin(IV), must predominate in the porewater experiments. This mechanism explains why the presence of oxygen and concomitant oxidation of tin(II) to tin(IV) so effectively decreases monomethyltin yields. We experimentally confirmed that MeI does not methylate tin(IV) under our experimental conditions. Only negative, i.e. carbanionic, methyl donors can methylate tin(IV).[14,20]

Methylation experiments in the presence of various ligands

Data in Table 4 demonstrate that in the absence or presence of oxygen, yields of monomethyltin decrease when comparing reaction media of aqueous sodium chloride (23 g kg^{-1}) with those containing in addition 105 mg dm^{-3} DOC. The DOC originates from unknown compounds in porewater or fulvic acid, or the known ligands salicylic acid or EDTA. The yields in air-free reactions vary from 17.8 % in saline solution to 0.038 % for fulvic acid in saline solution. Similar results occur for aerated solutions. Three possible processes could account for lower yields in the presence of ligands: (1) complexation of tin(II) by ligands; (2) oxidation of tin(II) by the ligands; and (3) binding of methyl iodide by the ligands. Similar yields in the absence of oxygen in the reaction media saline water, salicylic acid in porewater, and porewater make unnecessary discussion of those ligands' effects on methylation.

Previous speciation calculations by Ring and Weber[15] demonstrated that complexation of tin(II) by fulvic acid is an unlikely reason decreased methylation yields in its presence. Even using stability constants observed for the very strong bonding of copper(II) by fulvic acid, in the presence of tin speciation calculations showed a predominance of $Sn(OH)_2$. In contrast the decreased yield with EDTA might be due to complexation.

Among solutions containing DOC, only fulvic acid, which oxidizes or reduces a variety of substances under environmental conditions, is likely to prevent methylation of tin(II) by oxidizing it. Omar and Bowen[21] observed oxidation of tin(II) by humic matter. Since fulvic acid has a reduction potential of approximately 0.5–0.7 V at pH 0,[22] and the standard reduction potential for reduction of tin(IV) to tin(II) is 0.15 V, the oxidation is thermodynamically favored. However, two other prerequisites for oxidation are not well known for fulvic acid. They are a sufficiently fast rate and an ample oxidizing capacity to effect enough oxidation of tin(II) to measure decreased yields. Thus, our experiments do not demonstrate the presence or absence of oxidation effects.

The third possibility, the binding of methyl iodide to EDTA or, especially, fulvic acid is reasonable. Both solutions contain 100 μmol methyl iodide. The EDTA and fulvic acid solutions, respectively, contain 18 and 7 μmol of carboxyl groups. Even if an unlikely 100 % yield of carboxyl group esterification occurred, sufficient methyl iodide would be available for methylation of tin(II). Monomethyltin yields in porewater decrease by a factor of only approximately two when decreasing the amount of reactant methyl iodide from 100 to 20 μmol.

The above discussion, however, does not rule out binding of methyl iodide to fulvic acid by well-known, non-specific hydrophobic interactions.[23] For example, hydrophobic butyltin compounds bind to hydrous iron oxides coated with fulvic acid.[24] Attempts to prove the existence of non-specific interactions by comparing monomethyltin yields with fulvic acid and fulvic acid presaturated with methyl iodide failed.

The anaerobic/aerobic ratio of monomethyltin yields (Table 4) for different ligands show that only the porewater, is *significantly* more sensitive to oxygen than the saline solution. A low sensitivity to oxygen suggests binding of tin(II) by ligands in the medium. Speciation calculations in our previous study[15] demonstrated that in saline solutions in the presence or absence of fulvic acid, hydroxide (OH^-) was the major ligand between pH 6 and 8. Possibly pH-7 porewater has ligands that compete with hydroxide, but do not bind tin(II) so strongly as to decrease methylation.

CONCLUSIONS

The decrease in tin methylation under aerobic conditions and in the presence of fulvic acid might have important implications for our understanding of methylation in marine sediments. Gilmour *et al.*[9,10] argued that sulfate-reducing bacteria are essential

mediators for methylation of tin in marine sediments. Reduction of tin(IV) to tin(II) in the sulfidic zone of the sedimentary column is likely, thus making possible its methylation by oxidative addition of a carbocation donor through a process similar to that studied in these model experiments. Data in this paper indicate that tin(II) is rapidly oxidized by contact with air, and that the resulting tin(IV) does not methylate. We therefore expect that methylation in sediments will occur essentially within the anoxic zone and be minimal on the oxic surface layers. At the surface tin(II) would be oxidized and then precipitate or be adsorbed on the solid phase. Gilmour *et al.*[9,10] corroborate this conclusion. In the sulfidic zone aqueous tin(II) can either be methylated by methyl donors or be precipitated as sulfide. Thayer and co-workers[25] proved that methyl iodide reacts with SnS to form monomethyltin. A better understanding of the geochemistry of tin across redox boundaries is necessary, however, before the consequences of the results presented here can be fully appreciated.

If the reduction in monomethyltin yield in the presence of fulvic acid is due to binding of methyl iodide, important environmental results will occur. Humic substances are ubiquitous and MeI is one of the available, potential methylating agents in the aquatic environment. If the interaction of fulvic acid and methyl iodide prevents methylation of metals, it suggests that environmental methylation might be in intracellular process.

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