The speciation of alkyltin compounds in the marine environment

by

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Abstract

An analytical method has been developed for the determination of alkyltin compounds at ng levels in environmental samples, converting these tin species to their corresponding hydrides, other than tetramethyltin. For this method, the acidity of the solution, Na BH_4 concentration, and gas flow rates were optimized. A suitable hydride trap such as 3% OV-1 on Chromosorb W was used to separate common interfering compounds and to obtain good peak separation. The samples analysed in an air-hydrogen flame burning in a quartz-tube furnace placed on the optical axis of AAS under the optimized conditions.

Water, organisms and sediment samples from the Cilician basin of the Mediterranean and other seas were analysed for total, acid extractable and alkyltins. Methyltins were occasionally observed in some natural waters. Mono- and di-methyltin compounds were found in polluted sediments, wehreas unpolluted coastal water sediments only contained primarily trimethyltin. The net methylation rate is evidently independent of inorganic tin content susceptible to biosynthesis reaction. Biomethylation reaction can occur towards timethyltin in both oxic and anoxic non-polluted sediments, e.g. in Saanich Inlet. Methyltin per cent in the fish is about 3 - 6% of total content while limpets contain significant organotin compounds ranging between 35 - 75% of the total tin values. No tri-methyltin was detected in macroalgae although limpet, fish and sediment have certain levels.

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Introduction

The chemical behaviour of any element in the environment depends on the nature of its components. Because of their general toxic properties, the role that heavy metals play in the environment has recently been the subject of increased study. It was observed that heavy metals in their inorganic forms exhibit relatively low toxicity towards biota when compared to those metals with certain carbofunctional groups attached. The biotransformation of toxic substances in the environment is therefore of vital importance from the standpoint of public health (TOLBA, 1980). The toxicity of a metal depends on the chemical form in the environment as well as on its uptake route. For example, alkylmercurials are from 10 - 100 times more toxic than inorganic mercury compounds and similar effects are noted for organotins as quoted by JEWETT et al., (1975).

Tin, one of the naturally methylated elements in the environment has become of particular interest in recent years. Because, although it has been suspected that the alkyl forms of tin might be biosynthesized steadily in the environment (WOOD and GOLDBERG, 1977; RIDLEY et al., 1977) no adequate analytical technique was found to confirm this supposition up to 1978. Application of borohydride to form stable metalhydrides has made it possible to measure the tin compounds at their natural levels. However, no great attempt has been made so far to define the natural biomethylation products of tin in different marine environments so as to supplement and confirm the laboratory findings of GUARD et al. (1981), HALLAS et al. (1982), CHAU (1980) and BRINCKMAN et al. (1981).

Based upon the studies of HODE et al. (1979) and BRAMAN and TOMPKINS (1979) a method has been developed and applied to the marine environmental samples for the speciation of tin. This article covers the analytical work to adapt the hydride generation method to the analysis of inorganic tin and alkyltins in sediments and organisms, and their distribution in those samples.

Experimental

Apparatus: A Varian-Techtron Model AA-6 atomic absorption spectrophotometer and a Linear Instruments Corporation Model 252 integrating recorded or a Varian Model A-25 recorder were used to obtain all the data. The apparaturs for the reduction of tin species to the corresponding hydrides, their collection on a cold trap, and their determination by atomic absorption is illustrated in Figure 1. The air, hydrogen and helium flow rates were 150, 250 and 80 ml/min, respectively.

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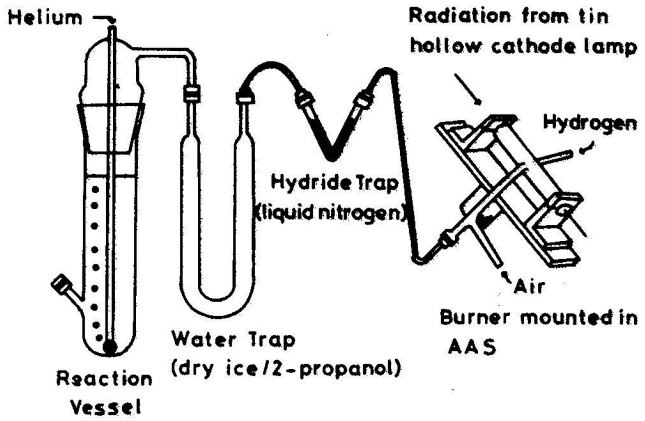

Figure 1. Apparaturs for tin analysis

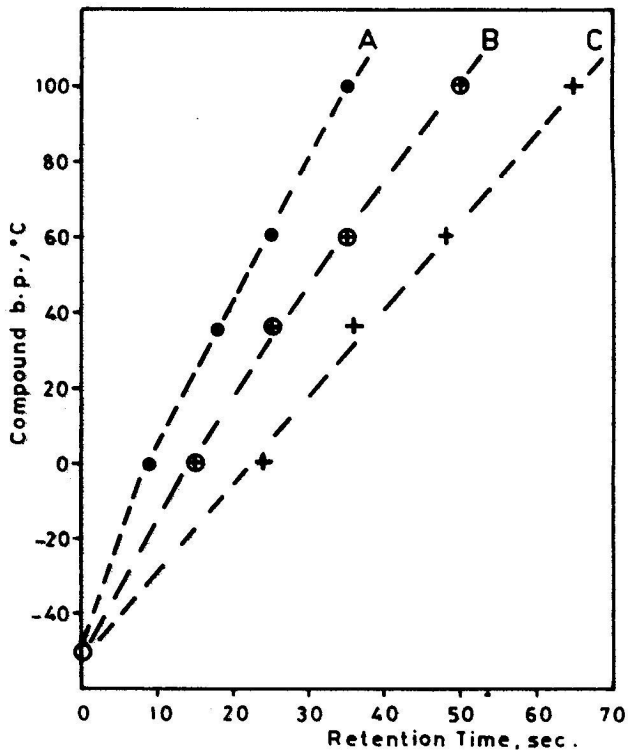

Figure 2. Effect of glass-wool (A) and OV.packed hydride trap (B: heated; C: not heated) on retention times of tinhydrides

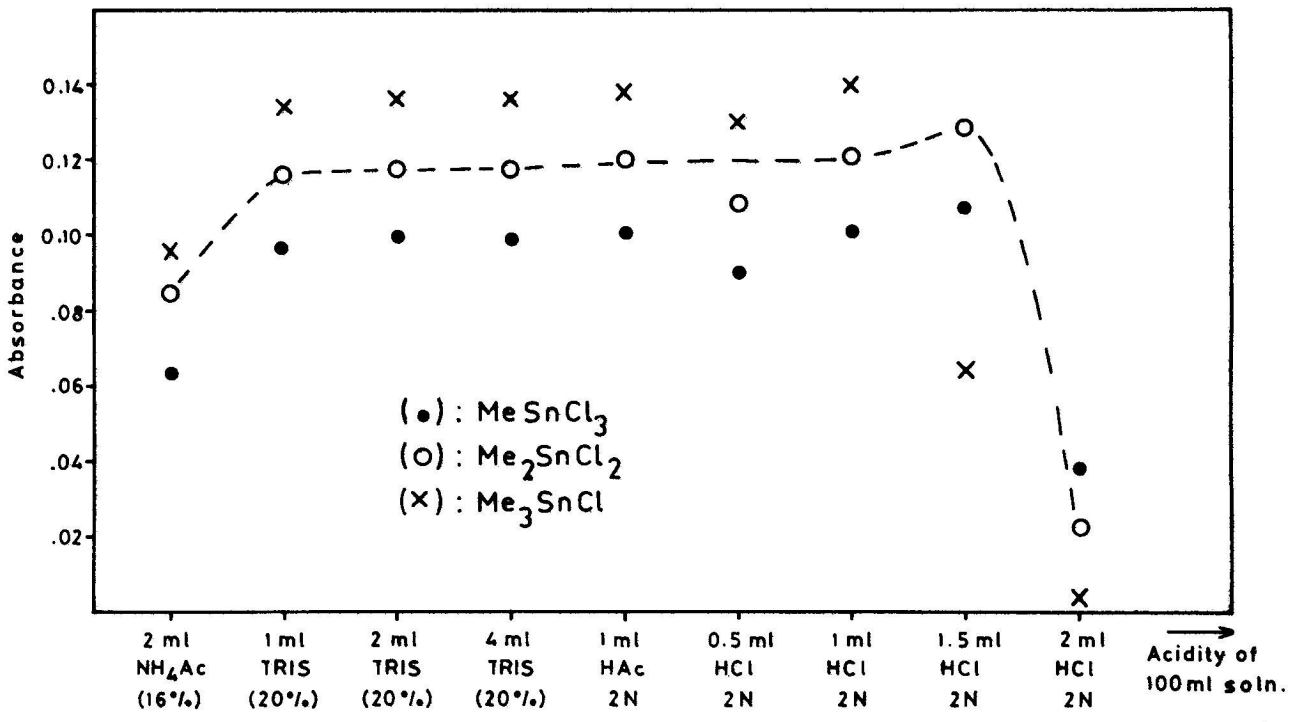

Figure 3. Effect of acidity on the recovery of methltins from water solutions

Reagents: 4% sodium borohydride solution was purified by adding 1 ml of 2N NaOH per 100 ml and filtering. If pure NaOH was not available, $NaBH_4$ was purified as follows: 4 g of $NaBH_4$ was dissolved in 25 ml of sea-water, then 0.5 ml of 2N NaOH was added and stirred for 15 minutes. Finally it was filtered through a Whatman number 2 filter paper and diluted to 100 ml with d.d. water. This purification procedure is as effective as the electrolysis procedure described by HODGE et al., (1979) and the direct filtration procedure given above. Other reagents were used as received.

Standards: All organotic and $SnCl_4$ standards were obtained from Ventron (Danvers, Mass.) and prepared in d.d. water or ethanol as described by HODGE et al., (1979).

Water analysis: 100 ml of water sample was placed in a reaction vessel and 1 ml of 20% TRIS-HCl buffer solution was added. After degassing with helium carrier gas for one minute, the procedure given by HODGE et al., (1979) was followed. Later the procedure was modified by substituting a reaction vessel of 750 ml capacity, subsequently increasing the volume of $NaBH_4$ and TRIS buffer to 5 ml and doubling the stripping time. The volatile tetramethyltin was investigated by degassing the solution for 5 - 10 minutes prior to sodium borohydride addition.

Sediment analysis:

i) Acid extractable tin: 1 g of dried sediment sample was leached with 10 ml of cold 6N HCl for two weeks, and agitated at 24 h intervals. The final volume was then brought up to 20 ml with d.d. water. 0.05 - 0.1 ml of the leachate was taken for analysis. After the addition of 1 ml of 2N acetic acid (HAc) the solution was diluted to 100 ml in the reaction vessel and reacted with 1 ml of 4% $NaBH_4$ following the same procedure given above for water analysis.

ii) Organotin analysis: Two different procedures were followed to extract organotin compounds from dried and homogenized samples: (a) 0.5 - 1 g of tin-polluted sediment that contained low calcium carbonate was sonicated with 40 ml of 0.1 N HCl for one hour. The pH of the solution was adjusted to 4 - 5 with dilute NaOH prior to the analysis. Then the sample was analysed by adding 1 ml TRIS-HCl and 1 ml $NaBH_4$ to 100 ml final volume. (b) 1 - 5 g of unpolluted samples was shaken ultrasonically with 30 - 50 ml of d.d. water and then analysed following the addition of 1 ml TRIS-HCl and 1 ml $NaBH_4$.

Sea plant and organisms analyses:

i) Total tin: 1 - 2 g of the dried samples were completely digested with HNO_3 and $HClO_4$. The residues were dissolved in 50 ml of 0.2N HNO_3. 5 - 10 ml of the solution was transferred to the reaction vessel, diluted to 100 ml with d.d. H_2O and reacted with 1 ml $NaBH_4$. The standard addition method was followed for each sample.

ii) Organotins: (a) Dried and homogenized limpet shell samples in 40 ml of d.d. water were sonicated for one hour and analysed by adding 1 ml of TRIS-HCl and 1 ml of $NaBH_4$ to 100 ml of the solution, (b) The soft parts of limpet, fish tissue and macroalgae (0.5 - 2 g) in 50 ml of 0.04N HCl were homogenized using a Virtis Homogenizer and a pyrex homogenizing cup. The solution was transferred to the reaction vessel and reacted with 1 ml of borohydride.

In order to overcome foaming problems, helium entry in the reaction vessel was shortened and held above the 100 ml volume line. The solution was stirred and hydrides were stripped entirely from the solution by the hydrogen bubbles produced from $NaBH_4$.

Results and discussion

Methodology

Buffering: The efficienty of stannane and methyltin hydride generation is strongly dependent on the pH of the solution. The recoveries do not change between pH 2 and 6. Where the pH is less than 2, trimethylstannane yield is sharply reduced (Figure 3). In order to eliminate any incomplete recovery at lower pH the TRIS-HCl buffer (20% by weight) was used in water analysis. This hydride method is not able to differentiate between Sn (II) and Sn (IV); both species are reduced with the same yield under the operating conditions followed during this work.

Cold-trapping of hydrides and sensitivity: In the beginning, a glass wool-packed hydride trap was used, described by HODGE et al., (1979) later the 3% OV-1 on Chromosb W packed trap was tested to increase the retention times of methyltin hydrides in the trap with respect to SnH_4 (Figure 2). As seen in Figure 4, a glass wool trap is not suitable for separating monomethyltin hydride from the broad peak of SnH_4 produced from polluted sediment samples. Moreover, before methyltin hydrides distril in the OV-trap, all volatile gases in the trap, such as H_2S, CO_2 and other metal hydrides, are removed efficiently. Also sensitivity was increased by placing the OV-trap in a pre-heated porcelain cup. A 0.15 ng Sn (IV) detection limit for both Sn (IV) and methyltins in the 100 ml-volume was obtained.

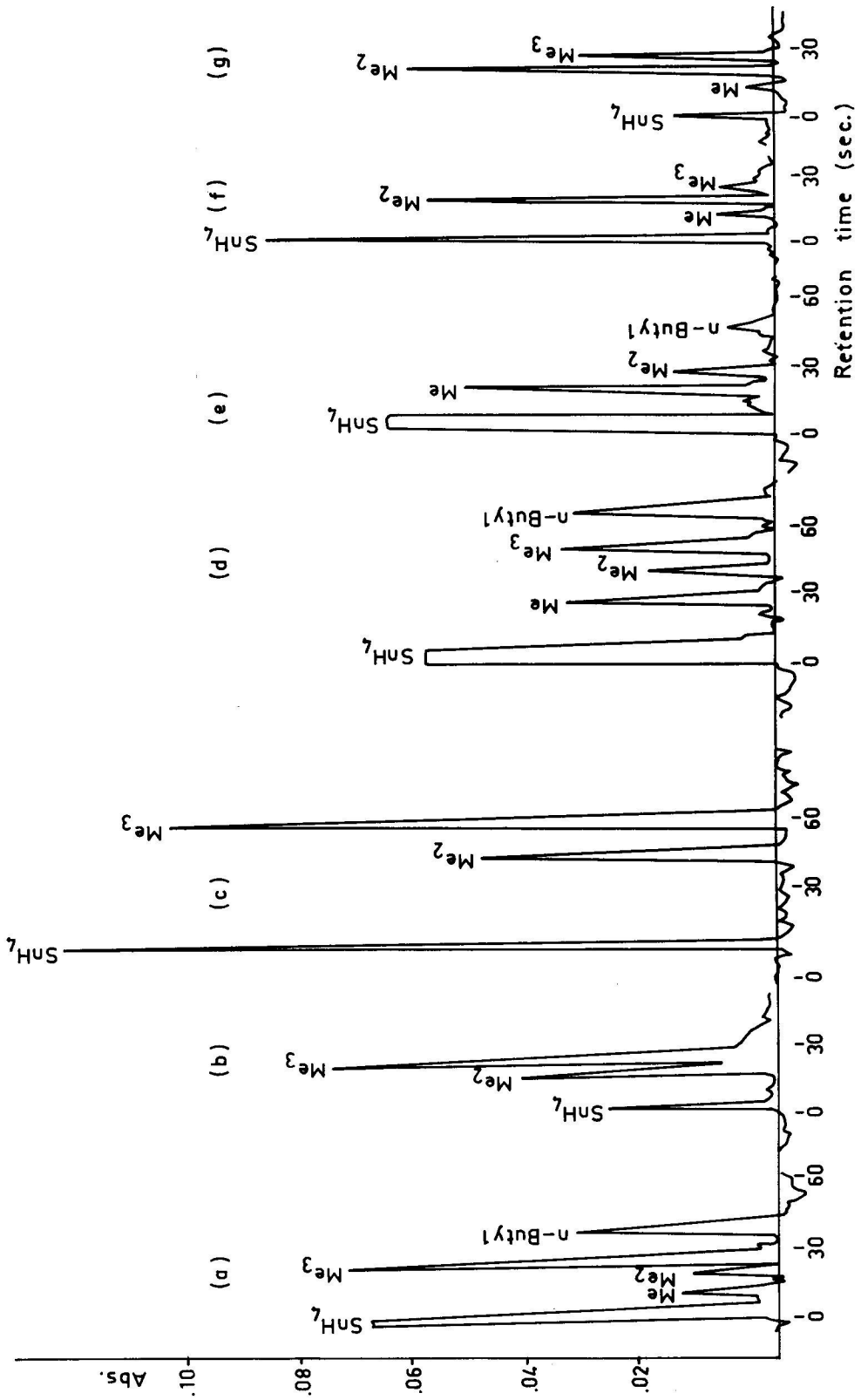

Figure 4. Chromatograms obtained from sediments:
(a) Göksu Delta using glass-wool trap,
(b) Seyhan Delta using glass-wool trap,
(c) Seyhan Delta sample,
(d) Palace Moat (Tokyo),
(e) Mersin Harbour and organisms,
(f) Limpet shell,
(g) Fish tissue, using OV-trap (in c-g) plus heat (in e-g)

Sn (IV) and methyltin preservation: The results of 3 month preservation studies in Nalgene plastic bottles showed that 1 ml of concentrated HCl per lire of sea-water was adequate for storage of Sn (IV) and methyltin standards at ng levels in sea-water kept in the refrigerator. ANDREAE (1981) used nitric acid for preservation, but we observed that methyltins were not recovered completely under his conditions. Further nitrate ion interfered strongly at a pH of less than 2 and no methyltin hydride peak was detected. Some other workers have also pointed out the interfering effect of nitric acid in the hydride system (BROWN et al., 1981).

Extraction efficiency of organotins from sediment: The sediments from the Mediterranean coastal waters (except Mersin harbour) contain high calcium carbonate (SHAW and BUSH, 1978) and therefore the addition of acid does not help the release of organotin compounds from the sediments. On the contrary, CO_2 production decreases the yield of organotin extraction. Extensive study with these sediments indicated that water alone can extract organotins into the solution. Also the sediments from San Diego Bay, Palace Moat (Tokyo), Chesapeake Bay, the Baltic Sea and Mersin Harbour contain high water extractable inorganic tin and some hydrophobic materials. So extraction efficiency of organotins is proportional to the amount of sample weighed and acid in the solution. It was found that 0.5 - 1 g of sediment in dilute acid is sufficient to obtain a stable baseline (40 ml of 0.1N HCl is adequate for the extraction). Hydrogen sulphide, produced in some sediment analyses, was removed by using a lead acetate column placed between hydride trap and burner (ANDREAE, 1981).

Environmental

Water: The results obtained from the water analyses are given in Table 1. Previous data (HODGE et al., 1979; BRAMAN and TOMPKINS, 1979) and our results imply that methyltin distribution in the water is not ubiquitous and probably originated from the seasonal change in microflora population in semi-enclosed coastal waters, while inorganic tin generally ranges bewteen 3 - 6 ng/l. The levels of inorganic tin in rain-water are between 1 - 3 ng/litre.

Sediments: The results of water extractable methyltins and cold 6N HCl extractable inorganic tin analysis are given in Table 1.

In order to correlate biologically available tin and the levels of methyltins, the sediments were digested by cold 6N HCl as described by SEIDEL et al., (1980). Total methyltin and acid extractable tin contents of the sediments are illustrated in Figure 5. The highest total methyltin concentration, 21 ng/g, was found in the coastal water sediments of Turkey, whereas heavily polluted Chesapeake Bay sample contained 0.6 ng/g total methyltin. Although there is no apparent linear correlation between net methyltin synthesis and tin content that is susceptible to biomethylation in the sediment, the amount and source of pollutants entering the aquatic environment alters the distribution pattern of methyltins in the sediment. Monomethyltin is the main product of biosynthesis reaction in partly anoxic sediment from highly polluted sites such as Mersin harbour, Chesapeake Bay and San Diego Bay which have heavy shipping activities and are influenced by sewage sludges and river-borne particulate loads. The main form of methyltins in unpolluted Mediterranean coastal sediments is trimethyltin compound. In general no monomethyltin was found in oxic-coastal and delta sediments along the north-eastern Mediterranean. The values obtained from polluted-anoxic sediments suggest that the appearance of monomethyltin is the result of biomethylation of inorganic tin rather than the degradation of tri-and dimehtyltin compounds, since, in anoxic-polluted Baltic Sea and Cheasapeake Bay sediments, no trimethyltin was found above the detection limit of the method and in anoxic-nonpolluted Saanich Inlet sediment no dimethyltin was detected.

The core samples, 60 cm long, from the fresh water Palace Moat (Tokyo) which received atmospheric dust and gases from the highly polluted city of Tokyo (GOLDBERG et al., 1976) were analysed at 4 cm intervals. No remarkable changes in Me- and Me_3-Sn concentrations were observed. As seen from Table 2, more remarkable is the observation that n-butyltin in the same core decreases below 35 cm (1958) and is not detectable below 45 cm (1953). Since the major transport path is via the atmosphere, this suggests that n-butyltin could be transported atmospherically. This finding suggests that n-butyltin and dibutyltin detected in Lake Michigan water (HODGE et al., 1979) could have been a result of atmospheric input. A slight increase in dimethyltin concentration was also found near the surface (Table 2).

Organisms: The analyses of limpets and green macro-algae (Chlorophyta) from unpolluted waters of the Mediterranean Sea indicate that mono-, di- and tri-methyltin exists in sea-water (Table 1).

Two types of macro-algae samples contain only dimethyltin and to some extent monomethyltin, while limpet and fish also accumulate trimethyl. This indicates that dimethyltin, biosynthesis is performed by the algae itself and/or bacteria attached to the algae.

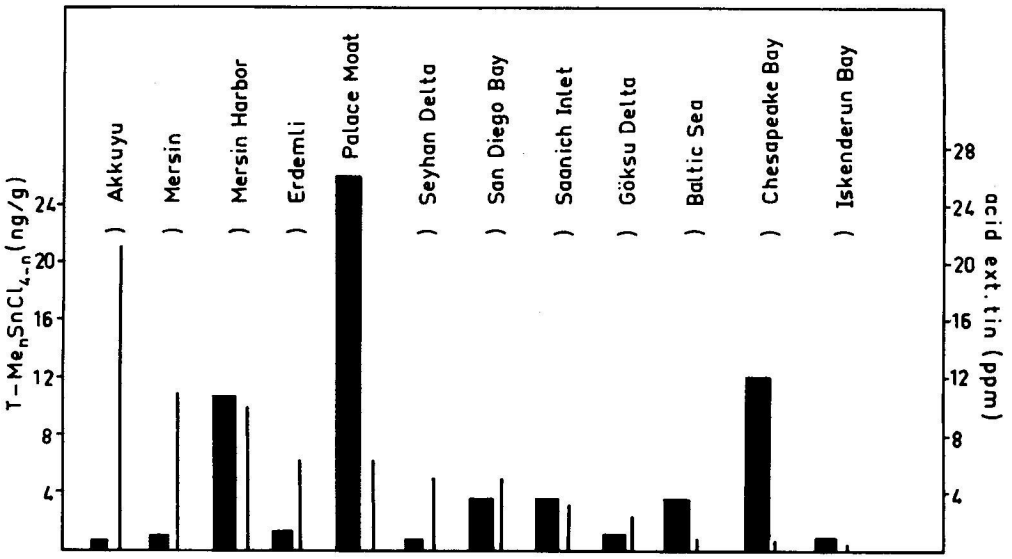

Figure 5. Graphical representation of average values of acid extractable tin (▬▬) and total water extractable methyltin (———) in the sediments

Material & Location[a)]	Inorg.tin (ppb)	$MeSnCl_3$ (ng/l or ng/g,dry weight)	Me_2SnCl_2	Me_3SnCl
Water				
Rain,La Jolla (USA)	1-3	n.d.-10	n.d.	n.d.
Seawater,SanDiego (USA)	3-6	n.d.	n.d.	n.d.
Lamas Harbour (Turkey)	3.5-6	n.d.-4.5	n.d.-1.2	n.d.
Sediment	acid ext. tin(ppm)			
Akkuyu,Turkey	0.5	n.d.-0.4	8.1	11.8
Erdemli,Turkey	1.1	n.d.	n.d.-1.8	4.4
Mersin Harbour,Turkey	11	7.7	2.2	0.5
Mersin Harbour,Turkey, (entrance)	2.1	0.2	0.5	0.1
Mersin,Turkey	0.7	n.d.	2.6	8.6
Seyhan Delta,Turkey	0.6	n.d.	1.3	3.9
Iskenderun Bay,Turkey	0.8	n.d.	n.d.	0.35
Göksu Delta,Turkey	1.0	n.d.-0.7	0.7	1.6
San Diego Bay,USA	3.6	2.4	2.3	n.d.-0.2
Saanich Inlet,Canada (core sample)	3.8	0.6	n.d.	2.6
Baltic Sea (core sample)	3.7	0.5	0.3	n.d.
Chesapeake Bay,USA (2 core samples)	12	0.6	n.d.	n.d.
Palace Moat,Tokyo (core sample)	26	3.8	1.3	1.0
Organism	T-Sn(ppb)			
Fish(U.moluccensis)from Mediterranean coast	260	27	2.6	1.2
Fish(M.barbatus)from Mediterranean coast	86	0.8	2.9	1.3
Limpet: soft part	50-75	1.3-4.8	1.8-18	0.8-63
(Patella caerulea)shell Lamas Harbour,Turkey.	13	0.4-2.8	0.2-1.2	0.7-2.8
Chlorophyta,Lamas Harbour	37	n.d.	12	n.d.
Seaweed, Lamas Harbour	250	16.8	37	0.9

a) See Figure 6 for sampling sites of the sediment samples from the northeastern Mediterranean coastal waters.

n.d. not detected

Table 1. Tin and methyltin compounds in water, sediment and organisms

Table 2. Alkyltin distribution in the sediment from the Palace Moat, Tokyo, Japan (ng/g, dry)

Depth in core (cm)	Total [a] tin (ppm dry)	Me_2SnCl_2	$n\text{-}BuSnCl_3$
0-4 (1975)	27	3.5	19
4-8	27	2.4	35
8-12	29	2.1	24
12-16	25	1.8	21
16-20 (1965)	21	0.7	20
20-24	18	1.2	10
24-28	20	0.9	14
28-32	17	0.8	8
32-36	8	1.4	7
36-40 (1955)	16	0.6	3
40-44	17	0.5	2
45-60 (1945-1954)	18	0.5-1.0	n.d.

(a) SEIDEL et al. (1980) ; n.d.: not detected

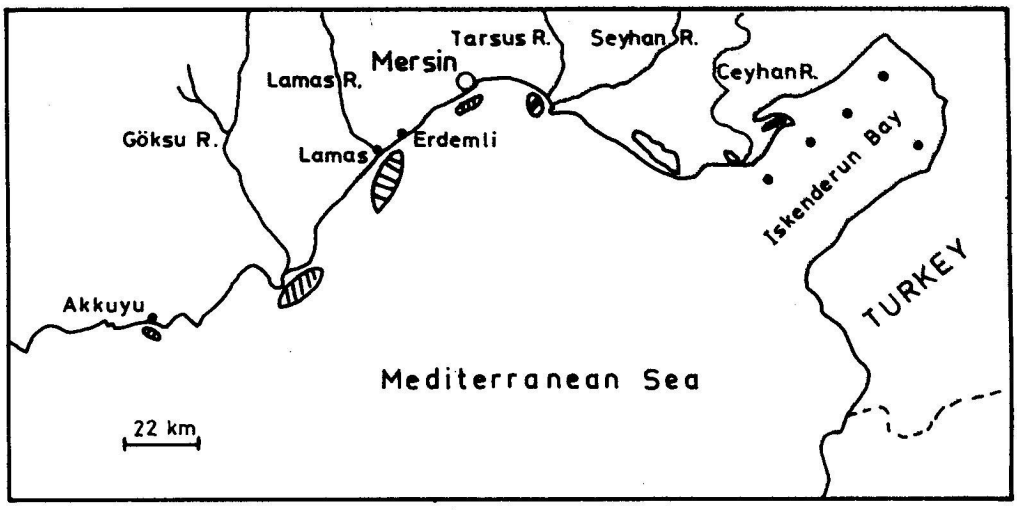

Figure 6. Sampling sites for sediments along the Mediterranean coast, Turkey

Composite fish samples of the Mullidae family, namely U. moluccesnsis and M. barbatus, containing about 0.3 and 0.1 ppm Hg wet weight respectively, were analysed. As seen in Table 1, these samples also contain high total tin as methyltins range between 3% and 6% of total tin. Monomethyltin was detected in U. moluccensis (homogenate of two fish tissues). At the moment, it is difficult to reach a conclusion as to whether the fish accumulates inorganic tin or organotins (subsequently being demethylated and converted to inorganic form in the fish body). Nevertheless, a value of 27 ng monomethyltin which is comparatively higher than di- and trimethyltin in the tissue of U. moluccensis (which is also able to accumulate methylmercury in large amounts), implies that demethylation and transmethylation reaction with Hg^{2+} could be responsible.

Conclusions

Methodology studies indicate that chemical interferences can be minimized by using an OV-trap and TRIS-HCl buffer. The qualitative identification of methyltin species can be performed successfully by adding standards to the sample and separating the concentrated hydrides from each other without heating the OV-packed hydride trap.

No direct relationship exists between inorganic and total methyltin levels. Inorganic tin from anthropogenic sources does not increase the net methylation reactions in the sedimentary phase. Low trimethyltin concentrations in polluted sediments are presumably due to changes in the biomethylation reaction. This is an unexpected result. In other words, more toxic Me_3Sn^+ exists in unpolluted waters and can be accumulated by organisms of higher trophic levels. Biological synthesis is of Me_3Sn^+ can offer both in anoxic- and oxic-nonpolluted sediments. This suggests that either trimethyltin is produced to large extents in oxygenated environments or the demethylation rate of trimethyltin is significantly faster in partly anoxic-polluted sediments (Mersin Harbour and San Diego Bay).

Limpets can accumulate methyltins to high levels, reaching the values of 35 - 75% of total tin. Due to the incompleteness inherent in the organotin extraction procedure, stemming from methyltin to large molecule bonding in the limpet, and also in the sediment, this range must be an under-estimate.

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