OCCURRENCE AND FATE OF METHYLTIN SPECIES IN AQUATIC ENVIRONMENT

by

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ABSTRACT

Methyltin and butyltin species were determined in the waters, sediments and organisms from the NE Mediterranean and in the waters of Marmara and southern Black Sea. The methyltin speciation studies in the literature were also reviewed. The methyltin findings were examined to assess their distribution patterns in the different aquatic environments. Possible methylation pathways were proposed, considering the reaction mechanisms given for abiotic/biotic methylation processes under laboratory-simulated oxidizing/reducing conditions. The trimethyltin (TMT) form was found to be predominate in the unpolluted sea waters and sediments, while methylation reactions in the inorganic and organic tin-polluted sea waters, sediments, lake and river waters follow a different mechanism to yield monomethyltin (MMT) and dimethyltin (DMT) predominantly. In the unpolluted-anoxic sediment of Saanich Inlet no DMT was observed while MMT and TMT existed at measurable level (ng g^{-1}), which confirms the results of abiotic/biotic methylation products from model studies. The methyltin findings of different groups in the tin-polluted aquatic environments are generally consistent with the methyltins produced abiotically under the simulated reducing conditions. From model studies, it was seen that TMT existed only if MMT and/or DMT were available at comparable levels with TMT, indicating sequential type of methylation reaction whereas inorganic tin in the unpolluted sea waters and oxic sediments was methylated mainly to TMT, most probably following a different biomediated reaction mechanism in nature.

1. INTRODUCTION

In recent decades, the worldwide production and consequent use of organotin compounds as heat and light stabilizers biocides and fungicides have increased significantly (UNEP, 1989). The known toxic potential of organotins along with the development of analytical techniques for the quantitative speciation of organotin compounds at trace levels in the environmental samples (Braman and Tompkins, 1979; Hodge et al., 1979) has caused a great concern about the distribution, fate and impact of biomethylated tins and butyltins of anthropogenic origin in the environments as well as to study the biotic/abiotic methylation reactions, and degradation rates and ultimate products of butyl- and phenyltin compounds of man-made origin under the simulated environmental conditions . A review of the various aspects of phenyltin compounds, tributyltin and its derivatives along with the inorganic and methtylated forms of tin can be found in UNEP (1989) and Oceans'87 (1987).

It has been shown that tin in various oxidation states (0, II, IV) and methyltin compounds can be methylated by abiotic and biotic pathways to different methyltin compounds, depending upon redox potential of the studied environments (Ridley et al., 1977; Guard et al., 1981; Hallas et al., 1982; Rapsomanikis and Weber, 1985; Craig and Rapsomanikis, 1985; Donard and Weber, 1988). The ultimate results of these studies were reviewed briefly, regarding the environmental findings. The text also includes the detailed discussion of the aspect of methyl- and butyltin distributions observed in the waters, sediments and organisms from different environments, particularly from the Turkish coastal waters and in the basin waters of Marmara Sea.

2. MATERIALS AND METHODS

The water, sediment and organism samples collected from the coastal waters of Turkey were analyzed by AA-hydride derivatization technique after the adequate preteatments of samples (Tuğrul, 1982; Tuğrul et al, 1983; Yemenicioğlu et al., 1984; Kubilay, 1989). The method adopted for methyltin analysis was modified little for the determination of butyltin compounds. The sampling locations along the Mediterranean coastal waters, Turkey, are illustrated in Fig. 1.

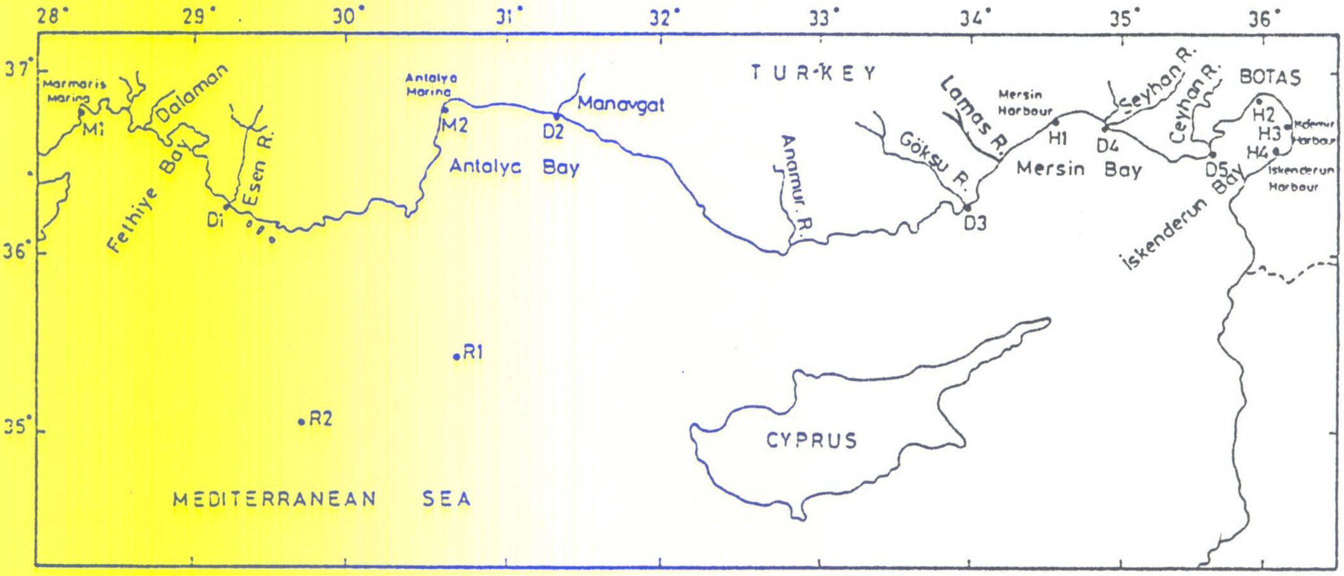

Figure 1. Sampling locations in the Mediterranean

3. RESULTS AND DISCUSSION

3.1. Methodology

We have carried out the alkyltin measurements only in the unfiltered water samples. Therefore, the data given in the text represent the total concentrations of hydride reducible organotin compounds existing in the subsurface waters of the sites studied. Valkirs *et al.* (1985) noted that, from the limited data on butyltin (BT) distributions in the suspended particulate samples, the BT concentrations in the particulate fraction represented a minor percentage of the detectable BT in the water samples, indicating minor contribution to the spatial distribution of BT.

The alkyltin measurements performed by our group in sediment and organism represent the water or weak acid-soluble and hydride reducible fractions of alkyltins available in the samples (Tuğrul et al., 1983).

The data compiled in the text have been obtained by using hydride generation (HG) -AA,HG-GC or HG-GC coupled with AA. The available analytical methods are capable of seperating and determining the principal species of tin (methyl-, ethyl-, butyl- and phenyltins) in water. It was noted that organic pollutants (e.g. oil and grease) in water can give rise to the drastic decreas in sensitivity of HG-AA technique (Valkirs et al., 1985). It is rather difficult to assess the spatial distributional pattern of the tin species due to some differences in sample storage, treatment and analysis methods followed by different groups and lack of intercomparison studies to determine the reliability of tin measurements in water sediment and organism samples. A recent intercomparison study conducted by the participation of four international research groups has shown that BT (and very likely methyltin) measurements need further development (Kubilay et al., 1990), particularly in the polluted samples. Nevertheless the relative abundances of BT determined by the groups in the same samples were found to be similar.
Therefore, the relative distributions of tin species were particularly taken into account for the environmental assessment of the measurement results.

3.2. **Environmental results**

3.2.1. **Methyltins in the Marmara Sea Basin**

The Marmara Sea situated between 40°15'-41° N latitute and 27°-29°30' E longitute is connected with the Black Sea through the narrow Strait of Bosphorus to the northeast and with the Aegean Sea through the Strait of Dardanalles to its southwest. Due to water exchanges between these two seas through the Marmara Sea, it has a permanently stratified water body with the less saline waters of the Black Sea origin in the surface layer (0-20m) and much higher saline waters of the Mediterranean origin below about 30m down to the basin bottom (Figure 2). So the biochemical properties of this sea are mainly dominated by the inflowing waters of the Aegean and Black Sea, and vertical mixing at halocline. Apart from natural processes inducing the biochemical characteristics of the Marmara, the coastal waters of this sea receive substantial amounts of organic and inorganic pollutants from domestic and industrial sources, influencing algal production and oxygen utilization rate in the lower layers of the Marmara Sea. The distributions of other parameters related to algal production and organic matter degradation with depth are also illustrated in Figure 2. As seen from the depth profiles of these physical and biochemical parameters, the algal production is limited in first 25 meters from sea surface. Because of the presence of permanent halocline, the salty waters below 30 m always has an oxygen deficiency, with a significant decline down to 300 m, depending on the sinking rate of organic matter from productive surface layers and the residence time of basin water in the Marmara.

The methyl- and monobutyltin measurements in the Marmara Sea were carried out in July, September and December 1988, and February 1989. It was seen that the distributional patterns of methyl- and monobutyltin compounds with time and space were too scattered to reach a general conclusion on their abundances in varying water characteristics of Marmara and to assess the significance of other physical and biochemical processes on the vertical distribution of alkyltin compounds. For instance, as seen in Fig. 3, mono-, di-, trimethyltin and monobutyltin species, ranging between 8-90, 2-27, 70-410 and 19-32 ng L^{-1}, respectively, were detected in the July samples collected from the depths of 50-100 meters whereas at other depths they were undetectable or at trace levels. The surface waters of the Marmara were more productive in July and February than in September and December. Methyltin compounds were mostly detected in these productive months, and particularly in February (see Fig. 2), trimethyltin predominated in the water columns of the sites investigated, indicating the importance relative abundances of microorganism population on the biomethyltion of tin in the water column. This finding is in good agreement with the ones obtained in the coastal waters of the Black Sea and Mediterranean. The July samples of the Marmara were stored refrigirated for about three months before processing, due to some instrunmentation problems. So, adsorption and decomposition processes could take place during the storage, which very likely influenced the aspect of methyltin distributions in the samples. Therefore, the higher MMT measured in some deep waters of Mediterranean origin might result partly from the degradation of TMT and DMT till analysis.

The residence time of the subhalocline waters of the Marmara was estimated to be about 6-7 years whereas the half-life of MBT is on the order of weeks. Therefore, it is not expected to have a homogeneous distribution for monobutyltin (MBT) compound of man-made origin in the whole Marmara basin waters. So, the patchy existence of monobutyltin below 30m water depth indicates intermittent input from commercial ships to the Aegean and Black Sea near to the two straits through which the water masses with the various concentrations of MBT are carried to the surface and lower layers of the Marmara Sea as well as direct discharge of butyltin compounds from different sources into the surface waters of the Marmara. The occasional detection of MBT and methyltins at intermediate water depths, particularly at 30-150 meters coincides with the oxygen deficient water masses, indicating that the MBT and, at least, an important fraction of methyltin compounds observed at these depths resulted from dissolution and decomposition of the sinking detritus from the productive surface layers, which carry butyl- and mehyltins actively and passively down. The MBT and MT compounds measured in the deep waters very likely originated from the sediments.

The vertical distributions of humic matter, dissolved organic carbon, total mercury and dissolved inorganic nutrients were examined to relate the depth profiles of alkyltins (see Fig. 2) with the variations in other chemical parameters. No reliable conclusion predicting the pathway of the alkyltin transport in the Marmara basin waters, could be derived from the several parameters measured simultaneously. Nevertheless, we suggest that, in the relatively less contaminated basin waters of the Marmara, methylation reaction takes place in the whole water column to yield TMT predominantly, particularly at the depths between 50-150 meters in which the majority of fast sinking organic detritus oxidized or dissolved, indicating an abundance in bacteria density at these depths. Also, as seen from the DO profile, some sharp decreases were observed in the water layers between 50-250 meters. It has been shown that methylation reactions proceeds fast in the reducing environment with other adequate reaction conditions. If all

TMT were carried from upper layers we had to measure less TMT concentration and its degradation products, DMT and MM.

3.1.2. Methyltins in the Mediterranean and other seas

The concentrations of methyl- and butyltin species measured in the subsurface waters of Turkish harbours, marinas, estuaries, coastal and open seas are given in Table 1. Some of these data have been published elsewhere (Kubilay et al., 1990). As seen from the table, TMT was generally found to predominate in the methyltin-contained subsurface water samples from both unpolluted and butyltin-polluted seas. In relatively productive and less contaminated seas, e.g. Black Sea coastal waters and the region within the Rhodes cyclonic gyre formed permanently between Cyprus and Rhodes Island in the eastern Mediterranean, TMT concentration was much greater than DMT and MMT. Furthermore, no positive relationship was seen between the methylated tin and man-made butyltin concentrations measured in the sea waters analysed. We have not observed methyltin species in most of the subsurface butyltins contained water samples which were not included in Table I.

The results of the present study clearly indicate that only the existence of butyltin compounds in sea water ranging between some tens and hundred ng L^{-1} does not give rise to the natural occurance of methyltins at ng L^{-1} level in the marine environments investigated. Since biochemical methylation reactions need adequate environmental conditions, such as continuous tin source, optimum water temperature, sufficient microorganism population and methyl sources, etc., for aerobic water environments.

The results obtained from the tin speciation studies appeared in the literature , which covered inorganic tin and methyltin in the same sample, are compiled in Table II . If the data contained inorganic tin, but indicated undetectable MT concentration they were rejected and not considered in discussion on the aspect of methyltin distributions.

The tin data compiled in Table II point out that tin is methylated to DMT predominantly when there exists a continuous inorganic tin discharge to the surface water. e.g. the Bay of Iskenderun receives a significant amounts of inorganic tin from the steel and fertilizer complexes located on the eastern part of the bay (Yemenicioglu et al., 1987). The tin concentrations measured in the waste waters of these complexes ranged from 15 to 1100 ng L^{-1}. MMT determined in these waters was likely to originate directly from methylation reaction. Because it is well known that MMT significantly tends to adsorb on sinking particulates in sea water (Hodge et al., 1979; Tuğrul et al., 1983). But Braman and Tompkins (1979) determined the three forms of MT (DMT form predominantly) in the bay waters of the United States. The greatest concentrations of inorganic tin, MMT and DMT were determined by Maguire et al. (1982) in the Canadian Harbours. Their findings also verify our conclusion for inorganic tin-polluted waters. In the San Diego Bay waters, which receives butyltins from the hulls of boats in different sizes, only MMT and DMT were detected occasionally (Hodge et al., 1979).

In the estuarine waters, DMT was found to be the predominant form of the methyltins. The occasional appearance of MMT in these waters can be attributed to its removal by fast sedimentation in these relatively shallow waters. The ultimate conclusion derived from the tin speciation studies is that the production of methyltins in both polluted and unpolluted waters is not dominated by the continuous tin input only. Other environmental conditions should be adequate to produce measurable methyltin species.

3.2. Lake water

As seen from Table II, the aspects of the MT distributions in the waters of various lakes studied are different. TMT was the predominant form in some lakes whereas at undetectable level in the others. These findings predict that biomethylation reaction in these lake water environments proceeds on different pathways induced by various microbial population, and physical and chemical properties of the lakes. In the tin-contaminated Canadian lakes and Lake Michigan, only MMT and DMT were detected at relatively high concentrations (Hodge et al.,1979; Maguire et al., 1982). It was also stated that the presence of MMT and DMT in the Canadian lakes investigated, which do not receive waste waters directly was atributed to the atmospheric transport of methyltin through precipitation. If it were so MMT and DMT concentrations measured in the US lakes (Braman and Tompkins, 1979) had to be at comparable levels with those in the Canadian lakes. The low MT levels measured by the same group in some Canadian waters justify the reliability of the lake data. Accordingly, the high MT levels in the Canadian lakes could not only result from the methyltin production in the lake, but also from soil within the catchment areas of the lakes through surface run-off.

3.3. River water

The aspects of methyltin species distributions in the river waters show the similar pattern observed in the inorganic tin-polluted bay and estuarine waters. The greatest MMT and DMT concentrations were seen in the Canadian rivers as in the lakes (Maguire et al., 1982). Only the polluted waters of Rhine river contained relatively high concentrations of MMT and DMT, 70 and 210 ng L^{-1} respectively. Braman and Tompkins (1979) observed that more than 50% of total dissolved tin was generally in the methylated forms whereas the majority of dissolved tin in the Canadian river waters is transported in the inorganic forms to the receiving lake and coastal sea waters.

3.4. Rain water

From the limited MT data available in rain water, we can state that tin may be transported to the open seas in methylated forms, which are released from soil and coastal marine environments through the formation of volatile MT compounds, such as methyltin hydrides, tetramethyltin and methylalkyltin compounds observed in natural environments and produced by abiotic and biotic methylation reactions under the simulated oxidizing/reducing environmental conditions (Donard and Weber, 1988; Jackson et al., 1982) as well as from anthropogenic sources.

3.5. Sediment

The results of alkyltin measurements carried out by Tuğrul et al.(1983) and Kubilay et al.(1990) in the sediment samples from the coastal waters , harbours and river deltas are compiled in Table III.. Tuğrul et al.(1983) have also determined the cold 6N HCl acid extractable inorganic tin in the samples. As seen from Fig. 4 no direct relationship exists between inorganic tin and total methyltin levels in the sediments. On the contrary, the total concentration of water extractable methyltins measured in the unpolluted sediments exceeds the levels in the tin-polluted sediments. However, the aspect of the methyltin distribution appears to change in different sediment environments. In general, no MMT at ng level was available in most of the unpolluted oxic-coastal and delta sediments. It is interesting to note that the ratios of Me/Me_3 and Me_2/Me_3 in the four oxic-delta sediments sampled in 1988, are consistent with the ones of Tuğrul *et al.* (1983) given in Table III.

The methyltin distributions in the inorganic tin-polluted Iskenderun Bay have shown the similar pattern in both sea water and sediment, except that TMT was detected in the sediments. Since TMT is released more easily from sediment to overlying water with respect to MMT and DMT dissolution, its level in sediment becomes less than MMT and DMT when there exist MMT and DMT sources from the surface waters through particle sinking. In the butyltin-tin polluted San Diego Bay and Mersin Harbour, biomethylated forms of tin in the sediments tend to emphasize the mono- and dimethyltin species. It should be noted that the MMT and to a less extent DMT transport to sea bottom may be of great importance on the distributional pattern of methyltins in the sediments of these polluted waters. The release of MT, especially TMT form, from sediment to overlying water column should also be taken into account when studying the sources and fate of methyltins in the polluted waters. For example, occasional detection of TMT in the Turkish harbours and marinas point out that TBT is likely to react with methylating agents by bio-mediated pathway to yield TMT (Brickman et al., 1981) in addition to TMT synthesis in water column and release from sediment.

Another remarkable finding from the sediment analyses is that the anoxic-unpolluted Saanich Inlet contained MMT and TMT only, no DMT was detected in this core sample. The deep waters of Saanich Inlet was found to be generally anoxic throughout the year (Murray et al., 1978). In reducing water environments, inorganic tin is transported in the reduced form to the sea bottom, which is easly utilized in the abiotic/biotic methylation reaction taking place in the sediment to yield TMT and MMT (Donard and Weber, 1988). Guard et al. (1981) also observed that, in anaerobic estuarine sediments, TMT can yield only volatile tetramethyltin by both biotic and abiotic pathways. No other hydride reducible (water soluble) methyltin was detected by Guard and co-worker. They suggested that the DMT released from the proposed reaction mechanism may be removed from the ecosystem as the very insoluble $(CH_3)_2SnO$ but more likely accumulates in the form of complexes with sulfur-containing ligands found insediments. These two findings indicate that the biochemical methylation reaction of tin follows a different pathway in the Sn(II) amended reducing environment.

Craig and Rapsomanikis (1985) observed that methylating agents can transfer methyl groups by oxidative abiotic reaction to Sn(O) and Sn(II) to yield

MMT, DMT and tetramethyltin, but no TMT at trace level while Hallas et al. (1982) detected the formations of DMT, TMT and to a less extent MMT by biomediated reactions in the sediment. The detection of low MMT with regard to DMT and TMT was due presumably to the inefficient extraction of MMT from the sediments (Tuğrul et al., 1983). Nevertheless, their MT findings from the simulated environment were similar with the MT distributions in the tin-polluted sediments (Tuğrul et al.,1983; Aboul Dahab, 1988).
From the study of Rapsomanikis and Weber (1985) it is evident that the abiotic methylation of inorganic tin (Sn^{+2}) in the reducing environments is a sequential kind of reaction with diminishing yield at each step while the outcomes of biomediated chemical reactions of Sn(IV) and Sn(II) carried out under the simulated environmental conditions clearly pradict that the formations of different methyltins in volatile and nonvolatile forms are very likely in different aquatic environments, as shown in the present study.

Aboul Dahab (1988) has determined very high concentrations of water extractable methyl- and butyltins in the sediments from Alexandria coastal belt (Table IV). The MMT and TBT compounds were found to be the predominant forms while TMT was mostly at undetectable level. This result is in good agreement with the ones of Tuğrul et al. (1983) in the tin-polluted sediments. But his total MT concentration values are much greater than the ones given in Table III, due presumably to the differences in the extraction methods followed. Only our recent MT measurements in the delta sediments are at comparable level with his measurement results. He also abtained a close relationship between the total methyl- and butyltin concentrations. Total BT/total MT ratio was found to range between 1-3. The sole sample from the off Eastern, which contained DMT only, has a BT/MT ratio of 6.

3.6. Organism

The methyltin measured by Tuğrul et al. (1983) in various marine organisms are displayed in Table V. Briefly, fish and limpet accumulate methyltins in their edible tissues, indicating the MMT, DMT and TMT productions in the ambient waters. As seen in Fig. 5, total-tin and methyltin concentrations in the adible tissue of limpet changed monthly(Yemenicioğlu, 1983), with the greatest concentrations in spring and early summer months indicating short half-life and fast accumulation of MT in limpet. The rate of inorganic tin input from Lamas stream, water temperature and natural assemblage of microorganisms in the area are very likely to influence the accumulation and excretion rates of methyltins. Since limpet is a filter feeder and inhabits the tidal zone it is difficult to assess the degree of methylation of inorganic tin by the organisms itself. The methyltin content of the limpet shell (see Table V) demonstrates the significance of accumulation of bacterial-origin methyltins in the shell of limpet.

Chlorophyta sample accumulated only DMT whereas seaweed collected from the same location contained MMT and DMT almost at the same level, and trace amount of TMT, indicating different methylation pathways. Seidel et al. (1980) also observed DMT and tetramethyltin only in some macroalgae samples from different sites of the US coastal waters.

4. CONCLUSIONS

The little or remarkable differences in the sampling, treatment and measurement methods followed by various groups make it difficult to assess the spatial distributions of alkyltins using the published data . Therefore, a comprehensive intercalibration study is needed to improve the reliability of alkyltin measuerments in the environmental samples.

The detection of TMT and MBT compounds in the water column of the Marmara Sea basin predicts the significance of vertical transport of organotin compounds by fast sinking particulate matters. The similar mechanism is very likely to occur in the transport of MMT and to a less extent DMT in polluted water environments.

In the relatively less contaminated and productive seas, and unpolluted oxic sediments, the TMT was the predominant form of methyltins produced by biochemical reactions whereas the MMT and DMT forms predominated in the tin-polluted sea, lake and river waters and in the tin-polluted harbour and bay sediments.

The distribution patterns of methyltin species in waters, sediments and organisms from polluted and unpolluted environments indicate that different biomediated methylation reactions take place in aerobic and anaerobic water environments. It was also understood that, in anoxic nonpolluted waters, methylation reaction of tin very likely follows a different pathway to yield water soluble MMT and TMT, and volatile tetramethyltin, stannane and methylstannanes, but trace amounts of DMT occasionally. The unexpected aspect of methyltin distributions in the Saanich Inlet sediment, which did not contained measurable DMT, can be confirmed by a tin speciation study to be conducted in the redox gradient zone and anoxic sediments of Black Sea.

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Table I. Concentrations of butyl- and methyltins measured in the coastal waters of Turkey (as alkyltin chloride, ng l^{-1}).

Sampling Site	Sampling Station	Sampling Date	MBT	DBT	TBT	MMT	DMT	TMT
Marmara Sea		July 1988	nd-37	-	-	nd-48	nd-14	nd-50
		Sep. 1988	nd-17	-	-	nd-28	nd-55	nd-16
		Dec. 1988	nd	-	-	nd	nd	nd
		Feb. 1989	nd	-	-	nd	nd-1.2	nd-10
Dardanalles		July 1988	nd	-	-	17-63	nd	nd
Bosphorus		July 1988	2.7-7	-	-	nd-1.1	nd-2.2	nd-15
Black Sea		Sept. 1988	nd-35	-	-	nd-5.1	nd-80	nd-35
		Jan. 1989	nd	-	-	nd	nd	nd-12
İskenderun Harbour	H4	May, 1988	8	56	83	nd	nd	7.4
		Nov., 1988	8	23	31	nd	nd	13.7
		Feb., 1989	27	7	32	nd	nd	nd
Mersin Harbour	H1	Nov., 1988	12	44	31	nd	nd	39.7
Botaş	H2	May, 1988	140	nd	9	nd	nd	5.3
		Nov., 1988	311	nd	nd	nd	nd	17.1
İsdemir	H3	Nov., 1988	633	nd	nd	nd	1.0	2.8
		March, 1989	77	nd	nd	nd	nd	nd
Antalya Marina	M2	Feb., 1989	102	nd	nd	nd	nd	nd
Göksu Delta	(D3)	Oct., 1988	212	nd	nd	nd	nd	27.5
		Feb., 1989	268	nd	nd	nd	nd	nd
Reference Stations	R2	July, 1988	nd	nd	nd	nd	7.5	266.7
	R1	Oct., 1988	nd	nd	nd	nd	18.0	129.2

nd: not detected (below the detection limits of the applied method).

Table II. Methyltin concentration in saline, lake, river and rain waters (ng L^{-1} as Sn)

	Sn(IV)	MeSn	Me_2Sn	Me_3Sn	Ref:
<u>Saline water</u>					
Bay waters	2-62	nd-15	0.7-7	nd-1	1
	(54-73%)	(<18%)	(8-39%)	(<20%)	
" "	nd-207	nd-1.1	0.6-1.7	0.6-0.95	1
	(10-54%)	(17-44%)	(24-40%)	(12-34%)	
" "	6-38	1-4	5-15	nd	4
İskenderun Bay:					
July, 1982	11- 175	6-83	4- 18.3	nd	6
Aug., 1982	26- 7710	5.5-10	5- 12	nd	6
Sep., 1982	219- 237	nd	9- 12.5	nd	6
Nov., 1982	13- 207	nd	0.5-1.4	nd	6
Ap., 1983	3.5-604	-	-	-	6
Canadian Harbours	80- 2100	370-1200	340-400	nd	5
Estuarine waters	3 - 20	nd-8	0.9-3.3	nd-1.1	1
	(27-88%)	(low-66%)	(7-71%)	(low-29%)	
" "	1 - 4	nd-0.1	0.5-1.2	nd-0.5	3
Lamas Estuary	4.1 - 5.5	0.6-2.2	0.6	nd	7
Göksu "	3.2 - 27	nd	0.6- 1.5	nd	6
" "	12 - 49	1.8-4.8	2.3-20.5	0.9-1.5	6
Lamas "	9 - 15	nd	0.9- 3.6	nd	6
<u>Lake water</u>	3-10	nd-1	0.56-1.2	3.3-7.6	1
	(46-65%)	(max.5%)	(6-8%)	(28-46%)	
" "	2.4-3.5	2.6-4.5	nd-5.5	nd-1.3	1
	(47%)	(31-52%)	(37%)	(low-8.9%)	
" "	84- 490	3-9	nd-31	nd	4
Canadian Lakes	40-2500	110-250	30-90	nd	5
<u>River water</u>	nd-4.1	0.5-12	0.4-7.5	nd-1.8	1
	(17-52%)	(19-76%)	(5-37%)	(low-8.9%)	
" "	1-25	nd-0.5	nd-0.4	nd-0.3	3
Canadian Rivers	20-120	370-680	140-210	nd	5
Missisipi "	128	1.3	3	0.1	3
Rhine "	18	70	210	1.5	3
<u>Rain water</u>	3-41	0.6-22	nd-1.9	nd-0.61	1
	(2-92%)	(2-66%)	(low-20%)	(low-7.5%)	
" "	1-3	nd-5	nd	nd	2

1:Braman and Tompkins (1979); 2:Tuğrul et al., (1983); 3:Byrd J.T. and M.O. Andrae (1982); 4:Hodge et al. (1979); 5:Maguire et al. (1982); 6:Yemenicioğlu (1984)

Table III. Concentrations of methyltins and monobutyltin in the sediments from Turkish coastal waters and in the core samples from other seas (ng g^{-1} dry weight as alkyltin chloride).

Station	Smp.date	$MeSnCl_3$	Me_2SnCl_2	Me_3SnCl	$BuSnCl_3$	Me/Me_3	Me_2/Me_3
Manavgat(D2)	1988	15	36	143	100	0.10	0.25
Eşen(D1)	1988	38	58	107	260	0.35	0.54
Seyhan(D4)	1988	65	81	159	100	0.41	0.51
Seyhan(D4)	1980	nd	1.3	3.9	na	<0.1	0.33
Göksu(D3)	1988	375	477	1696	980	0.22	0.28
Göksu(D3)	1980	nd-0.7	0.6	1.6	na	<0.4	0.37
Iskenderun Bay,80		nd	nd	0.35	na	<0.3	<0.3
Iskend. Bay	1982	0.6	2.4	0.5	na	1.2	4.8
Iskend. Bay	1982	0.2	1.3	0.1	na	2.0	13.0
Iskend. Bay	1982	0.2	0.9	0.1	na	2.0	9.0
Taşucu Bay	1980	0.1	0.2	1.0	na	0.1	0.2
Akkuyu	1980	nd-0.3	8.1	11.8	na	<0.1	0.7
Lamas	1980	nd	nd-1.8	4.4	na	<0.1	<0.4
Mersin	1980	nd	2.6	8.6	na	<0.1	0.3
Mersin Harb.	1980	7.5	2.1	0.5	na	25.0	4.2
Mersin Harb.	1980	0.2	0.5	0.1	na	2.0	5.0
San Diego Bay,	81	2.3	2.3	nd-0.2	na	>10	>10
Baltic Sea,	-	0.5	0.3	nd	na	>5	>3
Chesapeake Bay,	-	0.6	nd	nd	na	>6	-
Saanich Inlet,	-	0.6	nd	2.6	na	0.2	<0.1

nd: not detected ; na: not analyzed.

Table 4. Spatial concentrations of tin species (ng g^{-1} as Sn) in Alexandria coastal belt (from O. Aboul Dahab, 1988).

	I Ref. St	II Agamy	III Mex Bay	IV Western Harbour	V Off Sewage outfall	VI Off Eastern	VII Eastern Harbour	VIII Eastern coast	IX Abu Kir
Station No.	4	1-3	5-11	12-14	15	16	17-18	19-26	27-35
No. of samples	1	3	7	3	1	1	2	8	9
Inorg.Sn	310	488	2147	4720	2430	1080	3645	1075	2252
MMT	0	20	69	1000	85	0	500	41	127
DMT	15	12	35	77	70	45	23	23	43
TMT	0	0	0	60	0	0	23	0	3
Total MT	15	32	104	1136	155	45	545	64	173
% MMT/Total MT	0	63	68	88	0	0	91	68	70
% DMT/Total MT	100	37	32	7	45	100	4	32	30
% TMT/Total MT	0	0	0	5	0	0	4	0	0
MBT	0	41	57	330	45	55	138	60	83
DBT	10	17	49	305	65	60	120	63	67
TBT	35	40	187	975	185	160	260	63	252
Total BT	45	97	294	1610	295	275	518	186	401
% MBT/Total BT	0	38	19	22	15	20	27	32	20
% DBT/Total BT	22	15	16	19	22	22	23	34	15
% TBT/Total BT	78	47	65	59	63	58	50	34	65

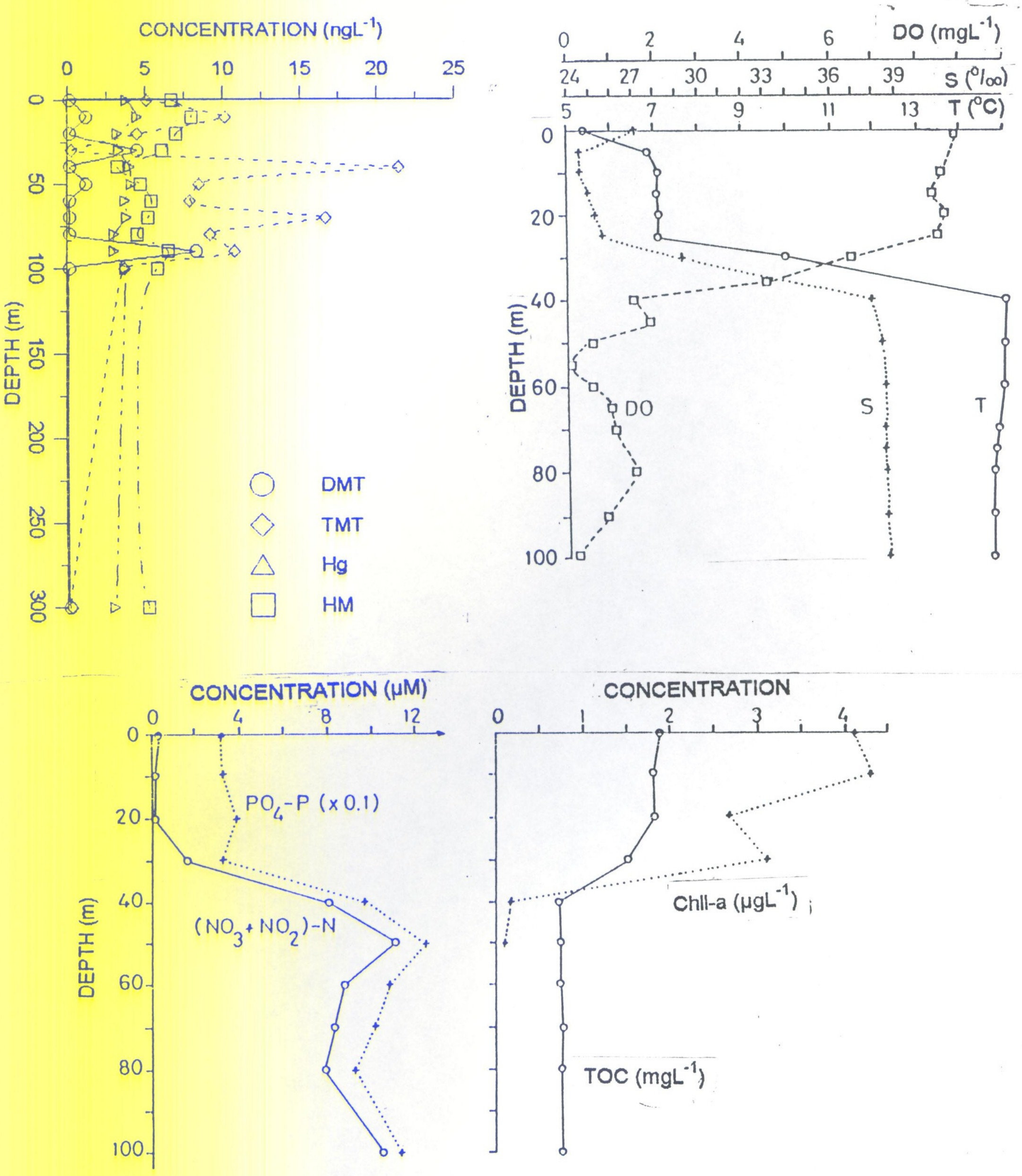

Fig. 2. Vertical variations of DMT, TMT, total Hg, dissolved oxygen (DO), temperature, salinity, humic matter (HM), nutrients and total dissolved organic carbon (TOC) in the basin water of the Marmara, February, 1989.

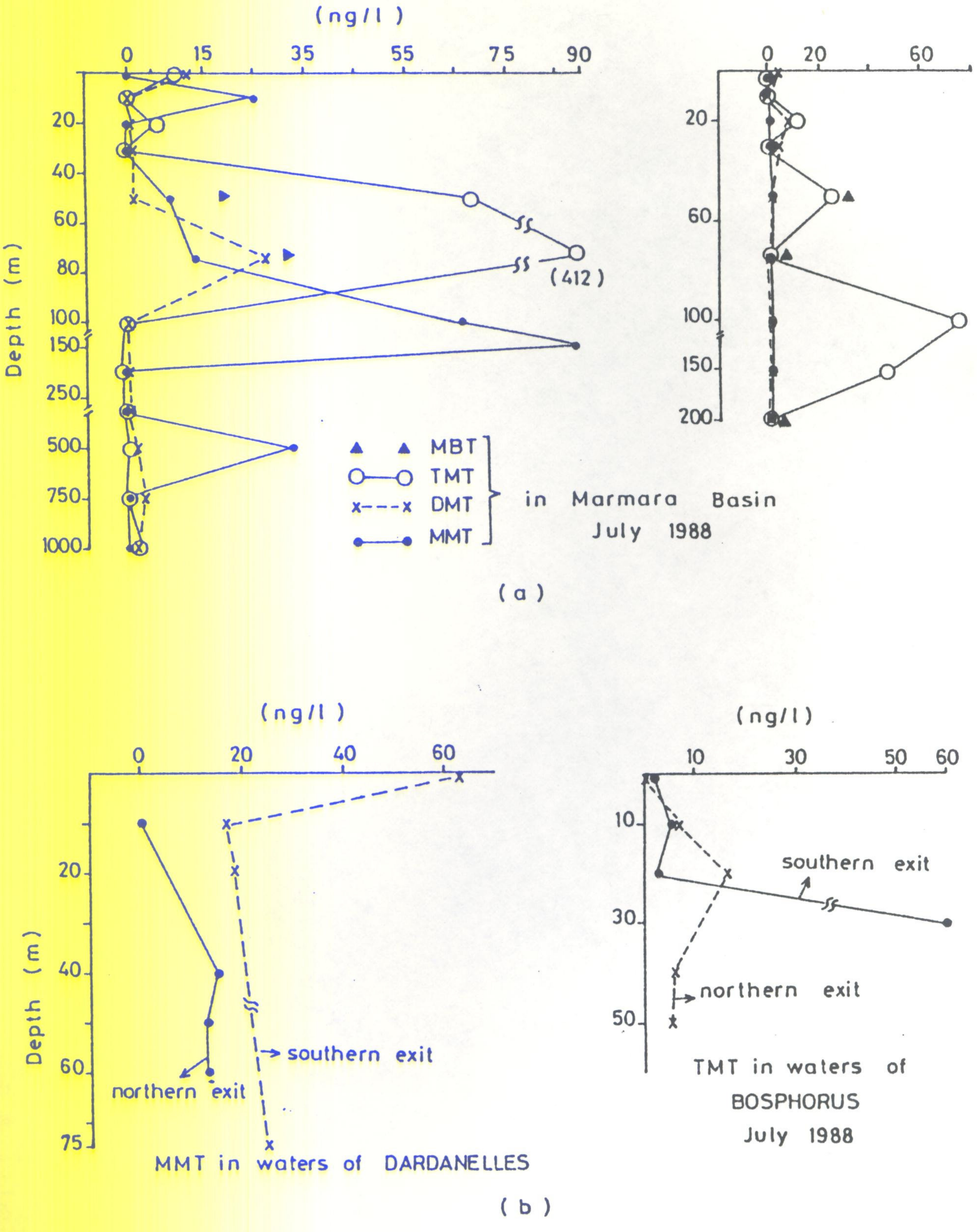

Fig. 3. Vertical distribution of methyltin concentrations in the waters of Marmara Sea and two straits, July 1988.

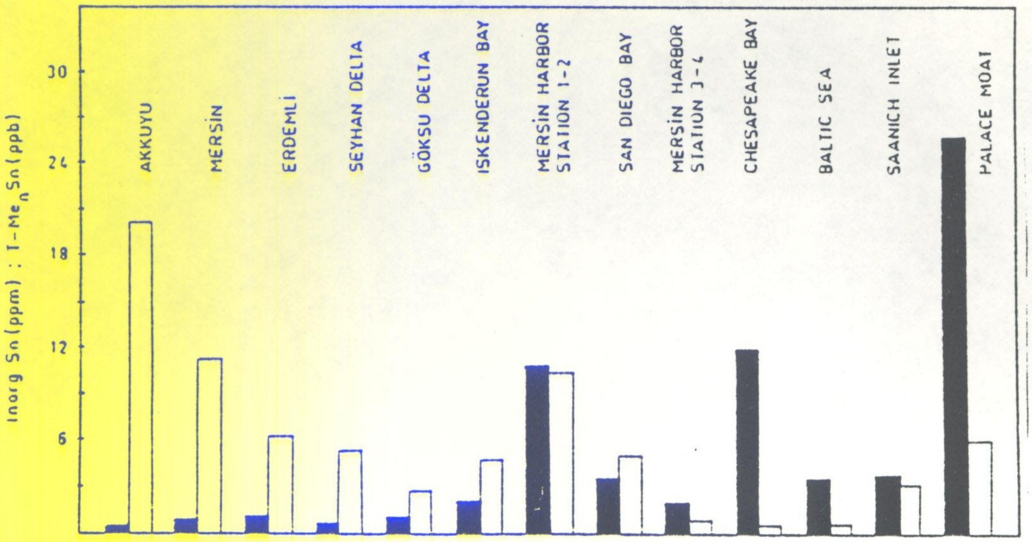

Fig. 4. Average values of 6 N HCl extractable inorganic tin(■)and total water extractable methyltin (□) in sediments from different environments.

Table V. Average organotin, total tin concentrations (ng g^{-1}, dry weight) and methyltin ratios in marine organisms from the northeastern Mediterranean coast, Turkey (from Tuğrul et al., 1983).

Species	T-Sn	Me-Sn	Me_2-Sn	Me_3Sn	Tin % in T-MeSn	Me/Me_3	Me_2/Me_3
<u>Fish</u>							
U. moluccensis	260	27	2.6	1.2	6	23	2.2
Mull. barbatus	86	0.8	2.9	1.3	3	0.6	2.2
<u>Limpet</u>							
Patella caerulea							
<u>Shell</u>							
L.H. in.(Oct.'80)	13	2.8	1.2	0.7	16	4	1.7
L.H.out.(Oct.'80)	n.a.	0.4	0.2	2.8	-	0.14	0.07
<u>Soft tissue</u>							
L.H. in.(June'80)	75	1.3	12	34	36	0.04	0.4
L.H. in.(June'80)	64	2.1	18	63	76	0.03	0.3
L.H.out.(June'80)	50	4.8	4.2	35	52	0.14	0.1
L.H.in.(Oct.'80)	n.a.	2.4	7.8	0.8	-	3	9.8
L.H.out.(Oct.'80)	n.a.	1.3	1.8	10.4	-	0.13	0.2
<u>Brown macro-algae</u>*	9	n.d.	0.5	5.8	41	(a)	0.09
<u>Chlorophyta</u> (L.H., Apr.'80)	37	n.d.	12	n.d.	18	(a)	(b)
<u>Seaweed</u> (L.H., Dec.'80)	250	16.8	37	0.9	11	19	41

(a): very small; (b): very large; L.H.in., Lamas Harbour inside; L.H.out., Lamas Harbour outside; n.d. not detected; n.a. not analyzed; * 40m depth near L.H

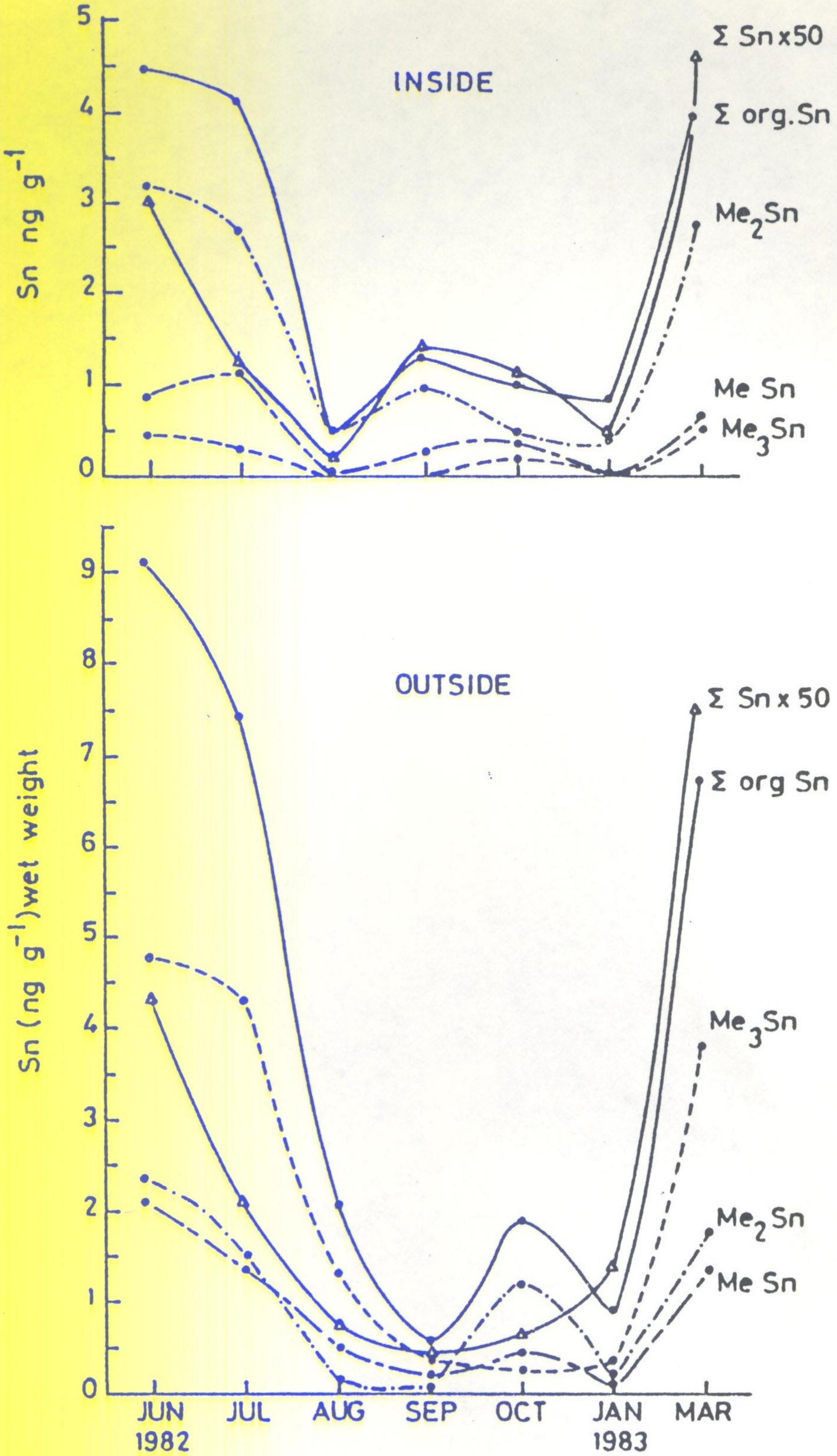

Fig. 5. Monthly variation of tin species in the edible tissue of limpet from Lamas Harbor.