

DISTRIBUTION OF TIN IN THE NORTHEASTERN MEDITERRANEAN

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ABSTRACT

Concentrations of tin, one of the naturally methylated elements, was determined in sea water, sediments and organisms, collected from the Northeastern Mediterranean. A hydride generation technique was employed, in which the tin and methyltin, were converted to their hydrides. The hydrides produced were detected by atomic absorption spectrophotometer. On the average, the inorganic tin content of sea water samples ranged between 1.1-236 ng/l. Although the dominant methyltin species was dimethyltin, all forms of methyltins (mono, di and tri-methyltins) were detected. The sediment samples were analyzed for the acid extractable tin content and the concentrations were found to range between 0.17-2.30 ug/g (dry weight). Methyltin concentration ranged between 0.1-9.7 ng/g (dry weight). The organism (Limpet) samples were analyzed for their total tin and methyltin contents. Total tin ranged between 7.2-564 ng/g (dry weight), and the methyltins ranged between 0.5-13.9 ng/g (dry weight).

INTRODUCTION

Inorganic and organic tin compounds have several industrial and agricultural applications, many of which are dispersive and eventually they enter into the marine environment. Once they entered into the marine environment, the tin compounds subjected to photo-or biological degradation, biomethylation 2, 3 and chemical reactions 1. Inorganic tin compounds are relatively nontoxic, but organotin compounds are toxic to most of the aquatic and terrestrial organisms 1. The toxicity varies depending on the degree of substitution and the nature of the organic group 4,5. Wood and Goldberg (6) placed tin in the very toxic group due to the powerful toxic effect of organotin compounds relative to its inorganic form. Some laboratory experiments demonstrated that inorganic tin and trimethyltin can be biomethylated in the marine environment 2,3. The biomethylation of toxic substances in the environment is of vital importance from the stand point of public health 7.

Based up on the work done by Hodge 8 a hydride generation technique was employed for the speciation of tin compounds in the marine environment.

MATERIALS AND METHODS

Instrumentation:

A Varian-techtron Model AA-6 Atomic Absorption Spectrophotometer (AAS) was used for the analysis of the samples. The output is routed to a Varian-Model A-25 strip chart recorder set on 2 mV to read full scale for 0.2 absorbance unit. The water trap (12x1.5 cm i.d.), Hydride trap (14x0.6 cm i.d.) packed with 3% OV-1 on chromosorb W AW-DMC SGO/80, quartz-tube burner (8x0.8 cm i.d) and the reaction vessel (250 ml capacity) are illustrated in Figure 1. The operating parameters are: Wave length; 286.3 nm, slit width; 0.5 nm, lamp current; 3mA and the gas flow rates were adjusted as follows: air; 150 ml/min, hydrogen; 250 ml/min; helium; 80 ml/min.

Background correction was used throughout the analysis, under these operating conditions the detection limits are 0.2 ng for methyltins and inorganic tin.

Reagents and standards:

All standards and reagent solutions were prepared with distilled deionized water (ddw):

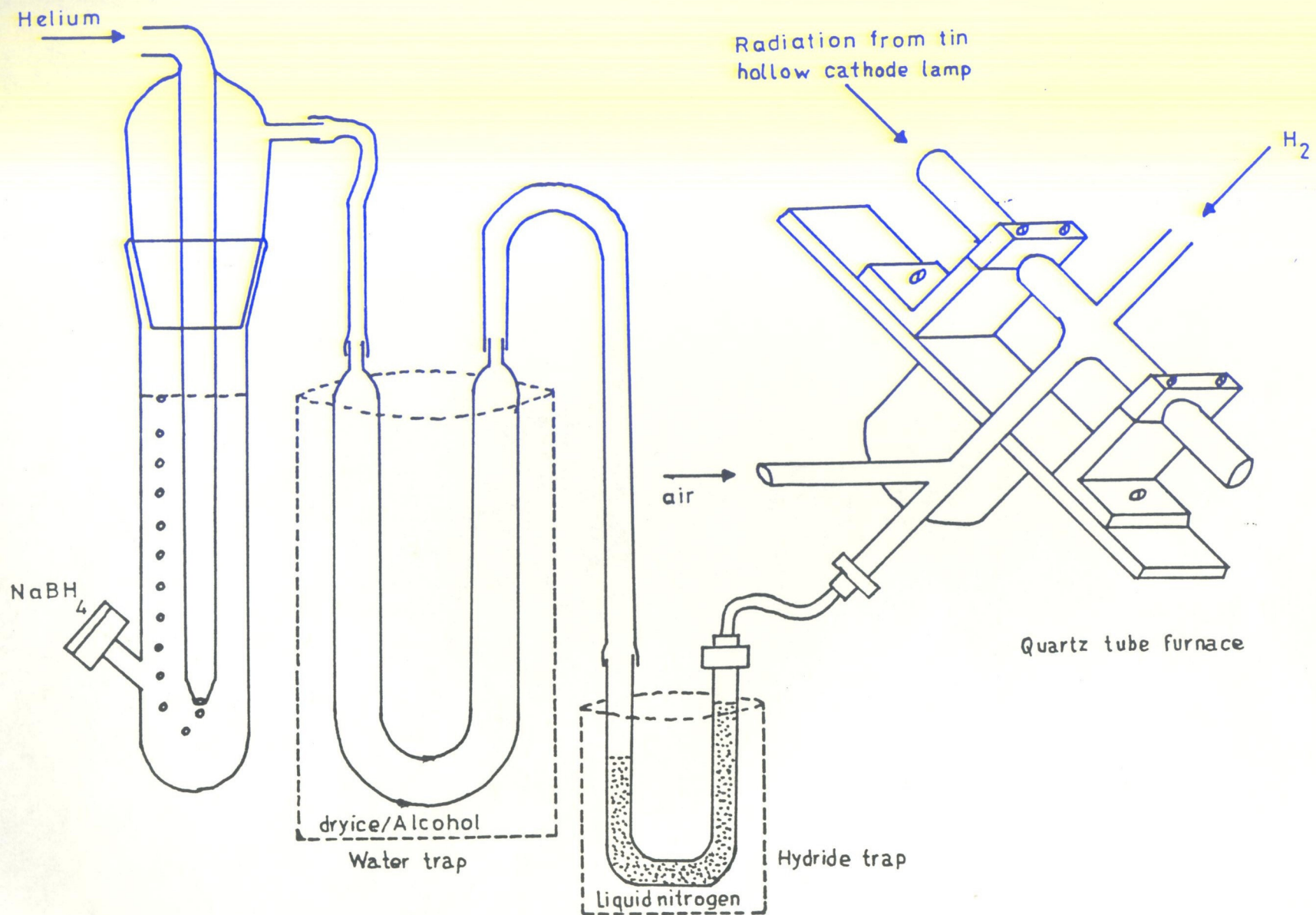


FIGURE:1 Apparatus setup.

HCl (Analar), HNO_3 (Merck, GR), HClO_4 (Aristar), NaOH (Baker Analyzed Reagent) and TRIS-HCl (Ventron, Denv. Mass.) were used as received. All methyltins and Sn(IV) standards were obtained from Ventron (Danv. Mass.) and prepared as described by Hodge 8. 4% NaBH_4 (MCB Reagents) were purified before use. Most of the inorganic tin blank arise from this reagent. Purification was done as follow: 4 g of NaBH_4 was dissolved in 25 ml of sea water, then 0.5 ml of 2N NaOH added and stirred for about 15 min with a magnetic stirrer. Finally the solution was gravity filtered through Whatman No:2 filter paper and diluted to 100 ml with ddw.

Sampling and Sample Preservation:

Sea water samples were collected from a rubber boat upwind of the ship, with a polyethylene bucket from the surface and transferred into 2 l capacity acid cleaned bottles. In order to avoid the hydrowire contamination a nylon hydrowire was used for sampling. Then the samples are brought to laboratory within a few hours and analyzed or 2 ml of concentrated HCl was added and preserved in refrigerator until the analysis time.

Sediment samples were taken by a Vaan-Veen type grab sampler which collects the top 10 cm and are placed into precleaned nylon bags. After expelling the air, the bags were sealed and preserved in deep-freezer at about -30°C until the analysis time.

Organism samples were collected on the rocks by hand. After washing with ddw. They were placed in the pre-cleaned nylon bags and brought to laboratory with in a few hours. After expelling the air, bags were sealed and preserved in a deep freezer until the analysis time.

Sea water Analysis:

For inorganic tin determination a 100 ml capacity reaction vessel was used. 100 ml of sea water was transferred into the reaction vessel. If smaller amount of sample was to be analysed the final volume was adjusted to 100 ml with ddw. Then 2 ml of 20% (w/v) TRIS-HCl was added and purged with helium for a few minutes. During this purging the hydride trap was out of liquid nitrogen. If concentrated HCl were added to the samples for preservation, analysis carried out without TRIS-HCl addition. Then the procedure given by Hodge 8 was followed.

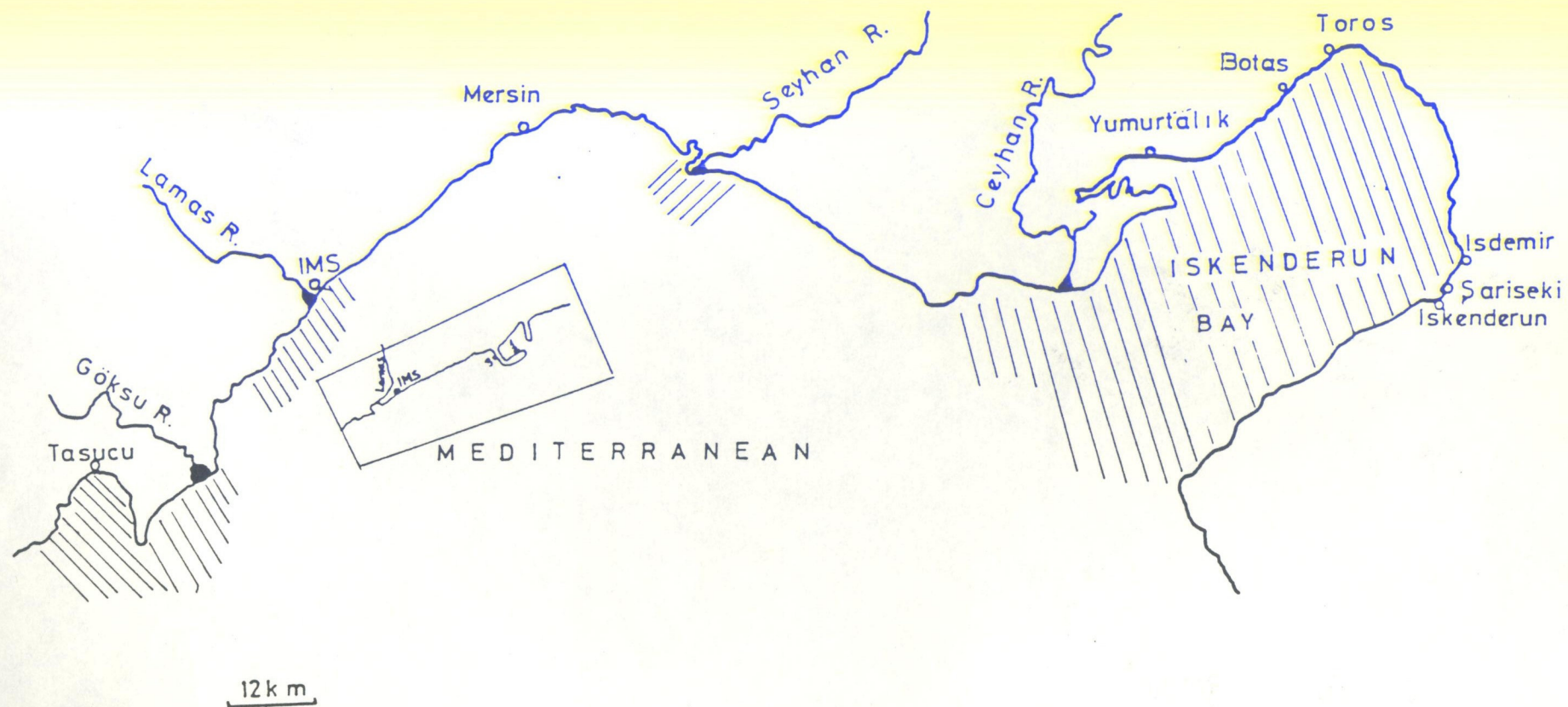


FIGURE 2 Sampling Areas.

Methyltin species were determined by using 250 ml of sea water samples and 2 ml of TRIS-HCl. Analysis were performed using the same procedure as above by injection of 2 ml of 4% NaBH_4 . The stripping time for hydrides was extended to 7 minutes.

The qualitative and quantitative determinations was done by standard addition method.

Sediment Analysis:

Acid Extractable:

Acid extractable tin analysis was performed by using same method as described Seidel 9 and Tuğrul 10.

Methyltins:

1-5 g of the dried and grounded sediment sample, depending on the concentration of methyltin content, were covered with 40 ml of ddw. The samples were then shaken with ultrasonic apparatus for 30 minutes. The samples then transferred into the reaction vessel and ddw was added to adjust final volume to 100 ml. 1 ml of 20% (w/v) TRIS-HCl was added and reacted with 1 ml of 4% NaBH_4 following the procedure given for water analysis. Analytical calculations and peak identification were done by standard addition method.

Analysis of Organisms:

Total tin Analysis:

4-5 g of wet tissue (soft part) of the limpet samples were digested in concentrated HNO_3 as described by Tuğrul 10. 0.5-1 ml portion of the resultant solution was transferred into the reaction vessel and ddw was added to adjust final volume to 100 ml. The analysis were carried out as described in sea water analysis by the addition of 1 ml of 4% NaBH_4 .

Methyltin Analysis:

0.5-2 g dried (soft part) of limpet samples were placed 20 ml of 0.04 N HCl and homogenized into solution by using Bühler "H0" homogenizer with stainless-steel blades and shaft and pyrex homogenizing cup. The homogenized sample was then transferred into the reaction vessel and diluted to 100 ml with ddw. In order to prevent foaming, during the degassing, the helium bubbler was shortened and the reaction vessel was degassed above the solution. The analysis

carried out by the addition of 1 ml 4% NaBH_4 following the same procedure used for sea water analysis. The solution was stirred with a magnetic stirrer during the collection of the hydrides. Standards were run under the same conditions.

RESULTS AND DISCUSSIONS

Water:

Beside sea water, samples obtained from Lamas River were also analyzed for their inorganic and methyltin content. The lowest inorganic tin concentration in Lamas River water was measured in winter, 1981 (2.0 ng/l) and the highest was measured in spring, 1983 (7.8 ng/l) with an average of 4.3 (ng/l). The highest value measured coincides with snow melt. Methylated tin species were not detected in the riverine water samples.

Compared with continental and USA rivers, the tin concentrations in Lamas river water is very low.

In Lamas river estuary dimethyltin observed in winter and spring 1983 sampling period, but all forms of methyltins were observed in summer, 1983 sampling period when the inorganic tin concentration in water column is very high when compared with the other sampling periods (see Table 1). On average the inorganic tin concentration in this estuary ranges between 1.70-104.72 ng/l.

Sea water samples from Göksu river estuary and Tasucu bay contain inorganic tin in the range of 21.70-96.61 ng/l (average). Dimethyltin was found in spring, 1983, and all forms of methyltins like Lamas river estuary, observed in summer, 1983.

The behavior of the methyltins in Lamas river and (Göksu river estuary and Tasucu bay) Tasucu area have shown the same variations.

The inorganic tin content of Iskenderun bay water ranges between 51.77-732.97 ng/l (average). the methyltin distribution of this area differs from those of Tasucu area and Lamas river estuary. Methyltins were observed almost of all sampling period with the exception of spring, 1983. No trimethyltin were detected in this area.

The occasional appearance of methyltins above the detection limit of the method employed (at ng levels), most probably originate from the seasonal changes in micro organisms population able to methylate inorganic tin and to degrade the methyltins. In additions, the changes in some physical parameters such as, salinity, temperature, light intensity and turbidity could be important.

Constant detection of dimethyltin in winter and spring time at three sampling area, namely Iskenderun bay, Lamas river estuary and Tasucu area (Göksu river estuary and Taşucu bay), suggested that, dimethyltin formation by microorganisms is favoured in colder season.

As mentioned above the methyltins were detected in Iskenderun bay water samples at almost all sampling periods (an exception was spring, 1983). The industrial activities established on the shores of Iskenderun bay, discharge their waste into the sea without any pretreatment. Extensive shipping and boating activities also exists in the bay. The tin levels in discharged water samples from these industrial activities are given in Table 1.

The appearance of methylated tin species in Iskenderun bay water at every sampling period indicate that, if there is a continuous inorganic tin flux into a productive coastal water, and if the inorganic tin concentration is well above the natural levels, inorganic tin is steadily biomethylated.

Sediment:

The sediment samples collected from north-eastern Mediterranean were analyzed for their tin speciation. In order to correlate the inorganic tin that is susceptible to biomethylation and the methyltin content, the sediments were digested with 6 N cold HCl as described by Seidel 9 and Tuğrul 10. As can be seen from Table 3, there is no significant seasonal and regional variations in the acid extractable tin concentrations of the sediments. No direct relationship were found between inorganic tin and methyltin content. The methyltins were detected in sediment samples at every sampling period. Like water samples, in sediment samples also the dominant methylated tin species were dimethyltin. In Taşucu and Lamas river estuary sediments, at cold seasons, only dimethyltin were observed and at summer and spring all forms of methyltins were detected. In water samples from the same locations all forms of methyltins were detected only in summer. Sediments from Iskenderun bay was found to contain all forms of methyltins while sea water samples from same locations contains only mono-and

dimethyl-tins, and trimethyl tin were not observed in these water samples.

Organisms:

Two sampling stations were chosen in Lamas harbour (Fig.2) station 3 is out side of the harbour and is under the influence of fresh Lamas river water (this influence were confirmed by the measurement of some parameters, namely S‰, T°C, DO and conductivity). Station 1 is inside the harbour and the river water influence is not as strong as at st.3.

The total tin concentration of samples obtained from st.3 is maximum in summer (Table 4) while at st.2 this maximum occurs in autumn, 10% of the total tin was found to be in organic form for both stations. But in st.3 the dominant tin species was trimethyltin while at st.1 the dominant tin species was dimethyltin. The methyltin content of the organisms at st 1 decreases rapidly from 11% to 3% (in summer and autumn respectively) while at st.3 both in summer and autumn the organic tin was 10% of the total tin and reaches 3% in winter. In spring 26% of the total tin is in the organic form, dimethyl tin being the dominant species. On the other hand at Taşucu harbour limpet samples contain highest amount of methyltin in spring period (70%) and no trimethyltin was detected in these samples with the exception of summer. The dominant methylated tin was found to be monomethyl tin. Samples from Yumurtalık and Iskenderun harbour contain small amount of organic tin and the methylated tin was monomethyl tin only. Samples of these areas contain very high amount of inorganic tin.

CONCLUSION:

The present study provides evidence that tin can be biomethylated by the microorganisms in the marine environment and can be mobilized in the ecosystem. Methylated products could be the result of degradation of organotins, such as phenyl, butyl-tin, as well as the methylation of inorganic tin. Existence of methylated tin species in the organisms even at the time of their absence in water column suggested that either methylation continues in the organisms itself or accumulated by the organisms when these species exist in the water column. Because of the increased toxicity of tin in the organic form, the studies on the environmental samples must be extended and sublethal effects must also be studied in the laboratory experiments.

TABLE. 1: Average Concentrations of Tin Species in
Sea Water and River Samples (ng/l)

Sampling area and season (a)	Sn _i (a-b) (c)	Me-Sn (a-b) (c)	Me ₂ -Sn (a-b) (c)	Me ₃ -Sn (a-b) (c)
<u>Lamas River:</u>				
Summer, 1982(2)	2.7-4.5 3.60	-	-	-
Autum, 1982(3)	3.8-6.5 5.27	-	-	-
Winter, 1983(2)	2.0-2.9 2.45	-	-	-
Spring, 1983(3)	3.6-7.8 5.30	-	-	-
Summer, 1983(2)	2.5-4.2 3.35	-	-	-
<u>Lamas River Estuary:</u>				
Summer, 1982(2)	1.2-2.2 1.70	-	-	-
Autum, 1982(4)	8.1-18.6 13.72	-	-	-
Winter, 1983(20)	6.4-20.9 12.77	-	2.9	-
Spring, 1983(13)	5.7-33.6 12.80	-	7.5	-
Summer, 1983(4)	18.2-250.2 104.72	5.8-11.0 8.70	1.3-21.6 10.90	2.0-9.7 4.92

Table.1 Cont'ed

Taşucu Area

Autum, 1982(9)	8.0-52.2	-	-	-
	27.59			
Winter, 1983(11)	12.6-450	-	-	-
	96.61			
Spring, 1983(18)	2.0-76	-	1.3-3.1	-
	21.70		2.20	
Summer, 1983(5)	1.20-49.2	3.8-9.9	4.8-41.8	2.0-3.2
	25.02	7.0	22.84	2.53

İskenderun Bay

Summer, 1982(13)	11.5-7711	11.7-20.7	8.5-19.0	-
	732.97	15.02	14.65	
Autum, 1982(20)	2.5-237	-	1.1-25.9	-
	68.32		6.69	
Winter, 1983(8)	9.3-207	-	1.1-2.9	-
	51.77		1.96	
Spring, 1983(9)*	3.5-604	-	-	-
	156.5			

* These samples are stored in refrigerator for a long time (about 4 monthes) before analysis.

(a): Numbers in paranthesis indicate the number of samples analyzed.

(a-b): Indicates measured lowest and highest concentrations of tin species

(c): Indicates the average tin species.

(-): Not detected

Sn: Inorganic tin.

Me-Sn: Monomethyl tin

Me₂-Sn: Dimethyl tin

Me₃-Sn: Trimethyl tin

TABLE.2: Inorganic tin levels in discharged water samples from Industrial activities established on the shores of Iskenderun bay. (ng/l)

Sampling source	Sampling date	inorganic tin [*]
Isdemir (Iron and steel complex)		
Discharge 1	September, 1982	15
Discharge 2	September, 1982	16
Discharge 3	September, 1982	1115
Toros Fertilizer Plant		
Discharge 1 (basic)	September, 1982	-
Discharge 2 (asidic)	September, 1982	65
Sarıseki Fertilizer and Phosphoric acid complex	September, 1982	240

(-): Not detected

(x): No methyltins were detected in these samples.

TABLE.3: Average concentrations of acid extractable tin (ug/l) and methyl tins (ng/g) in sediment samples (dry weight).

Sampling area and season (a)	Acid extractable tin (a-b) c	Me-Sn (a-b) c	Me ₂ -Sn (a-b) c	Me ₃ -Sn (a-b) c
Iskenderun Bay				
Summer, 1982(9)	0-54-0.90 0.75	0.1-0.8 0.44	0.3-4.5 2.13	0.1-0.7 0.4
Autum, 1982(7)	0.38-0.89 0.66	0.1-0.3 0.2	0.1-1.6 0.44	0.1 0.1
Taşucu Area				
Spring, 1980(9)	0.41-1.46 0.87	0.1-0.7 0.25	0.2-2.1 1.08	1.0-9.9 4.28
Summer, 1982(2)	0.65-0.95 0.80	0.1-0.2 0.15	0.1-0.2 0.15	0.6-1.3 0.95
Winter, 1983(10)	0.61-0.81 0.70	-	0.1-0.6 0.30	-
Spring, 1983(6)	0.17-0.72 0.52	0.2-0.3 0.27	0.2-1.0 0.6	-
Lamas River Estuary				
Spring, 1980(2)	1.06	0.2	1.3	3.1
Winter, 1983(5)	0.87-1.51 1.39	-	0.3-0.90 0.65	0.1-0.25 0.2

(a): Indicates the number of samples analyzed

(a-b): Indicates the lowest and highest measured tin concentrations

(c) : Indicates the average tin concentration.

(-) : Not detected

(Me-Sn): Mono methyl tin

(Me₂-Sn): Dimethyl tin

(Me₃-Sn): Trimethyl tin

TABLE.4: Average total tin and methyltin concentrations
in limpet samples (ng/g dry weight).

Sampling area and Period	Av.Length (cm) (a)	Σ Sn	Me-Sn	Me ₂ -Sn	Me ₃ -Sn	Percent organictin
Lamas harbour Station 3						
Summer, 1982	3.2(36)	123.48	2.90	2.70	6.90	10%
Autum, 1982	3.4(25)	23.27	0.70	1.15	0.60	10%
Winter, 1983	3.3(15)	54.15	0.9	0.25	0.60	3%
Spring, 1983	3.1(9)	51.45	2.80	3.10	7.60	26%
Lamas harbour Station 1						
Summer, 1982	3.5(25)	54.03	2.0	3.35	0.75	11%
Autum, 1982	3.8(27)	67.26	0.79	1.29	0.5	4%
Winter, 1983	3.0(10)	24.0	-	0.8	-	3%
Spring, 1983	3.3(9)	37.36	1.4	5.5	1.1	21%
Taşucu harbour						
Winter, 1983	2.9(14)	450	13.9	3.5	-	4%
Spring, 1983	3.5(4)	19.3	9.0	4.6	-	70%
Summer, 1983	3.3(24)	108.3	13.85	6.65	1.0	20%
Autum, 1983	3.6(4)	71.6	6.4	2.7	-	20%
İskenderun harbour						
Summer, 1982	3.5(11)	26.50	3.4	0.7	-	2%
Autum, 1982	3.0(21)	226.8	2.05	-	-	1%
Spring, 1983	3.7(8)	294.0	0.9	-	-	0.3%
Summer, 1983	3.0(19)	350.97	3.55	0.6	-	1%
Yumurtalık harbour						
Summer, 1982	3.7(28)	342.78	4.5	-	-	1%
Autum, 1982	3.1(27)	147.36	2.6	-	-	2%
Winter, 1983	3.0(15)	67.55	0.3	-	-	0.4%
Summer, 1983	3.2(11)	68.27	3.9	-	-	6%
Autum, 1983	2.5(16)	52.75	1.58	-	-	3%

(a): Indicates number of organism analyzed

(-): Not detected

(Σ Sn):Total tin

(Me-Sn):Mönomethyl tin

(Me₂-Sn):Dimethyl tin

(Me₃-Sn):Trimethyl tin

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