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TWO TOXICANTS, MERCURY AND TIN IN THE GULF OF ISKENDERUN

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ABSTRACT

The concentrations of total mercury and tin in the sediment samples collected from İskenderun bay were determined by utilizing atomic absorption spectrophotometer. Mercury concentration of the samples was determined by cold vapor, and tin concentration by hydride generation techniques. The highest mercury concentrations were measured infront of İSDEMİR (Iron and stell complex) with a value of 550 µg/g (dry weight). The mercury concentrations were found to decrease with distance from the shore. Sediment samples were analysed for their acid extractable tin content and the highest value was obtained infront of İSDEMİR with an average of 1.03 µg/g (dry weight). The gradual decrease of tin concentrations in sediment samples with the distance from the shore was relatively much less than mercury concentrations. Sea water and biota samples obtained from the same region were also analyzed for their mercury and tin content.

INTRODUCTION

The naturally occuring toxic elements and compounds do not cause serious public health problems. Because under natural conditions their distribution is relatively constant, and regulated by natural biological actions which effect their degradation and synthesis. The continuing and immense variety of industrial activities cause disturbances of the natural balances and release of toxic elements and compounds in to the marine environment. Microorganisms in the marine environment can produce methylated forms of some metals among which Hg and Sn are very toxic 1,2. The biomethylation of toxic substances in the environment has a vital impertance from the public health stand point 3.

In this work an attempt was done to give chemical and biological distribution of mercury and tin in the North Levantine Basin of the Mediterranean Sea. In addition chemical speciation of tin was also studied.

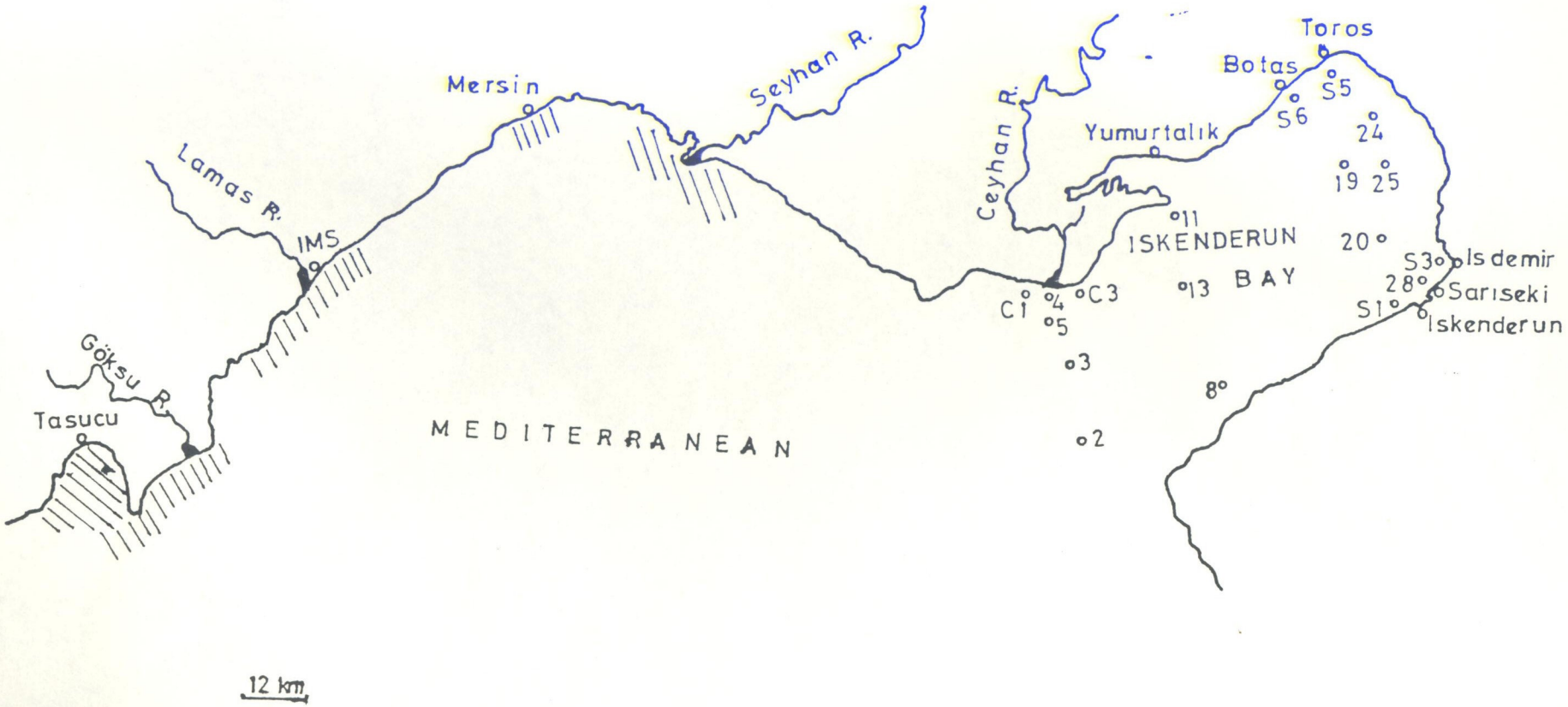
MATERIAL AND METHODS

Sampling: Sediment samples were collected by means of a Van-Veen type grab sampler which collects about top 10 cm. The samples were transferred into acid cleaned polyethylene bags and sealed after expelling the air. The samples were stored in a deep-freezer at -30^{o}C until the analysis time.

Sea water and discharge (effluent) samples were collected in plastic containers. Preservation of samples for mercury analysis was done by the addition of 10 ml of 5·% $KMnO_4$ and 10 ml of concentrated H_2SO_4 per liter. Samples for tin analysis preserved by addition of 1 ml concentrated HCl per liter and kept in refrigerator until the analysis time.

Fish samples were collected by deep trawling. Age of fish was determined by examination of otholiths and the results were supported by length distribution data 4, preservation of samples was done according to the procedure recommended in FAO Technical paper 5.

Sample preparation and analysis for total mercury was as follows: After the addition of 5 ml concentrated HNO_3 and 15 ml of 5% $K_2S_2O_8$ per liter of water sample, the samples were heated on water bath for 7-8 hours at 50-60^{o}C (this is necessary to completely decompose organomercurials). Then the samples were cooled down to room temperature, the permanganate enrichment technique was



SAMPLING STATIONS

used to concentrate mercury from large volumes of water samples 7. Concentrated samples were analyzed by cold-Vapor technique with Atomic Absorption Spectrophotometer (Variann Techton Mocel AA.6).

The acid extractable tin concentration in sediments were determined by following the procedure given by Seidel 8 and Tuğrul 9, and the methylated tin species were determined as described by Yemenicioğlu et.al., (This issue) by employing hydride-generation technique with an Atomic Absorption Spectrophotometer (Varian Model AA6.)

The organisms and water samples were analyzed for their inorganic and methyltins by using same procedures described by Yemenicioğlu et.al. (this issue).

RESULTS AND DISCUSSION

Sources: The results obtained from the analysis of effluent water samples are summarized in Table 1. During the course of analysis samples obtained from the same effluent were filtered and analyzed for their mercury content in the suspended loads (TSS). As can bee seen from table 1 most of the mercury measured in effluents is associated with the particulate materials. The mercury content of the river waters analyzed ranges between 17.8 and 38 ng/l, Lamas River having the lowest value and Ceyhan River highest. The mercury concentrations in the studied domestic and industrial effluent samples are well above those measured in the riverine samples. In some industrial and city sewage samples the mercury measured in suspended material is higher then the total mercury concentrations of the same effluent. This could be due to the high organic matterial content of these discharges which masks the Hg vapour or less possibly due to contamination during the filtration,

In some effluent and river water samples tin concentrations were also measured. As expected, inorganic tin concentrations in the effluent samples is much higher then the inorganic tin content of river water samples. Both in riverine and effluent samples the methyltin concentrations were below the detection limits of the method used.

Sea Water: The concentrations of total mercury and tin in sea water samples are given in Table 2. The total mercury associated with suspended sediments also measured in samples obtained from the same locations with sea water samples. The average total mercury concentration in sea water was 9.5 ng/l, and most of the mercury measured in sea water was found to be associated

with suspended sediment (70 to 100% excluding Seyhan River delta and Tasucu Bay). The findings of Tunçel et al. in sea water from the same locations 10 matches with our results where they found 75-80% of the mercury in sea water to be associated with the suspended sediments.

The average inorganic tin concentration in sea water samples excluding Iskenderun Bay was 34.2 ng/l. Tin concentration in Iskenderun Bay is 10 times higher then the values obtained from the other locations. This high value of tin is most probably a result of industrial input (see Table 1) and extensive shiping and boating activities in the bay. On the average the total organic tin composes about 50% of inorganic tin. An exception to this is Iskenderun Bay and Lamas River delta. Although the inorganic tin in Iskenderun Bay is the highest, the total organic tin rank at second. At Seyhan River estuary the inorganic tin is higher then other estuaries and organic tin concentrations is highest.

Organisms: The mercury and tin content of two species of MULLIDE family, namely U.moluecensis and M.barbatus were determined. The results are complied in Table 3. In general both mercury and tin concentrations of these two species increases by age. This is a reflection of the accumultion of mercury and up to some extent tin very efficiently by these species. Thus these two species of MULLIDE family can be used for the monitoring of the mercury pollution in the marine environment. Another interesting result is that; like mercury, U.moluccensis is able to accumulate larger amonut of tin then does M.barbatus. The mercury to tin ratio revels the fact that U.moluccensis accumulates mercury much more efficiently then tin, and M.barbatus concentrate larger amounts of tin then mercury. The total mercury data reported from Israili coast 11 and Turkish coast (this work) are in the same order for U.moluccensis.

Table 4 summarizes the methylmercury and total methylated tin concentrations in fish samples. All of the measured mercury in M.barbatus is in the form of methylmercury, while organic tin percent is about 52%. On the other hand in U.moluccensis methylmercury percentage is 60% and organic tin percentage is only 18.

Sediments: The average mercury and tin concentrations in sediment samples are given in Table 5. The highest mercury concentrations were measured in sediments obtained from Mersin region. This high mercury concentration may be a result of extensive shipping activity in the overlaying waters and discharge of city sewage. Samples obtained from Seyhan River delta also contain relatively high mercury concentrations. The main source of mercury in this region is the use of mercurials for agricultural purposes which eventually enters into the sea. The highes

acid extractable tin were measured in the samples obtained from Iskenderun bay. The sources of tin in this region is extensive shipping and boating activities in the bay since organotin compounds are used in antifauling paints and most important is the industrial discharges directly into the sea (tin and mercury levels in some of these industrial discharges is given in Table 1). The concentrations of both mercury and tin in sediment samples decreases with distance from the shore, and the decrease of tin concentrations is much less then mercury. This is an expected trend since both in effluents and in sea water mercury is mostly associated with suspended loads and they precipitate rapidly in the shallow waters.

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Table 1: Total Mercury and Inorganic tin Concentrations of Some Effluents in N.Levantine (ng/l)

Sampling station*	Total Mercury in water	Total mercury associated with TSS	Inorganic tin	%Hg associa with TSS
Iskenderun sewage (8)	37.6±25.5	27.6±22.2	-	73
Isdemir (Iron and stell Complex)				
Discharge I (8)	73.7±63.7	63.6±46.3	15	86
" II (8)	49.7±62.6	29.4±21	16	60
" III (8)	-	-	1115	-
Sarı Seki fertilizer and phosphoric acid complex				
Discharge (8)	261.7±228.2	158.8±161.6	240	60
Toros fertilizer plant				
Discharge I (acidic) (8)	36.7±35.1	208±36.9	-	100
" II (basic) (8)	84 ± 60	77±70.4	65	91
Ceyhan River (8)	38±27.4	40.2±43	-	100
Seyhan River (8)	23.3±25.6	14±12.5	-	60
Tarsus River (8)	22.3±21.3	18.8±9.7	-	84
Mersin city sewage (24)	77.9±11.6	158.2±251.7	-	100
Lamas River (8)	17.8±22.6	15.4±15.9	4.3	86
Göksu River (8)	26.2±17	31±18.1	-	100

*: Numbers in paranthesis indicates the number of samples analyzed -: Not analyzed ±: values indicate RSD

Table 2: Total Mercury and Tin Concentrations in the sea-water (ng/l)

Sampling location	Total Hg	Inorganic Sn.	Total Hg Associated with TSS (ng/l)	%Hg Ass. with TSS	Total org.Sn	%org. tin
İskenderun Bay	7.5	319	7.5	100	25.3	8
Seyhan River delta	7.5	49.7	3.5	31	27.3	55
Mersin Region	2.5	-	6.1	100	-	-
Lamas River delta (IMS Limonlu)	3.9	13.7	2.8	72	21.1	150
Göksu river Delta	13.5	30.8	11.2	83	14.3	46
Taşucu Bay	2.6	42.7	1.2	45	22.0	51

-: Not analyzed

Table 3: Total Mercury and tin Concentrations in Fish (ng/g wet wt)

Organism and Sampling area (a)	Age Group	Total Hg	Total Sn	No of samples	Hg/Sn Ratio
Upeneus moluccensis					
IMS (Limonlu)	I	63	36	4	1.75
	II	120	65	5	1.85
	III	305	52	4	5.87
İskenderun Bay	I	96	96	3	1.00
	II	348	324	4	1.07
Ceyhan River Estuary	I	200	67	3	2.99
	III	485	208	3	2.33
Mullus barbatus					
İskenderun Bay	II	36	50	4	0.72
	III	70	161	3	0.43
	IV	74	189	1	0.139
Ceyhan River Estuary	II	65	42	2	1.55
	III	73	43	2	1.70

Table 4: Methylmercury and total organic tin in fish (ng/g dry wt)

Organism	Age group	No of samples	Me. Hg^{-}	Org.Sn	%Me Hg^{-}	% Org. Sn
Upeneus moluccensis	II	9	59-10	18-5	60	18
Mullus barbatus	I	15	34- 5	-	98	-
	II	5	82-19	11·6-3	96	52
	IX	5	214-73	-	99	-

Table 5: Total mercury and acid extractable tin concentrations in sediments

Samplin Area*	Total Mercury (ng/g dry wt.)	Acid extractable tin (µg/g dry wt.)
İskenderun Bay (3) (3)	68	1.03
Seyhan River Delta (3)	76	0.76
Mersin (3)	440	-
IMS (Limonlu (10)	38	0.28
Göksu River Delta (12)	56	0.69
Taşucu Bay (2)	34	0.73

* : Number of samples analyzed are given in the paranthesis

-- : Not analyzed