CHEMICAL AND BIOLOGICAL DISTRIBUTION OF MERCURY IN THE NORTH LEVANTINE

by

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1. INTRODUCTION

It is well known that mercury is a cumulative pollutant, and its concentration is progressively enhanced at each trophic level in food chains. Because of its low solubility in seawater, mercury accumulates in sediments. Its transportation to the marine environment is due to industrial discharges and continental weathering, and mercury undergoes many biological and chemical transformations into various forms. Both inorganic and organic forms of mercury can be accumulated directly from seawater by marine organisms.

Several organomercurial compounds, such as phenylmercuric chloride and phenyl mercuric acetate, are used as fungicides on cotton and other plants along the southeast coast of Turkey (GTHB, 1983). These compounds are generally applied during the peak season of rainfall in this region, and mercury is thus transported to the sea. As a result of the application of these fungicides at certain times, seasonal variations in mercury concentrations in some marine organisms have been observed in this area (Tugrul et al., 1980). The work described here is an attempt to determine the chemical and biological distribution of mercury in the North Levantine Basin (Fig. 1). This might contribute to the elucidation of the biogeochemical cycle of mercury in the region.

2. MATERIALS AND METHODS

Samples were collected during 1981 and 1983 from the locations shown in Fig. 1. Sediment samples were collected with a Van Veen type grab sampler. Care was taken not to contaminate the samples. Samples were transferred to precleaned plastic containers and deep-frozen at -20°C until they were analysed. Seawater and effluent samples were collected in plastic containers. Samples were preserved by the addition of 10 ml of 5% $KMnO_4$ and 10 ml of concentrated H_2SO_4 immediately after collection.

Samples of fish and crustacea were collected either by gill nets or by trawling. Age of the fish was determined by examination of otoliths and the results were supported by length distribution data of 1752 individual fish given elsewhere (DAE, 1981). Preservation of the biological samples was done according to the procedure recommended in FAO Technical paper No. 158 (Bernhard, 1976).

Samples of algae (Caulerpa prolifera) were collected by hand. After washing with double-distilled water, they were placed in precleaned glass containers and frozen at -20°C.

Tar-ball samples from the sea surface were collected with a Neuston net, and those from the bottom were collected by hand by divers.

Organomercurial (mainly methylmercury) concentrations in fish, crustacea and algae was determined by following the procedure given by Boveng (1970). Methyl mercury concentrations were determined with a Varian Aerograph Model 2700 gas chromatograph equipped with Ni-63 electron capture detector. The analytical column used was a 6 feet long, 2 mm i.d. coiled glass (Pyrex) column packed with 1.5% OV-17 + 1.95% OV-210 on Varaport 30 (80-100 mesh size).

Sample preparation and analysis for total mercury was as follows:

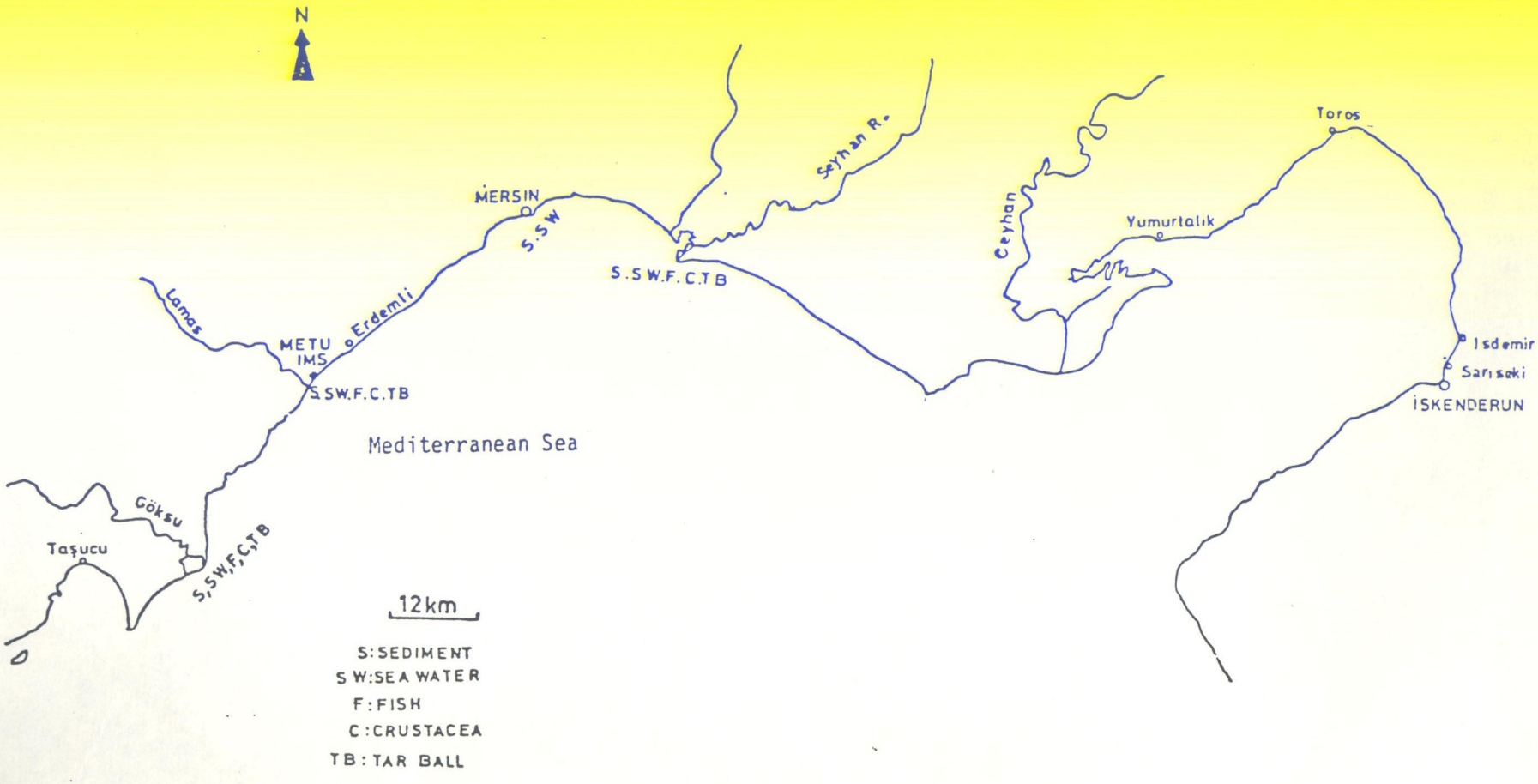

Fig. 1 Sampling Stations

After the addition of 5 ml concentrated HNO_3 and 15 ml of 5% $K_2S_2O_8$ per litre of water sample (sea water and effluent), the samples were heated at 50-60°C on water baths for 7-8 hours to completely decompose organomercurials. After cooling, the permanganate enrichment technique (Topping and Pirie, 1972) was used to concentrate mercury from large volumes of water samples. Concentrated samples were analyzed by using an atomic absorption spectrophotometer (Varian Techtron Model AA-6), employing the cold-vapour generation technique.

3. RESULTS AND DISCUSSION

Sources: The measured average total mercury concentrations in source samples, together with their standard deviations, are given in Table I. The same samples were analyzed for the mercury contents of the suspended solids, and these results are also given in Table I.

As can be seen, some of the sources are the rivers. Average total mercury concentrations in river waters lie between 25 and 59 ng l^{-1}. With the exception of the Lamas river, at least 90% of the mercury is associated with the suspended (particulate) material.

The domestic and industrial discharges contain on average twice the mercury content of the rivers. Possibly due to the high content of organic matter in these discharges, in some cases the mercury concentrations associated with suspended matter appears to be higher than the total content. Such results possibly indicate contamination of the samples during filtering process. Anyway, in order to come to a conclusion for the effects of effluents on the marine environment the fluxes have to be considered.

Sediments: The mercury concentrations measured in sediment samples are given in Table II. From the results given in this table it is clear that the highest concentrations were measured in the samples obtained from Mersin Harbour. The main reason for relatively high mercury concentrations in this region is due to the harbour activities and direct sewage discharge without any pretreatment. The methylmercury level at the sewage outfall (Mersin) was much higher than the natural levels in the marine area of Mersin Harbour, but a decrease in methylmercury concentration was observed with distance from the outlet of the sewage.

The measured total mercury concentrations in the N. Levantine are more or less similar to those from other regions of Mediterranean such as Israeli coasts (Roth and Hornung, 1977), and Tuscany coast (Renzoni et al., 1973).

Seawater: The measured total mercury concentrations in the seawater samples on the average was 13 ng l^{-1} (Table III). Of course these low concentrations were obtained outside Mersin Harbour where the mercury concentrations were 30 ng l^{-1} which is more than twice that of the other locations.

In this work an attempt was made to determine mercury in seawater after filtering it through 0.45 um filter paper. It was found that the concentrations were below the detection limits. This observation matches with the results reported by Tuncel et al. (1980) from the same region, where they found 75 to 80% of the mercury in sea water associated with the particulate material.

When the total mercury concentrations of N. Levantine are compared with the ones reported from Western Mediterranean those by Fukai and Huynh-Ngoc (1976) the values of N. Levantine are half those of the Western Mediterranean. In order to be able to speculate on the reasons for this behaviour the physicochemical properties of the water masses have to be studied extensively.

Tar balls: Tar balls are the derivatives and/or degradation products of crude oil, fuel oil, etc. We expected them to concentrate mercury, especially organomercurials, since before forming the tar lumps these substances are good solvents for these compounds. But the analysis of 16 tar ball samples showed that they do not contain mercury. In contrast to mercury, lead concentrations in tar balls were relatively high, i.e. between 5 to 303 $\mu g\ g^{-1}$. It was also observed that the lead present was in the

Table I. Total mercury concentrations of some effluents in N. Levantine
(Concentrations in ng l^{-1})

Effluent	No of samples analyzed	Total mercury a) ~~associated with TS b)~~	Total mercury a), associated with TS b)	% Mercury associated with TS b)
Iskenderun Sewage	5	45 ± 25	46 ± 25	100
Isdemir Iron and Steel				
Complex Discharge I	5	121 ± 97	84 ± 38	69
" " II	5	50 ± 182	44 ± 44	88
Sariseki Fertilizer Plant Discharge	5	135 ± 182	202 ± 149	100
Toros Fertilizer Plant Discharge (Acidic)	5	54 ± 31	68 ± 44	100
Toros Fertilizer Plant Discharge (Basic)	5	187 ± 269	106 ± 53	57
Ceyhan River	5	59 ± 33	54 ± 32	92
Seyhan River	5	49 ± 43	45 ± 39	92
Tarsus River	5	60 ± 37	56 ± 45	93
Mersin City Sewage	5	129 ± 162	131 ± 146	100
Lamas River	5	38 ± 46	19 ± 14	50
Goksu River	5	25 ± 14	32 ± 20	100

a) ± values show the standard deviations
b) TS stands for Total Suspended Material

Table II. Mercury concentrations in sediments

Sampling location	No of analyses (a)	Wet Wt.	% E.O.M. (b)	Total Mercury (ng g^{-1})
Seyhan R delta	3	1.56	0.4	76
Mersin Harbour	7	3.75	2.7	480 ± 40
Mersin	6	1.90	2.4	440 ± 30
IMS (Limonlu)	10	--	1.4	28 ± 6
IMS (Limonlu Harbour)	3	1.61	--	49
Goksu R delta	12	1.46	0.8	56 ± 8

a) No of analysis for total mercury
b) % Extractable organic material which can be extracted with methanol + benzene (50 % by vol.)

Table III. Total mercury concentrations in the sea water

Sampling location	No of samples analyzed	Total Hg (a) (ng/l)
Iskenderun Bay	10	12 ± 7
Seyhan R. delta	5	13 ± 3
Mersin Harbour	8	30 ± 9
IMS (Limonlu)	10	12 ± 2
Goksu R. delta	7	13 ± 2

a) ± Values are the standard deviations.

Table IV. Mercury concentrations in Caulerpa prolifera

Sampling mercury (a) Location (ng/g)	No of Analyses	Wet Wt. / Dry Wt.	Total Hg (a) (ng/g)	Methyl mercury (a) ng/g
Göksu R. delta	4	10.5	64 ± 18	5 ± 6
IMS (Limonlu)	8	9.0	70 ± 12	9 ± 7
Seyhan R. delta	5	11.4	67 ± 21	6 ± 5

a) The results are given on dry weight basis and ± values are the standard deviations

fraction which is insoluble in hexane, benzene and methanol but soluble in pyridine. The lead present in pyridine gave reactions with dithiazone.

Beijer and Jernelöv (1979) showed that mercury undergoes transalkylation reactions with alkyllead compounds. Most probably this mechanism is valid for the tar balls too, where a transalkylation takes place and volatile alkylmercury compounds form.

Organisms:

(i) Caulerpa prolifera: in this work the macro-alga Caulerpa prolifera was analyzed for total mercury and the measured concentrations are given in Table IV. On the average the total mercury concentrations were 67 ng g^{-1} (dry weight). The methylmercury formed about 8 to 13% of the total mercury observed in algae. Stary et al. (1980) has shown that in algae inorganic mercury accumulates much more rapidly than organic, and algae do not convert inorganic mercury into the organic form. The same authors have also shown that methyl and phenylmercury is converted into the inorganic form, by the action of algae. Most probably this is the case for Caulerpa prolifera too.

(ii) Crustacea and fish: from the results given in Table V, it is seen that mercury concentrations measured in Portunus pelagicus show a great variation.

The studies on Mugil auratus have shown that mercury concentrations in this organism is independent of age, size and weight. A carnivore species Saurida undosquamis has the capability of regulating mercury concentrations very efficiently. Thus both M. auratus and S. undosquamis cannot be used for montitoring of mercury in the marine environment. On the other hand Mullus barbatus and Upeneus moluccensis which belong to the Mullidae family are good indicators of mercury pollution in marine environment since both of them accumulate mercury efficiently and this is very well reflected in age groups too (Table V).

Table VI shows the methylmercury concentrations and percentages of the methylmercury in the organisms. With the exception of U. moluccensis almost all of the measured total mercury is in the form of methylmercury. In U. moluccensis methylmercury percentage varies between 56 and 100, and it is independent of total mercury, i.e. in two species where total mercury was 220 ng g^{-1}, all of the mercury was methylmercury while in another two species containing 715 ng g^{-1} and 114 ng g^{-1} total mercury the measured methylmercury percentage was only 56.

Different organs of two different species were analyzed and the results are given in Table VII. During the growth period Penaeus kerathurus changes its carapace frequently (DAE, 1981). Although the total mercury concentrations measured in carapace are very low, still it gives an indication of an excretion route of mercury. Via carapace, mercury from a living organism is excreted and settled to sediment. This mechanism is more efficient when the species is juvenile since moulting of carapace is more frequent.

The mercury concentrations measured in P. Pelagicus in this work are close to the ones reported from Oslofjord (Andersen and Neelaktan, 1974). The mercury concentrations in shrimp (not P. kerathurus) samples from Pacific and Atlantic showed two times higher mercury concentrations than those from N. Levantine (Klein and Goldberg, 1970; Bertine and Goldberg, 1972). The values reported for M. auratus from Israeli coast (Yannai and Sachs, 1978) are more or less the same as the ones given in Table V.

The total mercury data reported by Hornung et al. (1980) for S. undosquamis and U. moluccensis shows that the total mercury levels measured in both places (Turkish coast and Israeli coast) are the same.

Table V. Total mercury concentrations in the muscle tissue of fish and crustacea

Organism	Age Group	No of Samples	Total Mercury (ng g^{-1}) Wet Wt. Min.	Max.	Average	Total Mercury (ng g^{-1} Dry Wt.)
Penaeus Kerathurus	--	35	10	133	38 ± 25	152 ± 100
Portunus pelagicus	--	20	32	269	107 ± 67	470 ± 277
Mugil auratus	II	2	19	22	21	80
	III	4	23	54	38	160
	IV	5	16	44	22 ± 17	93 ± 68
	V	3	12	27	20	84
	VI	3	17	20	19	80
	VII	4	9	40	22	90
	VIII	4	19	27	22	94
	IX	4	13	25	19	77
	X	2	17	22	20	80
	XI	1	-	-	29	116
Mullus barbatus	0	6	17	79	38 ± 24	170 ± 111
	I	70	14	169	48 ± 23	224 ± 108
	II	8	30	134	73 ± 40	314 ± 176
	III	7	34	369	129 ±120	496 ± 305
	IV	7	20	294	175 ±102	559 ± 354
Upeneus moluccensis	0	22	14	99	27 ± 19	90 ± 20
	I	50	30	150	64 ± 30	256 ± 106
	II	28	56	371	122 ± 41	550 ± 300
	III	9	149	424	262 ± 87	1344 ± 290
	IV	5	290	746	499 ±192	2503 ±1209
Saurida undosquamis	0	24	10	133	35 ± 15	159 ± 72
	I	59	21	154	50 ± 26	200 ± 96
	II	57	25	165	58 ± 28	233 ± 120
	III	13	36	129	81 ± 30	348 ± 150

Table VI. Methylmercury concentrations in fish and crustacea

Organism	Age group	No of samples	Methylmercury (ng g^{-1}) Min.	Max.	Mean	% Methylmercury
Penaeus kerathurus	--	11	51	131	91 ± 40	99
Portunus pelagicus	--	7	94	290	170 ± 80	99
Mugil	VII	4	11	38	21	95
	VIII	4	16	30	20	90
	XI	1	--	--	30	100
Mullus	I	24	28	37	34 ± 7	98
	II	5	46	102	82 ±19	96
	IX	5	132	305	214 ±73	99
Upuneus moluccensis	II	9	48	72	59 ± 10	60
Saurida	I	3	19	28	25	100
	II	4	30	55	43	98
	II	3	66	152	91	100

a) The given figures are the arithmetic mean of the measurements and ± is the standard deviation.

Table VII. Mercury Concentrations in different tissues of Penaeus kerathurus and Upeneus moluccensis (ng g^{-1})

Organism	Length or Age Group	Tissue Analyzed	Total Mercury (a)
Penaeus kerathurus	120 mm	Muscle	60
		Carapace	9
	150 mm	Muscle	92
		Carapace	6
	180 mm	Muscle	112
		Carapace	4
	200 mm	Muscle	100
		Carapace	3
Upeneus	160 mm	Whole body	1851
	III	Gonads	168
		Fin and Bones	38
		Bones	118

a) For Penaeus kerathurus the results are given as dry wt. and for Upeneus moluccensis wet weight.

4. CONCLUSIONS

In U. moluccensis, a species of the Mullidae family, total mercury content increases almost exponentially with the increasing age group. This trend is not that obvious for M. barbatus which is another member of the same family. Ninety-eight per cent of the total mercury measured in M. barbatus was found to be in the form of methylmercury, while in U. moluccensis on the average only 60% was methylmercury. The biological methylation plus transmethylation reactions of mercury compounds provides an explanation for the presence of methylmercury in fish, even though the mercury in the studied sources are either in inorganic or other organic forms.

In order to complete the biogeochemical cycle of mercury and/or toxic elements in the bioshphere more refined and extensive physico-chemical and biochemical information is necessary.

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