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Mercury in Water, Organisms and Sediments from a Section of the Turkish Mediterranean Coast

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Samples of water, marine organisms and sediment collected along the Turkish Mediterranean coast in the vicinity of Mersin were analysed for total mercury. The levels of mercury found in the samples from this area are generally low in comparison with the levels found in other regions of the Mediterranean.

The harmful effects of toxic chemicals to the marine environment, particularly in coastal areas, are well known. A geographical area of particular concern is the Mediterranean Sea. This essentially closed basin is bordered by many countries, some of which are highly developed industrially. There is a large input of polutants into the Mediterranean from land-based sources (Helmer, 1977). Until recently no attempts were made to control the input of toxic chemicals to the sea and as a result severe pollution problems, especially in localized areas, have been observed (Osterberg & Nickes, 1977).

In the wake of the world-wide concern over the harmful environmental effects of mercury, several investigations of the levels of mercury in the Mediterranean marine environment have been carried out in recent years (Thibaud, 1971; Cuacciolo *et al.*, 1972; Robertson *et al.*, 1972; Renzoni *et al.*, 1973; Selli *et al.*, 1973; Roth & Hornung, 1975; Fukai & Huynh-Ngoc, 1976; Grimanis *et al.*, 1976). These studies – primarily in the western regions of the Mediterranean – have demonstrated that although in general the levels of mercury are similar to those found in other regions of the world, elevated levels are seen in certain coastal areas. Information about the eastern regions of the Mediterranean is quite limited.

The study reported here was carried out to make a survey of the levels of mercury in the marine environment in an area of the eastern Mediterranean along the Turkish coast comprising the Mersin harbour area and the region to the west of Mersin.

Materials and Methods

Water

Water samples were collected at three locations, as shown in Fig. 1. At Ovacik samples were collected at five stations; at Limonlu at three stations; and at Mersin at nine stations, both inside and outside the harbour. The samples were collected over 1 year at approximately 2-monthly intervals at Ovacik; Limonlu and Mersin samples were collected only twice.

The samples were taken with 1.5 l. Nansen or 2.5 l. Niskin plastic water samplers. Immediately after collection they were transferred to 1 l. polyethylene bottles. A preservative solution consisting of 10 ml 2% $KMnO_4$ and 10 ml concentrated H_2SO_4 was added to the samples within 3 h of collection.

Due to the extremely low levels of mercury in unpolluted seawater, a concentration step was needed before analysis. The permanganate enrichment technique (Topping & Pirie, 1972; Harsanyi *et al.*, 1973) was used. Samples concentrated 80 times were analysed by atomic absorption spectrometry using a cold-vapour apparatus of our own design.

To study the loss of mercury from seawater samples during storage, 25 1-l. seawater samples were collected from a selected location. The samples were divided into five

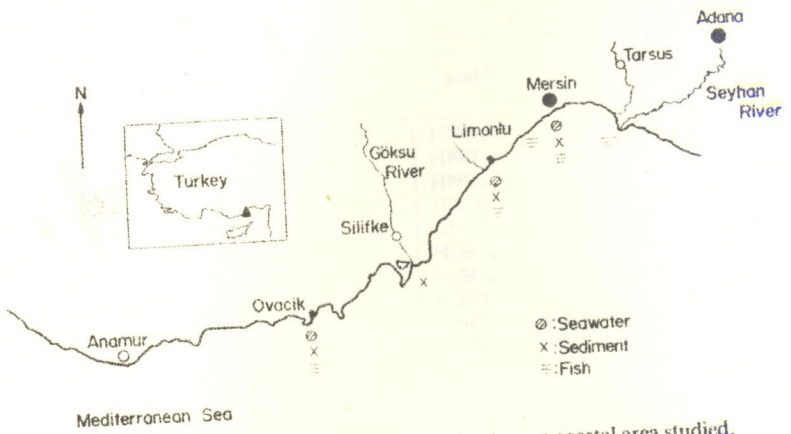

Fig. 1 Sampling locations in eastern Mediterranean coastal area studied.

groups, each group containing five samples. To each sample in the first group were added 50 ml HNO_3; to each in the second group, 50 ml HNO_3 + 10 ml 2% $K_2Cr_2O_7$; to each in the third group 10 ml H_2SO_4 + 10 ml 2% $KMnO_4$; to the fourth group samples no additions were made. The remaining five samples were analysed within 24 h. The four groups of treated samples were stored for 6 months and then analysed.

Organisms

Seven different species of fish and one species of shrimp were analysed. The organisms were collected mainly near the coast between Mersin and Limonlu; a few samples from the Seyhan Delta were also analysed. Specimens were collected both by deep trawl and with gill nets. After collection the samples were taken in an ice box to the laboratory where they were positively identified and the lengths and weights recorded. Each specimen was stored in a plastic bag at −40°C until analysis.

For analysis 0.5–1 g of muscle tissue was carefully removed from the dorsal area (or abdomen in the case of the shrimp) and digested with 3 ml HNO_3 at 140°C for 3 h in Teflon-lined high-pressure decomposition vessels. After dilution the digested samples were analysed by cold-vapour atomic absorption spectrometry.

Sediment

Sediment samples were collected at four locations, as shown in Fig. 1, with two stations at each location. All samples were collected with a Van Veen type grab sampler. After collection the samples were placed in plastic bags and stored wet at −40°C.

For analysis the frozen sediment was thawed and 5–7 portions in weights of 0.05–0.3 g (wet) were selected from each sample. Each portion was digested with 2 ml HNO_3 in high-pressure decomposition vessels at 140°C for 9 h. After dilution the digested samples were analysed by cold-vapour AAS. All samples were analysed wet to avoid any mercury losses during drying. To express analytical results on a dry-weight basis. the samples were dried at 110°C for 24 h and the percentage of water calculated.

To study the effect of acid mixture on the extraction of mercury from marine sediments, a sample was dried and 0.05 g portions digested with different acids and acid mixtures at 150°C for 5 h. The diluted samples were then analysed for their mercury content. To determine the dependence of extraction efficiency on digestion time, 0.05 g portions of the same sediment sample were digested with 2 ml HNO_3 for periods of time from 1 to 9 h.

Results and Discussion

Water

The average concentrations of mercury in the water samples analysed are presented in Table 1. The values in this table from Ovacik are the averages of the samples taken during the last three sampling periods because the initial samples collected were used to develop the procedure as a routine method. The mercury concentrations given for each station at Limonlu and Mersin are the averages of two sample collections. The number of replicate analyses at each station does not allow computation of standard errors, but ten replicate analyses of a single water sample showed a relative standard deviation of about 10%, covering the entire procedure from enrichment to analysis steps.

The data in Table 1 indicate that the levels of mercury in water samples from the region of the Mediterranean studied are low. The samples from Mersin harbour show mercury concentrations 2–3 times higher than the samples collected at Ovacik and Limonlu, although still comparable with the levels found in other regions of the Mediterranean (UNEP, 1977). No differences in mercury levels between surface and bottom samples was observed.

Due to the low concentrations of mercury in unpolluted seawater, a problem of storage arises. If the samples must be kept for several days, either on board ship or in the laboratory, before analysis, it is necessary to ensure that no loss of mercury occurs during this period. The mechanism of mercury loss, although not fully understood, is probably due to both adsorption on the walls of the container and volatilization (Rosain & Wai, 1973). Many different preservatives have been recommended in the literature among them HNO_3 (Rosain & Wai, 1973), H_2SO_4–$KMnO_4$ mixture (Harsanyi *et al.*, 1973) and HNO_3–$K_2Cr_2O_7$ mixture (Christman & Ingle, 1976).

The ability of various preservatives to prevent loss of mercury from seawater samples was tested. The results given in Table 2 indicate that no solution can preserve samples with 100% efficiency, but the HNO_3–$K_2Cr_2O_7$ appears to be the best, resulting in only a 20% loss in 6 months. This is in good agreement with the work of Christman & Ingle (1976) who found a 100% retention with the same preservative over a period of 6 days.

TABLE 1

Mercury in seawater at three locations along the Turkish Mediterranean coast.

Location	Station	Depth (m)	Mercury concentration (ng $l.^{-1}$)
Ovacik	1	0	9
	1	3	8
	2	0	8
	2	5	8
	3	0	7
	3	50	8
	4	0	8
	4	5	10
	5	0	7
	5	20	8
Limonlu	6	0	10
	6	20	12
	7	0	10
	7	20	11
	8	0	11
Mersin harbour	9	20	24
	10	10	27
	11	20	23
	12	10	23
	13	20	23
	14	10	40
	15	5	21
	16	5	24
	17	10	19

TABLE 2

Loss of mercury from seawater samples during storage.*

Preservative	Mercury concentrations (ng $l.^{-1}$)		% mercury lost
	Initial	Final	
None	10	1	90
HNO_3	10	3	70
H_2SO_4:$KMnO_4$	10	5	50
HNO_3:$K_2Cr_2O_7$	10	8	20

*All samples were stored for 6 months.

TABLE 3

Total mercury ($\mu g\ kg^{-1}$ wet wt) in some marine organisms.

Species	Length (mm)	No. of specimens	Range	Mean
Mullus barbatus	98–192	9	20–80	40
Mullus surmuletus	150–175	5	40–80	70
Boops salpa	187–204	4	2–4	3
Mugil auratus	241–295	5	10–30	20
Upeneus moluccensis	135–148	5	110–130	120
Sardina pilchardus	157–165	5	40–60	50
Seriola dumerilii	181	1	–	100
Peneus kerathurus	168–170	6	10–40	20

Organisms

Total mercury was determined in several different marine organisms, some of economic importance in the area studied. As seen from the data in Table 3, the levels of mercury in the organisms studied were low in all cases. The highest concentrations of mercury were found in a species of fish, *Upeneus moluccensis*. The mercury levels in marine organisms in the area studied are considerably lower than those reported along the Israel coast (Roth & Hornung, 1975).

Sediment

To ensure complete extraction of mercury from the sediment samples, several different acids and acid mixtures

TABLE 4

Extraction of mercury from a marine sediment.*

ml : acid	No. of analyses	Mercury found ($\mu g\ g^{-1}$ dry wt) Mean	Std deviation	% relative std. dev.
1:HNO_3	11	0.65	0.05	7.7
2:HNO_3	5	0.60	0.04	6.7
3:HNO_3	5	0.56	0.02	3.6
4:HNO_3	5	0.54	0.02	3.7
5:HNO_3	5	0.56	0.02	3.6
1:H_2SO_4	4	0.16	– †	–
3:H_2SO_4	4	0.38	– †	–
5:H_2SO_4	5	0.45	0.03	6.7
1:HNO_3:0.5 $HClO_4$	6	0.50	0.03	6.0
1:HNO_3:1 $HClO_4$	6	0.59	0.04	6.8
1:HNO_3:1 HF	7	0.49	0.06	12.2
1:HNO_3:3 HF	7	0.54	0.12	22.2
2:HNO_3:H_2SO_4	16	n.d.	–	–

*0.05 g dry sediment was used in all cases.
† The number of analyses was not sufficient to calculate the standard deviation.
n.d. – none detected.

TABLE 5

Effect of digestion period on extraction of mercury from sediments.*

Time (h)	No. of analyses	Mercury found ($\mu g\ g^{-1}$ dry wt) Mean	Std dev.	% relative std dev.
1	8	0.62	0.07	11.3
3	6	0.60	0.04	6.7
5	7	0.54	0.05	9.3
7	7	0.58	0.03	5.2
9	7	0.59	0.02	3.4

*0.05 g dry sediment was digested with 2 ml HNO_3.

TABLE 6

Mercury in sediments taken from four locations along the Turkish Mediterranean coast.

Sampling location	N*	Mercury concentration ($\mu g\ g^{-1}$) Mean	Std deviation
Ovacik	5	0.019	0.006
	5	0.036	0.005
Goksu delta	6	0.037	0.004
	5	0.058	0.008
Limonlu	6	0.022	0.002
	6	0.034	0.004
Mersin harbour	6	0.44	0.03
	7	0.48	0.04

*N refers to the number of subsamples analysed from each grab.

were evaluated for their efficiency in extracting mercury from a selected sediment sample. The results summarized in Table 4 indicate that HNO_3 alone is quite sufficient for extracting mercury from marine sediments of this type and leads to the best precision in replicate analysis of a single sample. A surprising result was the discovery of the absence of any mercury absorption for the sample digested with HNO_3–H_2SO_4 mixture. In 16 replicate analyses with this commonly used mixture no mercury was found. A large non-specific background absorption was observed, however, during the analysis which might, if not corrected for, be erroneously taken as mercury absorption.

In addition to the acid used, the length of the digestion period may affect the amount of mercury extracted. From the results given in Table 5 it is seen that an increase in the digestion time does not increase the amount of mercury found, but it improves the precision of replicate analyses of a sample.

TABLE 7

Comparison of Hg in area studied with other regions of Mediterranean.

	Water (ng l^{-1})	Organisms ($\mu g\ kg^{-1}$ FW)		Sediment ($\mu g\ kg^{-1}$ DW)	Reference
		Family Mullidae	Family Clupeidae		
Turkish coast (this work)	15 (8–25)	40 (20–80)	50 (40–60)	140 (28–460)	–
Israel Coast	60 (10–180)	310 (50–560)	76 (30–120)	130 (10–570)	Roth & Hornung, 1975
St Gibraltar	110 (60–110)	–	–	–	Robertson *et al.*, 1972
Off Cyprus	120 (90–140)	–	–	–	Robertson *et al.*, 1972
Tuscany coast	(< 20–200)	–	–	(40–1300)	Renzoni *et al.*, 1973
S. W. Med.	24 (16–30)	-	–	–	Fukai & Nyunh-Ngoc, 1976
W. Ligurian Sea	21 (17–30)	–	–	–	Fukai & Hyunh-Ngoc, 1976
Alboran Sea	–	–	–	260	Robertson *et al.*, 1972
Tyrrhenian Sea	25 (20–30)	–	–	(50–1570)	Fukai & Hyund-Ngoc, 1976 (water) Selli *et al.*, 1973 (sediment)
Off Pescara	–	100 (55–143)	–	–	Caracciolo *et al.*, 1972
Saronikos Gulf	–	–	–	500	Grimanis *et al.*, 1976
Piraeus Harbor	–	–	–	10 000	Grimanis *et al.*, 1976
Off Monte Carlo	–	–	–	300	Robertson *et al.*, 1972
Off Marseilles	–	–	205	–	Thibaud, 1971
Off Sète	–	–	235	–	Thibaud, 1971

The analytical results for the sediments taken from four locations are presented in Table 6. The mercury levels in all samples, with the exception of those from Mersin harbour, are low. The Mersin harbour sediments show elevated mercury levels, in comparison with nearby regions, possibly as a result of the extensive shipping activities.

Conclusions

The average results obtained in this work are presented in Table 7 together with values reported from other regions of the Mediterranean. The low concentrations of mercury found in general in all samples from the eastern Mediterranean area studied support the view that as yet this region is relatively unpolluted. However, the higher concentration of mercury in the water and sediment samples from Mersin harbour, compared to nearby areas, demonstrate the effects of man's activities. Considering the Mediterranean as a whole, the mercury levels in this region are lower than other regions of the eastern Mediterranean; and in comparison with the western regions which have been most extensively studied, the difference is more pronounced. It is believed that the data presented provide some information as to the natural background levels of mercury in this particular region, and perhaps the Mediterranean as a whole.

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