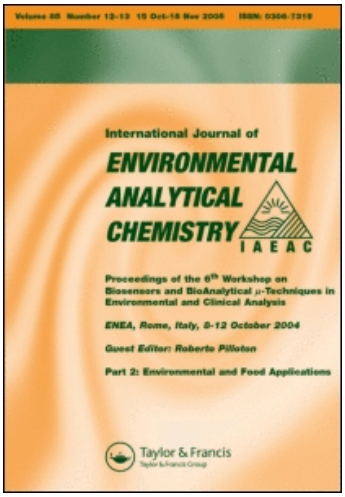

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Heavy Metal Concentrations in Water, Sediment and Fish from Izmit Bay, Turkey

K. Taymaz[ab]; V. Yigit[a]; H. Özbal[ac]; A. Ceritoglu[a]; N. Müftügil[a]
[a] Department of Nutrition and Food Technology, Marmara Research Institute, Gebze, Turkey [b] Revenue Canada Customs and Excise, Laboratory and Scientific Services, Ottawa, Canada [c] Chemistry Department, Bogaziçi University, Istanbul, Turkey

To cite this Article Taymaz, K. , Yigit, V. , Özbal, H. , Ceritoglu, A. and Müftügil, N.(1984) 'Heavy Metal Concentrations in Water, Sediment and Fish from Izmit Bay, Turkey', International Journal of Environmental Analytical Chemistry, 16: 4, 253 — 265
To link to this Article: DOI: 10.1080/03067318408076956
URL: http://dx.doi.org/10.1080/03067318408076956

Intern. J. Environ. Anal. Chem., 1984, Vol. 16, pp. 253–265
0306-7319/84/1604-0253 $18.50/0

Printed in Great Britain

Heavy Metal Concentrations in Water, Sediment and Fish from Izmit Bay, Turkey

K. TAYMAZ,† V. YIGIT, H. ÖZBAL,‡ A. CERITOGLU and N. MÜFTÜGIL

Marmara Research Institute, Department of Nutrition and Food Technology Gebze, Turkey

(*Received March 29, 1983; in final form August 4, 1983*)

Mercury, cadmium and lead levels in water, sediment and fish samples from Izmit Bay, Turkey have been determined. Sampling and analysis methods are described. Variations of heavy metal concentrations from different sampling stations are discussed. Results indicate that the levels of mercury and cadmium were highest in the vicinity of a chlor-alkali plant while the highest concentration of lead was near a metallic pipe factory. The amounts of heavy metals found in the shoreline sediment samples were similar to those found in fish species from the bay.

KEY WORDS: Heavy metal, metal contamination, metal pollution.

INTRODUCTION

Hundreds of chemicals that are produced by different industries find their way into the environment. Heavy metals such as cadmium, lead and mercury have long been recognized as a serious threat to human health. Recently, there has been a growing interest in their effect on life in the sea. As a result, a number of studies has been done to

†Revenue Canada Customs and Excise, Laboratory and Scientific Services, Ottawa, Canada.

‡Bogaziçi University, Chemistry Department, Bebek, P.O. Box 2 Istanbul, Turkey.

measure heavy metal concentrations in either water, sediment or fish samples with the resultant setting of limits for these metals in water and fish products by many agencies and governments.[1]

However, the relationship between the heavy metal concentrations in water, sediment and fish samples has never been monitored. This work is the first to actually monitor the concentration of these heavy metals in water, sediment and fish samples at the same time.

Izmit Bay, 48 km long and 2–10 km wide, is located on the Eastern shore of the Sea of Marmara in Northwestern Turkey (Figure 1). The Bay was selected as an area where heavy metal concentrations must be determined for the following reasons:

a) Both a large local population and heavy industry result in the excessive input of domestic and industrial waste water.
b) There is a slow circulation of the Bay's waters.
c) There has been a significant deterioration of the quality of the Bay's waters during the past 15–20 years.[2]
d) The pre-industrial custom of heavy fishing in the Bay area still continues.

EXPERIMENTAL

Apparatus

Nansen sampler, polyethylene and glass bottles, Parr digestion bomb 4745 equipped with polytetrafluoro ethylene (PTFE) vials were used. A hydrostatically damped corer was purchased from Hydrobios, Kiel.

The GC was a Varian 2100 equipped with a 2.5% carbowax column (2 m). Conditions were: EC detector 235°C, injector 200°C, column 150°C, carrier gas N_2 150 mL/h. A Varian 1200 Atomic Absorption Spectrophotometer equipped with quartz absorption cell (Cole–Parmer), carbon rod atomizer (Varian CRA 90) and recorder (Varian A-6) was used. CRA conditions for Cd were: 228.8 nm; 0.5 nm slit; 4.7 amp; dry 200°C, 20 s; ash 450°C 15 s; atomize 1500°C 1.5 s; ramp rate 400°C/sec, and for Pb were: 283.3 nm; 0.5 nm slit; 5.0 amp; dry 150°C, 20 s; ash 450°C, 15 s; atomize 1600°C, 2.5 s; ramp rate 350°C/sec.

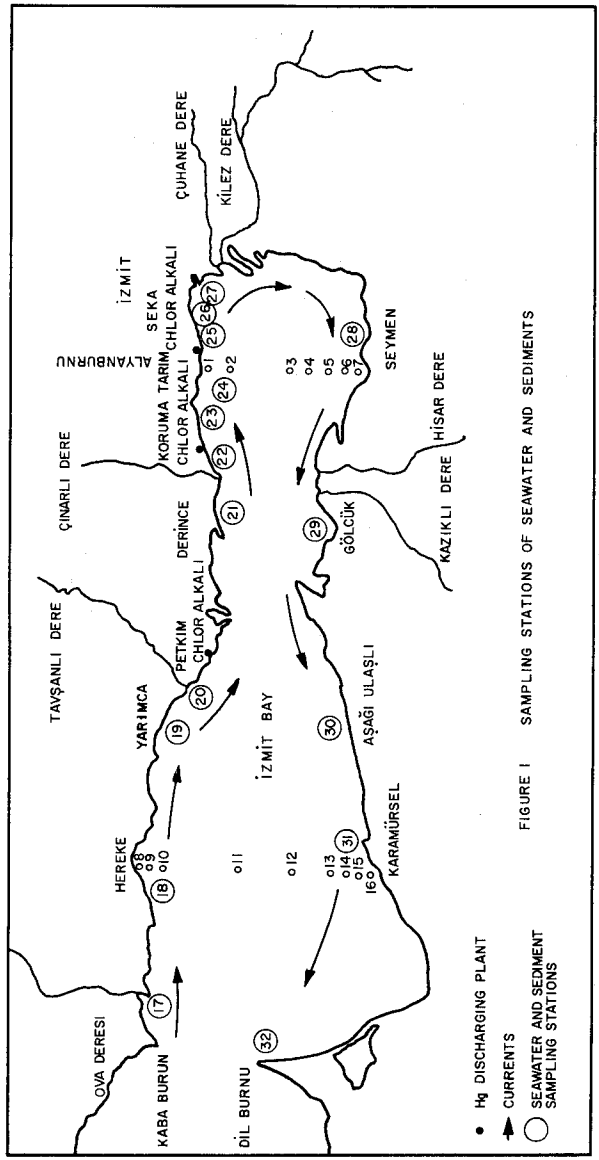

FIGURE 1 SAMPLING STATIONS OF SEAWATER AND SEDIMENTS

Reagents

Standard solutions of the metal ions and cysteine-hydrochloride were purchased from Fisher. Nitric acid (Suprapur), sodium sulfate (proanalysis grade), HC1 and NH_4OH (reagent grade) were purchased from Merck. Freon TF was purchased from Dupont. Ammoniumpyrrolidine-dithiocarbamate (APDC) was from Fluka AG of Switzerland.

SAMPLE COLLECTION

Water

Inshore samples were directly taken into plastic bottles. Deep water samples were collected by a Nansen sampler in plastic bottles, acidified to pH 2 with HNO_3 and stored at $-25°C$.

Sediment

Inshore sediment samples were directly collected in glass bottles. Subsurface sediment samples of the two cross-sections were taken with a hydrostatically damped corer and stored at $-25°C$ in glass containers.

Fish

Cod, anchovy, sand smelt, scad, red mullet, mackerel, garfish, pickerel and linnaeous from the Bay were cleaned. The head, tail and gills were discarded. Half to one kg of each sample was homogenized with water in the blender (4 fish/1L water, w/w), and immediately frozen.

ANALYSES

Water

Before the determination of organic mercury in water, the clean-up procedure of Westöö[3] was followed and the separation and quantification of organic mercury was achieved by means of gas chromatography. Inorganic and metallic mercury were determined

using a cold vapour technique. The analysis of cadmium and lead were done according to the method of Danielsson.[4] The cations were complexed with APDC and extracted into Freon TF. The measurements were done using an atomic absorption spectrophotometer equipped with a carbon rod atomizer.

Sediment

The samples were dried at 55–60°C (2 h) and sieved through a 180 mesh surface. A portion of the sieved particles (1.0 g) was digested with HCl/HNO_3 3/1 v/v (30 mL), at 90°C (1 h). The mixture was then diluted to 50 mL with water and total mercury concentration was measured with AA using the cold water mercury vapour technique.

A second weighing from the sample was taken (0.1 g) and digested with conc. HNO_3 (25 mL) in PTFE vials in Parr digestion bomb at 70°C (1 h) followed by additional treatment at 140°C (2 h). The mixture was cooled and quantitatively transferred with water (10 mL) into a separatory funnel. The metal ions (Cd and Pb) were complexed with APDC and their concentrations were determined as described in water analysis, above.

Fish

The homogenized fish tissue (0.5 g) was digested with HNO_3/H_2SO_4 (2/5 v/v, 28 mL) at 150°C (1 h). The total and organic mercury were determined as described in the water analysis. Cd and Pb determinations were achieved using 0.1 g of homogenized fish sample. The procedure was the same as that of sediment samples.

RESULTS AND DISCUSSION

The sampling stations for water and sediment are shown in Figure 1. More emphasis was given to the highly industrialized northern coast of Izmit Bay. Fish were collected from the local fishermen. Water samples were taken periodically. The two cross-sections, Alyanburnu–Seymen and Hereke–Karamürsel, were selected in order to determine the extent of toxic metal contamination. Water samples

at various depths and sediment samples at each station were collected. Analyses were done at least in duplicate and average results were calculated.

Water

Concentrations of Hg, Cd and Pb found in water from inshore sampling stations are given in Table I. The amounts of heavy metals found in the samples from the stations at the two cross-sections are listed in Table II.

TABLE I

Concentration of Hg, Cd and Pb in nearshore waters of Izmit Bay, October, 1980[a]

Sampling station no.	Total Hg (ppb)	Organic Hg MeHg (ppb)	Organic Hg EtHg (ppb)	Cd (ppb)	Pb (ppb)
17	1.4				
18	1.6	Trace	Trace		
19	4.0	1.0	1.0		
20	12.0	1.0	2.0		
21	2.7			0.02	2000
22	11.0	2.0	3.0		
23	2.5			0.02	2000
24	4.0				
25	23.0	7.0			
26	4.0			0.02	1500
27	0.8				
28	5.0				
29	5.0				
30	0.8				
31	1.3				
32	0.4				

[a]Blank spaces indicate that these samples could not be analyzed at this time.

Close examination of the results indicated that considerable variation (0.4–23 ppb) in Hg concentration along the coastal waters is present (Figure 1, Table I). Coastal waters near densely populated and industrialized areas were found to contain higher levels of Hg (stations 19, 20, 22, 24, 25, 26, 28 and 29). Highest levels of mercury

TABLE II

Concentration of Hg, Cd and Pb in the surface and deep-water samples taken from the two cross-sections June-July 1980

Station no.	Depth (m)	Hg (ppb)	Cd (ppb)	Pb (ppb)
First cross-section: Alyanburnu–Seymen				
1	Surface	0.85		
	7	0.40		
2	Surface	0.32		
	15	0.20		
3	Surface	0.37	0.10	0.15
	34	0.47		
4	Surface	0.25		0.30
	34	0.37	0.07	
5	Surface	0.32	0.47	1.25
	30	0.20		
6	Surface	0.32	0.17	0.83
	35	0.37	0.17	0.40
7	Surface	0.32	0.12	0.80
	17	0.32		
Second cross-section: Hereke–Karamürsel				
8	Surface	1.30		
	44	0.80		
9	Surface	1.30		
	10	1.30	0.64	0.10
10	Surface	0.92		
	10	0.80	0.74	0.25
	65	0.50		
11	Surface	0.60		
	10	0.50	0.24	11.50
	95	0.60	0.11	0.60
12	Surface	0.50		
	10	0.60	0.24	1.90
	95		0.13	
13	Surface	0.60	0.40	1.10
	10	0.50	0.33	2.70
	95	1.00		
14	Surface	0.70	0.98	2.20
	10	0.50		0.30
	95	0.60	0.42	1.00
15	Surface	0.50	0.18	0.70
	14	0.60		
16	Surface	0.60		
	11	0.70	0.30	1.95

were found at stations 20, 22 and 25, which are located near three chlor alkali plants, a pulp and paper mill and a refinery, respectively.

The natural levels of Hg in seawater and in groundwater are 1–3 ppb and 5 ppb,[5] respectively and mercury contamination of up to 1 ppb in drinking water is safe according to WHO.[6] The water samples from the stations away from the industrialized areas were found to contain less than 3 ppb of mercury. These results indicate that the contamination has not reached the areas away from the polluting industries.

The level of cadmium in the Bay varied from 0.02 to 0.98 ppb (Tables I and II). The acceptable limit of Cd in water is 10 ppb[7] which is much higher than the amounts found in the Bay.

The lead levels in the samples from stations 21, 23, and 25 were alarmingly high (1.5 to 2.0 ppm). These high values were explained as contamination from metallic pipe factories located near the sampling stations. The amount of lead in the samples from the two cross-sections ranged between 0.30 and 11.50 ppb (Table II).

The lead concentration of nonpolluted seawater is usually between 1 and 8 ppb[8], and uncontaminated natural waters contain 0.1 ppm of lead.[6] Therefore, the amount of lead found at the two cross-sections are well below the natural level of 0.1 ppm. In general, the heavy metal content of the shore water samples were higher than those from the two cross-sections.

The variation of Hg, Cd and Pb by depth (Table II) could be due to the circulation of water in the bay.

Sediment

Hg, Cd and Pb concentrations in the shoreline sediments and in the two cross-sections of Izmit Bay are presented in Tables III and IV respectively.

The mercury concentration of nearshore sediments ranged from 80 to 270 ppb (Table III). The highest level of Hg was at station 22, which is in the vicinity of the chlor alkali plant discharge. The level of mercury in the sediment is 4 to 100 times higher than the amounts found in water samples from the same areas.

The Cd concentration of the sediment samples along the shore ranged from 290 to 1380 ppb (Table III). These values are again considerably higher than those found in water samples from the

TABLE III

Concentration of Hg, Cd and Pb in the shoreline sediments (on dry weight basis) June 1980

Sampling station no.	Hg (ppm)	Cd (ppm)	Pb (ppm)
17	0.14	0.30	6.70
18	0.13	0.82	8.50
19	0.17	0.24	8.20
21		0.30	48.50
22	0.27	1.38	11.50
25	0.09	0.46	28.50
26		0.88	14.00
27	0.08	0.29	6.50
29		0.68	6.50

TABLE IV

Concentration of Hg, Cd and Pb found in the sediments taken from the two cross-sections (on dry weight basis)

First-cross-section: Alyanburnu–Seymen				
Station no.	Depth (m)	Hg (ppm)	Cd (ppm)	Pb (ppm)
1	7	6.10	2.13	59.50
2	15	5.00	0.47	46.00
3	34	4.50	0.60	31.00
4	34		0.24	5.00
5	35	5.70	0.81	25.00
6	30	5.30	0.60	29.00
7	17			
Second cross-section: Hereke–Karamürsel				
9	10	0.75	0.46	25.60
10	65			
14	30	0.40	0.12	20.50
15	14		0.36	24.50

same area. The levels of Cd in the sediment samples from the two cross-sections ranged from 120 to 810 ppb (Table IV). These values are again higher (100 to 4000 times) than the amounts found in water samples from the same locations.

The sediment sample from station 1 had an alarmingly high level of cadmium (2130 ppb). The source of contamination at this station could not be determined. The considerably high level of Cd at station 2 (1380 ppb) could be due to the chlor alkali plant located nearby.

The distribution of lead along the shore of the Bay ranged from 6500 to 48500 ppb (Table III). These values are 14 to 25 times higher than the levels in shoreline water samples. Generally, the sediment samples taken from the vicinity of chemical plants contained higher levels of lead.

The sediment samples from the two cross-sections contained 5000 to 59500 ppb of lead (Table IV). These values are 9000 to 35000 times higher than those found in water samples from the same location. The highest value of lead was found in the sediment sample from station 1 (59500 ppb), which also contained the highest levels of Cd and Hg.

All of these results point out that the heavy metals tend to accumulate in the sediment. Besides the chemical plants, these metals could be transported into coastal waters and sediments, either as adsorbed or suspended riverborne sediments, from the urban and industrial centers around the Bay.

The sediment samples from the two cross-sections contained higher amounts of Hg, Cd and Pb than the shore area. On the other hand, heavy metal content of the water samples from the two cross-sections were lower than the values found in shoreline samples. It has been reported that the heavy metals tend to accumulate in sediments and the concentration is dependent on grain size and organic carbon content.[9]

Fish

The concentration of the three heavy metals found in fish samples are shown in table V. The highest values of Hg were in scad and anchovy. According to the United States Food and Drug Administration, fish samples containing up to 0.5 ppm of Hg are considered safe.[10] The amount of consumption is also important. It is stated that a weekly intake of 0.008 mg of Hg/kg of body weight is safe.[11] The results indicate that the fish from Izmit Bay do not have high enough levels of Hg to affect human health.

TABLE V

Concentration of Hg, Cd and Pb in fish samples November, 1980

Fish species	Total Hg ppm	Me-Hg ppm	Et-Hg ppm	Cd ppm	Pb ppm
Cod	0.015	0.003	0.002	0.220	9.600
Anchovy	0.040	trace	trace	0.160	15.620
Sand smelt	0.003			0.200	6.250
Scad	0.030	0.008	0.010	0.600	10.000
Red Mullet	0.015				
Mackerel	0.010			0.470	4.370
Garfish	0.003			0.320	7.500
Pickerel	0.012			0.280	6.720
Linnaeous				0.160	7.810

The alkyl mercury content of the cod, anchovy and scad was investigated and scad was found to contain the highest amount (Table V). Mercury that reaches receiving waters as metallic Hg, inorganic mercury salts or organomercurials is transformed into methyl mercury which accumulates in fish and shellfish.[12] It is reported that levels as low as 0.1 ppb of methyl mercury in water interferes with the growth and photosynthesis of certain species of phytoplankton,[13] and that 5 ppb has an effect on the mobility of fish.[14] Alkyl mercury content of the fish from the Bay will be surveyed more extensively in the future.

The average Cd level in the fish caught in the Bay is 0.3 ppm. Scad, which is the permanent inhabitant of the Bay, has the highest concentration of Cd (0.6 ppm). According to the literature, fish samples generally contain 0.79 to 0.88 ppm of Cd.[15] It is suggested that the maximum permitted concentration of Cd in food should be 0.014 mg/kg of body weight.[11]

The lead concentration of the fish varied between 4.37 and 15.62 ppm in the Bay. These values are quite high. The recommended allowable limit of inorganic Pb in food is 2 ppm[5] and Pb level of up to 5 ppm is allowable in canned fish in the United Kingdom.[11]

Hg, Cd and Pb levels found in shoreline sediments (Table III) and amounts found in fish from the Bay (Table V) are similar in

magnitude, suggesting that there may be a relationship between the heavy metal content of shoreline sediments and fish species. Perhaps the heavy metal levels of sediments could be used for pollution assessment of fish.

CONCLUSIONS

It was found that the parts of the Bay were not polluted. The vicinity of chemical plants and populated areas showed the highest levels of mercury, cadmium and lead.

The heavy metal content of shoreline water samples were higher than those from the two cross-sections. The sediment samples contained greater amounts of mercury, cadmium and lead than the water samples, and the sediment samples of the two cross-sections had considerably higher amounts of Hg, Cd and Pb than shoreline sediments.

There is an indication of a correlation between the heavy metal concentration of the fish specimens and shoreline sediments.

Acknowledgement

This work was supported by North Atlantic Treaty Organization (NATO) project number 1967.

References

1. OECD (Organization for Economic Co-operation and Development). Utilization and Environmental Levels of Certain Chemical Substances; A Case Study Report from Japan, OECD, Environment Directorate, Paris (1976).
2. N. Kor, H. Goknil, A. Ayalp, M. Karpuzcu and R. Demirlikan, Izmit Körfezi Kirlenmesinin Kontrolü, MAG 318, **369** Ankara (1974).
3. G. Westöö, *Acta Chem. Scand.* **22,** 2277 (1968).
4. L. Danielsson, B. Magnusson and S. Westerland, *J. Anal. Chim. Acta* **98,** 47 (1978).
5. T. M. Leatherland, J. D. Burton and M. J. McCartney, *Nature* **232,** 112 (1971).
6. WHO (World Health Organization), Pollution Control in Europe, Copenhagen Regional Office, April (1972).
7. WHO (World Health Organization) International Standards for Drinking Water, Geneva, 3rd ed. (1971).
8. H. W. Durum and J. J. Haffty, Implications of the Minor Element Content in Major Streams: *Proceedings of the Symposium on Geochemical Evolution*, Amer. Assoc. for the Advancement of Sci. Denver, 29 Dec. (1961).

9. V. C. Anderlini, O. S. Mohammad, M. A. Zarba, S. W. Fowler and P. Miramand, *Bull. Environm. Contam. Toxicol.* **28,** 75 (1982).
10. D. R. Buhler, Mercury in the Western Environment, *Proceedings of a Workshop.* Portland, Oregon, Feb. 25–26, pp. 48, 83, (1971).
11. H. Waldron, *Chem. in Britain* **11,** 354 (1975).
12. S. P. Jensen and A. Jernelov, *Nature* **223,** 753 (1969).
13. R. C. Harris, *Science* **170,** 736.
14. P. E. Lindahl and E. Schwanbom, *Oikos* **22,** 210 (1971).
15. L. Fishbein, Chromatography of Environmental Hazards, (Elsevier, Holland 1972), Vol. 2, Page 60.