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Pollution Monitoring Using Marine Sediments: A Case Study on the Istanbul Metropolitan Area

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Abstract

Heavy metal concentrations of surfical sediments around the Istanbul metropolitan area are generally higher than the average shale values, with the highest contents occurring near the confluence of the Istanbul Strait (Bosphorus) with the Sea of Marmara. The metal distribution, together with that of organic carbon, suggests a significant contribution from munipical wastewater discharges. A total of 28 sites were sampled twice, with a 10-month interval (February and December 1996) to assess changes in the sediment composition. Analyses of the two batches of sediment samples suggest no significant changes in Cu, Pb and Zn; increases in Fe and Mn, and decreases in Hg and Ni contents over this time interval. Despite the high population density and industrialization in the area, these sediments have not been significantly contaminated in comparison with similar marine areas elsewhere in the world. This is mainly due to the dynamic two-layer circulation system of the area.

Key Words: Pollution, Marine Sediments

Denizel Sedimentler ile Kirlenme İzlenmesi: İstanbul Metropolitan Alan Çalışması

Özet

İstanbul metropolitanın civarındaki denizel yüzey sedimanlarının ağır metal içerikleri şeyl ortalaması ile karşılaştırıldığında genellikle yüksektirler. En yüksek değerler İstanbul Boğazı'nın Marmara Denizi girişinde bulunmaktadır. Metal ve organik karbon değerlerinin dağılım paternleri atık su deşarjlarının önemli ölçüde etkisi olduğunu göstermektedir. 28 istasyondan 10 ay aralıkla iki kez (Şubat 1996 ve Aralık 1996) sediment örneklemesi yapılmıştır. Bu iki set örneğin analiz edilmesi sonucunda Cu, Pb ve Zn içeriklerinde zaman içerisinde önemli bir değişiklik gözlenmezken, Fe ve Mn'ın arttığı, Hg ve Ni içeriklerinin de azaldığı saptanmıştır. İstanbul'un yoğun nüfusu ve endüstriyel faaliyetleri gözönüne alındığında, denizel sedimentlerinin, dünyanın benzer diğer bölgelerindekiler kadar kirlenmediği ortaya çıkmaktadır. Bu durum büyük ölçüde bölgenin iki tabakalı yüksek enerjili dinamiğinden kaynaklanmaktadır.

Anahtar Sözcükler: Kirlenme, Deniz Üstü Sedimanları,

Introduction

Surfical sediments are a feeding source for biological life, a transporting agent for pollutants and an ultimate sink for settling organic and inorganic matter. Their composition constitutes an important criterion for the assessment of long-term water quality. The metal content of sediments has natural and anthropogenic components. In heavily polluted sediments, the anthropogenically introduced components by far exceed the natural component, and because of their bio-availability constitute a hazard to the marine ecosystem. Interactions between solid sedimentary matter and dissolved metals play an important role in the regulation of dissolved metal concentrations (which are the most bioavailable) in the water.

İstanbul is the most heavily populated and industrialized metropolitan area of Turkey, situated on both sides of the Strait of Istanbul (Bosphorus) (Figure 1). The İstanbul Metropolitan area, with about 15% of the population of Turkey and 40% of the industrial activity, is the major source of pollution for the Sea of Marmara (Orhon et al., 1994). Previous work in the area includes studies on the chemical and physical oceanography of the Strait and the Sea of Marmara (Baştürk et al., 1988; DAMOC, 1971; Özsöy et al., 1986; Özsoy et al., 1988), and a few investigations on the metal concentrations of bottom sediments (Ergin et al., 1991; Bodur and Ergin, 1994). The Strait of İstanbul is characterized by a two-layer flow system, with less saline Black Sea water entering the Sea of Marmara as the surface current, and more saline Mediterranean water flowing to the Black Sea as the under current. The velocity of the surface currents is between 0.20 and 5 m/sec, and that of the under current between 0.05 to 2.50 m/sec (Özsoy, 1986). As a consequence of such strong current activity, coarse-grained sediments of mainly sand and gravel composition cover the floor of the Strait. Fine-graind (silt and clay) sediments with varying proportions of sand occur near the confluence of the Strait and the Sea of Marmara. A mixture of coarse- and fine-grained material is found at the Black Sea entrance of the Strait.

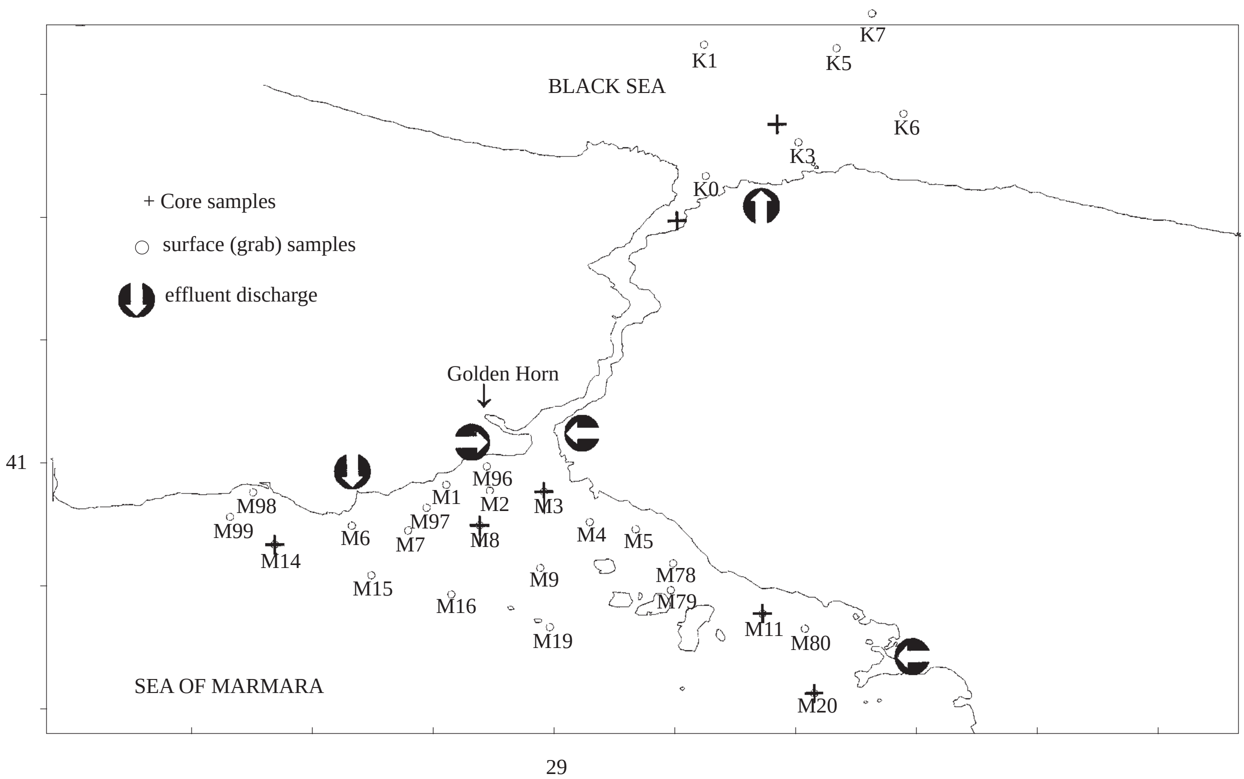

Figure 1. Sampling locations

Sampling and Analytical Methods

Surface sediment samples were collected from 28 sites by Van veen grab on the board of R. V. Arar of IMSM (Institute of Marine Sciences and Management, Istanbul University) (Figure 1). Each site was sampled twice, during February and December, 1996, to monitor possible temporal changes in the metal concentrations of the sediments. Surface sediment samples were taken from the uppermost part of the sediment with spoons and spatulas and deposited into plastic bags which were kept in a room at 4°C until granulometric and chemical investigations were carried out in the laboratory. Gravity core samples were also obtained from seven sites. Each core was sliced into 2 cm sections with a plastic spatula for metal analysis.

Pretreatment of the samples

The entire apparatus was pre-cleaned by soaking in 50% HNO_3 for 24 hrs. Samples were extruded from the plastic bags and mixed by plastic spatula in a glass mortar before drying at 110°C in the oven. Dried samples were ground for homogenization in a pre-cleaned agate mortar.

Organic carbon (C_{org}) content was determined by the Walkey-Blake method by oxidation via sulphochromic acid and back titraiton of the excess dichromate (Gaudette, 1974; Loring and Rantala, 1992). All metals were determined by flame atomic absorption spectrophotometer (AAS) after a total digestion, involving $HF+HClO_4+HNO_3$ acid mixture, except for Hg, which was analyzed by Hydride Generator-AAS. The precision of the total digestion was 2-14% (Table 1) as determined from five replicates. The precision for all the metals was better than 10% at, 95% significance level, except for Ni, which was 14%. The accuracy of the analyses was checked against the International Standards (BCR Reference Material CRM 142; and AQCS Reference Materials SL-1 and SL-7) (Table 2). The difference between measured and reference concentrations were generally small, except for Fe and Ni in CRM 142 and Zn in SL-1. The metal data were normalized to Al (weight ratios) to minimize the grain-size and $CaCO_3$-dilution effects.

Table 1. Precision of the metal analysis from five replicate samples.

Element	Mean	Precision (%)
Pb (ppm)	30	2
Cu (ppm)	20	8
Zn (ppm)	104	4
Hg (ppb)	2946	2
Fe (%)	4.6	8
Mn (ppm)	257	4
Al (%)	6.6	8
Ni (ppm)	15	14
Cr (ppm)	63	4

Precision at 95 % significance level $\%P=((2\sigma)/Conc.)\times 100$

Results

Organic Carbon (C_{org}) Distribution

The C_{org} contents of the surficial sediments collected in February and December, 1996, were found to have the same range (0.2-2.35 %) and similar distributions (Figure 2). High (>1.5 %) values were found along the coast near the confluence of the Istanbul Strait with the Marmara Sea. The Black Sea sediments (K0 to K7) are characterized by intermediate values of (0.71-1.34%) C_{org}.

The C_{org} contents of the sediment samples collected in February and December, 1996, were found in general to be generally similar (Table 3). Despite this similarity, the C_{org} contents at some sites located in the area close to the Strait/Marmara Sea confluence (sites M3 and M1) and Prince's Islands (sites M78 and M79) appear to have increased by as much as 110% during the ten-month period. Some decreases (<50%) in C_{org} at three sites K6, M6 and M4) may indicate the dynamic circulation and pollution of this marine environment.

Table 2. The accuracy of metal analysis.

Int.St.Reference Material (matrix)	Element	Reference Conc. (ppm) Confidence interval	Measured
CRM 142 (Light sandy soil)			
	Mn	569	574
	Fe	19600	25800
	Pb	37.8	35
	Cu	27.5	25
	Zn	92.4	92
	Ni	29.2	14
	Cr	74.9	85
SL-7 (Soil)			
	Mn	604-650	634
	Pb	55-71	60
	Zn	110-113	91
SL-1 (Lake sediment)			
	Fe	65700-69100	61400
	Pb	30-45	41
	Cu	24-36	28
	Zn	213-233	147
	Ni	36.9-52.9	39
	Cr	95-113	98

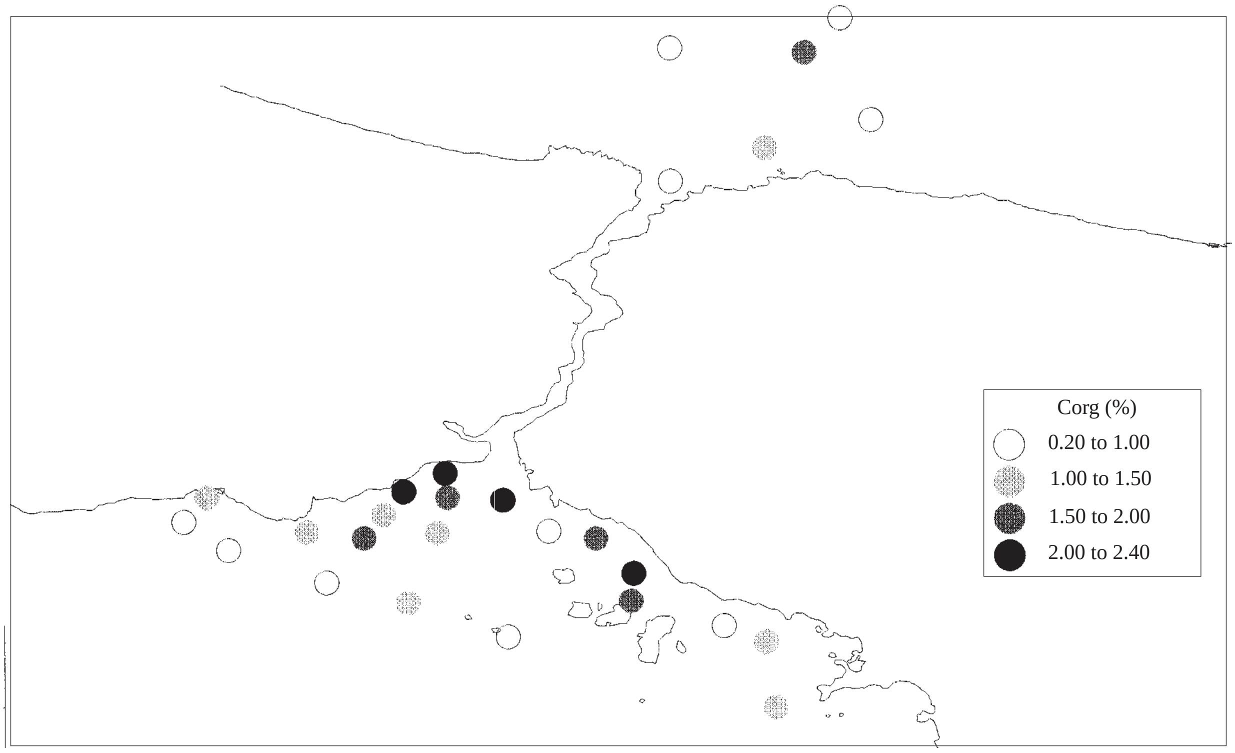

Figure 2. Distribution of corg content of the sediment samples collected in December, 1996.

Table 3. Basic statistical parameters and results of F-Test performed on analyses of two batches of 28 sediment samples collected during February 1996 and December 1996.

C_{org}&	February 1996		December 1996		F-Test	
Metals	Mean	Variance	Mean	Variance	F-calculated	F-Critical
C_{org}%	1.31	0.24	1.26	0.34	1.41	1.92
Cu (ppm)	37.48	179.8	32.44	320.5	1.78	1.92
Pb (ppm)	34.7	138.0	32.35	178.8	1.29	1.92
Zn (ppm)	95.51	723.8	89.2	1332.8	1.84	1.92
Hg (ppb)	360.7	107441.3	251.8	25256.0	4.25	1.94
Al(%)	5.80	3.63	5.29	2.44	1.48	1.92
Cr (ppm)	131.93	15116.1	104.13	7996.2	1.89	1.91
Fe (%)	2.35	0.94	2.92	0.44	2.13	1.91
Mn (ppm)	204.6	4130.2	253.2	9159.8	2.21	1.92
Ni (ppm)	37.04	233.3	27.00	79.69	2.92	1.91

The highest annual primary productivity was determined in the southern shelf of the Sea of Marmara, with a rate of 161 gCm^{-1}, where major rivers drain (Ergin et al., 1993). The study area has the second highest average annual primary productivity rate (104 gCm^{-2}). This area is affected by the organic-rich surface inflow from the Black Sea and also from the sub-halocline waters (regenerated-new production; Polat, 1989). C_{org} contents in sediments from the Sea of Marmara show no direct relationship with primary productivity (Ergin et al., 1993). The range of C_{org} content found by Ergin et al. (1993) (0.37-2.16%) is similar to that in the present study. Ergin et al. (1993) suggest that productivity and organic carbon accumulation in the sediments are strongly affected by the inflow of relatively organic-rich Black Sea waters, by the southerly major rivers and by the inflow of organic-poor Aegean or Mediterranean waters. On the other hand, Kıratlı and Algan (1994) point out that the increasing anthropogenic discharges in the eastern Marmara support the accumulation of C_{org} in the sediments. Tuğrul and Polat (1995) pointed out that the pollution load from Istanbul constitutes 40-60% of the total anthropogenic discharges.

The spatial distribution pattern of the C_{org} content of the surface sediments indicates an increasing trend along the coast near the confluence of the Istanbul Strait and the Sea of Marmara, suggesting the effect of the munipical waste-water discharges in this area (Figure 2). High primary productivity-induced organic carbon accumulation cannot explain such a distribution. Likewise, the decreasing trend of C_{org} with depth and in eastward and westward directions from the confluence might imply the dilution of C_{org}-rich sediments with C_{org}-poor sediments.

Table 4. Metal concentrations in surface sediments of the İstanbul as compared to the metal abundances in shale and to those in sediments from other marine environments in the world.

Metal	This study (for the sampling period of December, 1996)	elements in shale[1]	Average abundance of part: sample number is 7)	Sea of Marmara[2] (Northeastern (İstanbul)	Golden Horn estuary[3]	New Yors Harbour[4]	Thermaikos Bay[5]	Southern California[6]	Bristol Channel[7]
	Range	Mean							
Al (%)	0.8-8	2.44	9.2	NA	NA	NA	NA	NA	NA
Fe (%)	2-4	2.9	4.7	2.8	2.6-3.8	3.3-3.7	NA	0.8-4.0	2.4-3.9
Mn (ppm)	100-540	253	850	365	333-565	260-550	463-1935	NA	355-620
Pb (ppm)	12-58	32	20	55	124-702	140-830	20-150	4-23	20-145
Hg (ppb)	84-526	251	300	NA	NA	NA	NA	NA	NA
Cu (ppm)	5-80	32	50	48	333-3900	180-248	17-51	3-20	22-36
Zn (ppm)	48-237	89	90	101	450-8750	260-345	73-203	14-105	59-116
Cr (ppm)	11-509	104	100	102	242-485	NA	121-294	11-71	82-103
Ni (ppm)	1-41	27	80	58	98-167	NA	60-224	2-29	21-50

[1]Krauskoph (1979);[2] Bodur and Ergin (1994); [3]Ergin et al. (1991);[4]Williams et al. (1978);[5] Voutsinou et al. (1995); [6] Chow and Earl (1979) in Katz and Kaplan (1981);[7] Chester and Stoner (1975). NA=Not Analysed.

Metal concentrations and distributions

The Cr, Ni, Pb, Zn, and Hg contents of some Istanbul sediment samples were twice as high as the average abundances in shale (Table 4). Most of the high metal concentrations are found in the nearshore sediments of the Marmara Sea close to the confluence of the Strait (Figure 3). This again indicates the effect of the land-based pollutant inputs. The metal values determined in this study are compared with the results of a previous investigation by Bodur and Ergin (1994) in Table 4. In general, the results of the two studies are in agreement, with the exceptions of Ni, Pb and Cu. These differences might have been caused by the low accuracy of our Ni measurement (Tables 1 and 2) and in part by the small number of samples analysed by Bodur and Ergin, (1994) (i.e., n=7).

The Istanbul sediments were found to be less polluted than those of similar marine environments, such as the New York Harbour; the metal concentrations are considerably lower than those of the heavily polluted Golden Horn sediments but comparable to those of Thermaikos Bay, Southern California and the Bristol channel (Table 4). The dynamic circulation system in the area with a strong dual-flow regime is the main cause of the relatively low level of metal contamination in the Istanbul sediments.

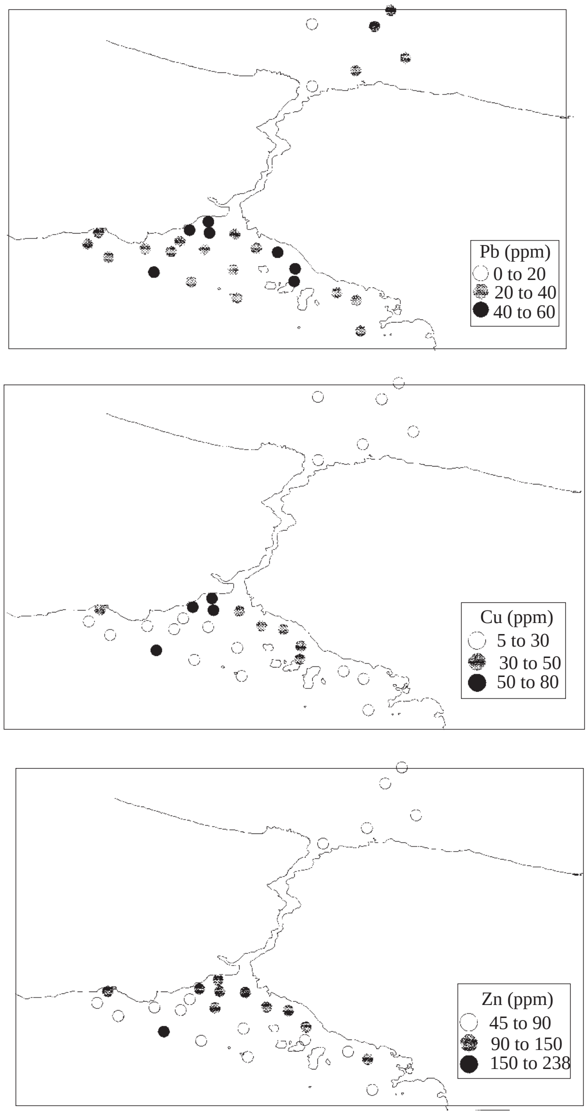

Figure 3. Distribution of Cu, Pb and Zn concentrations of the sediment collected in December, 1996.

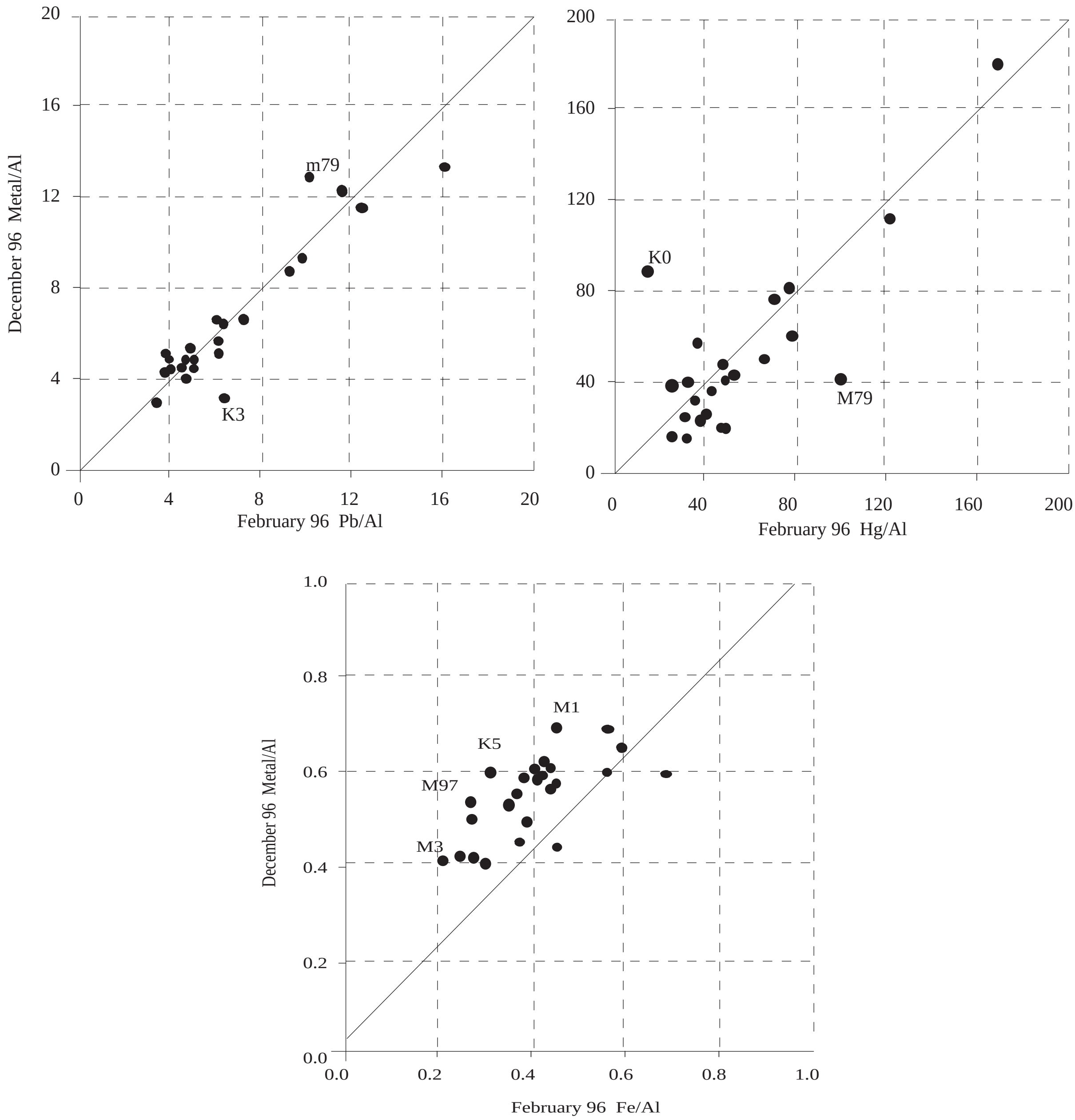

Figure 4. Aluminum-normalized plots Pb, Fe and Hg contents of the February, 1996, samples versus those of the December, 1996, samples.

Temporal variation of metal concentrations

Comparison of the two-data sets belonging to the two batches of sediment samples suggests that in general, the Cu, Pb, Zn and Cr contents did not change significantly over the 10-month period (Table 3). Changes of up to about 50% in these metal concentrations were observed at only at a few sites, such as M79 (29% increase in Pb) and K3 (50% decrease in Cu and Pb) (Figure 4).

The Fe and Mn contents of the sediments increased, whereas the Hg and Ni contents decreased over the 10-month sampling interval (Table 3; Figure 4). Sediments at most sites showed Fe enrichment, which amounted to a 53% increase at Site

M1 (Figure 4). The most notable increases (up to 175%) in Mn concentrations were observed at sites M11, K5 and M3. The Hg and Ni contents generally decreased over the 10-month period (Table 3). A marked decrease in the Hg content was seen at Site M79, whereas a significant increase in this element was seen at Site K0 (Figure 4). The most notable decrease in Ni content was observed at Site K-3. The temporal variability of Ni data can be explained in part by the low precision and accuracy of the Ni analyses (Tables 1 and 2).

The extreme local variations in some metal contents therefore may not always show the effects of the increase or decrease of metal pollution in time. Such a significant change in metal concentrations in sediments in such a short period is generally unusual, as shown by the Cu, Pb, Zn and Cr data sets. However, considering the dynamic nature of this marine environment in terms of pollution sources and water circulation, some local temporal variations in the metal contents may be real.

Depth/concentration profiles of metals

Aluminum-normalized depth/concentration profiles at Sites M-8 show increasing Cu, Pb, Zn and Hg contents in the top 15 cm of the sediment section (Figure 5). At site K0, the metal profiles show a general upward increasing trend, with some irregularities, which may be due to sediment mixing by current and biological activities. The last stage increase in the metal concentrations at this site starts at the same depth (i.e., 15 cm below sea floor) as at Site M-8. The sedimentation rate for the Site M-8 was given as 190 cm 1000 y^{-1} by Ergin et al. (1994) by the ^{210}Pb method. On the basis of this rate, the bottom of the core M-8 (90 cm) represents the 450 year BP (before present) and the top 15 cm the last 75 years. The small enrichment of Pb, Cu, Zn and Hg in the last 75 years may imply the increasing anthropogenic influences.

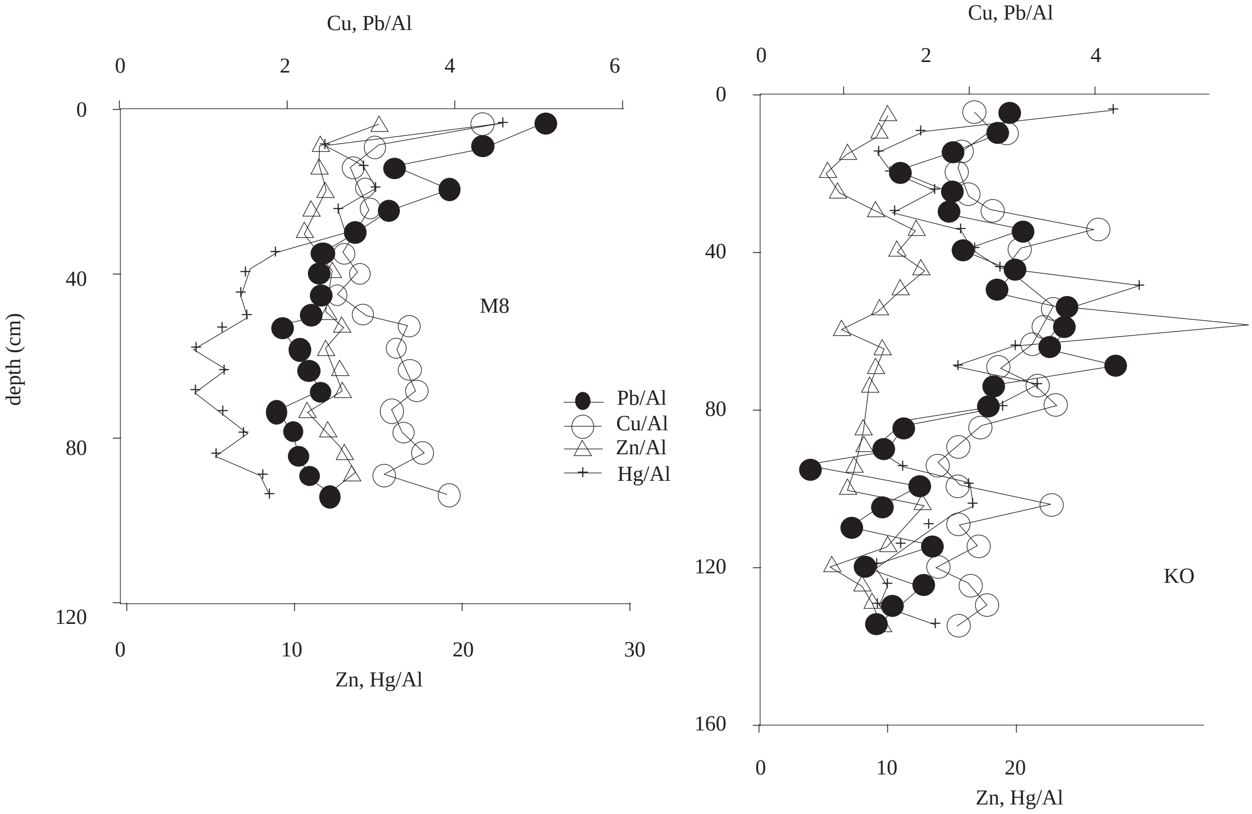

Figure 5. Depth profiles of the Cu, Pb and Zn along the cores M8 and K0.

Conclusions

Heavy metal contents of the surface sediments from the Istanbul metropolis did not demonstrate serious contamination compared to similar marine environments. This is mainly due to the efficient two-layer circulation in the area. Local enrichment of metals and C_{org} is related to the municipal waste water discharges. There was no significant increase in the Cu, Pb and Zn contents, whereas some enrichment in Fe and Mn, and decreases in the Hg and Ni contents of the sediments were discernible during the 10-month sampling interval. Longer term monitoring by sediment sampling and analysis is necessary to assess the processes controlling the variations in the metal contents of the sediments.

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