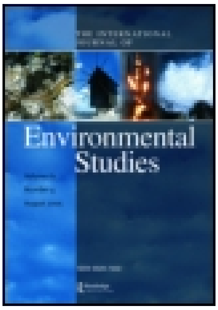

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Geologic assessment of environmental impact in bottom sediments of the eastern Aegean sea

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GEOLOGIC ASSESSMENT OF ENVIRONMENTAL IMPACT IN BOTTOM SEDIMENTS OF THE EASTERN AEGEAN SEA

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Surficial sediment samples collected from 46 stations in the eastern Aegean Sea were analyzed for their texture and heavy metal contents. The results obtained, together with the available data from others, are discussed with reference to the unusual geological sources and anthropogenic activities. It has been found that the sediment compositions varied regionally and in response to textural and compositional variations, and the heavy metal concentrations are mostly at or near natural levels in relation to their source rocks and other uncontaminated marine sediments. The concentrations of Cu, Zn, and Hg, particularly off the Meriç River mouth and in the inner Gulf of İzmir, are comparable to levels reported from other metal-contaminated areas. These metals apparently are being discharged from the industrial and urban centers. These results also necessitate further metal analysis in dated core sediments.

Keywords: Pollution; geological source; heavy metals; sediments; Aegean Sea.

1. INTRODUCTION

It has been widely recognized that sediments deposited in coastal marine environments near large industrial and urban areas are excellent recorders of both natural and human-induced impact[1–5]. Prerequisited are needed that must be met when choosing sampling and analytical techiques and adjustments for textural and compositional effects of the sediments[6,7]. Not paying attention to the types of land-based geological sources and thus geochemical anomalies may

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further lead to misinterpretation of the data obtained. The Turkish coastal marine waters, the eastern Aegean Sea in particular, are such environments where both anthropogenic activities and geochemical anomalies are expected to interact with each other.

In this context, this paper aims to present data on the distribution of heavy metals in the superficial bottom sediments of eastern Aegean Sea and to discuss them with particular reference to the geological unusual sources and anthropogenic activities. Thus, this paper intends to be the first in the field of sedimentary records of environmental pollution in the eastern Aegean Sea, on large scale.

2. ENVIRONMENTAL SETTING

The Aegean Sea forms the northeastern part of the Mediterranean Sea and is bounded to the northerly Black Sea through the Sea of Marmara (Figure 1) via its straits "Çanakkale or Dardanelles" and "İstanbul or Bosphorus". The study area extends from the Meriç River mouth in the north and the Bodrum-Marmaris peninsulas in the south (Figure 1). The coastal physiography of the eastern Aegean Sea is dominated by the NE-SW-to ENE-WSW-trending gulfs. The geology of the surrounding land regions is characterized by the occurrence of various rock types (ophiolite series, metamorphic rocks etc) and associated metallogenic ore/mineral deposits of economic importance (Figure 2).

The oceanography of the Aegean Sea is governed by the northerly inflow of Black Sea waters of brakish character and the southerly inflow of Mediterranean waters of saline character[10]. Meriç, Madra, Bakirçay, Gediz, K. Menderes, B. Menderes and Dalaman Rivers are the main suppliers of terrigenous material into the Aegean Sea.

3. MATERIAL AND METHODS

Fourty-six sediment samples were taken from different parts of the eastern Aegean Sea in water depths ranging from 12–640 m with a Dietz LaFonde bottom grab during the 1987 cruise of R/V Bilim (Figure 1). Grain size analysis of the sediments was performed according to Folk[11], whereby mud denotes a mixture of clay (< 0.002 mm), and silt (0.002–0.063 mm in diameter) fractions. Total carbonate contents of the sediments were determined using a modified gravimetric-volumetric method described in Müller[12].

The concentrations of Fe, Mn, Co, Cr, Ni, Cu, and Zn were determined by an atomic absorption spectrophotometer (Varian AA-6 Model), after total digestion

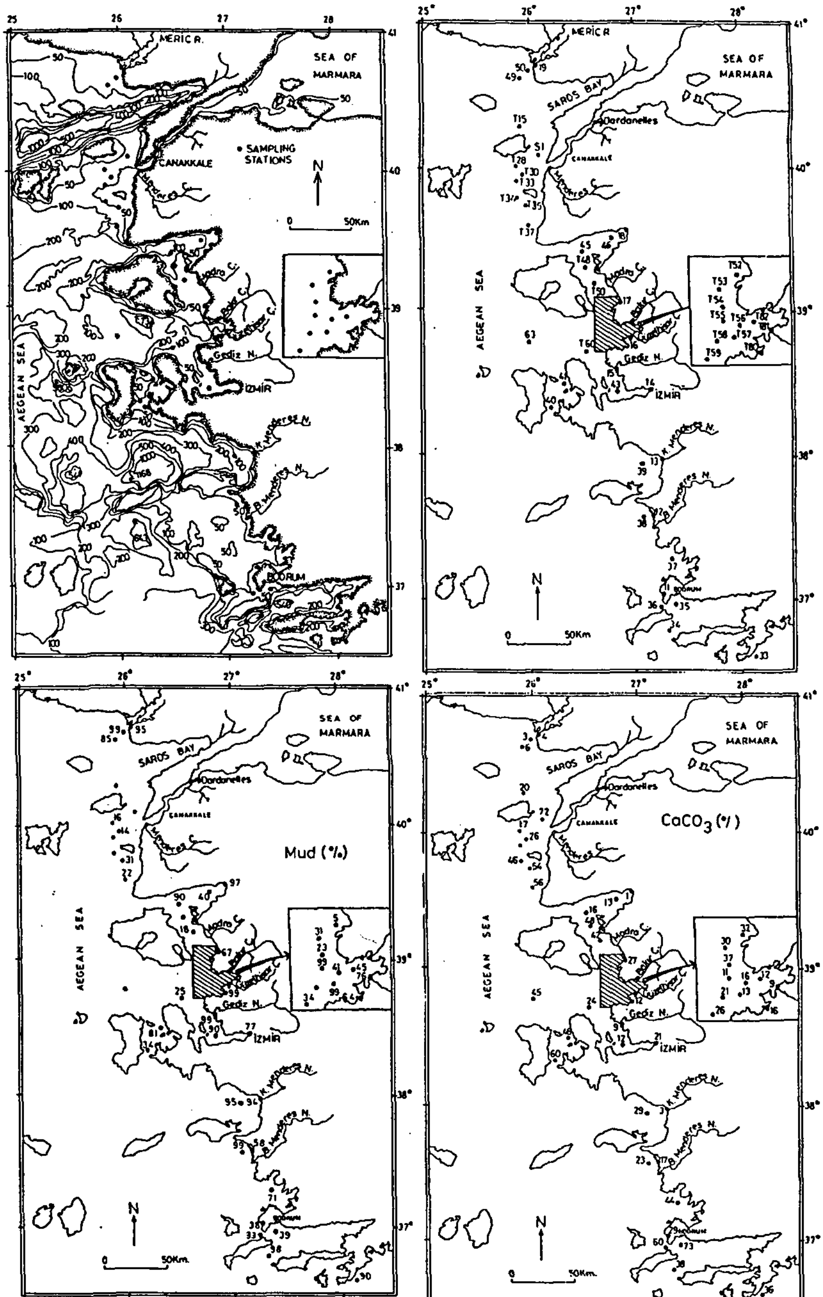

FIGURE 1 Map of study area showing bathymetry (top left), sediment sampling stations (top right), mud (bottom left) and carbonate (bottom right) contents in the sediments.

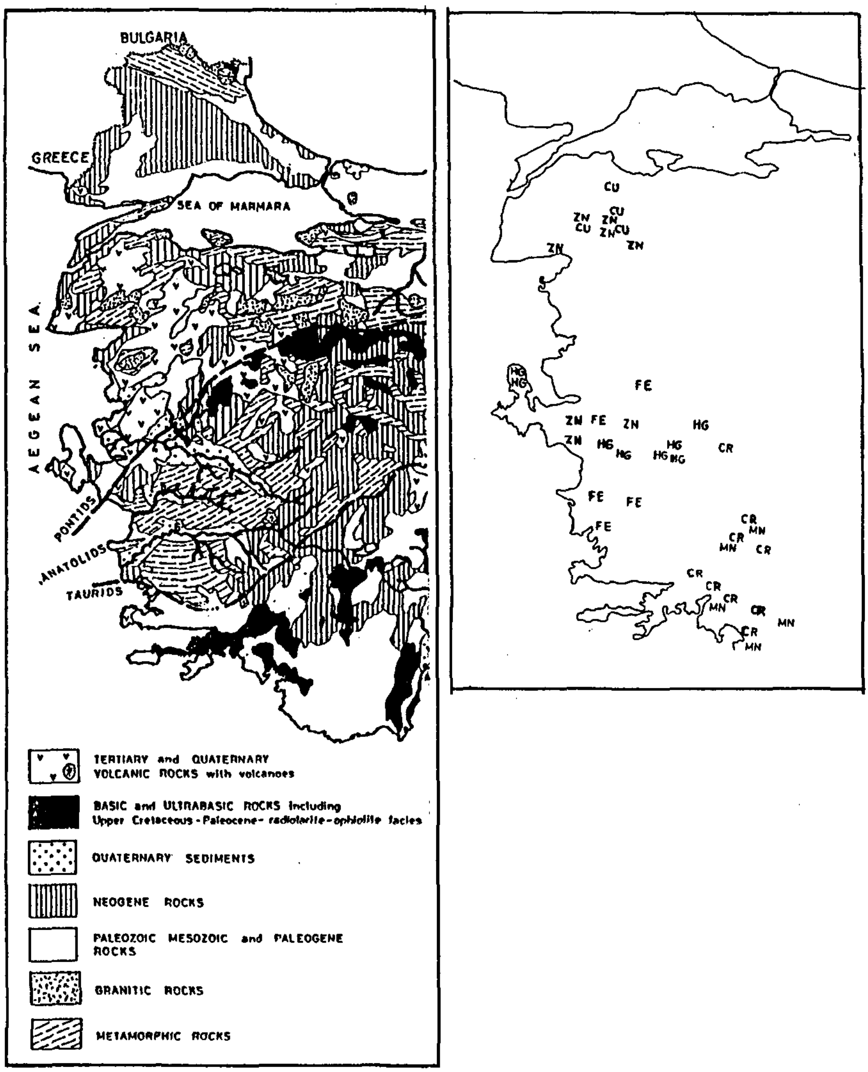

FIGURE 2 Maps illustrating land-geology and important ore/mineral deposits surrounding the eastern Aegean Sea (Compiled from Evans[8]: left; and M. T. A.[9]: right).

of ground of bulk samples with a hot HF-HNO_3-acid mixture. Precision and accuracy of the analysis were checked using international standards (CRM 142 from BCR in Belgium) and blanks. The precision was found to be generally between 1 and 11%. Total mercury contents were measured by using the cold-vapor technique, as described in UNEP/FAO/IOC/IAEA (1984) Reference

Methods. Additional data on metal contents of clayey sediments from the B. Menderes River was kindly provided by H. E. Sevim[13].

4. RESULTS AND CONCLUSION

4.1. Sediment Texture and Composition

Studied surficial sediments from the eastern Agean Sea varied widely in their texture[14]. Fine-grained-sediments, muds (sediments consisting of silt and clay) occurred mainly off the river mouths (areas of high land-based terrigenous input) and in coastal embayments (areas of low-energy, quite conditions; Figure 1). For example, sediments deposited off the mouths of rivers Meriç, Menderes, as well as, in the gulfs of Edremit, İzmir and Gökova showed high mud contents (> %90 of the bulk sample; Figure 1). The coarse-grained sediments, characterized by high sand and gravel contents, are confined to regions with high biogenic production and high-energy conditions. The biogenic constituents in the coarse-grained sediment fraction are mostly made of the remains of various benthic organisms which resulted in the presence of high carbonate contents (> %30 $CaCO_3$) in sediments (Figure 1).

4.2. Metal Concentrations in Marine Sediments

As it is known, carbonates are poor in many heavy metals[15] (Table I) and thus their presence in the terrigenous sediments have a dilution effect on the metal contents measured[14]. Therefore, a normalization of the metal data[23] should be made on carbonate-free basis. Figures 3 and 4 show the concentrations of the metals investigated on carbonate-free basis.

4.2.1. *Iron* Carbonate-free Fe contents ranged from 1.4 to 5.9% (Figure 3) and these values are largely comparable with those of the average composition of crustal rocks (Table I). The highest Fe values (%5.9) are formed off the mouths of Gediz and Menderes Rivers (Figure 3) which drain the Fe-rich mineral deposits and metamorphic rocks outcroppings on the coastal hinterland (Figure 2).

4.2.2. *Manganese* Except for two samples (2040 and 4234 ppm Mn), sediments mostly contained Mn in the range of between 151–1301 ppm (Figure 3), values similar to those of the average composition of crustal rocks (Table I). The highest Mn contents (2040 and 4234 ppm) are formed off the Bodrum-Marmaris peninsulas (Figure 3), areas which receive significant input from the land-based Mn-rich source rocks (Figure 2). At this stage, it is difficult to

TABLE I Comparison of data from surface marine sediments obtained in this study with others

Sample/ location	*Fe*	*Mn*	*Co*	*Cr*	*Ni*	*Cu*	*Zn*	*Hg*
This study	0.6–5.7	103–2625	2–41	9–132	11–406	3–77	19–162	
This study*	0.8–5.9	151–4234	3–76	13–487	19–634	4–80	28–205	17–1278[a]
B. Menderes River[14]	2.6–5.1	553–2061	17–61	133–425	138–734	33–77	105–346	32–220
Polluted sediments								
Golden Horn Estuary[b] (Marmara Sea)	1.5–5.1	156–610	9–28	162–620	61–151	280–3700	430–9900	
German Bight[1] (North Sea)	4.5	1600	20	90	45	40	400	1600
Skagerrak[16] (North Sea)	3.2–3.9	370–1037	20–52	83–104	63–78	30–62	175–223	5–858[17]
W. Baltic Sea[18]	2.7–3.6	468–1562	7–16	30–49	23–43	20–44	87–285	50–760
Tokyo Bay[5]	2.9–4.0	350–1670		29–126	16–44	16–79	106–405	
Gulf Aqaba[19] (Red Sea)	1.4–3.2	212–562	22–44		19–89	8–25	32–180	
Haifa Bay[20]						99	348	1040
Humber Estuary[4]	4.4	677		212	55	70	319	
Ganges Estuary[21]	1.2–4.6	254–800	14–64	21–100	8–57	4–53	12–611	
Crustal rocks								
Average[22]	5.0	950	25	100	75	55	70	80
Shales[15]	4.7	850	19	90	68	45	95	400
Sandstones[15]	0.9	X0	< 1	35	2	X	16	300
Carbonates[15]	0.4	1100	< 1	11	20	4	20	200

*Carbonate-free data; a) G. Evans (1986, personal communication)

distinguish diagenetic Mn-enrichment in the surface sediments, although it can not be ruled out.

4.2.3. *Cobalt* Co concentrations, except for one value 76 ppm at a station in the north, varied between 6 and 48 ppm (Figure 3), whereby most of the values fell in the range of average composition of crustal rocks (Table I). High Co contents are usually confined to sediments with higher Mn contents (Figure 3). This may suggest a common source and/or common mechanism of enrichment, both due to geochemical processes.

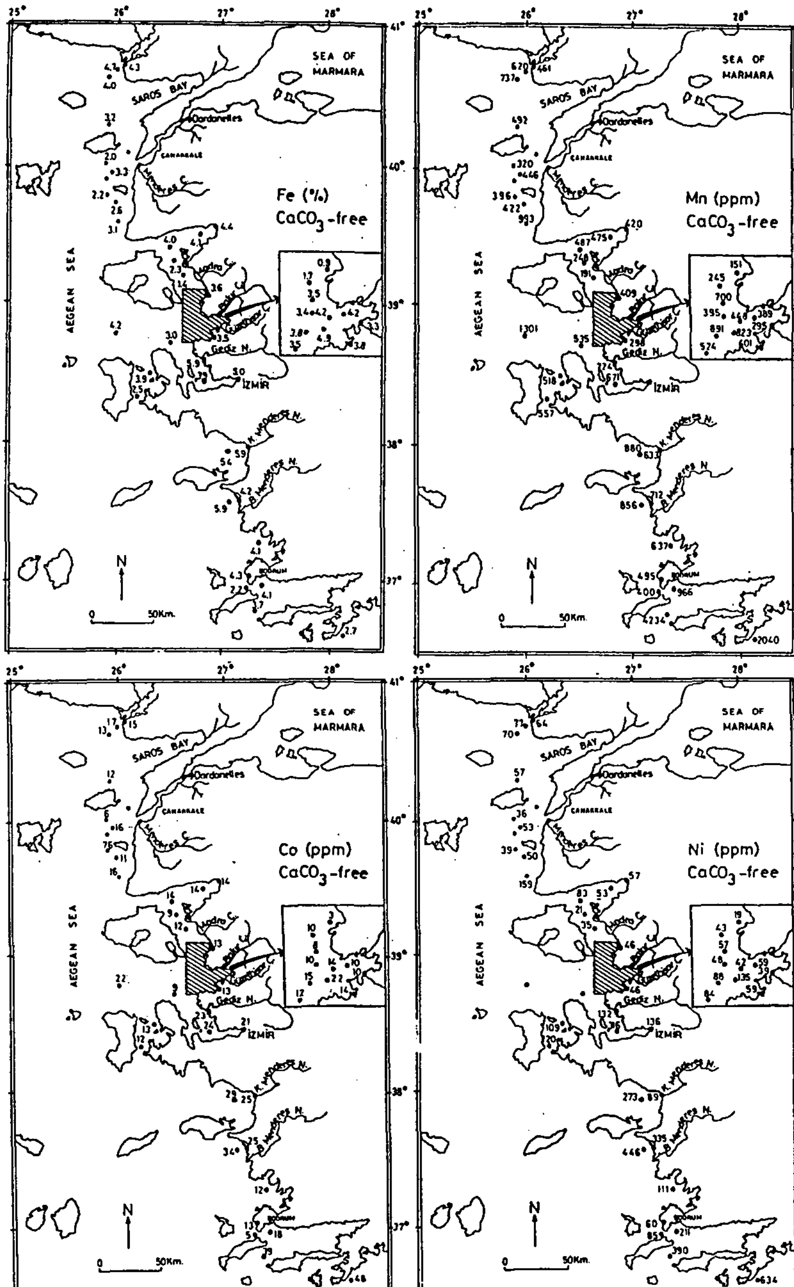

FIGURE 3 Normalized to carbonate-free metal concentrations in surface sediments of the Eastern Aegean Sea used in this study.

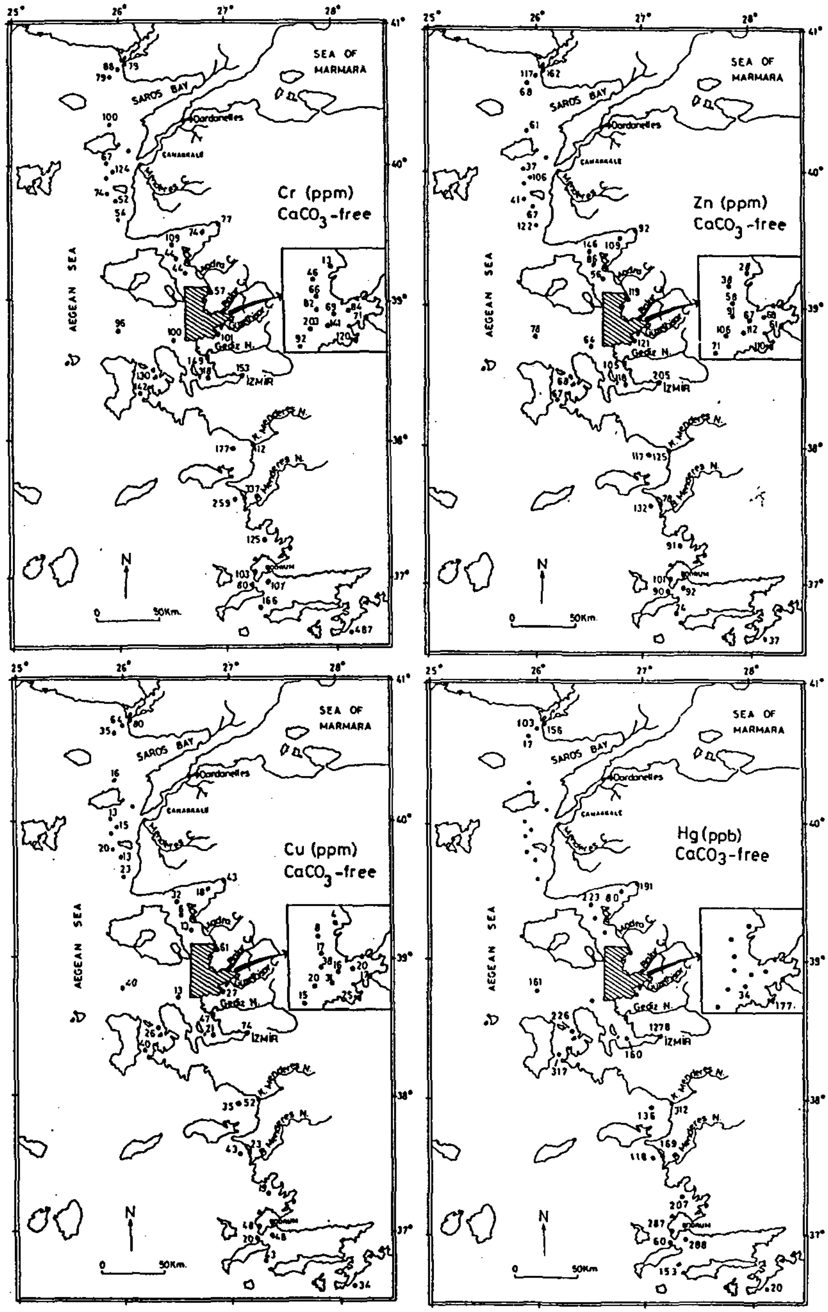

FIGURE 4 Normalized to carbonate-free metal concentrations in surface sediments of the Eastern Aegean Sea used in this study.

4.2.4. *Chromium* Cr concentrations were generally low (13–203 ppm) in the northern part and high (107–487 ppm) in the southern part of the study area (Figure 4). The crustal rocks contain, on average, 100 ppm Cr (Table I).The very high Cr contents in the southern part of the study area (259–487 ppm) are obviously due to the presence of volcanic and ophiolitic rocks and associated chromite deposits on land (Figure 2). Similar high Cr contents are also known to occur in the bottom sediments of the adjacent, Sea of Marmara (Golden Horn Estuary) which are derived from the anthropogenic activities[24] (leather tanning and electro-metal industries). See also Table I for other Cr contaminated coastal sediments in other regions.

4.2.5. *Nickel* Ni concentrations follow the distribution pattern of Cr. Sediments from the northern part are generally low (36–135 ppm) in Ni, whereas those from the southern part of the study area display higher Ni values (60–634 ppm; Figure 3). The presence of high Ni contents in the south, relative to average crustal composition (Table I), reflect contributions from the Ni-rich source rocks (volcanics, ophiolitic series, chromite deposits, etc; Figure 2) on land.

4.2.6. *Copper* The majority of Cu concentrations (4–61 ppm; Figure 4) are mostly similar to those of average crustal rocks (Table I). The relative high Cu contents are found off the Meriç River mouth in the north (64–80 ppm), and in the inner Gulf of İzmir (74 ppm; Figure 4), which clearly reflect contribution from anthropogenic activities, as it is also known for other contaminated regions (Table I). In particular, the offshore-decreasing Cu contents from 80 ppm near to 35 ppm off the mouth (Figure 4) must be ascribed, at least in part, to the anthropogenic activities, because there exist no Cu-rich geological sources in the surrounding land regions (Figure 2).

4.2.7. *Zinc* Like Cu, Zn appears to be enriched in the inner Gulf of Izmir (205 ppm) and off the Meriç River mouth (162 ppm; Figure 4). Especially the nearshore (162 ppm)—to offshore (68 ppm) decrease in Zn contents (Figure 4) indicate transport and thus dilution of metal pollutants in offshore waters. Similar high Zn levels have been reported from other regions which have been subject to environmental pollution (Table I). Otherwise, the most of the Zn levels (28–132 ppm) obtained in sediments are comparable with the average composition of crustal rocks (Table I). It is difficult to establish whether the slightly high Zn contents (146 ppm) in the Gulf of Edremit can be related to the Zn-Cu ore deposits widely occurring on land (Figure 2).

4.2.8. *Mercury* The concentrations of Hg in the sediments varied between 17 and 1278 ppb, being maximum (1278 ppb) in the inner Gulf of İzmir, near the town of İzmir (Figure 4). It seems that the Hg contents in the inner and western parts of the Gulf of İzmir must be derived to a large extent, from the unusual geological source rocks and associated Hg-mineral deposits commonly occurring on land (Figure 2). However, the maximum Hg level in sediments near the town of İzmir can be, in part, indicative of environmental pollution because the inner Gult of İzmir is one of the most polluted coastal embayments of Turkey[25]. The Hg-levels obtained in this study are comparable with other Hg-contaminated sediments from coastal regions (Table I). Otherwise, the average concentration of Hg in crustal rocks amounts to 80 ppb (Table I), considerably lower than those found in this study.

4.3. Comparisons of Metal Data with that in Polluted Coastal Marine Sediments

The concentrations of the metals Fe, Mn, Co, Cr, Ni, Cu, Zn, and Hg, together with those from various other sources and regions are listed in Table I for comparative basis. This shows that most of the metal levels obtained in this study are in good agreement with those of an average composition of crustal rocks, and the deviations can be explained by variations in texture and lithology. Hence, these metal levels can be ascribed to the weathering products of geological sources (Table I). Exception do occur, however, for Cr and Ni which are overwhelmingly high but well coinciding with the unusual geological sources around the study area (i.e. mafic and ultramafic rocks and associated ore deposits of economic importance, Figure 2).

To test the metal levels in this study with respect to environmental impact, available metal data from several polluted coastal marine environments are presented in Table I for comparison. Obviously, the concentrations of Zn, Cu and Hg are comparable to levels reported from other urbanized and industrialized areas (Table I). Thus the highest concentrations of Zn, Cu, and to some extent, Hg obtained in this study could be related in part to the anthropogenic activities, although these metal levels alone cannot suggest that the eastern Aegean Sea is polluted. The concentrations of these metals, relative to average crustal rock composition, are enriched by factors mostly less than 2, hence at or near the natural background values. The discharge of municipal and industrial waste waters are the dominant sources of the heavy metals studied.

Further investigations are needed to show the chronology of metal enrichment in these sediments by using dated core sediments.

4.4. Metal Concentrations in River Sediments

Data was only available for the B. Menderes River[13]. As shown (Table I), metal concentrations measured in the fine-grained, clay fractions of sediment in the

B. Menderes River are largely comparable with those obtained in the marine sediments off the mouth of this river. The predominantly geological origin of these metal levels are also inferred from the data obtained in short sediment cores where metal concentrations remained nearly the same throughout the cores[13]. This would suggest a slight anthropogenic metal input in this region.

5. CONCLUSIONS

Surface sediments in the eastern Aegean Sea showed significant variations regionally in their metal contents in response to textural and compositional variations, and the heavy metal concentrations measured were found to be affected by the both geological and anthropogenic contributions. The majority of the metal levels obtained are comparable with the average composition of crustal rocks, and deviations from them for the contents of Cr, Ni, Hg, and Zn are due to anomalies in the geological sources on the surrounding land. For example, elevated concentrations of Fe are related to ultramafic rocks; Cr and Ni to ultramafic rocks, and associated chromite deposits; Zn to Pb-Zn-Cu ore deposits; Hg to Hg-mineral deposits; and Mn to Mn-carbonate deposits. All are of economic importance. Anthropogenic contribution was assessed for the high concentration of Zn, Cu, and Hg off the Meriç River mouth and in the inner Gulf of İzmir. These metals apparently are being discharged from industrial and urban centers. Further sediment investigations are suggested to record the anthropogenic impact on metal distribution in sediment by using dated cores.

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