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Heavy metal pollution in surface sediment and mussel samples in the Gulf of Gemlik

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Abstract Sediment quality data provide essential information for evaluating ambient environmental quality conditions. An evaluation is presented of heavy metal pollution, on the basis of statistical analysis of metal concentrations from the sediments of the Gulf of Gemlik, southeastern Marmara Sea, Turkey, which has been subject to high levels of pollution. The ranges for heavy metal concentrations (Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) at the <63 μm grain size were higher when compared with those obtained from >63 μm fractions. Not only large industrialized seaports but also resort areas throughout the Gulf are flagged as hotspots for elevated concentrations, generally higher compared to those from the other Turkish marine environment. The highest concentrations of Cr, Pb and Ni were measured in the outer part of the Gulf, while the highest concentrations of Cu were documented offshore the main rivers. While the concentrations of Cr, Fe, Mn and Ni in some stations approach the severe effect level given in various sediment quality guidelines, the concentrations of the most human-related metals (Cd and Zn) in the mussels collected from the Port Mudanya were higher than the acceptable values for human consumption set by various healthy organizations.

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Introduction

Heavy metal discharges to the marine environment are of great concern all over the world. Heavy metal concentrations in sediment, which is essential to the functioning of aquatic ecosystems, are many times greater than the same metals in the water column. The bioaccumulation of sediment-bound metals by benthic species is extremely important to the food webs and their eventual transfer back to man. Therefore sediments are used as environmental indicators to reflect the prevailing quality of marine or lake systems. Moreover, they permit the determination of metals even when the concentrations in water are undetectable with current methods (Gonçalves et al. 1994: Soares et al. 1999).

The Marmara Sea is a semi-enclosed deep basin between the Mediterranean and the Black Sea. The contaminants are introduced through water way into

Marmara Sea by a surface and deep currents from the Black Sea and Mediterranean Sea. The surface layer consists of low salinity (18–29‰) water of the Black Sea origin. The remainder of the water layer (below 20–25 m) is high salinity (~38.5‰) Mediterranean Sea water (Shiganova et al. 1995; Lee et al. 2002).

The Marmara Sea has been subject to very high levels of pollution due to several industrial complexes, municipal wastewater, agricultural chemicals, oil pollution and airborne particles. Large industrialized seaports are often flagged as hotspots for elevated concentrations of heavy metals in water and sediment. Mussels appear to be among the most sensitive organisms to heavy metals some of which are lethal even at low levels. Different countries employ mussels for pollution monitoring within the so-called "Mussel Watch Programme," such as Radioecology Laboratory of Cekmece Nuclear Research and Training Center (Topçuoğlu 2002). The production of mussel species (*Mytilus galloprovincialis*) from the Marmara Sea is 1019 and 862 tons annually in 2000 and 2001, respectively (D.I.E. 2003). The annual production of the other kind of mussel species (*Venus gallina) was* 1028 tons from the Marmara Sea in 1999.

Critical coastal and near-shore areas in the Marmara Sea include: (a) Izmit Bay, which receives waste from Turkey's most important industrial area as well as the domestic waste of the city of Izmit; and (b) the Gulf of Gemlik, which receives pollution from Lake Iznik as well as industrial and household waste from adjacent towns. The Gulf of Gemlik, a 31-km-long semi-enclosed trough located in the southeastern part of the Marmara Sea (Fig. 1), is considered to be one of Turkey's most industrialized regions and is contaminated by persistent organic and heavy metal pollutants. The main anthropogenic sources of pollutants are shipping, sewage treatment discharges, urban run-off and industrial activities. Around the eastern and southeastern coasts of the Gulf are clustered more than 40 moderate and big industrial plants. Gemlik and Mudanya towns are the most important industrial towns and marine export gates.

The Gulf is represented by stratified water layers; constituted by low salinity (23–29‰) Black Sea waters and high salinity (38.5‰) Mediterranean waters, with the pycnocline occurring at depth of about 15–25 m. Sub-halocline water masses are permanently depleted in dissolved oxygen, thus limiting benthic life in the Gulf. Although DO values decrease as low as 0.1–0.9 mg l^{-1} in summer, increasing vertical mixing in winter times changes anoxic conditions with DO concentrations around 1.3 mg l^{-1} (Yüksek et al. 2004). Massive algae blooms around shallow inner harbors can be seen during hot summers. Contrary to high industrialization in the south, the villages along the northern coast of the Gulf are important tourism centers. Tourist growth and coastal development have, however, mushroomed as a result of legislative and institutional arrangements designed to encourage tourism investment.

Industrial and municipal emissions especially along the eastern and southern coastal areas have environmental effects on ecosystems, humans, fishing potential and heavy metal content in bottom sediments. The concentrations of total-Cd in surface bulk sediments (0–3 cm) of the Gulf, for example, varied from <0.01 to 10.1 μg g^{-1} dry weight (dw), indicating heavy contamination throughout the Gulf but 4–5 times severely along the southern coasts (Ünlü et al. 2006). Domestic land-based load input plays a significant role in the pollution of this semi-enclosed embayment. Discharge of untreated sewage due to inappropriate and inadequate sewerage infrastructure constitutes the basic pollution problem in the receiving waters. Higher anthropogenic pressure is via rivers and their valleys which have long been productive agricultural lands. Kocasu River is main transport source of pollutants, with an annual suspended solid discharge of 6.5×10^5 t (Ergin and Bodur 1999). Karsak creek is another important pollution source in the east. This creek is connected to Lake Iznik to the east; two big towns and various industrial plants discharge waste and domestic sewerage into this channel.

Because of its sheltered basin morphology and low-energy current conditions, the sediments of the Gulf of Gemlik are characterized by their fine-grained nature, being rich in mud (>90%) and poor in sand (Ünlü and Alpar 2006). Depositional areas contain higher concentrations of contaminants than do areas of high energy. The specific objectives of this study were (a) to quantify heavy metal (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) levels at >63 and <63 μm fractions in the different environmental compartments of the Gulf of Gemlik; (b) to compare results with the similar works which have been carried out in the Marmara Sea, Aegean Sea, Bosphorus and Black Sea; and (c) to determine the concentration of the selected heavy metals in mussel tissues.

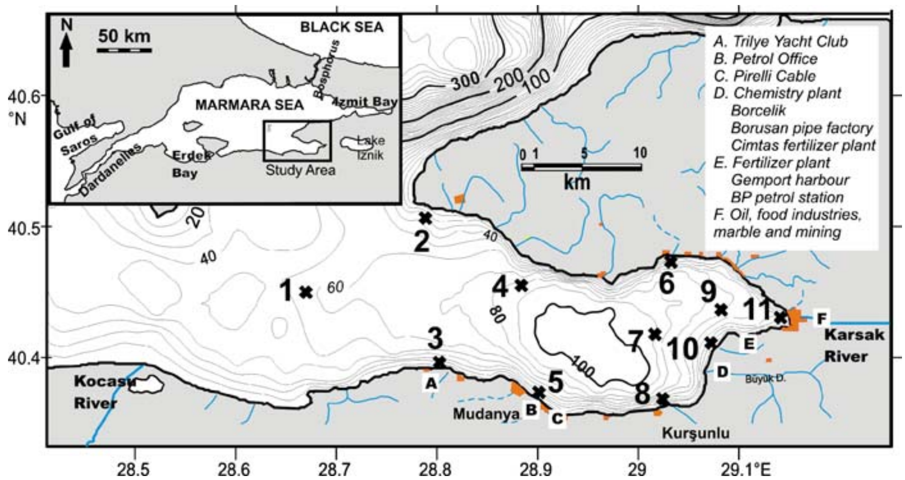

Fig. 1 Sediment sampling stations, industrial complexes and main pollutant rivers around the Gulf of Gemlik. The average and maximum depths are 59 and 107 m, respectively

Materials and methods

The surface sediment samples (three replicates) were collected from 11 sites (Fig. 1) using a van Veen-type grab sampler in June 2004. The collected sediments were composed after subsampled from the top 2 cm. They then were stored in plastic cups that were cleaned by 1:1 HCL and 1:1 HNO_3 until analysis. All samples were sieved with sieves of 500, 250, 125 and 63 µm mesh sizes. This wet sieving, a volume of 400 ml deionized water was used and the sieving was performed during 40 min. The sediment samples were dried at 85°C for 48 h, crushed and homogenized prior to the analysis.

The mussel (*M. galloprovincialis*) samples were collected from the Port Mudanya. Immediately after collection, the mussels were stored on ice in an insulated box and transferred to the laboratory and then frozen at −21°C. Prior to metal analysis, all the soft parts of ten mussels (7–8 cm shell length) were dissected. The sample was pooled and freeze-dried for 7–10 days to a constant weight. The dry/wet ratio was found to be 0.27± 0.03. The other analytical methods were previously described (Topçuoğlu et al. 2004).

One gram of the dry sediment sample was dissolved with 15 ml concentrated HNO_3 in a teflon beaker. The beaker placed on the hot plate and the nitric acid boiled for 2–3 min. 10 ml $HClO_4$ was added into the baker and kept at 170°C. After that, 10 ml hydrofloric acid was added and heating and boiling continued the residue dissolves. The HF was used in order to achieve complete dissolution. Finally the residue filtered using Whatman paper No. 41. The volume of the filtrate was made up to 100 ml with 5% HCl in a volumetric flask. The absorbance was read on an atomic absorption spectrophotometer (Varian Model Spectra AA.100/200). Values are expressed as the mean of three analyses for same sample. Errors were calculated from standard deviation of the absorbencies

The accuracy of the analysis was verified by analyzing the IAEA's certified reference material (lake sediment SL-1), by the same procedure used for the samples (Table 1). The average recovery of all analyzed metals in the reference material was 98.4%.

The metal data show normal frequency distribution and statistically tested before map production using the GEO-EAS program (v. 1.2.1) by the U.S. Environment Protection Agency (EPA 1991). The variograms for each element were checked for the appropriate variogram model, which mathematically specifies the spatial variability of the data set. Spherical models were chosen with parameters varied markedly between elements. Point kriging was chosen as gridding meth-

Table 1 Analyses of certified reference material (SL-1), for accuracy of AAS analyses used in the present study

Metal	Certified value (µg g^{-1})	Measured value (µg g^{-1})	Recovery %
Cd	0.26±0.05	0.27±0.07	103.8
Co	19.8±1.5	19.1±3.4	96.4
Cr	104±9	101.5±13.0	97.6
Cu	30±5.6	28.7±3.2	95.6
Fe%	6.70±0.35	6.80±0.81	101.5
Mn	3400±161	3250±260	95.6
Ni	44.9±8.0	41.9±4.7	93.3
Pb	37.7±7.4	38.4±2.8	101.8
Zn	223±10	225.6±17.0	101.2

od and the maps were produced using the Golden Software Surfer© 8 software and the chosen variogram model.

Results and discussion

It is well known that the heavy metal concentrations in sediment sample decrease with the increase of grain size. It is reported some advantages in using smaller fraction of the grain size (< 63 μm) (Förstner and Salamons 1980; Soares et al. 1999). First, such a grain size is similar to the suspended matter in the seawater. Lesser problems occur in comparison of the heavy metal levels for different studies. The separation method may be wet or dry. Both wet and dry sieving methods were applied in the separation of <63 μm grain size in the past (Groot et al. 1982; Lucas et al. 1986); both having some disadvantages. In another study, Soares et al. (1999) have shown that higher metal concentrations could be obtained in wet sieved samples if compared to the dry sieved fractions. We have used only wet sieving method in the present study. The heavy metal concentrations were analyzed using both <63 and >63 μm fractions after wet sieving.

Nine heavy metals were detected in sediment samples. The ranges for Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were between 13–24, 71–181, 23–58, 3.5–6.3 (%), 300–1560, 35–165, 0.1–67 and 88–185 μg g^{-1} (dry wt) at the <63 μm grain size fractions, respectively (Table 2). The highest concentrations occurred near the northeastern shore (stations #6 and 11) for Co, Fe, Cu and Zn and southwestern shore (station #3) for Cr and Ni. The highest concentrations of the Mn and Pb determined at the stations # 7 and 2, respectively. The lowest Pb concentrations were generally found near the southeastern shores (stations #8 and 10) where the highest concentrations of polycyclic aromatic hydrocarbons (PAHs) were documented very high (Ünlü and Alpar 2006).

The metal concentrations in the >63 μm fractions are generally lower when compared with the <63 μm fractions (Table 2). The only exceptions are for the deeper (65–95 m) stations # 4, 7 and 9 where >63 μm fractions were found a little higher for the Cu, Mn, Pb and Zn concentrations. A reason may be the quantity of grain size fractions in those samples where the ratios of coarse grained sediments are less than 2%. It is well known that the changes in the quantity of various grain size fractions influence the chemical compositions of the sediments (Romankevich 1984). Meanwhile, the heavy metal accumulation by fine grained sediment samples is especially related with the organic matter concentrations (Gonçalves and Boaventura 1991).

The minimum values at the range of Co, Cr, Cu, Fe, Mn, Ni and Zn concentrations at the <63 μm grain size in the present study are generally higher than the concentrations found in the other parts of the Marmara Sea, Black Sea, Bosphorus and Aegean Sea (Table 3). This result showed that the Gulf of Gemlik is a relatively polluted part of Marmara Sea. One reason is the low rate water circulation in this semi-enclosed embayment. The average current speeds of the upper Black Sea water, which usually flows counterclockwise, determined to be 13–17 cm s^{-1} at the entrance and 2–6 cm s^{-1} in the central and inner part. On the other hand, the average speeds of the underwater of the Mediterranean Sea water found as 9–10 cm s^{-1} at the entrance and 2.5–4.5 cm s^{-1} in the central and inner parts with the varying directions (Ünlü and Alpar 2006). The comparison of the heavy metal ranges has shown that the Gulf of Gemlik is more polluted than the northern coast of the Marmara Sea and even from Izmit Bay (except Cr). At the same time, the maximum values in the ranges of Fe, Mn and Pb in the present data are higher than those found in Erdek Bay (Fig. 1). On the other hand, Co, Cr, Cu, Ni and Zn levels are lower. The highest concentrations of heavy metals in sediment samples of the Turkish marine environment were reported as: Mn and Ni in the deep Marmara basins; Cr and Zn in Erdek Bay; Co in Izmit Bay; Pb in Bosphorus strait and Cu in the Black Sea.

The present status of heavy metals concentration in the Gulf of Gemlik was also compared with worldwide literature data (Table 3). The levels of heavy metals in the <63 μm grain size from the southern Marmara Sea were comparable to the data reported for the surface sediments from the coastal and estuarine areas all over the world.

Correlation matrix (Pearson method) was calculated for the heavy metals, TOC and grain size parameters (Table 4). There are no significant correlations between heavy metal concentrations except that Cr has relatively high correlation with Ni (0.86), Co with Mn (0.67) and Cu with Zn (0.60). Results suggest some important control of clay size sediments on the distribution modes of most of the analyzed heavy metals (Co, Cr,

Table 2 Heavy metal concentrations (μg g^{-1} dry weight) at the <63 μm and >63 μm fractions

Station	Fraction	Co	Cr	Cu	Fe %	Mn	Ni	Pb	Zn
1	<63 μm	19.3±1.2	143.5±1.5	37.4±0.2	4.76±0.06	544±28	136.8±1.2	53.1±6.2	140.5±0.7
	>63 μm	18.8±1.3	129.7±1.1	36.3±0.1	4.61±0.02	539±6	132.9±2.6	54.9±2.2	134.3±4.1
2	<63 μm	16.7±2.0	121.3±2.4	40.7±0.7	3.96±0.03	488±3	99.8±2.1	66.4±2.8	146.9±0.6
	>63 μm	6.9±0.6	30.0±1.5	5.3±0.6	3.82±0.02	300±1	6.3±1.0	34.5±2.9	28.2±5.4
3	<63 μm	18.4±2.0	180.3±4.9	49.9±0.3	4.10±0.03	432±1	162.4±7.3	26.9±15.3	129.0±7.2
	>63 μm	17.1±2.1	141.6±4.1	37.0±0.3	3.20±0.06	457±1	119.0±6.6	<0.1	112.3±0.3
4	<63 μm	21.0±1.4	126.9±2.6	42.5±0.4	3.96±0.04	674±7	140.9±1.5	55.3±8.5	144.8±1.0
	>63 μm	17.8±3.0	129.1±2.6	39.8±1.4	3.49±0.06	679±8	111.7±2.1	46.6±7.6	184.3±9.9
5	<63 μm	17.1±3.3	112.6±2.6	50.2±0.3	3.85±0.05	514±3	87.9±3.0	40.7±10.9	102.1±6.9
	>63 μm	11.9±2.3	76.7±1.2	22.9±0.3	2.11±0.02	413±1	53.6±2.3	<0.1	65.6±4.7
6	<63 μm	23.7±1.6	70.9±1.9	37.5±0.2	6.34±0.09	863±7	35.0±2.4	11.3±2.6	104.5±0.2
	>63 μm	22.3±0.7	42.3±2.6	22.7±0.4	4.35±0.10	507±4	10.7±2.4	<0.1	68.4±1.0
7	<63 μm	22.0±1.5	121.0±3.0	36.1±0.5	3.93±0.06	1554±15	142.7±1.5	41.5±14.2	122.6±2.5
	>63 μm	24.0±2.0	107.2±4.1	52.0±0.5	3.94±0.06	1119±11	118.7±7.0	56.0±14.2	127.0±5.0
8	<63 μm	16.2±1.2	107.7±2.7	26.3±0.3	3.74±0.01	532±5	90.3±0.3	<0.1	88.7±0.8
	>63 μm	12.7±1.1	58.3±0.7	14.4±0.2	2.20±0.02	342±2	53.2±1.1	<0.1	68.1±0.3
9	<63 μm	19.9±0.6	117.6±4.9	38.7±0.6	4.55±0.07	475±5	124.0±6.2	26.1±8.6	119.4±1.0
	>63 μm	20.4±1.5	93.3±3.4	38.0±0.3	4.96±0.06	510±8	100.5±3.9	29.3±8.8	122.1±2.2
10	<63 μm	18.7±0.9	94.0±0.6	32.7±0.8	4.20±0.03	593±3	108.9±4.6	<0.1	126.6±1.8
	>63 μm	10.3±2.1	63.9±3.6	12.0±0.3	2.72±0.01	829±6	52.0±2.5	<0.1	57.5±4.5
11	<63 μm	13.2±1.1	93.9±1.6	57.3±0.9	3.54±0.05	305±1	74.0±0.6	<0.1	184.8±12.0
	>63 μm	10.0±0.8	66.6±5.3	54.9±0.3	2.05±0.03	208±1	47.7±1.6	46.5±2.9	123.7±0.7
Range	<63 μm	(13–24)	(71–181)	(23–58)	(3.5–6.3)	300–1560	(35–165)	(0.1–67)	(88–185)
	>63 μm	(7–24)	(30–142)	(5–55)	(2.1–5.0)	208–1120	(6–133)	(0.1–56)	(28–185)
Mean±SD	<63 μm	19±3	117±28	41±9	4.4±0.8	634±336	110±37	29±24	128±26
	>63 μm	16±5	85±37	31±17	3.4±1.0	537±259	73±45	25±25	100+46
Crust	–	20	100	25	4.7	850	80	35	90
TEL	–		52.3	18.7			15.9	30.2	124.0
PEL	–		160.0	108.0			42.8	112.0	271.0

Range and mean values, metal abundances in the crust (Krauskopf 1979), threshold and probable effect levels were added in the bottom rows.

Mn, Ni and Pb) in this area. The organic carbon content varies between 0.1 and 3.1% throughout the study area; highest in the middle of the Gulf and offshore Gemlik Port (Ünlü and Alpar 2006). It shows consistency with the sediment textural characteristics and oxygen deficiency in the Gulf. Bathymetry and hydrodynamic processes seem to play an important role in the enrichment of organic carbon. Even the mixing processes of the surface water and coastal wave circulation cause decrements in organic carbon fluxes in front of the ports and rivers, observed increments in organic carbon contents may imply an increment in nutrient inputs from the rivers. No correlation of heavy metals was detected with the organic carbon content (except for Cu), suggesting a reduced control of TOC on the distribution patterns of the heavy metals, whose dispersion is probably driven by anthropogenic inputs in the region.

Relatively elevated concentrations of high metals were observed throughout the Gulf (Fig. 2). Lead, which is presumed to be non-essential elements for life, shows clear contamination in the open sea part. Its spatial distribution is almost opposite that of PAHs given by Ünlü and Alpar (2006). Cr and Ni contaminations are quite even throughout the whole Gulf. Mn is largely contaminating the central basin. Copper and Zinc are essential elements for all living organisms but elevated levels may cause adverse effects in all biological species. Copper contamination is much higher in the Gemlik Harbor and southwestern areas of the Gulf. The very much greater population densities and levels of industrialization in the town Gemlik almost certainly

Table 3 Comparison of the ranges of heavy metal concentrations (μg g^{-1}) in sediments from the Gulf of Gemlik with some literature data obtained from industrial regions and from Turkish marine environments

Location	Cd	Co	Cr	Cu	Fe %	Mn	Ni	Pb	Zn	Ref
Izmit Bay, Marmara Sea	n.a	43–105	6–81	13–49	1.4–4.0	112–678	34–98	23–52	45–114	(a)
Bosphorus Strait	2.3–3.3	9–22	22–62	7–46	1.1–3.1	112–147	17–59	35.6–135	43–119	(b)
Marmara Sea	n.a	10–30	58–166	12–92	1.1–4.7	196–5720	29–161	25–92	43–149	(c)
Erdek Bay, Marmara Sea	n.a	6–29	11–238	3–52	0.8–4.6	168–746	8–149	19–61	34–272	(d)
Gulf of Saros, Aegean Sea	n.a	n.a	n.a	6–44	0.3–4.6	114–1740	14–45	2–80	23–154	(e)
Turkish coast of Black Sea	<0.1–0.9	<0.1–6.4	11–116	4.0–96	0.5–5.4	207–871	14–66	<0.1–31	34–268	(f)
Northern coast of Marmara Sea	<0.1–0.5	4.3–11	27–62	12–31	0.6–1.5	273–385	30–54	21.6–32	34–51	(g)
Jurujuba Sound, Brazil	n.a	n.a	10–233	5–213	n.a	n.a	15–79	5–123	15–337	(h)
Phillip Bay, Australia	0.1–5.8	n.a	8–115	1–62	0.3–9	7–318	2–66	1–197	13–1600	(I)
Caspian Sea	0.2–0.3	0.7–24	2–103	1–58	0.2–4	45–1111	2–35	1–29	1–146	(j)
Montevideo Harbor, Uruguay	<0.1–1.6	n.a	79–253	59–135	n.a	n.a	26–34	44–128	174–491	(k)
Port of Barcelona, Spain	0.6–2.9	n.a	60–105	74–601	n.a	n.a	19–32	87–455	219–1165	(l)
Gulf of Gemlik, Marmara Sea	<0.02	13–24	71–181	22–58	3.5–6.3	300–1560	35–165	<0.1–67	88–185	(m)

n.a=not analyzed. (a) Ergin et al. 1991; (b) Güven et al. 1993; (c) Bodur and Ergin 1994; (d) Balkıs and Çağatay 2001; (e) Sarı and Çağatay 2001; (f) Topçuoğlu et al. 2001; (g) Topçuoğlu et al. 2004; (h) Baptista et al. 1999; (i) Fabris et al. 1999; (j) Mora and Sheikholeslami 2002; (k) Muniz et al. 2004; (l) Casado-Martinez et al. 2006; (m) this study.

account for this. Since there are no industrial sources nearby the southwestern coasts, however, it is assumed that these arise from the weathering of local metal-bearing rocks and lateral offshore transport of suspended material or from the activities of fishing boats in this area. Like cupper also Zinc shows a similar distribution pattern but zinc contamination is not so large. Zinc and Copper may have some interactions with organic matter (Table 4).

Elevated concentrations of high metals also suggest anthropogenic (domestic and industrial) inputs via the Kocasu River in the west and the Karsak River in the east. The abundance of metals was also related to presence of the Neogene sedimentary and volcano-sedimentary formations around the Gulf. The drainage basin of Kocasu River is 27,600 km^2, almost 80 times the total area of the Gulf. It includes some high-background (Fe-, Pb-, B-, S-, Am-, perlite, albite, kaoline, jips, marble, cement-rich) volcanosedimenter rocks (e.g. andasite, dasitic, rio-dasitic tuffs intercalated with mica/clay and mineral rocks), autigenic silicates and carbonates (Uz et al. 1995). It has been suggested that the terrestrial anthropogenic inputs via the rivers and from the surrounding area of the Gulf are the most important. There seems to be various sources of metal pollution (e.g. Cr, Cu, Ni, and Pb) in the Gulf and they seem to be easily transported over a large area. These metal contaminations show signif-

Table 4 Correlation matrix (Pearson method) calculated for the heavy metals, TOC and grain size parameters in the studied area

	Co	Cr	Cu	Fe %	Mn	Ni	Pb	Zn	TOC	Silt %	Clay %
Co	1.00	−0.06	−0.41	0.70	0.67	0.12	0.23	−0.40	−0.27	0.02	0.45
Cr		1.00	0.21	−0.35	−0.13	0.86	0.49	0.12	0.18	−0.01	0.54
Cu			1.00	−0.26	−0.37	0.00	0.11	0.60	0.58	0.34	0.05
Fe %				1.00	0.19	−0.42	−0.09	−0.31	−0.24	0.24	−0.05
Mn					1.00	0.14	0.17	−0.27	−0.12	−0.02	0.37
Ni						1.00	0.46	0.15	0.07	−0.20	0.73
Pb							1.00	0.17	−0.04	−0.33	0.52
Zn								1.00	0.21	−0.03	0.14
TOC									1.00	0.80	0.41
Silt %										1.00	0.23

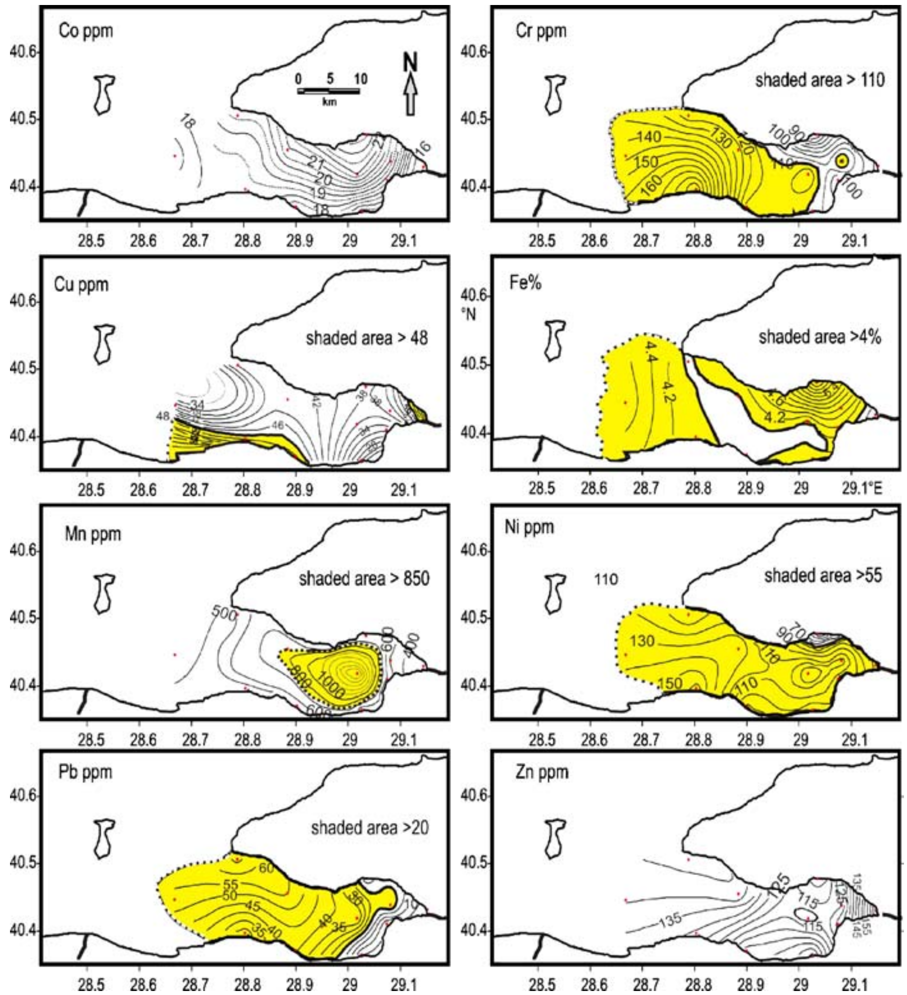

Fig. 2 Surface sediment concentrations (ppm) of Co, Cr, Cu, Fe (%), Mn, Ni, Pb and Zn in the Gulf of Gemlik

icant correlations with clay ratio (Table 4). Geochemical process in diagenic zones may also control the Fe and Mn distributions.

The main limitation of sediment chemistry data is that, by itself, it can not provide a basis for assessing the potential biological effects of contaminated sediments without the development or utilization of Sediment Quality Guidelines (SQGs). These guidelines are scientific tools that synthesize information regarding the relationship between the sediment concentrations of chemicals and any adverse biological effects resulting from exposure to these chemicals. For each parameter of interest, the guidelines have identified two numerical levels, the lower level is termed Sediment Quality Assessment Guidelines (ISQG) value and the higher level is called the probable effect level (PEL) value. Sediment chemical concentrations below ISQG values are not expected to be associated with any adverse biological effects, while concentrations above PEL values are expected to be frequently associated with adverse biological effects.

In this study, when compared with the priority toxic pollutants (listed in USEPA 1999), the concentrations of Cr, Cu, Pb and Zn have been found between the ISQG and PEL values (Table 2) which represent the range in which effects are occasionally observed. Except a limited area squeezed along the northern coast, the concentrations of nickel are above the PEL value throughout the Gulf, which is expected to be frequently associated with adverse biological effects. Nickel is used as a catalyst in industrial processes and in oil refining. The most important anthropogenic sources of nickel include fossil fuel combustion, smelting activities, and the electroplating industries along the southern coast.

Exposure of aquatic organisms to nickel contaminated sediments may result in a variety of adverse effects, including mortality, reduction in growth and avoidance reactions (CCREM 1987). Further studies are needed to confirm the potential pollution in sediment and its effects on the biological community.

The most likely route of human exposure to heavy metal is from consumption of contaminated mussels. Within the scope of the study, however, no systematic mussel collection was performed. Some mussels, however, were collected from Port Mudanya in September, 2004. Effluent discharges affect the region adversely and causing intensive fecal pollution. The total coliform concentration varied between 3 and 12 thousands CFU/100 ml and fecal coliform concentration varied between 2 and 10 thousands CFU/100 ml along the coast. These values vary between 0 and 97 thousands CFU/g, and between 0 and 6 thousands CFU/g in sediment, respectively (Alkan et al. 2000).

During the sampling of mussels (*M. galloprovincialis*), the seawater had a salinity of 24 psu, a temperature of 19°C, a pH of 7 (±0.1) and was oxygen saturated (7.5 mg/l). Nitrite, phosphate, ammonia and detergent concentrations were measured as 0.007, 0.15, 0.02, and 0.003 mg l^{-1}, respectively.

It is emphasizes in Table 5 that some heavy metal levels in the mussels from the Port Mudanya were higher than the acceptable values for human consumption set by various healthy organizations. For example the concentrations of the most human-related metals (Cd and Zn) are above the tolerance levels given by International Turkish Standards. Cadmium is also considerably high compared to daily tolerable Cd intake from food according to WHO/FAO committee's proposal (Merian 1991). Animals which have close relationship with sediment show relatively high body concentrations of cadmium (Kilgour 1991). Lead and nickel were significantly lower compared to mussels living in the northern margin of the Marmara Sea. Comparably low values of Cu concentration may be possible due to the ability of mussels to regulate Cu levels in their soft tissues.

Conclusion

An evaluation is presented of heavy metal pollution, on the basis of statistical analysis of metal concentrations in the sediments from the Gulf of Gemlik, a semi-enclosed embayment. The concentrations of heavy metals demonstrated uneven distribution patterns throughout the gulf. The concentrations of Cr, Fe, Mn and Ni in some defined localities approach the "severe effect levels" when compared with the Sediment Quality Guideline.

Our results showed that the sediment fraction with grain size <63 μm after wet sieving seems to be a useful method for evaluating heavy metal pollution. A comparison of the present results with those reported from other critical marine environments in the vicinity of the Marmara Sea, suggested that the heavy metal concentrations are generally higher in the Gulf of Gemlik.

The mussels collected from the gulf accumulate metals (Cd and Zn) which are above the tolerance levels of International Turkish Standards. From a nutritional point of view it is dangerous eating mussels with such high concentrations of Cd which is a very toxic metal (FAO 1989). On the basis of classification of environmental quality in fjords and coastal waters as proposed by Molvær et al. (1997) according to the basis of trace

Table 5 Comparison of the heavy metal concentrations obtained in the mussel samples collected from the Port Mudanya, Gulf of Gemlik, in September 2004 with other data from three different sites along the Marmara Sea and with the tolerance level in mussels given by the International Turkish Standards as modified on November, 14, 2002, by the Ministry of the Agriculture of Turkey

Samples	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Port Mudanya, Gulf of Gemlik (μg g^{-1} dry wt)	2.4±0.1	2.0±0.3	2.3±0.2	5.5±0.4	205.4±2.7	5.8±0.3	1.3±0.3	0.5±0.1	196±3.8
Average for Northern coasts of Marmara Sea (Topçuoğlu et al. 2004)	1.9±0.3	1.0±0.2	1.2±0.1	7.7±0.1	284.0±4.9	8.9±0.2	6.4±0.2	1.7±0.5	264±0.9
Tolerance level in mussel (mg/kg)	1.0	–	–	20	–	–	–	1.5	50

metal concentrations, the study region can be classed as slightly-to-moderately polluted. Even the metal accumulations of mussels may variable between stations, they are not found much different from those observed for the northern coasts of the Marmara Sea.

There are some limitations to this study. Much of the degradation in the Gulf of Gemlik is believed to be a result of human activities, increasing urbanization and industrial complexes on the land. Various physical–geochemical features influence the distribution of elements in the area, which are difficult to separate. Thus, pollution studies often do not distinguish between the forms but simply measure the total amount of metal present. Only by detailed, long-term monitoring of metal concentrations in different parts of the environment is it possible to distinguish between natural heavy metal contamination and that arising from human activities. Such kind of monitoring may also help understanding the complex and uncertain relationships between metal levels in sediment and the biota. Therefore, it is apparent that more studies are needed for clarifying the importance and role of the Gulf of Gemlik in the source and transportation of trace elements in the area. These studies can be geochemical composition of sediments, anthropogenic and natural inputs into the marine environment, and identification of major pollutants transported through water currents. Since anthropogenic sedimentation poses a significant threat to benthic ecosystems, pollutant monitoring of sediments should be continued. Moreover, it is well known that the sinking particulate matters are also important factor for checking of the heavy metal pollution in the marine environment. For this reason, it is important to determine heavy metal levels in collected sediment trap materials.

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