

Heavy Metal Concentrations in Surficial and Core Sediments from Izmir Bay: An Assessment of Contamination and Comparison Against Sediment Quality Benchmarks

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Abstract The levels of heavy metals were determined in surface and core sediments from the Izmir Bay in 2009. The highest concentrations of As, Cr, Cu, Ni, Pb and Zn were found in the inner bay due to industrial activities. In contrast, maximum levels of Mn, Co, Fe and Al were observed in the outer bay, due to geochemical structure. Cu, Pb, Zn, Ni, As, Cr and Co levels in the upper layer of core sediments were higher than the mean background values of bottom sediments. The enrichment of Cr, Mn, Pb, Zn, Cu and As in the bay seems to be driven by anthropogenic sources. It was found that the sediments in Izmir Inner Bay were generally polluted heavily with Cu, As, Ni, Cr, Pb and moderately with Zn according to the numerical Sediment quality guidelines of the USEPA.

Keywords Metals · Surface sediment · Core sediment · Enrichment factor · Contamination factor · Sediment quality benchmark · Izmir Bay (Eastern Aegean)

Izmir Bay (Eastern Aegean) is one of the great natural bays of the Mediterranean Sea, whose shoreline is dominated by Izmir Metropolitan Municipality. Izmir is an important industrial and commercial centre and a cultural focal point. The bay has a total surface area of over 500 km², water capacity of 11.5 billion m³, a total length of 64 km and opens in the Aegean Sea. The Gediz River, which flows to the northern part of the bay, is the second biggest river along the Eastern Aegean coast and this river is one of the major sources of anthropogenic input into the outer part of

Izmir Bay. The main industries in the region include food processing, beverage manufacturing and bottling, tanneries, oil, soap and paint production, chemical industries, paper and pulp factories, textile industries, metal processing, timber processing. Most of the industries in Izmir are located in the inner bay region (Kucuksezgin 2011).

Heavy metals, as defined by Nieboer and Richardson (1980), are normal constituents of the marine environment. Metals occur normally at low concentrations yet are capable of exerting considerable biological effects even at such levels (Rainbow 1992). All metals become toxic above threshold bioavailable levels (Blackmore 1998). Ag, Hg, Cu, Cd and Pb are particularly toxic. The elucidation of the comparative pollution of aquatic environments by heavy metals is possible by analysis of water, sediments and members of indigenous biota, i.e. biomonitors (Phillips and Rainbow 1993). Heavy metals readily enter the aquatic food chain and they may be biomagnified as they accumulate in higher trophic levels. They attain the highest concentration in higher consumer fish tissues at the top of the aquatic food chain (USEPA 1997). Measurement of persistent chemical concentrations in sediment cores can provide a valuable historical record of contamination.

Sediment cores contain information about the events that occurred in preindustrial time in the bays and its catchment area. Changes in metal concentration with depth in sediment cores can show long-term trends of metal input and thereby imply pollution. Vertical profiles of pollutant species in sediment cores have been commonly used as “pollution records”. Historical information about environmental contamination is a beneficial, even necessary, ingredient of attempts to decrease this contamination. This history can be used to establish background conditions and to evaluate how contaminant levels have responded to changes in population, land use, and human activities including actions (e.g., regulations,

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chemical restrictions) designed to reduce that contamination. This knowledge can be valuable in assessing the influence of past pollution control attempts and in designing and performing more effective programs in the future (Selvaraj et al. 2010; Liu et al. 2011).

There are various efforts to set national sediment quality criteria in many countries. Numerical sediment quality guidelines (SQG) have been used in North America for both freshwater and marine ecosystems (MacDonald et al. 2000). A number of studies have been carried out on the concentrations of heavy metals in the surficial sediment and biota (Parlak and Demirkurt 1990; Kucuksezgin 2011; Kucuksezgin et al. 2005, 2011), however no data are available from the published literatures discussing metal levels in the core sediments from Izmir Bay.

The purpose of this study is to investigate current metal distributions and concentrations in the surficial and core sediments, to compare other areas from Mediterranean Sea in order to obtain a global picture of the historic sediment quality of the Izmir Bay. This study also evaluates contamination level using enrichment factor analysis, the quality of sediment with the numerical SQG, ecological risk assessment finding the degree of contamination.

Materials and Methods

The surface sediment samples were collected using a Van Veen type grab sampler and the sediment core samples were obtained using a gravity corer from Izmir Bay during the cruise of R/V K. Piri Reis in spring 2009. 17 surface and 3 core sediments were sampled at different locations within the bay (Fig. 1) and dried, homogenized and reduced fine powder. For grain size correction, the $<63 \mu\text{m}$ fraction was chosen for analysis. A total of three sediment

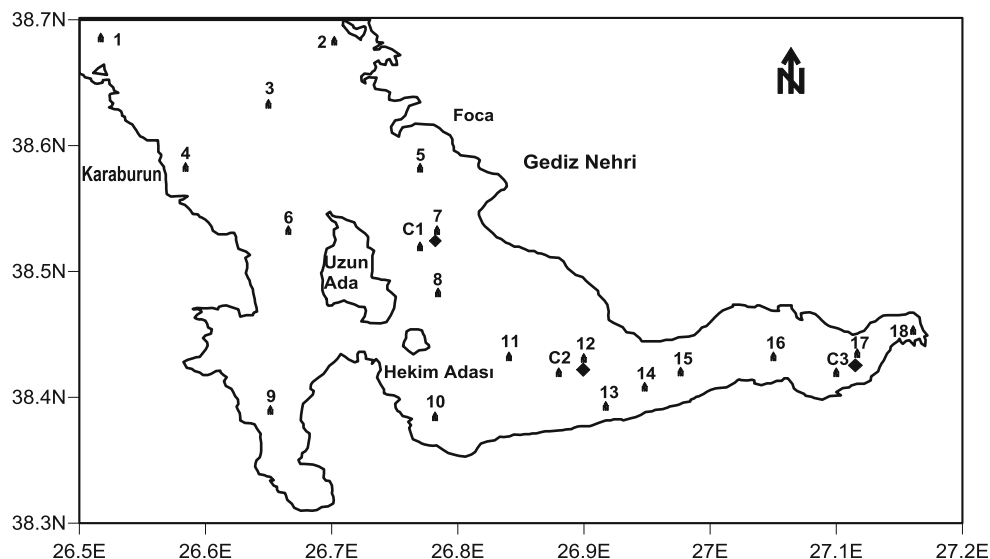
cores were cut into slices of 5 cm length and metals were analyzed in each slices of the core sediment.

Concentrations of metals were determined in the digested phase by inductively coupled plasma–mass spectrometer (ICP–ES/ICP–MS) analysis (ACME Analytical Labs, Vancouver, BC, Canada). Reference material (STD OREAS45CA) was used as a control for the analytical methods. Statistical analysis was performed using STATISTICA software package. Spearman Rank Order correlation test was used to determine linear relationships between metals and organic carbon concentrations.

Levels of heavy metal pollution in Izmir Bay were evaluated using two different techniques. One of them is enrichment factor (EF). Metal EF is used as an index to evaluate anthropogenic influences of heavy metals in sediments and is generally defined as the observed metal concentration (C_x) to the normalizing element Al (C_{ne}) ratio in the sample divided by the metal/Al ratio found in preindustrial reference value (crust). Commonly geochemical normalization of the heavy metals data to a conservative element such as Al or Fe, whose levels are unaffected by contaminant inputs, is employed in order to identify anomalous metal concentration. $EF = (C_x/C_{ne})_{sample} / (C_x/C_{ne})_{preindustrial\ reference}$; when $0.5 \leq EF \leq 1.5$, it suggests that the trace metals may be entirely from crustal materials or natural weathering processes. When $EF > 1.5$, it suggests that a significant portion of trace metals are provided by other sources (Zhang et al. 2007). In this study, metal concentration in bottom sediment of the core was used as the preindustrial reference (unpolluted) value and Al was used as normalizing element.

A contamination factor (C_f) to describe the contamination of a given toxic substance in a basin was suggested by Hakanson (1980). $C_f = C_e/C_b$; where C_e = concentration of the element in samples and C_b = background value for

Fig. 1 Location of stations in the Izmir Bay. The stations are plotted with different symbols where *Black circle* and *Black diamond* show surface and core sediment stations, respectively



the element. C_f , calculated as the ratio between the sediment metal content at a given station and the normal concentrations, reflects the metal enrichment in the sediment. C_f was classified into four groups in Hakanson (1980): $C_f < 1$, low contamination factor; $1 \leq C_f < 3$, moderate contamination factor; $3 \leq C_f < 6$, considerable contamination factor; and $C_f > 6$, very high contamination factor. The “degree of contamination”, C_d , is defined as the sum of all contamination factors of various heavy metals for a given basis. C_f for nine heavy metals (As, Cr, Cu, Co, Mn, Ni, Pb, Zn and Fe) in surface sediments was calculated using the raw elemental data. For the description of contamination degree, the following terminologies have been used: $C_d < 9$, low degree of contamination; $9 \leq C_d < 18$, moderate degree of contamination; $18 \leq C_d < 27$, considerable degree of contamination; and $C_d > 27$, very high degree of contamination.

Furthermore, potential acute toxicity of contaminants in sediment samples could be estimated as the sum of the toxic units (Σ TUs) defined as the ratio of the determined concentration to probable effect level (PEL) value (Pedersen et al. 1998).

The amount of organic carbon (%) was determined by spectrophotometrically in dried sediment samples following the sulfochromic oxidation method. The accuracy of this method is ± 0.017 % organic matter (Hach 1988). The sediment grain size was analyzed using the procedure of Folk (1980) and sand, silt, clay ratios were obtained. Textural classification of the sediment samples was based on the relative percentages of clay (<0.002 mm), silt (0.002–0.063 mm), sand (0.063–2 mm) and coarse sand-gravel (<2 mm).

Results and Discussion

In general particle size is fining in the sampling area except stations 1 and 4. Bottom sediments in these stations were relatively coarse with 84 %–96 % sand along the northwest coast of the outer bay while other stations were generally consists of clayey silt in the sampling area. According to grain size classification C1 and C3 were covered by silty clay along the core, while C2 was covered by clayey silt in the depth of 40–45 cm and silty clay in the other depths of this core.

Organic carbon (OC) concentrations in surface sediments from outer, middle and inner bay ranged from 1.2 to 29.2, 7.6–26.0 and 17.5–20.5 mgC/g, respectively (Table 1). The relatively high concentrations of OC at stations 9 and 10 reflect “high” organic matter flux to sediments due to the effect of anthropogenic and aquaculture activities. Surface sediments in the western coast of the outer bay (sta. 1) contained 1.2 mg C/g due to the grain size of the sediment from this station. The organic content of the muddy sediments are higher than sandy ones, with regard to clay particles tend to bind high quantity organic matter (Carvalho et al. 2005). The

relationship between metal concentrations and those of organic carbon have therefore also been examined for the present data set and no significant correlation was found between metals and organic carbon contents. The minimum, maximum and mean levels of metals, organic carbon determined in the surface sediments (as dry weight) from each sampling site as well as average crustal values (Turekian and Wedepohl 1961) are summarized in Table 1. Comparison of the metal concentrations with average crustal values revealed that most of the samples from the outer-middle, inner parts of the bay were polluted with As, Ni, Pb and As, Cr, Cu, Ni, Pb, Zn, respectively. On the contrary, the samples studied had lower Al, Co, Fe, Mn values at the inner bay and lower Al, Co, Cr, Cu, Fe, Mn, Zn concentrations at the outer-middle parts of the bay than the average crustal values, which indicated that there were no major sources of pollution for these elements in the bay.

The highest concentrations (as mg kg⁻¹) of Cr (112), Cu (66), Pb (82) and Zn (116) metals were found in the inner bay due to industrial activities compared to the middle and outer parts of the bay. In contrast, maximum levels of Mn (698), Co (18), Ni (117), Fe (34,200) and Al (22,400) were observed in the outer bay, due to geochemical structure (Ergin et al. 1993; Aksu et al. 1998). Increasing heavy metal concentrations tend to be associated with fine-grained sediments, and this can be seen in the high metal levels found in stations with high silt and clay contents except stations 1 and 4. All of the determinants were examined and Al, Co, Fe and Mn showed the least variability between the regions. The concentrations of As were, for all sites, greater than the elemental background levels.

According to our results; mean metal concentrations existed in the order of Fe > Al > Mn > Ni > Zn > Cr > Pb > Cu > As > Co, Fe > Al > Mn > Zn > Ni > Cr > Cu > Pb > As > Co and Fe > Al > Mn > Zn > Cr > Ni > Pb > Cu > As > Co in the outer, middle and inner parts of the bay, respectively. Fe, Al and Mn are the most abundant metals in all sediments because they are the most common elements in the Earth’s Crust (Turekian and Wedepohl 1961). Spearman rank-order correlation coefficients were computed between variables including all metals in the surface sediments of Izmir Bay. As results of the analysis, many metals turned out to be significantly positive correlated ($p < 0.05$). The highest coefficients were those for Fe–Ni ($r = 0.958$), Fe–Co ($r = 0.936$), Fe–Al ($r = 0.947$), Pb–Cu ($r = 0.838$), Cr–Cu ($r = 0.917$), As–Cr ($r = 0.828$), Ni–Co ($r = 0.929$), Al–Ni ($r = 0.945$), Zn–Cu ($r = 0.938$) and Co–Al ($r = 0.951$). The lowest correlation ($r = 0.337$) was observed between Zn and Ni.

The metal concentrations in sediments from the Izmir Bay were compared to the other studies performed in Mediterranean, Aegean and Marmara. Comparison of data

Table 1 Summary data showing mean \pm SE and range of heavy metal (mg kg⁻¹ dry weight) and organic carbon (mgC g⁻¹ dry weight)

Parameter	Outer bay	Middle bay	Inner bay	Average crustal ^b	BG ^c	TEL	PEL	SQG ^d non-polluted	SQG moderately polluted	SQG heavily polluted
Al	15,458 \pm 1,954 5,500–22,400	18,767 \pm 1,445 16,200–21,200	17,133 \pm 484 16,600–18,100	80,000	18,500	–	–	–	–	–
As	18.3 \pm 2.21 8.0–31	16.7 \pm 0.67 16–18	22.7 \pm 3.33 16–26	13	21	7.24	41.6	<3	3–8	>8
Co	12.5 \pm 1.54 4.0–18	16 \pm 1.53 13–18	14 \pm 0.58 13–15	19	15	–	–	–	–	–
Cr	59.3 \pm 6.90 23–87	71.3 \pm 4.48 65–80	98 \pm 10.7 77–112	90	61	52.3	160	<25	25–75	>75
Cu	20.3 \pm 2.79 5.0–32	27.7 \pm 1.20 26–30	53 \pm 10.2 33–66	45	20	18.7	108	<25	25–50	>50
Fe	24,317 \pm 2,841 8,700–34,200	31,000 \pm 1,411 28,200–32,700	27,700 \pm 1,069 25,800–29,500	47,200	30,000	–	–	–	–	–
Mn	411 \pm 43.9 211–698	513 \pm 45.7 467–604	513 \pm 11.9 491–532	850	455	–	–	–	–	–
Ni	77.4 \pm 10.3 26–117	90.7 \pm 7.80 77–104	76.7 \pm 5.33 66–82	68	97	15.9	42.8	<20	20–50	>50
Pb	22.7 \pm 2.27 8.0–35	27.3 \pm 0.88 26–29	56.7 \pm 15.3 29–82	20	13	30.2	112	<40	40–60	>60
Zn	63.3 \pm 7.55 22–97	91.7 \pm 2.85 86–95	167 \pm 25.4 116–196	95	59	124	271	<90	90–200	>200
Org. C	15.6 \pm 2.06 1.2–29.2	16.3 \pm 5.33 7.6–26	19.4 \pm 0.94 17.5–20.5	–	–	–	–	–	–	–
Σ TU ^a	3.24 \pm 0.40 1.17–4.67	3.80 \pm 0.24 3.41–4.25	4.56 \pm 0.43 3.77–5.26	–	–	–	–	–	–	–

^a Σ TU: Toxic unit^b Turekian and Wedepohl (1961)^c BG: Mean background values of bottom sediments from the three cores^d SQG: mg kg⁻¹

set revealed that levels of Cu, Ni, Cr, Pb and Zn were lower than previous study from Izmir Bay (Kucuksezgin et al. 2011). Arsenic and lead concentrations were similar to other regions around the Mediterranean, Aegean and Marmara Sea (Algan et al. 2004; Karageorgis et al. 2005; Accornero et al. 2008; Pekey 2006; Pazi 2011; Duman et al. 2012). Levels of Ni measured in Izmir Bay were slightly higher than the other areas except NW Mediterranean and NW Aegean, while Zn and Cr values were higher than NW Mediterranean, NE Mediterranean, Eastern Aegean, NW Aegean and Venice. Mn contents of the Izmir Bay are low compared to other areas except Venice. However, maximum values of Cu in Izmir Bay were higher than other areas except Marmara Sea and SW Mediterranean.

The vertical distribution patterns for As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the C1, C2, C3 cores from Izmir Bay are shown in Fig. 2. The vertical solid line in some of the

plots shows the average composition of sedimentary rock (Turekian and Wedepohl 1961). The mean concentrations for each element were lower than the background levels in earth crust except Pb, As and Ni in the core sediments. The high concentrations of Ni originated from the geochemical structure of the western Anatolia (Ergin et al. 1993). The levels of Ni, Fe, Zn, Cr and Co generally appeared to be uniformly distributed with depth (Fig. 2). Co, Mn, Fe levels did not indicate any significant anthropogenic input, thus are derived predominantly from lithologic material. Pb–Ni–As; Pb–Zn–Ni–As–Cr were anthropogenically enriched in top layers of C1 (outer), C2 (middle) and C3 (inner) from the Izmir Bay, respectively, but the decrease of these elements with depth in these cores was generally uniform. Pb, Cr, Ni, As concentrations in the top layer of C1, C2 and Cu, Pb, Zn, Ni, As, Cr and Co levels in the upper layer (0–5) cm of C3 core sediments were higher than the mean background values of bottom sediments

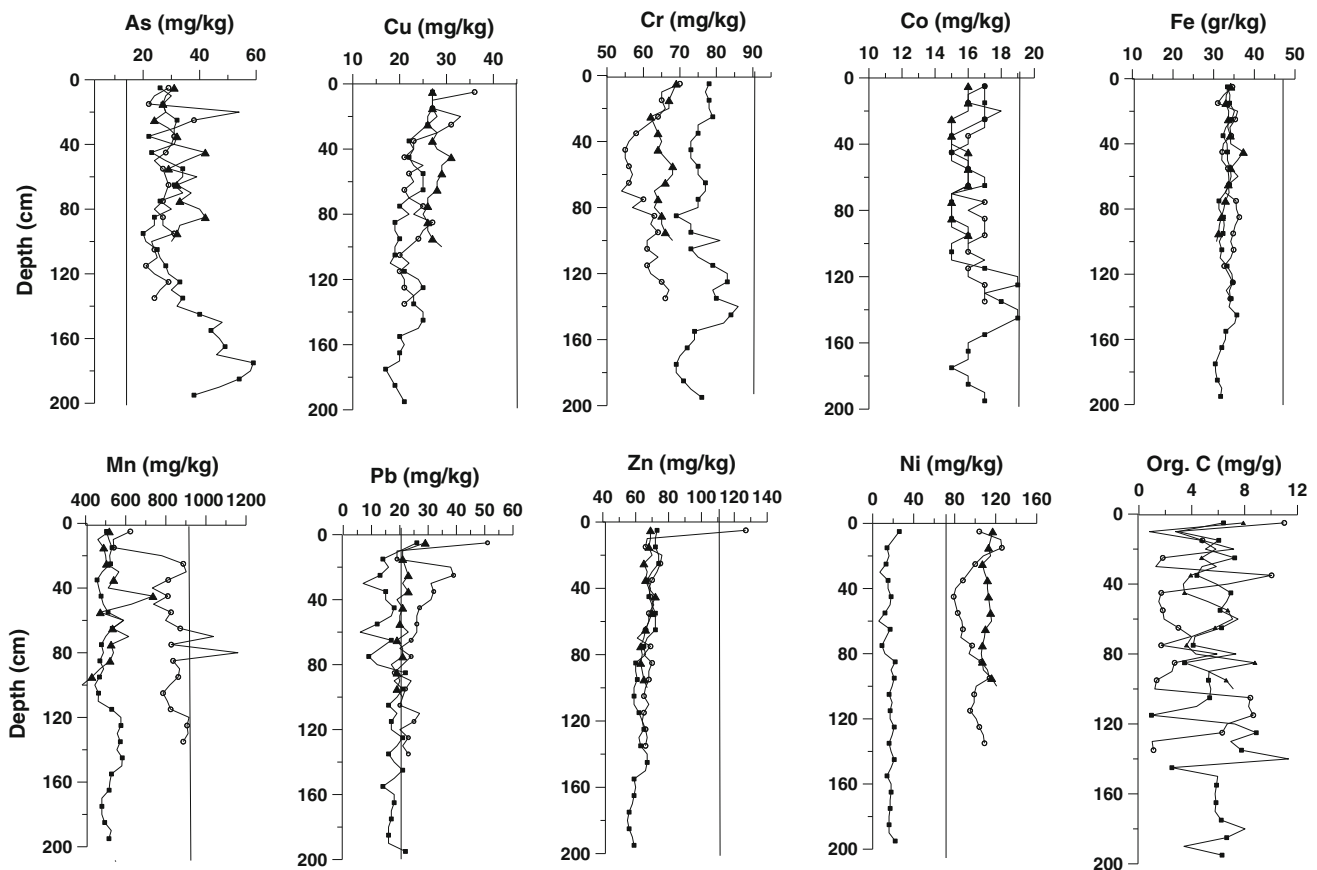


Fig. 2 Depth profiles of the concentration of metals (C1: Black square, C2: Black triangle, C3: circle) and Org. C in Izmir Bay's sediment cores. The line is the distribution of the elements of the Earth's Crust in Shale's Sedimentary Rocks (Turekian and Wedepohl 1961)

from the three cores (Table 1). The source of these metals can be attributed to the industrial activities. The average OC contents in C1, C2 and C3 were 0.95–11.3, 0.80–8.77 and 1.0–10.0 mgC g⁻¹, respectively. The levels of OC generally appear to be uniformly distributed with depth in C1 core sediments. OC values decreased along the C3 core sediment.

The contamination factors (*C_f*) were between low and moderate for Mn (0.46–1.53), Cu (0.30–1.60), Co (0.40–1.20), Cr (0.38–1.43), and As (0.38–1.48) and between moderate and considerable for Pb (0.62–6.31) according to the Hakanson (1980) classification in the bay. The *C_f* values of Ni were generally viewed to be low contamination in the study area, but the values of other metals were between low and moderate levels in the middle-outer bays. The *C_f* values of Cu, Zn and Pb were found to be of considerable contamination in the inner part of Izmir Bay sediments. The *C_f* values of metals except Cu, Zn and Pb were observed as moderately contaminated in the inner bay. The degree of contamination (*C_d*) values indicated moderate degree of contamination in the sediments from Izmir Bay, whereas station 17 showed considerable degree of contamination due to high *C_f* value of Pb in the inner bay.

An EF value of 1.5 indicates that the given element has principally originated from lithogenic source. EF of metals ranged between (Cr) 0.90–2.03, (Mn) 0.75–1.85, (Pb) 1.65–6.45, (Ni) 0.06–0.12, (Zn) 1.18–3.53, (Cu) 0.84–3.37, (As) 0.70–1.85, (Co) 0.65–1.39 and (Fe) 0.77–1.39 in the study area. The EFs of Ni, Co and Fe were lower than 1.5, while Cr, Mn, Pb, Zn, Cu and As enriched in the Izmir Bay. These results indicated that Cr, Mn, Pb, Zn, Cu and As (EFs > 1.5) came from human impacts.

Heavy metal levels were evaluated in surface sediments of the Izmir Bay in accordance with the numerical SQG of the USEPA. SQGs have been developed for many potentially toxic substances (i.e., trace elements, chlorinated organic, and polynuclear aromatic hydrocarbons) (MacDonald et al. 2000). SQGs were applied to this study for the assessment of the ecotoxicological sense of trace element concentrations in sediments with the threshold effect level (TEL) and probable effect level (PEL) values. The TEL (below which adverse effects are not expected to occur) and PEL (above which adverse effects are expected to occur) values are established for each SQG contaminant. Ni, Cu, Zn, Cr, Pb and As levels in the surface sediments of the Inner Bay exceeded the numerical TEL values stated in

the SQG, whereas Zn levels in the middle-outer parts of the bay were lower than the TEL. The minimum levels of Cu and Pb were below the TEL values, while the highest levels of Cu and Pb were above the TEL in the outer part of the study area. The only metal that exceeded the PEL value both in surface (26–112 mg kg⁻¹) and bottom layer of core sediments (109–156 mg kg⁻¹) was Ni at the entire sampling stations from the Izmir Bay. Additionally, Pb, Cr, Cu, Zn and As concentrations were below the PEL (Table 1). High concentration of Ni indicated that the source of Ni originated from parent rock weathering.

As, Ni, Cr, Cu, Pb, and Zn were assessed as the priority toxic pollutants based on the SQG of USEPA results. Numerical SQGs were used to identify contaminants of concern in aquatic ecosystem (MacDonald et al. 2000). Sediments were classified as non-polluted, moderately polluted, and heavily polluted, based on SQG of USEPA in Table 1 (Perin et al. 1997). Surficial sediment contamination was assessed according to SQG. It was found that the sediments in Izmir Inner Bay were generally polluted in heavy rate for Cu, As, Ni, Cr, and Pb and a moderately polluted rate for Zn. The contamination levels of Cr, Ni (considering maximum concentrations) and As were defined as heavily polluted in the middle-outer bays according to SQG, while Pb was specified as non polluted in the same stations.

The values of sum of TUs for each part of the study area based on concentrations of Ni, Cu, Zn, Pb, Cr and As were shown in Table 1. The toxic unit values ranged between 1.17 and 5.26. The sum of the toxic unit at the inner part of Izmir Bay exhibited higher level than other stations.

Metal contaminant sources to the Izmir Bay should include land-based point and nonpoint inputs, Gediz River discharge, and atmospheric inputs. This study presented the results of the surficial and vertical distribution of heavy metals and their accumulation in the Izmir Bay. Comparison of the metal concentrations with average crustal values revealed Al, Co, Fe, Mn values from inner bay and Al, Co, Cr, Cu, Fe, Mn, Zn levels from outer-middle parts of the bay were generally lower than those average crustal values, which indicated that no major sources of pollution for these elements in the study area. On the contrary, most of the samples from outer-middle, inner parts of the bay were observed to be contaminated with As, Ni, Pb and As, Cr, Cu, Ni, Pb, Zn, respectively. As were greater than the elemental background levels for all sites. Pb–Ni–As were both anthropogenically enriched in top layers of the three cores. The maximum EFs of Cr, Cu, Pb and Zn were calculated in the inner part of Izmir Bay. The elevated enrichment levels of Cr, Mn, Pb, Zn, Cu and As indicated anthropogenic pollution. This study indicated that the sediments in Izmir Inner Bay were generally polluted heavily with Cu, As, Ni, Cr, and Pb and moderately with

Zn as displayed by SQG. Furthermore, Ni concentrations at all sampling stations above the PEL value, which represented adverse effects, were expected to occur. On the other hand, Ni, Cu, Zn, Cr, Pb and As levels in the surface sediments of the Inner Bay were estimated above the TEL values. The degree of contamination in the sediments from Izmir Bay represented a moderate degree of contamination except inner bay that indicated a considerable degree of contamination.

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