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Sources of heavy metals in the Western Bay of Izmit surface sediments

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The study aimed to examine source apportionment of heavy metals of the surface sediments in the $< 63 \mu\text{m}$ size fraction. The sediment samples collected from 34 sites at the Western Bay of Izmit were subjected to a total digestion technique and analysed for major (total organic carbon, Al, Fe, Mg, and S) and trace (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, V, and Zn) elements by inductively coupled plasma-atomic emission spectrometry. The results were compared with the marine sediment quality standards, as well as literature values reported to assess the pollution status of the sediments. A factor analysis/multiple regression (FA/MR) multivariate receptor modelling technique was used for quantitative source apportionment to estimate the contributions from each source of contamination. Source fingerprints were obtained from the literature. A varimax rotated factor analysis was applied to the whole data set, and four probable source types were identified as the iron and steel industry, paint industry, crustal and sewage for heavy metals, explaining about 84% of the total variance. Source apportionment results derived from the FA and FA/MR methods agree well with each other.

Keywords: Surface sediment; Source apportionment; Factor analysis; Factor analysis/multiple regression; Heavy metals; Total organic carbon

1. Introduction

Sediment contamination poses one of the most harmful environmental hazards to marine ecosystems. While sediments may act as sinks, they also act as sources of contaminants in aquatic systems [1]. Sediments accumulate contaminants and serve as sources of pollution to the ecosystems with which they are connected. Pathogens, nutrients, metals, and organic chemicals tend to sorb onto both inorganic and organic materials, which eventually settle in depositional areas. If the loading of these contaminants into the waterways is sufficiently large, the sediments may accumulate excessive

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quantities of contaminants that directly disrupt the ecosystem, causing significant contamination and loss of desirable species. Without doubt, sediments are essential to the functioning of aquatic ecosystems [2]. Such trace elements as Cu and Zn are essential micronutrients for the normal growth and function of organisms. Other trace elements, i.e., As, Cd, Hg, Pb, and Sn, are considered to be toxic with respect to human health and aquatic life [3].

Grain size plays a significant role in determining elemental concentrations in sediments [4]. Salomons and Förstner [5] recommended a particle size fraction of $<63\text{ }\mu\text{m}$ for analysis as this would serve as the most approximate to be taken as equivalent to materials carried in suspension, the most important system for transport of sediments.

Pollution authorities use models to develop optimal control strategies for environmental pollutants. Receptor models infer contributions from different source types using multivariate measurements taken at one or more receptor locations [6, 7]. Several types of mathematical models have been used in the source apportionment studies. Factor analysis (FA) and factor analysis/multiple regression (FA/MR) analysis are parts of the multivariate model [8, 9].

This study aimed to identify the contributing source types and estimate the contributions of heavy metals to the Western Bay of Izmit. For this purpose, varimax rotated factor analysis (FA), reviewed by Henry *et al.* [10] and Gordon [11], and factor analysis/multiple regression (FA/MR), developed by Thurston and Spengler [12], were used to identify probable source types and to quantify their contribution.

2. Experimental

2.1 Study area

Izmit Bay is located on the northeastern Marmara Sea, latitudes $40^{\circ}41' - 40^{\circ}47' \text{ N}$, longitudes $29^{\circ}21' - 29^{\circ}57' \text{ E}$ (figure 1). It is an important semi-enclosed embayment situated close to Bosphorus and İstanbul, and has been strongly affected by constant population growth and industrialization [13]. The bay is about 45 km long,

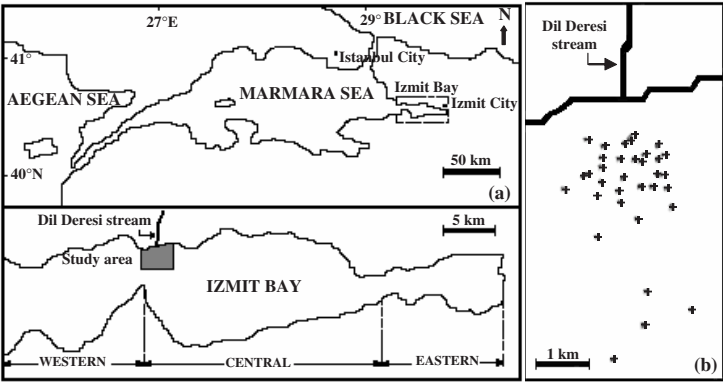


Figure 1. Map of (a) Izmit Bay and (b) sampling points.

1.8–9 km wide, and has an area of 261 km². It consists of three sections (western, central and eastern) connected to each other by narrow openings [14].

Sources of pollution include untreated or inadequately treated domestic sewage from 2 million inhabitants living around Izmit Bay [15] as well as solid and liquid wastes with limited treatment of organic matter from some 300 large industrial plants surrounding the bay. A petroleum refinery, supplying more than 30% of Turkey's demand, is situated on the northeastern coast. Bay waters carry heavy ship traffic [16].

One of the most important sources of pollution of Izmit Bay is Dil Deresi stream (with a total length of about 20 km and an average flow rate of 2 m³ s⁻¹), which flows into the Western Bay of Izmit. It is estimated that about 60% of the total waste water and 80% of the total TOC directly enters Izmit Bay through the Dil Deresi stream [17]. Additionally, the basin of the Dil Deresi stream is considered as one of the most highly industrialized areas of Turkey, hosting almost 120 industrial plants, such as paint (10 plants), chemicals (30 plants) and metal manufacturing and processing (50 plants), which are located along the basin and are subject to limited treatments. According to the figures of 1998, two major iron steel industries located by the Dil Deresi stream supply about 18% (1,953,000 tonnes) of steel production and approximately 23% of the total goods production (1,587,000 tonnes) [18]. Paint plants with the largest production capacity in Turkey are located here, and according to the 1999 data, nearly all of the 340,000 tonnes was produced in this location [19].

2.2 Analytical methodology

In April 2002, a total of 34 surface sediment samples were collected from the Western Bay of Izmit (figure 1). Water depth of the sediment samples ranged from 20 to 50 m. Sediment particle size fraction in the studied area is clay-silt as determined by Algan [20]. The samples were collected with a van Veen grab, and the upper 3–5 cm of the sediment was removed with a PTFE spatula to prevent contamination. These were immediately placed in polyethylene bags, refrigerated, and transported to the laboratory [21]. Samples were dried in an oven at 60°C for 3–4 days, lightly grounded in an agate mortar for homogenization, sieved to pass < 63 µm fraction and prepared for the chemical analysis.

An elemental analyser for C, H and N (Carlo Erba, EA-1106 model) was used to determine total organic carbon (TOC), with 1.0 N hydrochloric acid (HCl, Merck) added to the samples to remove inorganic carbonate phases [22].

The US EPA Method 3050B [23] and US EPA Method 6010B [24] were used, respectively, to digest and analyse Al, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Sn, V, and Zn.

Some 0.5 g of dried and homogenized sediment were weighed and placed into an acid-washed PTFE digestion vessel to which 5 mL of 1:1 nitric acid (HNO₃, Merck) was added, and the vessel covered with a watch glass. The sample was placed on a hotplate at ~95°C and refluxed for 5–10 min. The vessel was then removed from the hotplate and allowed to cool. After cooling, 2.5 mL of concentrated nitric acid (HNO₃) was added and the reflux repeated until brown fumes were no longer visible. The solution was evaporated to approximately 5 mL at ~95°C, without boiling, for 1 h. After cooling, 1 mL of water and 3 mL of 30% H₂O₂ were added and the solution heated slowly to start the peroxide reaction. The vessel was then cooled and 30% H₂O₂ in 1 mL aliquots added (less than a total of 10 mL). This was repeated

Table 1. Summary of data for SDN 1/2.^a

Metal	Observed \pm SD ($n = 10$)	Certified	Percentage recovery
Al	3.79 ± 0.1	3.75	101.1
As	51.1 ± 2.4	50.0	102.2
Cd	10.7 ± 1.1	11.0	97.3
Co	12.5 ± 0.84	12.1	103.3
Cr	153.0 ± 3.4	149.0	102.7
Cu	70.7 ± 2.1	72.2	97.9
Fe	3.59 ± 0.14	3.64	98.6
Mg	0.78 ± 0.1	0.76	102.6
Mn	799.0 ± 4.55	777.0	102.8
Ni	32.0 ± 2.8	31.0	103.2
Pb	123.5 ± 4.5	120.0	102.9
V	79.8 ± 2.42	77.7	102.7
Zn	450.0 ± 6.6	439.0	102.5

^a Concentration units are $\mu\text{g g}^{-1}$ for all metals except Al, Fe, and Mg, which are given in %. 'n' refers to the observations.

until the digestate appearance was unchanged. Acid-peroxide digestate was heated at $\sim 95^\circ\text{C}$ without boiling for 1 h, and 5 mL of concentrated HCl added to the sample digest and covered with a watch glass. The sample was placed on the hotplate at 95°C for 15 min. After cooling, digestate was transferred into a 50 mL volumetric flask, diluted to 50 mL with Milli-Q deionized water (analytical grade), and the flask transferred to a 125 mL high-density polyethylene (HDPE) sample bottle for storage. Sample solutions were analysed for major and trace elements following ICP/AES [24].

The detection limits of the measured elements in our study were defined as the concentration of an element which would give a signal three times higher than the standard deviation of 10 replicate analysis of one acid blank. The detection limits for trace elements were $10 \mu\text{g g}^{-1}$ for As, Ni, Pb, Sn, V, and Zn; $7 \mu\text{g g}^{-1}$ for Cu; $5 \mu\text{g g}^{-1}$ for Cr; $4 \mu\text{g g}^{-1}$ for Co; and $2 \mu\text{g g}^{-1}$ for Cd. For quality control, analytical blanks, duplicate samples and standard reference material SDN 1/2 (International Atomic Energy Agency, Monaco) were prepared with each batch of samples, which were then randomly analysed. Six analytical blanks were prepared in the same way as the samples to check for the existence of contamination during the digestion and analytical procedures. Blank subtraction is less than 5% for all the metals analysed by ICP-AES. The accuracy of the method was evaluated by analysing international certified reference material. The results (table 1) show a good agreement between the certified and analytical values, and the recovery ratios ranged from 97.3% for Cd to 103.3% for Co. The precision of the analytical procedures was better than $\pm 5.0\%$ RSD, with the exception of Zn (8.7%) and Cd (10.3%), all considered satisfactory.

2.3 Multivariate statistical methodology

Receptor models have widely been used in the field of air pollution control for several years [25, 26]. A few applications of this technique have been used to apportion pollution sources in marine environment [27, 28]. Elemental marker techniques and receptor modelling have not been applied previously to groundwater for source attribution, mainly due to the lack of quantitative information on the concentrations, behaviours, and characteristics of elements in groundwater systems. The original composition of a pollutant may be greatly altered at the sampling point, making

it almost impossible to determine the extent and/or source of contamination. Therefore, it is desirable to find and utilize pollution source characteristics or signatures, which are not modified during transport between source and receptor. Heavy metals are good candidates for this signature approach [29], because even if their chemical forms and absolute concentrations change as they move away from the source, individual elements with similar chemical characteristics are expected to be equally affected [6].

Factor analysis is a multivariate model for reducing matrices of data to their lowest dimensionality by the use of orthogonal factor space and transformations that yield predictions and/or recognizable factors [30].

The multivariate models deal with a series of m measurements of component i during sampling period or at sampling site k . From equation (1),

$$C_{ik} = \sum_{j=1}^p a_{ij} S_{jk}, \quad k = 1, \dots, m. \quad (1)$$

C_{ik} is used in multivariate models in order to predict the number of sources, p , and to determine the links between a_{ij} and S_j , whereas a_{ij} is the mass fraction of source contribution j possessing the property i at the receptor and S_j is the contribution of the individual sources.

For a source apportionment, it is necessary to perform an appropriate treatment of rotated scores to obtain the contribution of each source to C_{ik} . Several methods have been proposed in the literature to do this, the most popular of which are factor analysis/multiple regression (FA/MR) [9, 31], and absolute principle component score (APCS) [12, 32].

In the present study, a varimax rotated FA and source apportionment by FA/MR were applied to the elemental data to establish trends in a data matrix of 34 samples by 15 variables (Al, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Sn, V, Zn). Only those elements with observations higher than 80% were included in the FA. Lower quartiles of elements were used for the treatment of missing values, while samples with greater factor scores than or equal to 7.0 were excluded from the FA. All statistical calculations, including Pearson correlation coefficients, factor analysis and multiple regression, were performed using Statgraphics Plus 3.1 software [33].

3. Results and discussion

3.1 General characteristics of data

Table 2 summarizes the statistics for elemental concentrations at sampling sites, including mean concentrations with relevant standard deviation, geometric mean, minimum, maximum and median values. Each individual element displays a wide variation in elemental concentration as reflected by the large standard deviation values. The variations within elements may significantly affect the mean concentrations due to extremely high or low values. Median concentrations, on the other hand, will not be affected by extreme values, and are thus used for calculation in the present study. Median concentrations of trace and major elements are between $4.9 \mu\text{g g}^{-1}$ (Cd) and $36,500 \mu\text{g g}^{-1}$ (Fe) for the whole data set. The major elements Al, Mg, and S in sediment samples have median concentrations (as $\mu\text{g g}^{-1}$) of 30,100, 12,400, and 3900 for the whole data matrix, respectively. As can be seen in the table, heavy metals like Zn, Mn, Sn,

Table 2. Summary statistics (mean \pm SD, geometric mean, minimum, maximum, and median values) for elemental data in the Izmit Bay (concentration in $\mu\text{g g}^{-1}$).

Variable	Mean \pm SD	Geometric mean	Minimum	Maximum	Median
Al	30,400 \pm 7070	29,500	14,100	48,000	30,100
As	21.9 \pm 2.8	21.7	13.5	28.2	21.8
Cd	5.1 \pm 1.3	4.9	2.5	9.5	4.9
Co	18.3 \pm 6.4	17.5	12.1	47	17.3
Cr	75 \pm 16.7	72.9	38.9	112.4	74.3
Cu	66.4 \pm 16.6	63.9	24.5	102.4	67.6
Fe	35,800 \pm 5720	35,400	23,600	51,200	36,500
Mg	12,300 \pm 2770	11,900	5400	19,500	12,400
Mn	496 \pm 80	489	320	650	490
Ni	41.2 \pm 7.3	40.4	21.1	54.9	42
Pb	104.7 \pm 24.9	101.8	55.2	172	102
S	4100 \pm 1050	3980	1900	7500	3900
Sn	190 \pm 56.6	183.3	100	410	180
V	40.6 \pm 9.6	39.5	19	66	40
Zn	961 \pm 291	923.3	440	1900	930
TOC (% dry weight)	3.8 \pm 0.7	3.4	2.4	5.3	3.5

Table 3. Pearson correlation matrix for the metal concentrations.

	Al	As	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	S	Sn	V	Zn
Al	1.0														
As	0.6	1.0													
Cd	0.8	0.6	1.0												
Co	0.6	0.6	0.8	1.0											
Cr	0.7	0.9	0.6	0.6	1.0										
Cu	0.6	0.9	0.6	0.5	0.9	1.0									
Fe	0.8	0.8	0.7	0.7	0.9	0.8	1.0								
Mg	0.9	0.7	0.7	0.6	0.8	0.8	0.9	1.0							
Mn	0.6	0.8	0.6	0.5	0.8	0.7	0.8	0.8	1.0						
Ni	0.7	0.8	0.6	0.6	0.9	0.9	0.9	0.8	0.8	1.0					
Pb	0.7	0.6	0.9	0.7	0.6	0.7	0.6	0.7	0.6	0.6	1.0				
S	0.9	0.6	0.8	0.7	0.6	0.6	0.8	0.8	0.6	0.6	0.8	1.0			
Sn	0.7	0.6	0.8	0.9	0.6	0.6	0.7	0.7	0.6	0.6	0.8	0.8	1.0		
V	0.9	0.5	0.8	0.7	0.6	0.6	0.8	0.9	0.6	0.7	0.7	0.9	0.7	1.0	
Zn	0.6	0.6	0.8	0.9	0.6	0.6	0.7	0.7	0.6	0.6	0.8	0.8	0.9	0.7	1.0

and Pb have the highest median concentrations in the data set, 930.0, 490.0, 180.0, and 102.0 $\mu\text{g g}^{-1}$, respectively.

Total organic C (TOC) concentrations in the sediments display a wide range of 2.4–5.3% (table 2). The relatively high concentrations of TOC in the study area point to a high organic matter flux in sediments due to the direct discharge of untreated domestic sewage and insufficiently treated industrial wastes.

The degree of correlation between trace metals and other major constituents is often used to indicate the origin of the elements [34]. In this study, correlations between the element pairs were statistically tested. The relationship between two such parameters is shown on a Pearson's correlation coefficient matrix in table 3. There were significant statistical relationships between the elements when Pearson's correlation matrix was applied to the variables at a 95% confidence interval. The elements having high degrees of correlations ($0.8 \leq r \leq 0.9$) were As, Cr, Cu, Fe, Mn, and Ni, which indicates that they have similar anthropogenic sources. The table also shows that *S* and *V* values

Table 4. Trace-element concentrations ($\mu\text{g g}^{-1}$) from various sources.

Location	As	Cd	Cr	Cu	Pb	Zn
This study, range (median) ^a	13.5–28.2 (21.8)	2.5–9.5 (4.9)	38.9–112.4 (74.3)	24.5–102.4 (67.6)	55.2–172 (102)	440–1900 (930)
Average shale ^b	13	0.3	90	45	20	95
Soil ^c	1.8	0.2	100	55	13	70
Mean crust ^d	1.5	0.11	100	50	14	75
Mean sediment ^e	7.7	0.17	72	33	19	95
Golden Horn Estuary, Turkey ^f	nd	nd	275–551	337–4432	141–797	511–9943
Sediment Management Standards ^g	57	5.1	260	390	450	410
Southern Baltic Sea, Poland ^h	nd	0.81	28.7	12.6	31.5	60.1
Southern Bay, Brazil ⁱ	18.1–56.2	0.07–0.11	11–25.1	22.7–28.1	42.0–43.5	94.2–114
Izmir Bay, Turkey ^j	25–30	0.22–0.42	208–308	32–70	36–62	99–260

^a This study; ^b [35]; ^c [36]; ^d [37]; ^e [38]; ^f [39]; ^g [40]; ^h [41]; ⁱ [42]; ^j [43]. nd: not determined.

of the Izmit Bay sediments not only indicate good correlations with each other ($r = 0.9$), but also correlate ($0.8 \leq r \leq 0.9$) with Al, Fe, and Mg. In addition, significant correlation coefficients ($0.8 \leq r \leq 0.9$) were obtained between the elements Cd, Co, Pb, Sn, and Zn.

3.2 Comparison with other studies

We compared our results with results reported in literature (table 4) to gather preliminary information about the level of pollution in Western Bay of Izmit. The values were compared with marine sediment quality standards, SQS [40], and background concentrations of elements [35–38]. Then, the values were compared with other results concerning sediments from various marine environments presenting various levels of contamination.

The following observations were made:

- (1) When compared with the elemental background compositions, surface sediments were observed not to be contaminated with Cr and Cu; however, other elements like As, Cd, Pb, and Zn with greater anthropogenic inputs were observed to be enriched in the Bay sediment samples.
- (2) Zinc and Cd values were higher than the State of Washington SQS values, but concentrations of As, Cu, Cr, and Pb were lower than the SQS values.
- (3) Chromium and Cu concentrations were at comparable levels with the unpolluted areas reported in the literature, but the concentrations found for As, Cd, Pb, and Zn were comparable with those in polluted areas (table 4).

3.3 Source apportionment and quantification

FA and FA/MR were used to identify the source types and to quantify the contributions of each source to the surface sediment quality of the Western Bay of Izmit. Results of the FA are given in table 5. Three factors having greater eigenvalues than unity and explaining the 74% of the total variance are extracted. The table also includes factor loadings, eigenvalues, variance explained by each factor, and communalities of elements included in the FA.

Table 5. Varimax rotated factor loading and corresponding probable source type.

Variable	Factor 1	Factor 2	Factor 3	Communality (Factors 1–3)
As	0.85			0.77
Mn	0.79			0.66
Cr	0.96			0.93
Cu	0.82			0.74
Ni	0.88			0.80
Fe	0.81		0.42	0.84
Mg	0.50		0.65	0.69
Al			0.85	0.74
Cd		0.66		0.48
Co		0.90		0.85
Pb		0.61		0.40
Zn		0.93		0.88
Sn		0.85		0.75
S			0.81	0.77
V		0.31	0.81	0.81
Eigenvalue	4.89	4.10	2.12	11.11 ^a
Percent of variance	32.6	27.3	14.1	74.0
Probable source type	Iron and steel industry	Paint industry	Crustal	

^a Sum of communality.

The FA has revealed two anthropogenic components which represent combined discharges of industries and sewages. One of the main purposes of the study was to differentiate between industrial and sewage discharges and to estimate their contributions separately. This aim was not accomplished in the FA discussed above, probably because the elements discharged from industries are also discharged from sewages, which in turn generate a certain degree of uniformity between elemental distributions. Although both sources discharge these anthropogenic elements, their quantities vary significantly, which results in different concentrations of elements in different locations. To illustrate, some elements can be found in very high concentrations near sewage discharge outlets, whereas others can be detected in rather high concentrations near industrial discharge pollutants.

A method needs to be used to separate the anthropogenic factor obtained in the FA into two factors, one representing the discharges from industries and the other representing discharges from sewages. To differentiate between the industrial and domestic discharges, the methods developed by Atgin [43] and Pekey *et al.* [44] were used in this study. In this method, Atgin generated dummy variables using chromium as the normalizing element due to its high concentration level in industrial discharges and very low concentration in sewages. Similarly, values for As in our study were high in industrial discharges and low in domestic discharges. Therefore, As was selected as a normalizing element and three dummy variables; namely, Cu/As, Cr/As, and Ni/As were generated for each sampling site and included in the data set. In this study, the concentrations of Cu, Cr, and Ni were very high in sewers compared with the industrially affected sites. The elements having similar distributions of element to As ratios (dummy variables) are expected to appear as the same factor. On the other hand, elements predominantly discharged from the industries are expected to appear as a separate factor.

With these considerations, the FA was repeated for the data set. Varimax rotated FA results are presented in table 6 with probable source types. The inclusion of the dummy variables produced the anticipated results, and the anthropogenic factor was split

Table 6. Varimax rotated factor loading and corresponding probable source type when the dummy variables are added.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communality (Factors 1–4)
As	0.92				0.90
Mn	0.81				0.71
Cr	0.92			0.31	0.95
Cu	0.69			0.62	0.93
Ni	0.77			0.48	0.85
Fe	0.80		0.47		0.90
Mg	0.52		0.58		0.64
Al			0.77		0.72
Cd		0.87			0.78
Co		0.87			0.89
Pb		0.83			0.70
Zn		0.86		0.36	0.90
Sn		0.81	0.40		0.85
S			0.85		0.89
V			0.83		0.84
Cu/As				0.91	0.91
Ni/As				0.81	0.86
Cr/As				0.71	0.82
Eigenvalue	5.94	4.82	2.39	1.89	15.04 ^a
Percent of variance	33.0	26.8	13.3	10.5	83.6
Probable source type	Iron and steel industry	Paint industry	Crustal	Sewage	

^a Sum of communality.

into two separate factors. In the table, the eigenvalue was set to 1.0 as a threshold in order to limit the number of extracted factors. Factor loadings equal to or greater than 0.3 were presented in the table, because those below 0.3 were considered insignificant. With few exceptions, communalities of elements were higher than 0.80, indicating that four factors were sufficient to account for most of the variances of the elements (table 6). The four factors were obtained, which explained approximately 84% of the total variance, with the first factor accounting for 33.0%, the second factor for 26.8%, the third factor for 13.3%, and the fourth factor for 10.5%.

The first factor was characterized by high loadings of As, Cr, Mn, Fe, and Ni, and a moderate loading of Cu and Mg, which are used as markers or tracers of iron and steel industry. Therefore, this factor was identified as the iron and steel factor.

The second factor was heavily loaded with Cd, Co, Zn, Pb, and Sn, which are known to exist in industrial wastewaters. According to the literature [15, 45], elements like Cd, Co, Pb, Zn, Pb, and Sn are known as the markers of paint industries, many of which are present in the study area. Therefore, this factor was named the paint industry factor.

The third factor displayed high loadings of S, V, and Al, moderate loadings of Mg, Fe, and Sn. All the elements in the third factor (with the exception of Sn and V) are usually found in crustal components. It can be argued, therefore, that the third factor originates from crustal contribution.

The fourth factor contained variables like Ni, Zn, and Cr with weak loadings, a moderate loading of Cu, and strong loadings of the three dummy variables. Elements like Cu, Cr, Ni, and Zn are most likely to exist in sewages [46–48]. The presence of dummy variables in this factor suggests that it represents sewage discharge into the Bay. Therefore, this factor was recognized as the sewage factor.

Table 7 Mean source contributions (in % \pm SD) and the predicted-to-observed ratios (P/O) of heavy metals and dummy variables calculated using FA/MR technique.

Variable	Iron and steel industry	Paint industry	Crustal	Sewage	P/O ratios	r^2
Al	18.8 \pm 2.3	15.6 \pm 2.3	62.1 \pm 4.6	3.5 \pm 0.5	0.93 \pm 0.09	0.72
As	76.8 \pm 6.5	13.4 \pm 2.4	3.6 \pm 0.5	6.2 \pm 0.8	0.94 \pm 0.08	0.88
Cd	13.4 \pm 1.5	62.7 \pm 5.9	13.8 \pm 2.2	10.1 \pm 1.4	1.08 \pm 0.07	0.79
Co	8.5 \pm 1.1	72.8 \pm 5.7	12.1 \pm 1.9	6.6 \pm 1.0	1.09 \pm 0.08	0.90
Cr	64.9 \pm 4.4	16.1 \pm 1.7	9.5 \pm 1.0	9.5 \pm 1.3	0.94 \pm 0.05	0.94
Cu	61.2 \pm 4.7	13.6 \pm 1.6	12.8 \pm 1.7	12.4 \pm 1.3	0.95 \pm 0.06	0.92
Fe	49.3 \pm 3.9	9.5 \pm 1.1	39.1 \pm 3.4	2.1 \pm 0.3	0.94 \pm 0.09	0.88
Mg	44.3 \pm 4.8	12.6 \pm 1.9	33.8 \pm 3.4	9.3 \pm 1.8	0.92 \pm 0.11	0.66
Mn	51.4 \pm 4.8	23.6 \pm 2.8	18.5 \pm 1.9	6.5 \pm 1.1	0.95 \pm 0.09	0.76
Ni	71.1 \pm 6.2	8.3 \pm 1.3	9.5 \pm 1.2	11.1 \pm 1.5	1.05 \pm 0.07	0.86
Pb	11.5 \pm 1.6	74.1 \pm 6.6	12.8 \pm 1.4	1.6 \pm 0.2	1.06 \pm 0.10	0.72
S	10.2 \pm 1.2	11.3 \pm 1.6	65.6 \pm 5.3	12.9 \pm 1.1	0.94 \pm 0.07	0.88
Sn	14.5 \pm 1.8	67.8 \pm 5.7	8.9 \pm 1.1	8.8 \pm 1.3	1.07 \pm 0.08	0.88
V	9.8 \pm 1.4	13.6 \pm 1.9	69.8 \pm 6.1	6.8 \pm 1.1	1.06 \pm 0.09	0.85
Zn	18.2 \pm 2.0	71.5 \pm 4.9	7.4 \pm 1.2	2.9 \pm 0.4	0.93 \pm 0.07	0.90
Cu/As	4.3 \pm 0.5	4.1 \pm 0.7	12.4 \pm 1.4	79.2 \pm 5.6	1.06 \pm 0.05	0.88
Cr/As	3.8 \pm 0.6	6.8 \pm 0.5	16.9 \pm 1.8	72.5 \pm 6.8	0.93 \pm 0.07	0.79
Ni/As	5.8 \pm 0.6	8.1 \pm 0.8	11.3 \pm 1.2	74.8 \pm 6.0	1.07 \pm 0.06	0.85

Although FA applied to the data set provided qualitative information about the source types, it does not supply adequate quantitative information regarding the contributions of each source type. A multiple regression method was applied to the data set to overcome this problem following the FA. The accuracy of the FA/MR exercise can be tested by calculating ‘predicted to observed’ ratios of the elements, since FA/MR gives the contribution of each source on the concentration of each element in the same sample. The predicted-to-observed ratios (P/O) of the elements varied between 1.09 (Co) and 0.92 (Mg). Table 7 indicates that these elements were predicted with an uncertainty of more than 10% by applying the FA/MR technique. The mean percent contributions of each of the sources on the observed Al, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Sn, V, Zn, Cu/As, Cr/As, and Ni/As concentrations are given in table 7. The correlations of the predicted and observed values, r^2 , are rather high (≥ 0.70), except for Mg (table 7). When the percent contributions of each source type obtained from the FA/MR technique were compared with the elemental concentrations, the combined percent contributions for each of the elements were very close to the observed results.

4. Conclusions

Concentrations of heavy metals in sediments collected from Izmit Bay were investigated to estimate the contributions of the pollution sources using multivariate statistical analysis. The FA and FA/MR model were successfully applied to the data set to apportion the probable sources of heavy metals in sediments and to quantitate the contributions of each source to the samples. Dummy variables were used to enhance the source identification capability of the FA and to differentiate between the contributions of the industrial and domestic discharges. The results indicate that iron, steel, and paint industries are among the most significant sources. The study also demonstrates that the source apportionment of metals in sediments using multivariate methods

is of concern, especially if the results can be used for modelling or environmental management.

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