

Seasonal and Spatial Variations of Ecological Risk from Potential Toxic Elements in the Southern Littoral Zone of İzmir Inner Gulf, Turkey

Ebru Yesim Ozkan (✉ ebruyesim.ozkan@ikc.edu.tr)

Izmir Katip Celebi Universitesi <https://orcid.org/0000-0001-9780-6534>

Şakir Fural

Kirsehir Ahi Evran Universitesi

Serkan Kükrer

Ardahan Üniversitesi: Ardahan Universitesi

Hasan Baha Büyükişik

Ege Universitesi

Research Article

Keywords: Potential toxic elements, Regional ecological risk assessment, Environmental degradation Biogenic silica, İzmir Inner Gulf, Geographical Information Systems.

Posted Date: September 20th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-782841/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

1 **Seasonal and spatial variations of ecological risk from potential toxic elements in the southern**
2 **littoral zone of İzmir Inner Gulf, Turkey**

3 **Ebru Yeşim Özkan**

4 *İzmir Katip Çelebi University, Faculty of Fisheries, Department of Marine Biology, Turkey*
5 *ebruyesim.ozkan@ikc.edu.tr*

6 **Şakir Fural**

7 *Kırşehir Ahi Evran University, Faculty of Arts and Sciences, Department of Geography, Turkey*

8 **Serkan Kükrer**

9 *Ardahan University, Faculty of Humanities and Literature, Department of Geography, Turkey*

10 **Hasan Baha Büyükişık**

11 *Ege University, Faculty of Fisheries, Department of Fisheries of Basic Sciences, Turkey*

12 **Abstract**

13 This study aimed to investigate the ecological risk level of İzmir Inner Gulf. Based on the findings,
14 port, industry, settlement and transportation activities generated Mo, Pb, Cu, Cd, Zn enrichment.
15 Modified hazard quotient (MHQ) point to a high level of pollution and toxic effects for Ni and Cr;
16 significant pollution and toxic effects for As and Hg, and moderate pollution and toxic effects for Pb,
17 Zn, Cu. According to the ecological contamination index (ECI), the inner gulf is significantly-highly
18 polluted. Toxic risk index (TRI) and potential ecological risk index (PERI) are also consistent with
19 these data. According to the ECI, the inner gulf is significantly/highly polluted. TRI and the PERI are
20 also consistent with these data. Cd has created a significant ecological risk in all seasons due to its
21 high toxicity. Cu and Pb have caused moderate ecological risk in local areas near the port. A moderate
22 potential ecological risk has been identified in all seasons throughout the inner gulf.

23 **Keywords:** Potential toxic elements, Regional ecological risk assessment, Environmental degradation
24 Biogenic silica, İzmir Inner Gulf, Geographical Information Systems.

25 **1. Introduction**

26 The marine environment is one of the world's most valuable yet understudied areas (Williams and
27 Antoine, 2020). This is why these habitats around the world have attracted great attention in providing
28 basic life to people. However, due to increasing population growth, migration to coastal areas has
29 brought great problems for aquatic environments. New difficulties and threats have emerged in marine
30 habitats during the last few decades as a result of increased urbanization and rapid industrialization. As
31 a result of industrial development, metals are becoming more common in the aquatic environment due
32 to their contamination, durability and ability to be included in the food chain (Ahamad et al., 2020;
33 Bastami et al., 2014; Xiao, 2015).

34 Analysis of water, sediments, and members of indigenous biota, i.e. biomonitors, can be used to
35 determine the relative pollution of aquatic habitats by metals (Atalar et al., 2013; Phillips and
36 Rainbow, 1993). Metals released into aquatic environments can be trapped on suspended inorganic
37 and organic colloidal sediments before sinking to the bottom sediments, where they can be
38 bioaccumulated and biomagnified in the food chain (Bat and Özkan, 2019; Bat et al., 2015; Nowrouzi
39 and Pourkhabbaz, 2014; Schiff and Weisberg, 1999).

40 Sediments, which are released into the overlying water by natural and anthropogenic processes such as
41 bioturbation and dredging, are an appropriate indication of marine ecosystem health and can represent
42 the level of water pollution. Sediments are also significant because they may help determine the

43 degree of pollution in the marine environment, protect the health of the aquatic system, and promote
44 effective coastal management. Sediments are commonly thought of as trace element scavengers
45 because of their propensity to transfer and store trace elements (Looi et al., 2019). Organic and
46 inorganic matter are found in sediments in rivers, estuaries, oceans, and other water supply systems
47 (Hasan et al., 2013; Siddiquee et al., 2006). They are linked to hydrological connectivity, vegetation
48 features, water quality, land use, and mineral type, in addition to acting as a reservoir for contaminants
49 such as metals (Ahamad et al., 2020; Li et al., 2013). Both natural and manmade components created
50 or derived from the environment usually end up in sediments (Singovszka and Balintova, 2019). As a
51 result, when metal is present, they represent a significant source of exposure for natural ecosystems as
52 well as human activities. As a result, when metal is present, they represent a significant source of
53 exposure for natural ecosystems as well as human activities. Metals from contaminated sediments can
54 enter the water column as non-point sources (Algül and Beyhan, 2020; Liu, J. et al. 2017). When
55 polluted sediments are disturbed, metals that are trapped in the sediment can be discharged into the
56 water column, damaging water quality and aquatic life (Looi et al., 2019; Li, et al., 2012). In the food
57 chain, these metals may be bioaccumulated and biomagnified. Metals in sediments come from either
58 natural sources like atmospheric precipitation, ore deposits, geological weathering, storms, wind
59 bioturbation, and wave-induced bedrock weathering, or anthropogenic sources like mining, shipping,
60 industrial emission, smelting, fuel generation, electroplating, sludge discharge, energy transmission,
61 dense urban areas, wastewater irrigation and agricultural activities (Sun et al., 2015; Muhammad et al.,
62 2011, Altın et al., 2009). As a result of their toxicity, bioaccumulation, non-degradability, and vast
63 sources, as well as their persistence in the aquatic environment, metals have piqued the interest of
64 researchers (Gao et al., 2016).

65 Metals have great ecological significance due to pose significant toxicity to consumers at the top of the
66 food chains and tendency to accumulate in both sediment and biota (Bat and Arıcı, 2018; Bat, 2017;
67 Bat et al., 2021). Metals absorb suspended particles and settle as sediment because they are weakly
68 soluble in water (Bat and Özkan, 2019; Algül and Beyhan, 2020; Yang et al., 2014). Metals released
69 from sediments into the overlying water generate secondary pollution, which can harm the aquatic
70 system's biological status (Bat and Kurt, 2020; Varol and En, 2012; Niu et al. 2015). As a result,
71 metals can enter the aquatic food chain, where they can accumulate in biota (Algül and Beyhan, 2020;
72 Alrabie et al., 2019; Bat and Arc, 2018; Bat, 2017; Bat et al., 2021). Metals, unlike other
73 contaminants, do not biodegrade and are subject to a worldwide ecological cycle in which natural
74 waters play a key role (Bat et al., 2018; Hasan et al. 2013; Siddiquee et al., 2006). They enter aquatic
75 systems as a result of soil and rock weathering, volcanic eruptions, and a variety of human activities
76 involving the mining, processing, or use of metals and/or compounds containing metal contaminants
77 (Singovszka and Balintova, 2019). Metals are found in low concentrations in natural aquatic
78 ecosystems, typically at the nanogram to microgram per liter range, yet even at these levels, they can
79 have significant biological consequences (Singovszka and Balintova, 2019; Atalar et al., 2013;
80 Rainbow, 1992). However, in recent years, high metal contamination levels have become a source of
81 growing concern, with concern of environmental pollution as a result of metal toxicity and buildup in
82 aquatic habitats (Hasan et al., 2013). As a result, metal contamination is a difficult environmental
83 problem that is attracting growing attention due to its potential to endanger human and ecosystem
84 health (Looi et al., 2019; Amin et al., 2009; Tang et al., 2014). Metal pollutants present in sediments
85 have been demonstrated to pose a risk to marine organisms in near-future ocean acidification
86 conditions, according to studies (Williams and Antoine 2020; Roberts et al., 2013). However, the
87 concentrations of metals in the surface horizons of the sediment alone cannot provide extensive
88 indications about the state of contamination of sediments (Singovszka and Balintova, 2019). This type
89 of data makes it impossible to distinguish between natural and anthropogenic enrichment. The metal

90 enrichment factor (EF) and geoaccumulation indices (Igeo) are two common indexes used to
91 determine metal concentrations of environmental significance (Singovszka and Balintova, 2019; Feng
92 et al., 2011). These indices are used to quantify contamination levels in sediments. The amount of bio-
93 available metal in sediment has a significant impact on sediment quality (Singovszka and Balintova,
94 2019). Methods of geochemical normalization such as sediment quality guidelines (SQGs), Igeo, EF,
95 ecological risk index (MRI), and possible ecological risk index (PERI) can be used to determine the
96 degree of metal contamination in sediment (Ali et al., 2015; Xu et al., 2017). The EF and Igeo indexes
97 are employed as indicators to identify and quantify the degree of elemental pollution, as well as to
98 evaluate the intensity of anthropogenic contaminants collected in sediment (Looi et al., 2019; Barbieri,
99 2016). To date, numerous studies have used the EF and Igeo to assess the contribution of
100 anthropogenic inputs of elements in sediment (Özkan, 2012; Özkan and Büyükkışık, 2012; Kaya et al.,
101 2017; Kükrer et al., 2020; Fural et al., 2020; Fural et al., 2021).

102 The main objectives of the current study are: (1) to investigate the extent and degree of metal
103 distribution and concentration in the sediment of İzmir Inner Gulf, (2) to assess the origin of these
104 metals using EF and Igeo, and (3) to evaluate contamination of sediment using the MRI, PERI, MHQ,
105 ECI and TRI. This study is also expected to provide the background levels of pollutants and help
106 develop regional sediment quality guidelines.

107 **2. Material and method**

108 **2.1. Study area**

109 There are many gulfs with interesting hydrographic and sedimentological features, extending in the
110 east-west direction on the coastal zone of the Anatolian peninsula facing the Aegean Sea. While some
111 of these gulfs maintain their natural state, some are under anthropogenic pressure. İzmir Gulf is open
112 to the anthropogenic effects of settlements, industry, transportation networks and agricultural
113 activities. The water exchange between the Aegean Sea and İzmir Gulf, which has a semi-closed
114 feature, is limited. This increases the likelihood of ecological risks created by potentially toxic
115 elements discharging into the gulf. The inner gulf is a point where many streams (mainly old Gediz
116 mouth, Bostanlı, Bayraklı, Manda, Arap, Meles, Bornova, Polygon, Ilıca) discharge. These streams
117 have carried urban and industrial wastes to the inner gulf for many years.

118 The annual average rainfall in İzmir is 711 mm. İzmir receives 314 mm. of precipitation in winter,
119 152.9 mm. in spring, 21.4 mm. in summer and 60.4 mm. in autumn (MGM, 2021). Accordingly,
120 almost half of the annual average rainfall occurs in the winter season. The wet season in İzmir is as
121 follows: winter> spring> autumn> summer.

122 The characteristics of the gulf currents are determined by the complex coastline, bottom topography,
123 islands, water exchange with the Aegean Sea, river inputs and atmospheric forces. The general current
124 of the gulf is in the form of a cyclonic (counterclockwise) cycle that covers the entire gulf. Although
125 this general current characteristic is always observed, it is interrupted from time to time depending on
126 the intensity of the wind and the water exchange with the Aegean Sea and hence, cyclonic-
127 anticyclonic cycles occur. However, this interruption does is short-lived and it returns to its previous
128 state (Beşiktepe et al., 2011).

129

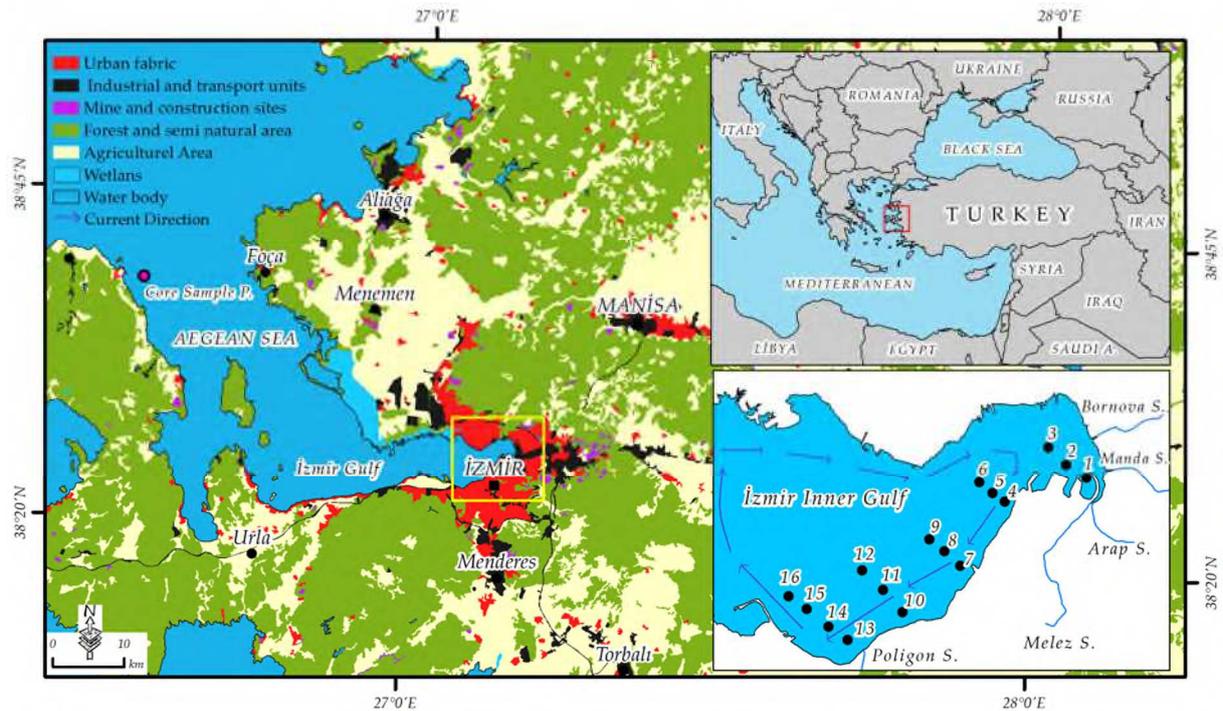


Figure 1: Location map of İzmir Inner Gulf

130

131

132 Major industrial activities in the region are food processing, beverage manufacturing and bottling,
 133 tanneries, oil, soap and paint production, chemical industries, paper and pulp mills, textile industries,
 134 metalworking and timber processing (Kontaş et al., 2004). Apart from these, the inner gulf was
 135 exposed to domestic wastes for many years and has gained a eutrophic character. The streams were
 136 planned to carry only rain water with the wastewater treatment plant (Grand Canal Project) which was
 137 put into operation at full capacity in 2002. This study examined the effect of the Great Canal Project
 138 on the cleansing process of the inner gulf.

139 İzmir Gulf is divided into three parts as inner, middle and outer gulf according to geomorphological
 140 and hydrographic features (Sunlu et al., 2012). The outer gulf is 45 km long in the northwest-southeast
 141 west direction and 20 km wide between Karaburun-Foça line. The middle and inner gulfs are 24 km
 142 long and 6 km wide in total in the east-west direction. The middle gulf, which is about 10 km long, is
 143 separated from the inner gulf by a very narrow sandbank of 13 m. deep, called the Yenikale Pass. This
 144 sandbank was formed as a result of the delta advancement of the Gediz River with the Pelikan and
 145 Karşıyaka mouths in the last few centuries (Özkan et al., 2008). The study area was bordered by the
 146 mouth of Çakalburnu Dalyan in the west and Bornova Creek in the east, where the Poligon Stream,
 147 Melez Creek, Manda Creek, Arap Creek and Bornova Stream, which form the southern shores of the
 148 İzmir Inner Gulf, are discharged (Figure 1).

149 2.2. Sampling and analytical methods

150 Within the scope of the study, samples were taken from 16 stations selected in the southern littoral
 151 zone of the İzmir Inner Gulf for four seasons (winter, spring, summer and autumn) in 2015. Surface
 152 sediment samples were taken with a core sampler. They were then placed in plastic bags and
 153 transported to the laboratory in ice boxes. Wet samples were used for Chl-a analysis. After the
 154 sediment samples were extracted with 90% acetone, they were measured spectrophotometrically
 155 (Strickland and Parsons, 1972). Samples for total organic carbon (TOC), biogenic silica (Bsi), CaCO₃
 156 and elemental analyzes were dried in a drying-oven and pulverized by pounding in a porcelain mortar.

157 TOC analyzes were performed by the Walkley-black method, which is performed by oxidation of
 158 organic matter with $K_2Cr_2O_7$ (Gaudette et al., 1974). $CaCO_3$ analyzes were carried out by the
 159 gasometric method based on the measurement of the partial pressure of the CO_2 gas released from the
 160 reaction of $CaCO_3$ with 10% HCl according to (Martin, 1972). Bsi measurements were performed with
 161 the method recommended by (De Master, 1981). Element analyzes were performed at Bureau Veritas
 162 Laboratory (Canada) using the ICP-MS method. Standard reference material, duplicate and blind
 163 sample reading methods were used for quality control of elemental analysis. Recovery values of metal
 164 measurements vary between 83% - 114%. Background data of a study conducted in İzmir Karaburun
 165 Gulf were used in the ecological risk index calculations. Metals background values as ppm; Fe
 166 (9.950), Ti (1.040) Mn (221), Cr (167), Ni (41.1), Zn (32), As (14), Co (8.7), Pb (6.35), Cu (5.8), Hg
 167 (1.67), Mo (0.3), Cd (0.05). The reliability of the metal content measurements is 95% (Özkan et al.,
 168 2017).

169 2.3. Ecological risk assessment methods

170 2.3.1. Enrichment factor (EF) and Geoaccumulation Index (I_{geo})

171 Various indices were used for ecological and ecotoxicological evaluation of metal
 172 concentrations. Two tools were used to determine whether the detected metals were of natural origin
 173 or of anthropogenic origin. The first of these tools is the EF and is mainly found by the ratio of the
 174 current metal concentration to the background concentration. EF is calculated by the following
 175 formula:

$$176 \quad EF = \frac{(C_i/C_{ref})_{sample}}{(B_i/B_{ref})_{background}} \quad (1)$$

177 Here, C_i is the metal concentration measured in sediment, C_{ref} is the concentration of the reference
 178 element selected for normalization in the sediment sample, B_i is the regional background value of the
 179 metal and B_{ref} is the background value of the reference element selected for normalization. EF
 180 provides the option to normalize metal concentrations and uses a reference element in EF calculations
 181 that is not affected by anthropogenic inputs and chemical reactions. In this way, the grain size is
 182 normalized. It applies the same to the reference sample as well (Ahmed et al., 2018). EF results were
 183 evaluated according to Sutherland (2000): $EF < 2$, minimal or no enrichment; $EF = 2-5$, moderate
 184 enrichment; $EF = 5-20$, significant enrichment; $EF = 20-40$, very high enrichment and $EF > 40$,
 185 extremely high enrichment.

186 Another index frequently used for the same purpose is I_{geo} and it has been formulated below (Müller,
 187 1969):

$$188 \quad I_{geo} = \log_2 \frac{C_m}{(B_m * 1.5)} \quad (2)$$

189 Here C_m is the measured concentration of the metal and B_m is the background value of the metal. The
 190 I_{geo} results were evaluated in the following manner: $I_{geo} \leq 0$ uncontaminated, $0 < I_{geo} < 1$
 191 uncontaminated to moderately, $1 < I_{geo} < 2$ moderately, $2 < I_{geo} < 3$ moderately to strongly, $3 < I_{geo} < 4$
 192 strongly, $4 < I_{geo} < 5$ strong to extremely, $I_{geo} \geq 5$ extremely.

193

194

195

2.3.2. Ecological Risk (MRI) and Potential ecological risk index (PERI)

The potential ecological risk index proposed by (Hakanson, 1980) was used to calculate the risks that metals could create separately (MRI) and in an integrated manner (PERI). The modified approach was preferred for calculating the individual ecological risks of metals (Brady et al., 2015). Accordingly, the EF was used in the calculation instead of the contamination factor:

$$MRI = Ef_i \times Tr_i \quad (3)$$

$$PERI = \sum_{i=1}^n MRI \quad (4)$$

Here, Ef_i refers to the EF and Tr_i refers to the toxic responsibility coefficient. Tr_i values for metals are as follows: Hg=40, Cd=30, As=10, Cu=Pb=Ni=Co=5, Cr=2, Mn=Zn=1 (Hakanson, 1980; Li et al., 2018; Rodríguez-Espinosa et al., 2018). The results are evaluated as follows: $MRI < 40$ low potential ecological risk, $40 \leq MRI < 80$ moderate potential ecological risk, $80 \leq MRI < 160$ significant potential ecological risk, $160 \leq MRI < 320$ high potential ecological risk, and $MRI \geq 320$ very high potential ecological risk. The PERI results are evaluated as follows: $PERI < 150$ low ecological risk, $150 \leq PERI < 300$ moderate ecological risk, $300 \leq PERI < 600$ significant ecological risk, $PERI \geq 600$ very high ecological risk (Hakanson, 1980).

2.3.3. Modified hazard quotient (mHQ) and ecological contamination index (ECI)

MRI and PERI are indices that are based on the amount of enrichment of metals in sediment. Apart from these frequently used indices, there are also indices created using the threshold values to determine the effects of metal content in sediment on aquatic biotome, such as threshold effect level (TEL), probable effect level (PEL) and severe effect level (SEL). mHQ and ECI are among these indices and are calculated in the following manner (Benson et al., 2018).

$$MHQ = \left[C_i \left(\frac{1}{TEL} + \frac{1}{PEL} + \frac{1}{SEL} \right) \right]^{1/2} \quad (5)$$

Here C_i refers to the measured metal concentration and TEL, PEL and SEL are the abbreviations for threshold effect level, probable effect level and severe effect level, respectively. TEL, PEL and SEL values are performed according to (MacDonald et al., 2000). mHQ findings are evaluated in the following manner; $MHQ < 0.5$ minor, $0.5 < MHQ < 1$ very low, $1 < MHQ < 1.5$ low, $1.5 < MHQ < 2$ medium, $2 < MHQ < 2.5$ significant, $2.5 < MHQ < 3$ high, $3 < MHQ < 3.5$ very high, $MHQ > 3.5$ extremely high/very severe.

ECI offers the opportunity to make an integrated, resource-specific assessment using a factor obtained from principal component analysis/factor analysis results (Benson et al., 2018). ECI is calculated in the following manner:

$$ECI = B_n \sum_{i=1}^n mHQ_i \quad (6)$$

Here, B_n is the inverse of the eigenvalue obtained from the principal component analysis for metals only with respect to multiplication. ECI findings are evaluated in the following manner: $ECI < 2$ uncontaminated, $2 < ECI < 3$ uncontaminated to slightly contaminated, $3 < ECI < 4$ slightly to moderately contaminated, $4 < ECI < 5$ moderately to considerably contaminated, $5 < ECI < 6$ considerably to highly contaminated, $6 < ECI < 7$ highly contaminated, $ECI > 7$ extremely contaminated.

234 2.3.4. Toxic risk index (TRI)

235 TRI is another index used to determine metals ecotoxicological effects (Zhang et al., 2016). The
236 following formula was used to determine the toxic risk index (TRI_i) of each metal in the study. Here C_i
237 refers to the measured concentration of the metal, TEL refers to “threshold effect level”, and PEL
238 refers to “probably effect level” (MacDonald et al., 1997).

$$239 \quad TRI_i = \sqrt{\frac{((C_i/TEL)^2 + (C_i/PEL)^2)}{2}} \quad (7)$$

240 The TRI value which represents the toxic risk of the area is obtained by summing the TRI_i values
241 calculated for each metal:

$$242 \quad TRI = \sum_{i=1}^n TRI_i \quad (8)$$

243 The following scale is used in the interpretation of TRI values: TRI ≤ 5 no toxic risk, 5 < TRI ≤ 10
244 low toxic risk, 10 < TRI ≤ 15 moderate toxic risk, 15 < TRI ≤ 20 considerable toxic risk, TRI > 20
245 very high toxic risk.

246 2.4. Spatial analysis and multivariate statistical analysis

247 Spatial analyzes were performed in Arc - Map 10.7 software using the Kriging interpolation method.
248 This method is an interpolation method that estimates the optimum values of the data at other points
249 using the data of the nearby points, and it is calculated in the following manner:

$$250 \quad N_p = \sum_{i=1}^n P_i \times N_i \quad (9)$$

251 In the formula; N refers to the number of sampling points, N_i refers to the geoid undulation values of
252 the points used in the calculation of N_p, N_p refers to the undulation value to be calculated and P_i
253 refers to each N_i value used in the calculation of N (ESRI, 2021).

254 Factor analysis, Spearman's rank correlation test and cluster analysis were performed to understand the
255 source identification and transport processes of metals and other variables used in the study. Anova
256 test was applied to determine seasonal differences between variables.

257 3. Result and discussion

258 3.1. Spatial and seasonal change of variables

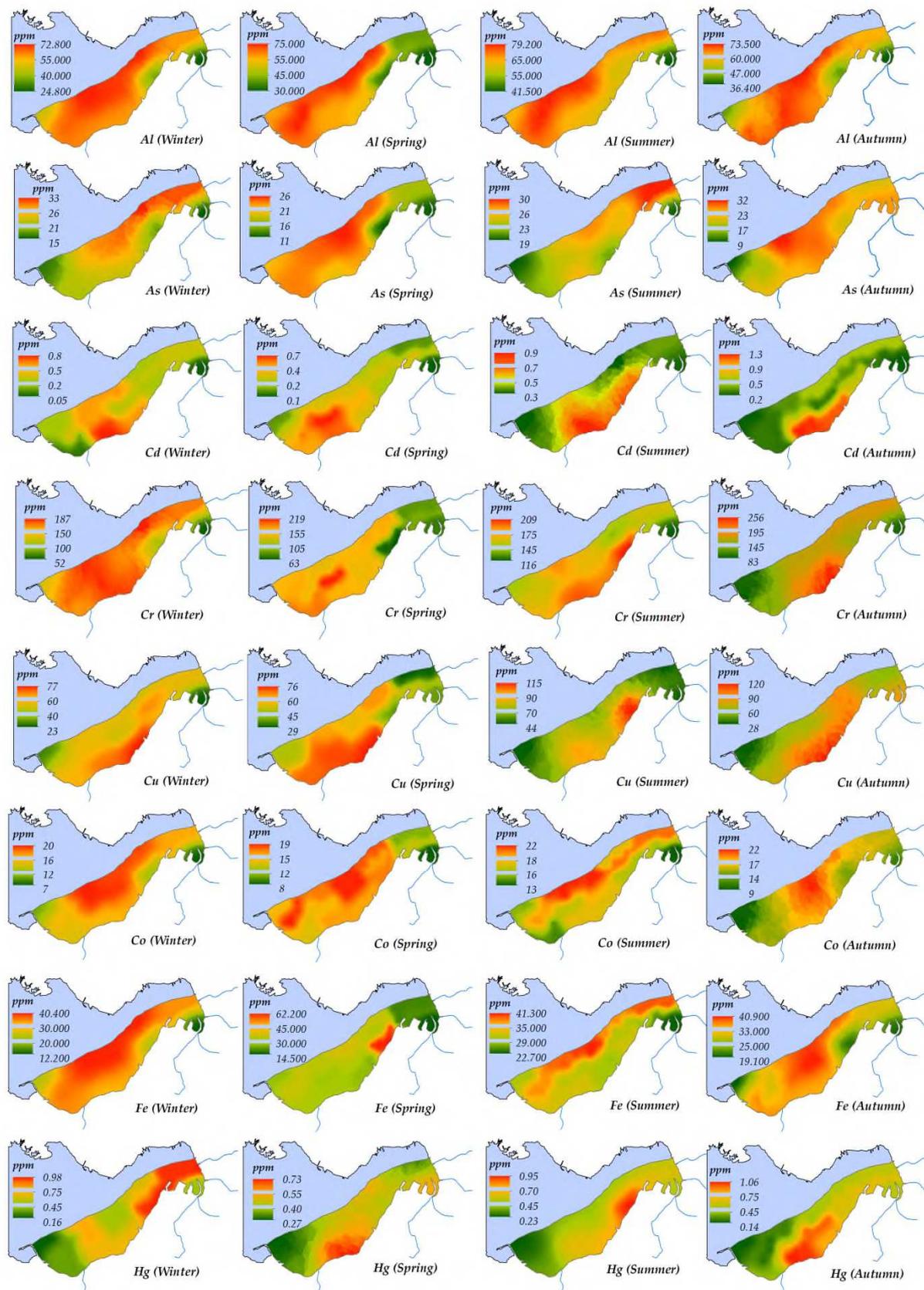
259 Average concentration of metals (ppm) were listed as Fe (32.510) > Mn (488) > Zn (220) > Cr (153) >
260 Ni (86.53) > Pb (79.42) > Cu (64.70) > As (23) > Co (16.4) > Mo (7.14) > Hg (0.52) > Cd (0.45) > Ti
261 (0.24). Maximum concentrations were found to be as follows: As was detected in ST 6 (33 ppm) in
262 winter, Cd was detected in ST 10 (1.32 ppm) in autumn, Cr was detected in ST 9 (256 ppm) in
263 autumn, Cu was detected in ST 9 (120 ppm) in autumn, Co was detected in ST 8 (22.50 ppm) in
264 autumn, Fe was detected in ST 4 (62.200 ppm) in spring, Hg was detected in ST 10 (1.06 ppm) in
265 autumn, Mn was detected in ST 4 (2.217 ppm) in spring, Mo was detected in ST 9 (21.70) in autumn,
266 Ni was detected in ST 8 (142.40 ppm) in winter, Pb was detected in ST 2 (208.50 ppm) in autumn, Ti
267 was detected in ST 14 (0.34) in summer and Zn was detected in ST 9 in autumn (429 ppm). According
268 to these data, the maximum concentrations were denser in the ST 9 and ST 10 during the autumn
269 season. As was in minimum concentration in autumn in ST 16 (9 ppm), Mn was in minimum
270 concentration in winter in ST 14 (267 ppm), Hg was in minimum concentration in autumn in ST 16

271 (0.14 ppm), Mo was in minimum concentration in spring in ST 16 (1 ppm) and Pb was in minimum
272 concentration in autumn in ST 16 (26.70). Cd (0.05 ppm), Cr (52 ppm), Cu (23 ppm), Co (7 ppm), Fe
273 (12,200 ppm), Ni (31.90 ppm), Ti (0.095 ppm) and Zn (67 ppm) detected at the minimum
274 concentrations in winter in ST 1 (Figures 2 and 3). Existence of a large number of metals at minimum
275 concentrations in winter. in ST 1 where Melez Creek, Arap Creek and Manda Creek discharge is
276 noteworthy. It can be argued that this situation occurred due to the decrease in sedimentation rate due
277 to the flow of stream waters discharging into the inner gulf during the rainy winter season.

278 According to spatial analysis data; As reached high concentrations in the mouths of Bornova Stream in
279 winter and summer, in Poligon Stream in spring and in the mouths of Melez Creek, Manda Creek and
280 Arap Creek in autumn. Cd and Mo were at maximum concentrations in stations close to the Poligon
281 Stream in all seasons. Cr and Co were in high concentrations at stations close to the mouth of the
282 Poligon Stream in all seasons except autumn. Cu was high at the mouth of the Poligon Stream in all
283 seasons except summer. In summer, high values were observed around ST 4. Fe was in high
284 concentration in the stations close to the mouth of the Poligon Stream in winter and autumn. Hg
285 reached high concentrations at the stations close to the mouth of Bornova Stream in winter, Melez
286 Creek, Arap Creek and Manda Creek in spring and at the stations close to the mouth of the Poligon
287 Stream in autumn. Mn was in high concentration near the mouth of Bornova Stream and Poligon
288 Stream in winter and especially at the mouth of Bornova Stream in summer. Ni was in high
289 concentration at stations close to Bornova Stream in winter and summer and to the mouth of Poligon
290 Stream in autumn and spring. Pb reached high concentrations at the mouth of the Melez Creek, Arap
291 Creek and Manda Creek in all seasons except winter, at the stations close to the mouth of the Poligon
292 Stream and at the mouth of Bornova Stream in winter. Zn was in high concentration at stations close to
293 the mouth of the Poligon Stream in all seasons.

294

295

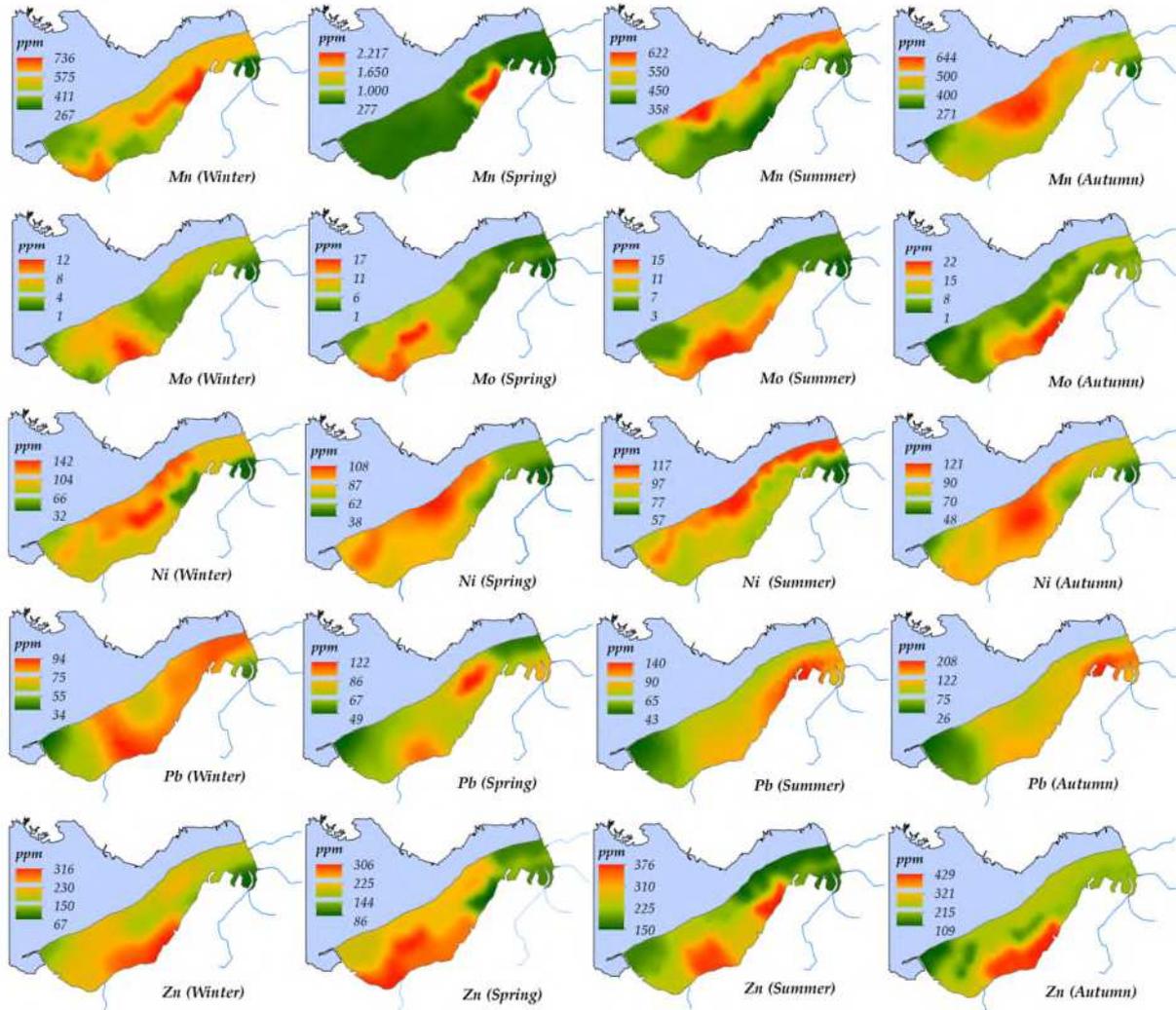


296

297

Figure 2: Spatial and seasonal change of metal concentration (part 01)

298



299

300

Figure 3: Spatial and seasonal change of metal concentration (part 02)

301

Table 1: Comparison of metal concentrations (ppm) in some gulfs in the Aegean Sea

Location	Al	As	Cd	Cr	Cu	Co	Fe	Hg	Mn	Ni	Pb	Zn	Reference
İzmir Inner G. (Turkey)	46.900	23.07	0.45	114.28	64.49	16.38	32.500	0.51	487	86.64	79.36	219	This Study
İzmir Inner G.(Turkey)	19.216		0.34	100.62	59.50		28.383	0.35	420		62.27	188.44	Gülsever et al., 2019
Aliğa G. (Turkey)	60.300	20.60		78.60	16.70		22.000		212	28.80	34.80	55.80	Palas,2020
Ayvalık G. (Turkey)		36.73	0.47	23.24	8.92	6.30	8.725		178	41.42	14.78	60.73	Tunca, et al., 2017
Edremit G. (Turkey)		35.50	0.23	29.10	5.05	7.34	20.819		202	56.09	9.36	43.04	Tunca, et al., 2017
Astakos G. (Gerece)			3.25	166	23				687		28	89	Panagos et al., 1989
Kalloni G. (Gerece)			3.20		48				910		96	103	Varvanas, 1989

302

303 The average metal concentrations of four seasons in the inner gulf of İzmir, metal concentrations of
 304 some of the gulfs in the Aegean Sea and the metal concentrations of a study conducted in 2019 in the
 305 İzmir Inner Gulf were compared. According to the findings; Al concentration was lower than Aliğa
 306 Gulf. As concentration was lower than that of Ayvalık Gulf and Edremit Gulf and higher than that of
 307 Aliğa Gulf. Cd concentration was lower than that of Edremit Gulf and higher than that of other gulfs.
 308 Cr concentration was higher than all gulfs except Astakos Gulf. Mn concentration was higher than all

309 gulfs except Astakos and Kalloni Gulfs. Cu, Co, Fe, Ni, Pb, Zn and Hg concentrations were higher
310 than all comparative Gulfs. When the metal concentrations were compared with the study conducted in
311 İzmir Inner Gulf in 2019, a decrease was observed in all values (Table 1).

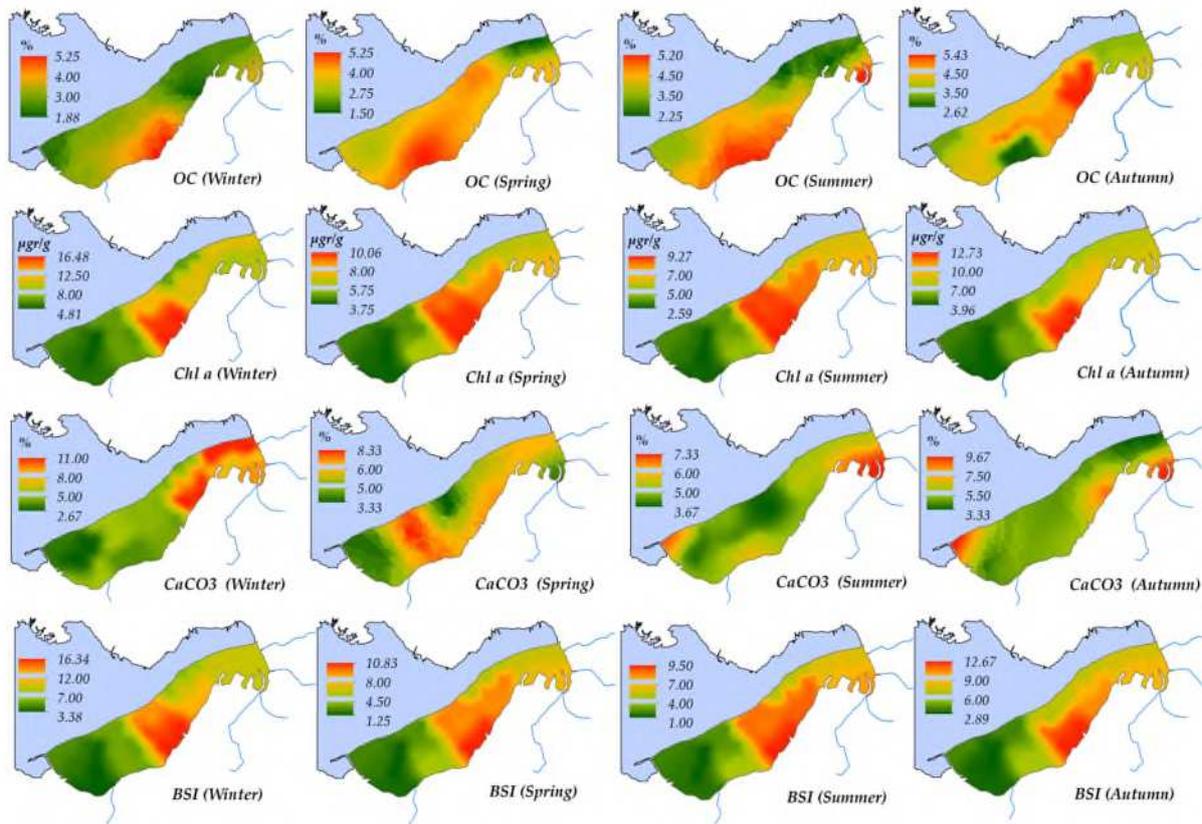
312
313 TOC concentration was found to be at maximum in ST 9 (5.25%) in winter, in ST 10 (5.25%) in
314 spring, in ST 1 (5.25%) in summer and in ST 4 (5.43%) in autumn. Minimum concentration was
315 determined in ST 16 (1.88%) in winter, in ST 3 (1.50) in spring, in ST 2 (2.25%) in summer, and in
316 ST 10 (2.62%) in autumn. According to the spatial distribution analysis, high concentrations of TOC
317 were detected at the mouth of the Poligon Stream in spring and summer. TOC concentration was
318 especially high in the mouths of Manda Creek, Arap Creek and Melez Creek in summer. This finding
319 shows that rivers are effective on seasonal and spatial distribution of TOC. Dense TOC concentration
320 in river mouths and around ST 10 strengthens the possibility of its allochthonous character.

321 Chl-a concentration was minimum in ST 14 and maximum in ST 9 in all seasons. According to spatial
322 analysis, maximum Chl-a concentration was detected in stations (ST 10 and ST 11) far from stream
323 inputs in all seasons although Chl-a was relatively moderate in the mouth of Manda Creek, Arap
324 Creek and Melez Creek in spring and summer. This situation shows that Chl-a is produced in the inner
325 gulf, has been subjected to minimum rainfall conditions and seasonal changes and is discharged by
326 rivers in minimal concentration.

327 Bsi was at maximum levels in ST 9 and at minimum levels in ST 14 in all seasons. The seasonal and
328 spatial distribution similarity between Bsi and Chl-a is striking. This shows that diatoms significantly
329 contribute to the phytoplankton biome. Increases in algae biome were found to be localized around ST
330 9 rather than the estuaries. Detailed temporal and spatial changes of TOC, Chl-a, CaCO₃ and Bsi are
331 presented in Figure 4.

332 CaCO₃ concentration was at maximum in ST 3 (11%) in winter, in ST 11 (8.33%) in spring, in ST 1
333 (7.33%) in summer, and in ST 16 in autumn (9.67%). Minimum values were identified in ST 14
334 (2.67%) in winter, in ST 7 (3.33%) and ST 15 in spring, in ST 15 (3.67%) in summer, and in ST 15
335 (3.33%) in autumn. According to spatial analysis, CaCO₃ reached high concentrations around ST 1,
336 ST 2 and ST 3 at the mouth of Arap Creek, Melez Creek, Manda Creek and Bornova Stream in winter,
337 summer and autumn (Figure 4). High CaCO₃ concentration at this point is related to the sedimentation
338 of the Miocene lacustrine CaCO₃ in Arap Creek and Melez Creek basins (MTA, 2021). The source of
339 the high CaCO₃ concentration detected in the stations close to the mouth of the Poligon Stream in the
340 spring is related to the upper Senonian clastic CaCO₃ rocks in the stream basin (MTA, 2021). There
341 are no geological formations that can be a source of CaCO₃ on the southern shores of the İzmir Inner
342 Gulf, except for the Poligon Stream, Arap Creek and Melez Creek basins. In this case, the CaCO₃
343 concentration is expected to reach the maximum concentration only in the specified river mouths.
344 However, the maximum concentrations identified in ST 11 (8.33%) in spring and ST 16 in autumn
345 (9.67%) were not related to stream inputs. The maximum values in ST 16 in the west of the mouth of
346 Poligon Stream and in ST 11 in the east were distributed in line with the flow directions. This situation
347 indicates that the currents in the inner gulf may have an effect on the spatial distribution of metals and
348 other variables, especially CaCO₃.

349



350

351

Figure 4: Spatial and seasonal change of TOC, Chl-a, CaCO₃ and BSI

352

3.2. Evaluation of metal enrichments

353

354

355

356

357

358

359

360

361

362

363

364

365

366

367

368

369

370

371

372

373

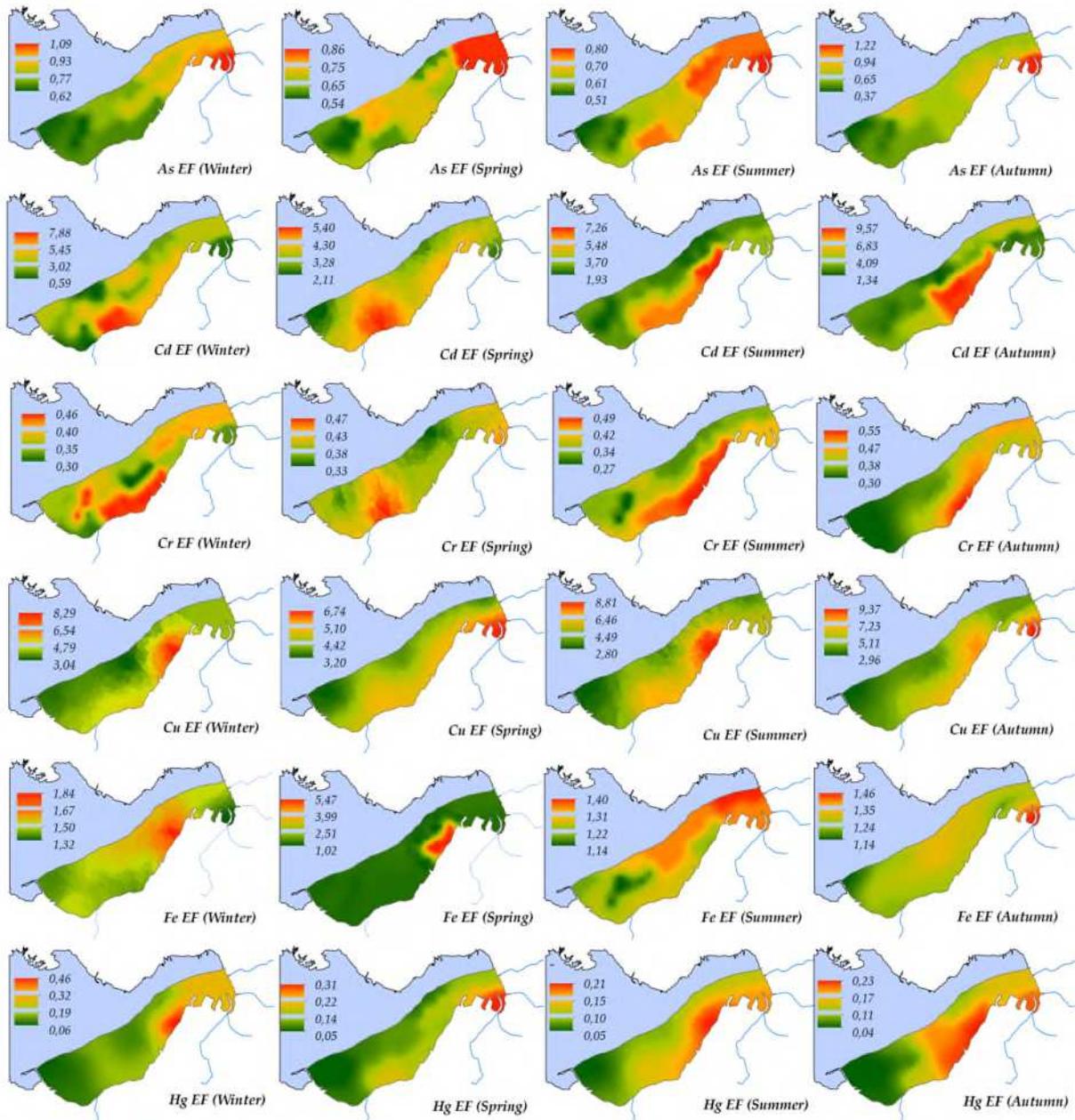
374

The metals were listed as follows according to EF general average data: Mo (9.80) > Pb (5.59) > Cu (4.86) > Cd (3.83) > Zn (2.92) > Fe (1.42) > Mn (1.03) > Ni (0.89) > Co (0.81) > As (0.71) > Cr (0.39) > Hg (0.14). Accordingly, Mo and Pb were significantly enriched while Cu, Cd, Zn were moderately enriched. Other metals were classified as “minimal or no enrichment” (Figures 5 and 6). The maximum EF for As (1.22) was identified in ST 1 in autumn and the minimum EF (0.52) was identified in ST 15 in the summer and autumn. According to spatial analyses, it was determined that high EF values were concentrated around ST 1, ST 2 and ST 3 where river mouths are located in all seasons, but As did not exceed the threshold value in any of the stations. Cd enriched significantly by reaching the maximum EF in winter (7.43), in summer (6.26) and in autumn (9.04) in ST 10 and in the spring (6.22), in ST 11. According to the spatial distribution analyses, the possible source of the anthropogenic effect around ST 10 and ST 11 is the Polygon Stream, where domestic waste and sewage discharge has been carried out for many years. As it is well documented, domestic wastes and sewage leaks are included among the most important anthropogenic resources of Cd (Merhaby et al., 2018). Ports and transportation networks are other important anthropogenic resources of Cd (Jeong et al., 2020). Accordingly, the possible source of high EF values around ST 4 is the port and the source of the high accumulation detected along the southern shores of the gulf is the highway. Because transportation networks can affect Cd, Pb and Zn concentrations up to 320 meters away (Viard et al., 2004). Cr was not enriched in any of the seasons. Maximum EF (0.58) was determined in ST 9 in autumn and minimum EF (0.27) was identified in ST 14 in autumn. Cu significantly enriched by reaching the maximum level in ST 4 in winter (8.88) and in summer (7.65) and in ST 1 in spring (6.80) and in autumn (9.57). There is no river input around ST 4, but there is a port that has been used for many years. Therefore, the likely source of Cu enrichment around ST 4 is the port. The Manda Creek, Arap Creek and Melez Creek,

375 which discharge into the inner gulf near ST 1, pass through the regions where industry and
376 urbanization activities are the most intense. In this case, the reason for the enrichment around ST 1
377 may be the discharge of domestic and industrial wastes to the inner gulf by the rivers. The fact that Cu
378 is affected by anthropogenic activities taking place in port regions has been identified in some busy
379 ports in various countries of the world (Chen et al., 2020; Jeong et al., 2020; Jahan and Strezov, 2018).
380 Fe did not show significant accumulation in other seasons, except for the significant level of
381 enrichment (5.47) in ST 4 in the spring. The only source for such unnatural accumulation around ST 4
382 is the port. Possible source of enrichment here may be the discharge from ships. Hg has not been
383 enriched in any season. However, maximum EF levels were detected in winter (0.46), in summer
384 (0.21) and in autumn (0.23) in ST 4 and in spring (0.31) in ST 1. According to the spatial distribution
385 of Hg, domestic and industrial wastes arrive through Manda Creek, Arap Creek and Melez Creek in the
386 spring and a small amount of anthropogenic effect is experienced as a result of the port in other
387 seasons. Hg not pose an ecological risk hazard due to enrichment. The maximum values detected in
388 three seasons in ST 4, where the port is located, may be related to the anthropogenic activities taking
389 place in the port area because Hg is an important pollutant in port areas (Chen et al, 2020; Jahan and
390 Strezov, 2018). Mn reached the maximum enrichment in winter (2.84), in spring (8.35) and in autumn
391 (1.20) in ST 4 and in summer (1.01) in ST 1. According to these data, there was a moderate
392 enrichment for Mn in ST 4 in winter and and significant enrichment in the spring. Mn did not exceed
393 the threshold value of 2 in any stations during summer and autumn. Spatial analyses showed that Mn
394 was enriched in winter and spring with anthropogenic effects originating from the port. Discharges
395 from ships, maintenance and shipping activities in ports can be a source of Mn (Oliveira et al., 2020).
396 Mo reached maximum enrichment in ST 10 in winter (19.94), in ST 13 in spring (19.98), in ST 9 in
397 summer (19.29) and in ST 9 in autumn (27.16). Mo was very highly enriched in autumn and
398 significantly enriched in other seasons. According to spatial analyses, in winter, Poligon Stream
399 discharges Mo which has a significant anthropogenic effect. Mo is an important pollutant for sediment
400 and undersea fauna in coastal areas (Rumisha et al., 2012). Ni did not demonstrate any anthropogenic
401 accumulation in any season. However, the maximum enrichment in the mouths of the Manda Creek,
402 Arap Creek, Bornova Stream and Melez Creek in the spring and the mouth of the Bornova Stream in
403 the summer shows that the streams discharge Ni with minimal anthropogenic effect. Pb enriched
404 significantly by reaching maximum values in winter (10.54) in ST 4, in spring (13.15) in ST 1, in
405 summer (10.21) in ST 2 and in autumn (12.42) in ST 1 and ST 2. Possible source of the enrichment in
406 winter is the port and the source of the enrichment in the stations at the mouths of the Manda Creek,
407 Melez Creek, Arap Creek and Bornova Stream in other seasons is industrial- domestic wastes and the
408 port. Pb is an important anthropogenic pollutant in port areas (Che et al, 2020; Jeong et al., 2020). Zn
409 showed maximum enrichment in winter (4.41) in ST 9, in spring (4.25) in ST 11, in summer (4.51) in
410 ST 4 and ST 10 and in autumn (5.03) in ST 9. According to this finding, Zn enriched in the lower
411 limits of the significant level in autumn and enriched moderately in other seasons. Spatial analyses
412 show that Zn was enriched in spring and summer near the mouth of the Poligon Stream. Zn is a major
413 pollutant that can result from domestic waste and sewage (Merhaby et al., 2018). Poligon Stream has
414 been an area where domestic wastes and sewers have been discharged for many years. Possible reason
415 for the enrichment in ST 4 is the port because, Zn is a metal that is frequently encountered in port
416 areas and can easily be absorbed into the underwater fauna (Beneditto et al., 2019).

417

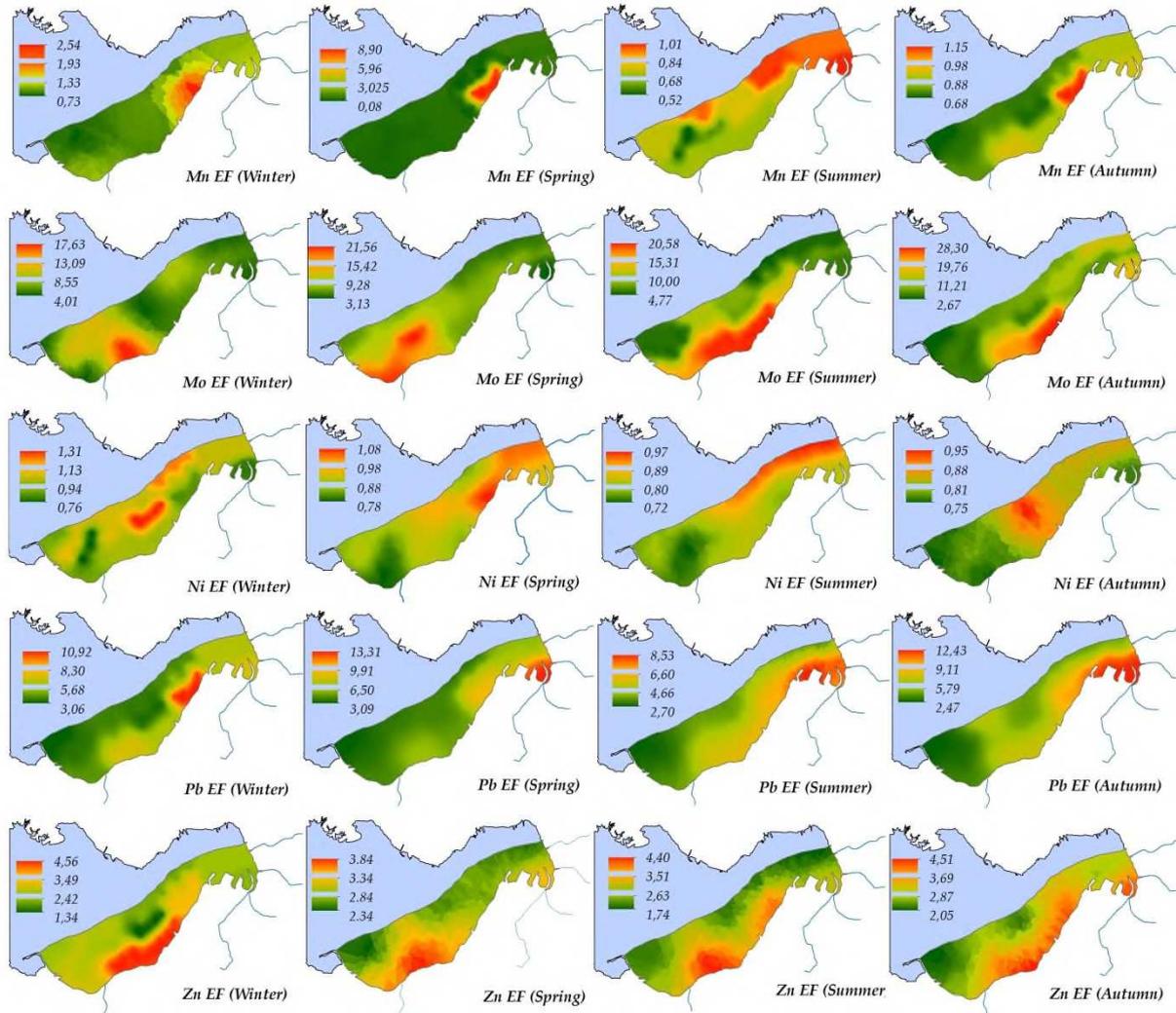
418



419

420

Figure 5: Spatial and seasonal change of EF (part 01)



421

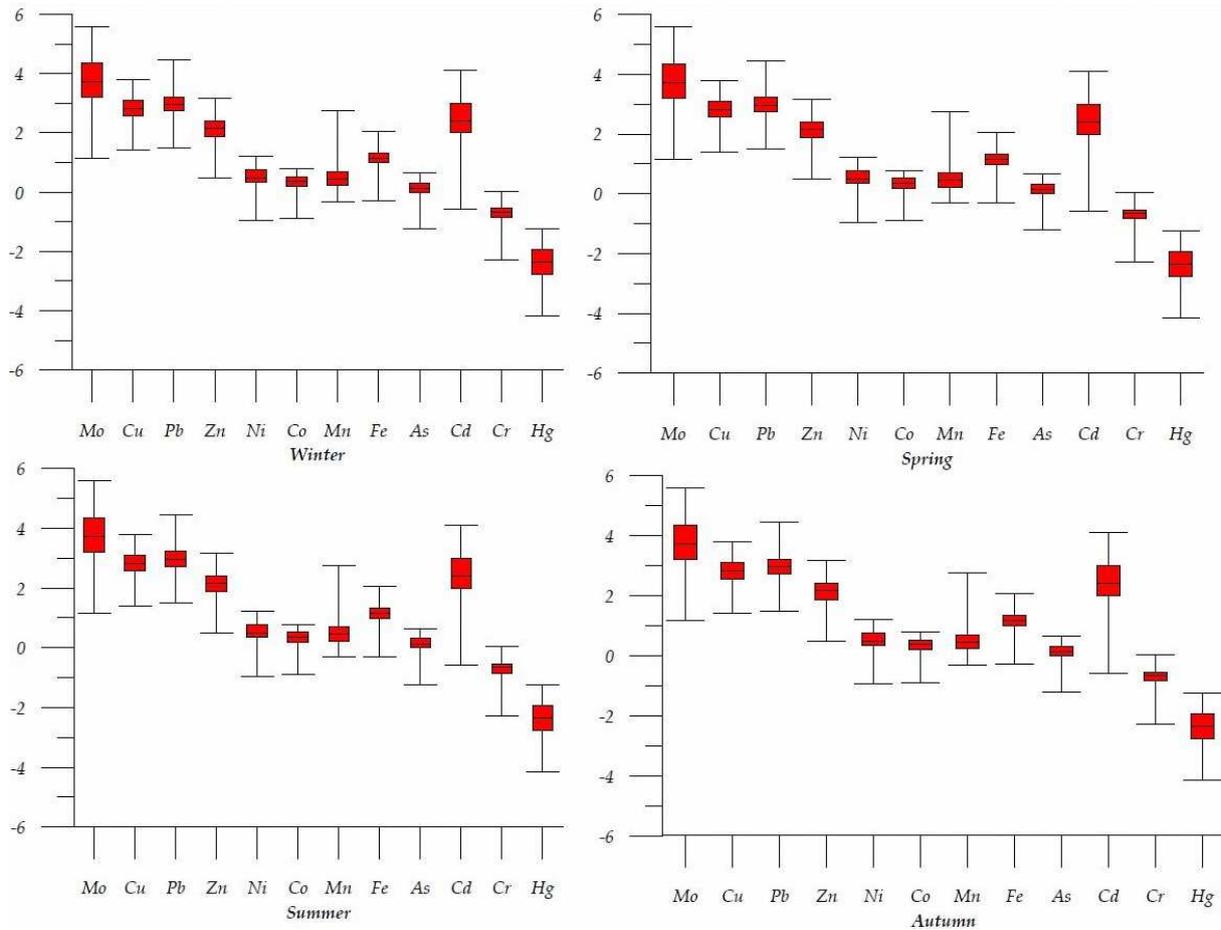
422

Figure 6: Spatial and seasonal change of EF (part 02)

423 Based on the average of all seasons, I_{geo} was listed as: Mo (3.68) > Pb (2.97) > Cu (2.82) > Cd (2.39) >
 424 Zn (2.11) > Fe (1.08) > Mn (0.47) > Ni (0.43) > Co (0.30) > As (0.09) > Cr (-0.77) > Hg (-2.40)
 425 (Figure 7). According to these data, İzmir Inner Gulf was moderately contaminated with Mo; slightly
 426 contaminated with Pb, Cu, Cd, Zn, Fe, Mn, Ni, Co, As while it was not contaminated with Cr and Hg.
 427 However, the minimum and maximum values observed in some stations resulted in the seasonal and
 428 spatial change of the pollution degrees. Possible sources of metals with an anthropogenic effect are
 429 defined in the EF section.

430

431 .



432

433

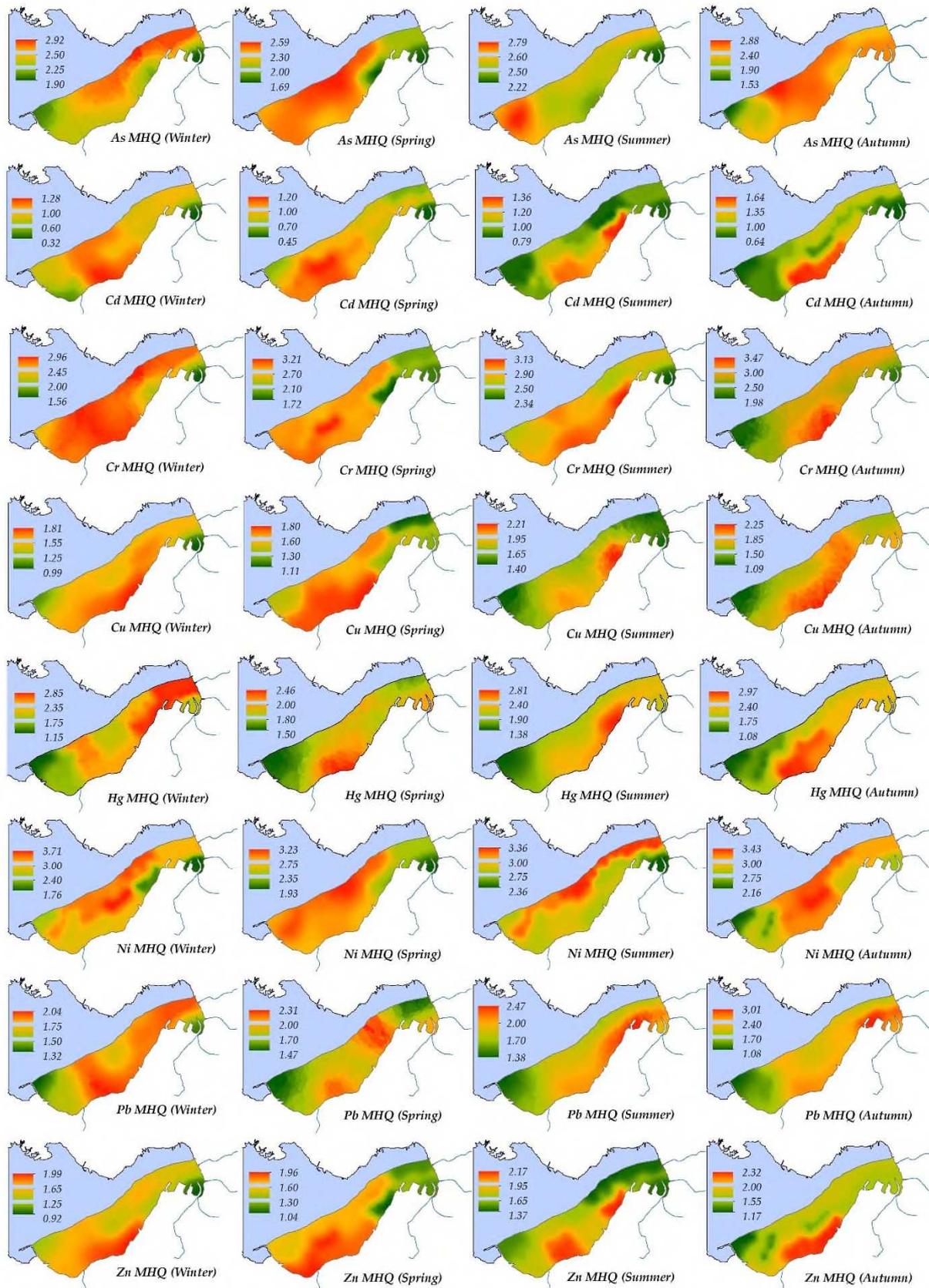
434

Figure 7: Box and whisker plot of I_{geo} values

435 3.3 Ecological and ecotoxicological risk assessment of metals

436 According to the average data, the mHQ index ranked as Ni (2.87) > Cr (2.65) > As (2.42) > Hg (2.03)
 437 > Pb (1.83) > Zn (1.63) > Cu (1.63) > Cd (0.93). Accordingly, high level of risk was identified for Ni
 438 and Cr, significant level of risk was identified for As and Hg, medium level of risk was identified for
 439 Pb, Zn, Cu and very low level of risk was identified for Cd. Maximum mHQ was detected for Ni
 440 (3.71) in winter in ST 10, for Cr (3.21) in spring in ST 11, for As (2.92) in winter in ST 6, for Hg
 441 (2.85) in winter in ST 2, for Pb (2.47) in summer in ST 4, for Zn (2.32) in autumn in ST 9, for Cu
 442 (2.24) in summer in ST 4, for Cd (1.28) in summer and in winter in ST 10. Minimum mHQ was
 443 detected for Ni (1.76) in winter in ST 1, for Cr (1.56) in winter in ST 1, for As (1.53) in autumn in ST
 444 16, for Hg (1.08) in autumn in ST 16, for Pb (1.08) in autumn in ST 16, (0.92) for Zn in winter in ST
 445 1, for Cu (0.99) in winter in ST 1 and for Cd (0.32) in winter in ST 1. Spatial analyses show that the
 446 minimum mHQ was concentrated in the ST 1 located at the mouth of the Manda Creek, Melez Creek,
 447 Arap Creek and in winter (Figure 8). It is believed that this situation is caused by the high flow rates
 448 into the inner gulf from the streams in the winter months, when the maximum precipitation falls,
 449 slowing down the sedimentation and distributing the transported metals within the inner gulf.

450



451

452

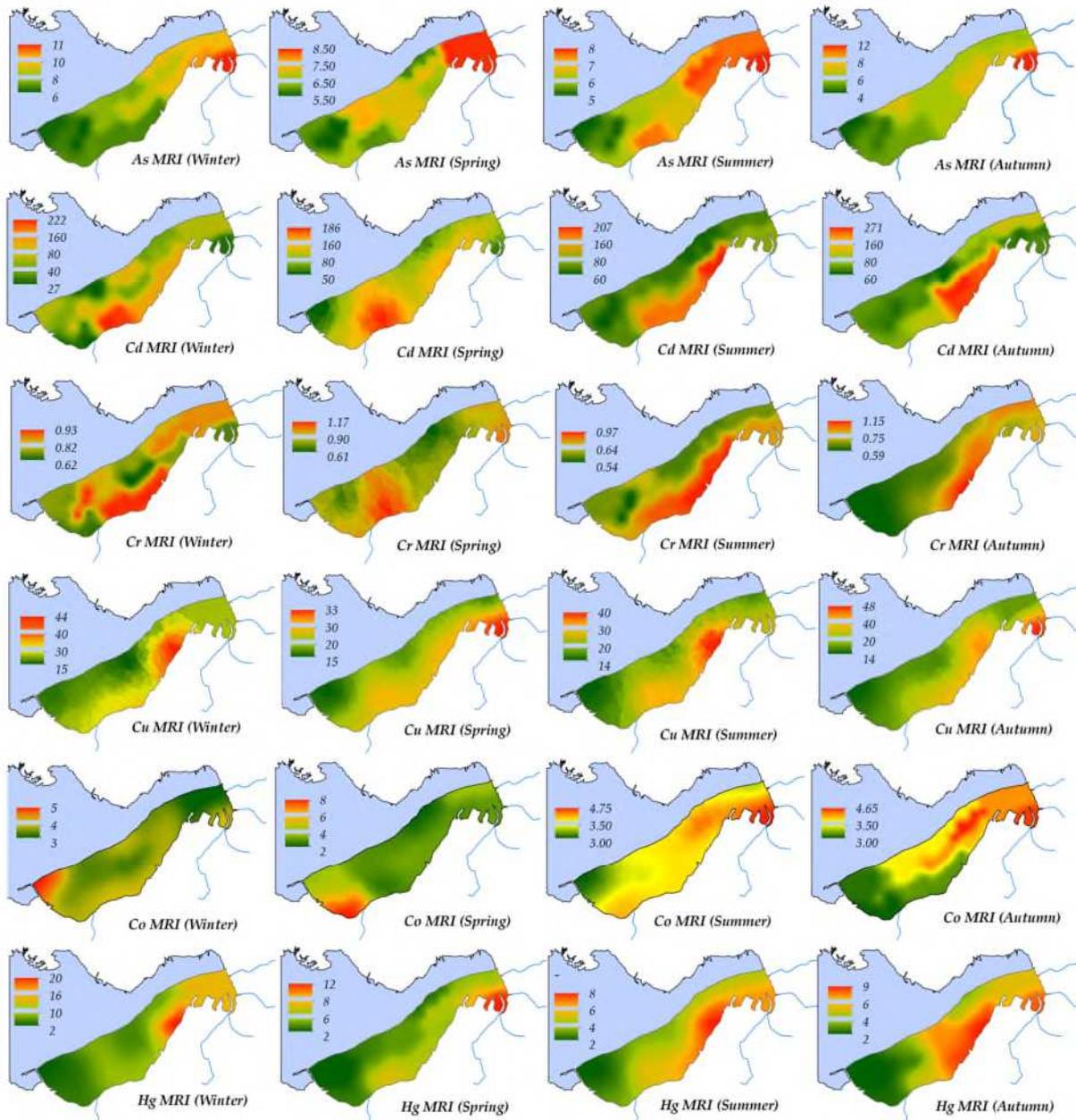
453

Figure 8: Spatial and seasonal change of MHQ

454 ECI values ranged from 3.80 to 6.26 in winter and averaged 5.56. ECI reached a maximum (6.26)
455 around ST 3 in winter. This situation indicates that the ST 11 environment was highly polluted.
456 Minimum ECI (3.80) was observed in ST 1. Accordingly, ST 1 pointed to a mild to moderate
457 contamination level in winter. The ECI was between 4.30 and 6.11 in the spring and averaged 5.46. In
458 ECI reached to the maximum (6.15) level in ST 11 and created a high degree of pollution. In the
459 spring, the minimum ECI (4.30) was observed around ST 4. At this point, moderate pollution was
460 detected. ECI was 5.86 in summer on average, ranging from 5.00 to 6.49. The maximum value (6.49)
461 was observed in ST 10 near the mouth of the Poligon Stream in the summer and a high degree of
462 pollution was detected. The minimum value (5) was observed in ST 16, which was moderately dirty.
463 In autumn, the maximum ECI (7.11) was observed in ST 9 and the minimum ECI (3.84) in ST 16. ECI
464 was 5.82 on average. Accordingly, there was high pollution around ST 9 and slight-moderate pollution
465 around ST 16. The average ECI of four seasons was 5.67. Accordingly, the whole inner gulf was
466 highly polluted in winter. According to the spatial analyses data, the maximum ECI was concentrated
467 in ST 9 ST 10 and ST 11, the stations close to the mouth of the Poligon Stream (Figure 10). This
468 situation shows that the Poligon Stream plays an important role in the pollution of the inner gulf.

469 According to the four-season average data of MRI, Cd (114.79) > Pb (27.97) > Cu (24.29) > As (7.09)
470 > Hg (5.64) > Ni (4.45) > Co (4.07) > Zn (2.92) > Mn (1.03) > Cr (0.78). Accordingly, while Cd
471 created significant ecological risks in all seasons throughout the inner gulf, other metals did not create
472 ecological risks in any season. However, the MRI values detected in some seasons were observed to
473 create an ecological risk. According to spatial analyses, As did not pose an ecological risk, but reached
474 its maximum ecological risk level around ST 1 in winter (10.95), spring (8.49), summer (8.02) and
475 autumn (12.06). This finding shows that in case of an increase in anthropogenic resources, the streams
476 and ports passing through the city and industrial zone may create a risk of As pollution in the inner
477 inner gulf. As values were at minimum in winter (6.17), spring (5.57) and autumn (5.27) in Station 14
478 and in summer (5.20) in Station 15. Cd was at the maximum ecological risk level in ST 10 in winter
479 (222), summer (187) and autumn (271) and in ST 11 in spring (186). A high degree of ecological risk
480 has been identified in the vicinity of the aforementioned stations. This situation is attributed to the
481 anthropogenic Cd sources in the Poligon Stream basin. Minimum ecological risk values for Cd were
482 determined in winter (27) in ST 13, in spring (51) in ST 16, in summer (59) in ST 15 and in autumn
483 (57) in ST 15.

484

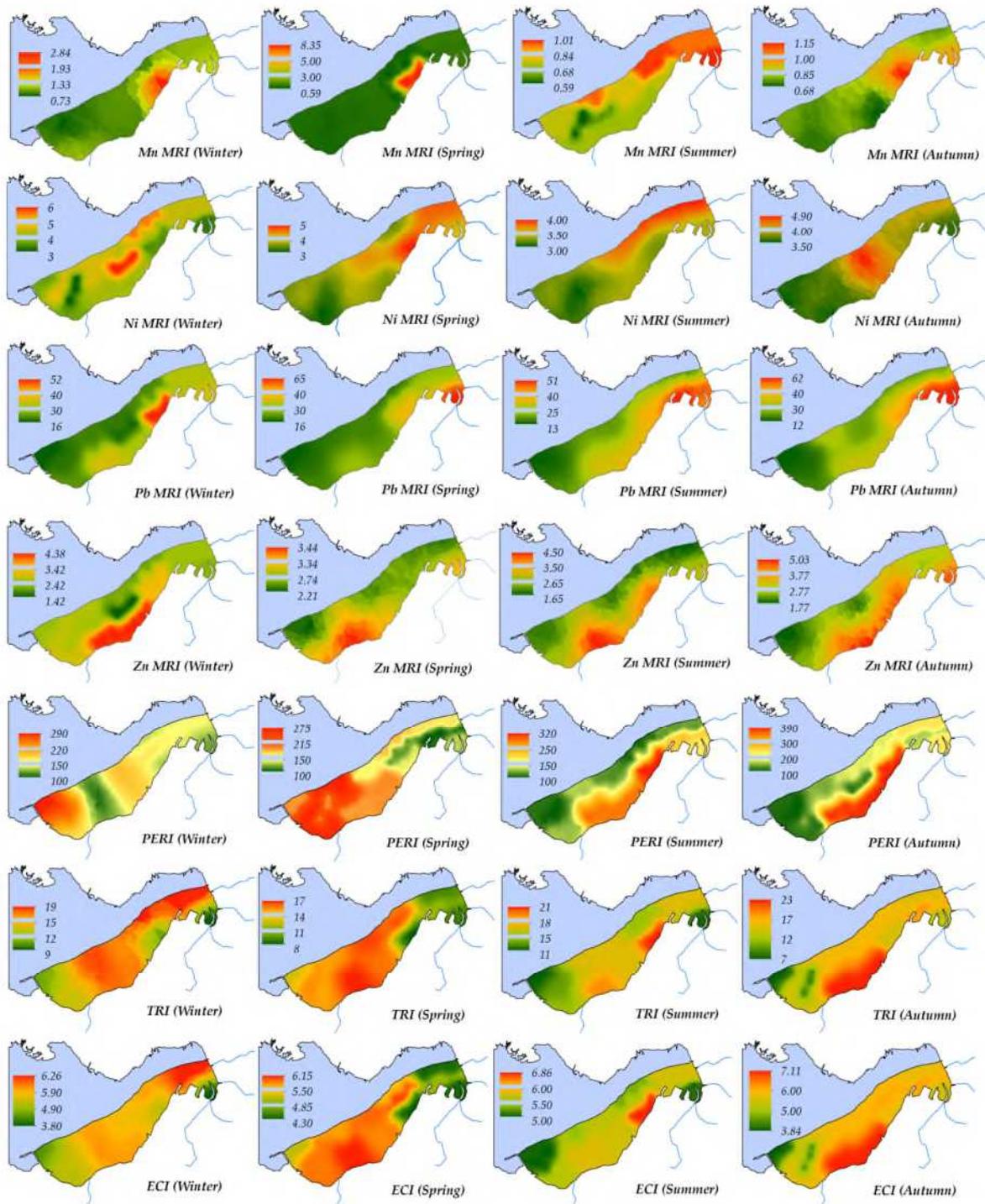


485
486

Figure 9: Spatial and seasonal change of MRI (part 01)

487 Cr did not create an ecological risk in any station and season. Maximum ecological risk values for Cu
 488 were identified in winter (44) in ST 4, in spring (34) in ST 1, in autumn (41) in ST 5 and in summer
 489 (48) in ST 1. Accordingly, Cu was found to create a moderate ecological risk in winter and autumn in
 490 ST 4 and ST 5 near the port and in summer in ST 1 where Arap Creek, Melez Creek and Manda Creek
 491 discharge. Minimum ecological risk values for Cu were identified in winter (15.50) in ST 16, in spring
 492 (15.88) in ST 15, in summer (14.19) in ST 6 and in autumn (14.26) in ST 16. Co, Hg, Mn, Ni and Zn
 493 did not create an ecological risk in any station or season. Figures 9 and 10 present the spatial
 494 distribution analyses of these metals. Pb reached the maximum ecological risk value in winter (52) in
 495 ST 4, in spring (65) in ST 1, in summer (51) and autumn (62) in ST 2 and created a moderate
 496 ecological risk in the aforesaid station areas. According to spatial analyses, Pb created an ecological
 497 risk due to the the harbor in winter and due to anthropogenic effects discharged by the Manda Creek,

498 Arap Creek, and Melez Creek in other seasons. Minimum values for Pb were observed around ST 16
 499 in all seasons.



500

501 Figure 10: Spatial and seasonal change of MRI, PERI, TRI and ECI (part 02)

502 PERI average for four seasons was 193. Accordingly, a moderate potential ecological risk was found
 503 to exist in the inner gulf. When examined seasonally; winter average of PERI was 187. There was a
 504 moderate ecological risk in the inner gulf during the winter season. PERI increased to the maximum in
 505 winter (314) in ST 10, creating a significant potential ecological risk. The reason for this situation was
 506 the Cd discharged by Poligon Stream. PERI was at minimum levels (95) around ST 13. Low potential

507 ecological risk was detected in ST 1, ST 6, ST 8 and ST 12 in winter and moderate potential
508 ecological risk was detected in other stations (Figure 10).

509 PERI average for spring was 190, and the maximum (270) and minimum value (100) were observed in
510 ST 11 and ST 16 respectively. A moderate ecological risk existed in the whole inner gulf in the spring
511 except for ST 15 and ST 16. Cd was the reason for the ecological risk. In the spring, high (265) MRI
512 values around ST 4 (263) and ST 2, where the port is located, drew attention. This indicates that ports
513 have an impact on the potential increase in ecological risk.

514 PERI average for summer was 184. There was a moderate potential ecological risk in the inner gulf in
515 summer. PERI created a significant potential ecological risk by reaching the maximum (308) in ST 4,
516 while the minimum value (110) was observed in ST 15. Low ecological risk was identified in ST 3, ST
517 4, ST 5, ST 6, ST 14, ST 15 and ST 16 in summer.

518 PERI average for autumn was 210 and a moderate ecological risk was identified in the inner gulf.
519 PERI was found to be at the maximum (373) level in ST 4 and at the minimum (106) level in ST 15.
520 Accordingly, there was a significant ecological risk around ST 4, low ecological risk around ST 8, ST
521 13, ST 15, ST 16 and moderate potential ecological risk in other areas.

522 Generally speaking, a moderate ecological risk has been identified in all seasons throughout the İzmir
523 Inner Gulf. Ecological risk is low in certain stations in some seasons while it is significant in some
524 stations in some seasons. Figure 10 presents the detailed spatial distribution of PERI.

525 According to average values, TRI was (16.65) in winter, (15.65) in spring, (17.93) in summer and
526 (17.85) in autumn. Accordingly, a significant toxic risk existed in all seasons. The order of
527 responsibility of metals from TRI is Ni> Cr> As> Hg> Pb> Zn> Cu> Cd. According to the spatial
528 distribution of TRI, the maximum value was determined in ST 9 (25.17) in autumn and the minimum
529 value in ST 16 in autumn. Maximum TRI values were observed in ST 11 near the mouth of the
530 Poligon Stream in winter and spring, in ST 4 near the harbor in summer, and in ST 9 in the autumn
531 (Figure 10). Accordingly, anthropogenic activities in the harbor and Poligon Stream cause an increase
532 in the toxic risk in the inner gulf.

533 **3.4. Multivariate statistical analysis**

534 Four factors with an eigenvalue > 1 were identified for factor analysis. These factors explained 79.59%
535 of the total variance. The first factor explained 38.44% of the variance and consisted of TOC, Mo, Cu,
536 Pb, Zn, Cd and Cr. This factor represented the anthropogenic effect. Mo, Cu, Pb, Zn and Cd are
537 elements of anthropogenic origin, which are in the moderate-significant class according to EF and I_{geo} .
538 TOC, on the other hand, is related to eutrophication, which is one of the most important problems of
539 the İzmir Inner Gulf. Cr is the only element in this factor with a low enrichment value. It is also
540 included in the second factor with a weight close to its load in the first factor. This indicates that Cr
541 has mixed resources. The second factor explained 19.04% of the total variance and consisted of Ni,
542 Co, As, Cr, Ti (positive load) and $CaCO_3$ (negative load). This factor represented lithogenic sources.
543 All elements included in the factor were lithophile elements with low enrichment and I_{geo} values. The
544 third factor explained 15.24% of the total variance and consisted of Chl-a, Bsi, and Hg. This factor
545 represented primary production. It consisted of Chl-a and biogenic silica accumulated in the sediment,
546 as well as Hg. The participation of Hg in this factor may be related to the transport of algae from water
547 to sediment, depending on the uptake. The fourth and the final factor explained 6.87% of the total
548 variance and consisted of Fe and Mn. This factor also represented rock erosion similar to factor 2.

549 However, the presence of these two elements in a different factor may be due to differences in
 550 transport processes (Table 2).

551 Table 2: Factor analysis

	<i>Factor 1</i>	<i>Factor 2</i>	<i>Factor 3</i>	<i>Factor 4</i>
TOC	0.50	-0.01	0.10	-0.14
CaCO ₃	-0.03	-0.60	0.29	0.10
Mo	0.86	0.23	-0.17	-0.01
Cu	0.88	0.14	0.15	0.00
Pb	0.58	0.04	0.42	0.10
Zn	0.91	0.26	-0.06	-0.08
Ni	0.03	0.96	0.08	0.08
Co	0.22	0.86	0.11	0.33
Mn	-0.17	0.00	0.14	0.96
Fe	0.06	0.67	-0.05	0.72
As	0.24	0.83	0.26	-0.02
Cd	0.85	0.14	0.04	0.04
Cr	0.70	0.64	-0.05	-0.09
Ti	0.27	0.88	-0.22	0.04
Hg	0.56	0.02	0.64	0.02
Chl-a	-0.01	0.00	0.94	0.04
Bsi	0.01	-0.06	0.96	0.06

552

553 Based on the correlation test, TOC had a positive but weak relationship with Mo, Cu, Pb, Zn, Cd and
 554 Cr. The role of TOC in transporting this element appeared to be low. CaCO₃ had a weak negative
 555 relationship with Mo, Ni, Co, Fe, Cr and Ti. Accordingly, CaCO₃ is believed to have no function in the
 556 distribution of metals. Cu, Pb, Zn, Cd and Mo with anthropogenic enrichment had strong positive
 557 correlations with each other. These elements are thought to share source and transport processes. Apart
 558 from these elements, Mo had a relationship with Ni, Co, Fe, As, Cr, Ti and Hg, but its relationship was
 559 weak with other elements except Cr. Ni, Co, Mn, Fe, As, and Ti displayed a strong relationship with
 560 each other and a relatively weak relationship with Cr. The low enrichment values of these elements
 561 and the relationships between them showed that they were transported from natural resources to the
 562 inner gulf by common transportation processes. Although Hg is an element that does not show
 563 enrichment, it had a weak correlation with Mo, Cd and Cu of anthropogenic origin, had a strong
 564 correlation with Pb and weak correlation with As and Ti, which are naturally sourced elements. This
 565 situation may refer to the similarity in the transportation processes rather than the common source.
 566 Chl-a, which represents primary productivity, had a positive weak relationship with Mn and Pb and a
 567 negative weak relationship with Ti. Similarly, Bsi showed a weak positive relationship with Pb and a
 568 negative weak relationship with Ti. This situation indicates that phytoplankton play a partial role in the
 569 transport of lead to the sediment. The 0.99 correlation between Bsi and Chl-a indicated that the
 570 contribution of diodes to the concentration of Chl-a was important, and that the diotames controlled
 571 the Chl-a concentration. The absence of a statistically significant correlation between these two
 572 parameters representing primary production and TOC suggests that the carbon source may be
 573 allochthonous (Table 3).

574

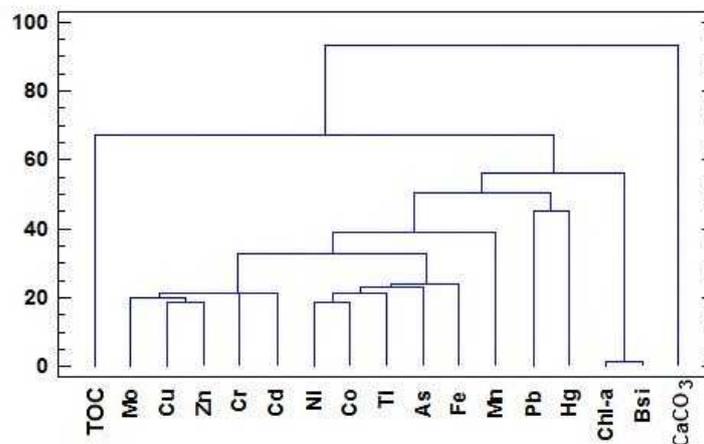
575

Table 3: Correlation analysis

	TOC	CaCO ₃	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr	Ti	Hg	Chl- <i>a</i>	Bsi
TOC																	
CaCO ₃	-0.05																
Mo	0.35	-0.28															
Cu	0.49	-0.01	0.65														
Pb	0.39	0.17	0.48	0.65													
Zn	0.50	-0.21	0.80	0.83	0.51												
Ni	-0.05	-0.43	0.32	0.04	0.02	0.23											
Co	0.00	-0.35	0.36	0.23	0.24	0.20	0.76										
Mn	-0.21	-0.04	-0.08	-0.03	0.16	-0.07	0.62	0.68									
Fe	-0.13	-0.39	0.25	0.00	-0.04	0.14	0.85	0.79	0.72								
As	-0.01	-0.13	0.39	0.26	0.34	0.28	0.75	0.76	0.60	0.67							
Cd	0.36	-0.16	0.70	0.65	0.50	0.75	0.21	0.24	-0.08	0.17	0.27						
Cr	0.33	-0.36	0.85	0.57	0.42	0.79	0.49	0.47	0.08	0.34	0.46	0.65					
Ti	0.03	-0.48	0.43	0.25	0.00	0.37	0.76	0.74	0.45	0.78	0.64	0.29	0.49				
Hg	0.23	0.19	0.33	0.55	0.80	0.38	0.09	0.22	0.18	-0.04	0.32	0.45	0.35	-0.06			
Chl- <i>a</i>	0.12	0.18	-0.17	0.11	0.43	-0.09	0.01	0.12	0.25	-0.04	0.19	0.05	-0.06	-0.29	0.60		
Bsi	0.14	0.20	-0.19	0.11	0.45	-0.10	-0.01	0.10	0.25	-0.06	0.17	0.04	-0.08	-0.31	0.60	0.99	

577

578 Two important clusters are noteworthy according to the dendrogram obtained from cluster analysis.
 579 One of them is the cluster representing the anthropogenic contribution among Mo, Cu, Zn, Cr, Cd, and
 580 the other is the cluster representing the natural processes between Ni, Co, Ti, As, Fe, Mn. These two
 581 clusters are also compatible with the factor analysis results. The high affinity between Chl-*a* and Bsi
 582 was also consistent with the results of factor analysis and correlation test. Although there was a
 583 relationship between Hg and Pb, the distance of these two elements was grand. A similar result was
 584 encountered in the correlation test and a high correlation was found between the two elements (Figure
 585 11). This similarity is thought to be based on common transport processes. TOC and CaCO₃ did not
 586 seem to play an important role in the transport and distribution of metals.



587

588

Figure 11: Cluster analysis

589 One-way ANOVA was performed at 95% confidence interval to identify whether there was a
590 difference between seasonal concentrations for each of the 17 variables measured in the study. While
591 there was a significant difference between the seasons in the concentrations of CaCO₃, Cu, Ti, Chl-a
592 and Bsi, no significant difference was found for the other elements. Multiple range test (LSD) was
593 performed to detect the seasons which created difference. Accordingly, the CaCO₃ concentration
594 varied in the spring, but it had similar levels in the other three seasons. Cu concentration showed a
595 significant difference between winter-summer, winter-autumn and spring-summer. From this point of
596 view, it can be argued that there is a difference between dry seasons and humid seasons in terms of
597 precipitation. For Ti, a difference was observed between summer-spring and summer-winter.
598 Considering that it is a lithophile element and is carried to the inner gulf by erosion, this difference
599 between rainy and dry seasons is significant. Chl-a and Bsi concentrations showed statistically
600 significant differences between winter-spring and winter-summer. This may be due to the fact that
601 abiotic factors such as light and temperature that affect primary production stimulate the increase in
602 plant biome with the arrival of summer.

603 **4. Conclusion**

604 According to results of the study, port management, industry, settlements and transportation activities
605 carried out in the inner gulf of İzmir caused Mo, Pb, Cu, Cd and Zn to be enriched with anthropogenic
606 effects and diverge from natural concentration levels. This was confirmed by multivariate statistical
607 analysis. The mHQ data showed high level of pollution and toxic effects for Ni, Cr, significant
608 pollution and toxic effects for As and Hg, and moderate pollution and toxic effects for Pb, Zn and Cu.
609 According to ECI data, the inner gulf is highly polluted and the Poligon Stream is at the forefront in
610 this pollution. Toxic risk has reached significant levels in the vicinity of the ports and near ST 10. Cd
611 created a significant ecological risk in all seasons due to its high toxicity. Cu and Pb caused moderate
612 ecological risk in local areas near the port. A moderate potential ecological risk has been identified in
613 all seasons throughout the inner gulf. However, a significant potential ecological risk has emerged in
614 ST 4 in some seasons due to the anthropogenic effects arising from the ports and a significant potential
615 ecological risk has been identified in ST 10 near the mouth of the Poligon Creek due to sewer
616 leakages. The results point to a moderate potential ecological risk and a high level of toxic risk in the
617 inner gulf of İzmir. Directions of currents, rivers and amount of precipitation have an impact on the
618 spatial-seasonal distribution of toxic and ecological risks. In order to ensure the sustainable use of the
619 inner gulf, port activities should be inspected, use of public transportation or metro should be
620 encouraged on transportation lines that are close to the shore and the rehabilitation tasks of rivers,
621 especially the Poligon Stream, should be reviewed.

622

623 **Acknowledgements**

624 This study was supported by the Scientific and Technological Research Council of Turkey (TUBITAK)
625 within the scope of project 114Y419. We thank TUBITAK for their support.

626

627

628

629

630

631

632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661

Declarations

Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

All authors approve the publication of the article in your journal

Authors Contributions

EYÖ, Conceptualization, Funding acquisition, Investigation, Project administration, Writing – original draft

Ş.F, Conceptualization, Data curation, Formal analysis, Software, Writing – original draft
Visualization

S.K, Conceptualization, Formal analysis, Methodology, Resources, Writing – review & editing

HBB, Conceptualization, Funding acquisition, Project administration, Validation, Writing – review & editing

All authors read and approved the final manuscript.

Funding

This study was supported by the Scientific and Technological Research Council of Turkey (TUBITAK) within the scope of project 114Y419. We thank TUBITAK for their support.

Competing interests

The authors declare that they have no competing interests

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

The datasets generated during and/or analysed during the current study are available in the [NAME] repository, [PERSISTENT WEB LINK TO DATASETS]

662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700

REFERENCES

- Ahmed, I., Mostefa, B., Bernard, A., Olivier, R. (2018). Levels and ecological risk assessment of heavy metals in surface sediments of fishing grounds along Algerian coast. *Marine Pollution Bulletin* 136, 322–333. <https://doi.org/10.1016/j.marpolbul.2018.09.029>.
- Ahamad M.I., Song J., Sun H., Wang X., Mehmood M.S., Sajid M., and Khan A.J. (2020). Contamination level, ecological risk, and source identification of heavy metals in the hyporheic zone of the Weihe River, China. *Int. J. Environ. Res. Public Health*, 17, 1070. <https://doi.org/10.3390/ijerph17031070>.
- Altın, A., Filiz, Z., Iscen, C.F. (2009). Assessment of seasonal variations of surface water quality characteristics for Porsuk Stream. *Environ. Monit. Assess.* 158, 51–65. <https://doi.org/10.1007/s10661-008-0564-3>.
- Algül F. And Beyhan M. (2020). Concentrations and sources of heavy metals in shallow sediments in Lake Bafa, Turkey. *Scientific Reports*, 10, 11782. <https://doi.org/10.1038/s41598-020-68833-2>.
- Alrabie, N. A. et al. (2019). Heavy metals concentrations in stormwater and tilapia fish (*Oreochromis niloticus*) in Kuala Lumpur holding and storage SMART ponds. *Pertanika J. Trop. Agric. Sci.* 42, 1, 225–236. ISSN 1511-3701; EISSN: 2231-8542.
- Ali, U. et al. (2015). Mass burden and estimated flux of heavy metals in Pakistan coast: sedimentary pollution and eco-toxicological concerns. *Environ. Sci. Pollut. Res.* 22, 4316. <https://doi.org/10.1007/s11356-014-3612-2>.
- Amin, B., Ismail, A., Arshad, A., Yap, C. K., & Kamarudin, M. S. (2009). Anthropogenic impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia. *Environmental Monitoring and Assessment*, 148, 291–305. <https://doi.org/10.1007/s10661-008-0159-z>.
- Atalar M., Küçüksezgin F., Duman M., Gönül T. (2013). Heavy metal concentrations in surficial and core sediments from İzmir Bay: an assessment of contamination and comparison against sediment quality benchmarks. *Bull Environ Contam Toxicol*, 91, 69–75. <https://doi.org/10.1007/s00128-013-1008-5>.
- Bat L, Özkan E.Y, Öztekin HC. (2015). The contamination status of trace metals in Sinop coast of the Black Sea, Turkey. *Caspian Journal of Environmental Sciences (CJES)*. 13, 1, 1-10. <http://aquaticcommons.org/id/eprint/21748>.
- Bat L. (2017). The contamination status of heavy metals in fish from the Black Sea, Turkey and potential risks to human health. In: Sezgin, M., Bat, L., Ürkmez, D., Arıcı, E., Öztürk, B. (Eds.) *Black Sea Marine Environment: The Turkish Shelf*. Turkish Marine Research Foundation (TUDAV), Publication No: 46, ISBN- 978-975-8825-38-7, Istanbul, pp. 322-418.
- Bat L, Öztekin A, Şahin F, Arıcı E, Özsandıkçı U. (2018). An overview of the Black Sea pollution in Turkey. *MedFAR.*, 1, 67-86.
- Bat L, Arıcı E. (2018). Chapter 5. Heavy metal levels in fish, molluscs, and crustacea from Turkish seas and potential risk of human health. In: Holban AM, Grumezescu AM. (Eds.) *Handbook of Food Bioengineering, Volume 13, Food Quality: Balancing Health and Disease*. Elsevier,

- 701 Academic Press, ISBN: 978-0-12-811442-1, pp. 159-196. <http://dx.doi.org/10.1016/B978-0->
702 12-811442-1.00005-5.
- 703 Bat, L., Özkan, E. Y. (2019). Heavy metal levels in sediment of the Turkish Black Sea Coast. In I.
704 Management Association (Ed.), *Oceanography and Coastal Informatics: Breakthroughs in*
705 *Research and Practice* (pp. 86-107). Hershey, PA: IGI Global. <http://doi:10.4018/978-1-5225->
706 7308-1.ch004.
- 707 Bat L, Kurt G. (2020). Use of polychaeta species as bioindicator for heavy metal pollution in marine
708 environments. (In): Bayram T, Zayachuk Y, Gupta DK. (Eds.) *Environmental Radioactivity in*
709 *Turkish Environment*. Sivas Cumhuriyet Üniversitesi Matbaası, ISBN 978-605-7902-40-5, pp.
710 259-281.
- 711 Bat L, Arıcı E, Öztekin A. (2021). Threats to quality in the coasts of the Black Sea: heavy metal
712 pollution of seawater, sediment, Macro-Algae and Seagrass. In: Shit P.K., Adhikary P.P.,
713 Sengupta D. (eds) *Spatial Modeling and Assessment of Environmental Contaminants.*
714 *Environmental Challenges and Solutions*. Springer, Cham. pp. 289-325.
715 https://doi.org/10.1007/978-3-030-63422-3_18.
- 716 Benedetto, A. M., Semensato, G. E., Carvalho, C., & Rezende, C. (2019). Trace metals in two
717 commercial shrimps from southeast Brazil: Baseline records before large port activities in
718 coastal waters. *Marine Pollution Bulletin*, 146, 667-670.
719 <https://doi.org/10.1016/j.marpolbul.2019.07.028>.
- 720 Beşiktepe, Ş. T., Sayın, E., İlhan, T., & Tokat, E. (2011). Investigation of İzmir Bay current dynamics
721 with the help of model and observation. 7th Coastal Engineering Symposium, 427-437.
722 Trabzon: TMMOB.
- 723 Bastami, K.D.; Bagheri, H.; Kheirabadi, V.; Zaferani, G.G.; Teymori, M.B.; Hamzehpoor, A.; Soltani,
724 F.; Haghparast, S.; Harami, S.R.M.; Ghorghani, N.F.; Ganji S. (2014). Distribution and
725 ecological risk assessment of heavy metals in surface sediments along southeast coast of the
726 Caspian Sea. *Marine Pollution Bull.* 81, 262–267.
727 <https://doi.org/10.1016/j.marpolbul.2014.01.029>.
- 728 Barbieri, M. (2016). The importance of enrichment factor (EF) and geoaccumulation index (I_{geo}) to
729 evaluate the soil contamination. *Geology & Geophysics, Scientific Reports*, 4, 7152.
730
- 731 Benson, N.U., Adedapo, A.E., Fred-Ahmadu, O.H., Williams, A.B., Udosen, E.D., Ayejuyo, O.O.,
732 Olajire, A.A., (2018). New ecological risk indices for evaluating heavy metals contamination
733 in aquatic sediment: A case study of the Gulf of Guinea. *Regional Studies in Marine Science*
734 18, 44–56. <https://doi.org/10.1016/j.rsma.2018.01.004>.
735
- 736 Brady, J.P., Ayoko, G.A., Martens, W.N., Goonetilleke, A. (2015). Development of a hybrid pollution
737 index for heavy metals in marine and estuarine sediments. *Environ. Monit. Assess.* 187, 306.
738 <https://doi.org/10.1007/s10661-015-4563-x>
739
- 740 Chen, Y., Liu, Q., Xu, M., & Wang, Z. (2020). Inter-annual variability of heavy metals pollution in
741 surface sediments of Jiangsu coastal region, China: Case study of the Dafeng Port. *Marine*
742 *Pollution Bulletin*, <https://doi.org/110720>. 10.1016/j.marpolbul.2019.110720.
743
- 744 De Master, D.J., 1981. The supply and accumulation of silica in the marine environment. *Geochimica*
745 *et Cosmochimica Acta* 45, 1715–1732. [https://doi.org/10.1016/0016-7037\(81\)90006-5](https://doi.org/10.1016/0016-7037(81)90006-5).

746
747 ESRI. (2021). [https://desktop.arcgis.com/en/arcmap/10.3/tools/3d-analyst-toolbox/how-kriging-](https://desktop.arcgis.com/en/arcmap/10.3/tools/3d-analyst-toolbox/how-kriging-works.htm)
748 [works.htm](https://desktop.arcgis.com/en/arcmap/10.3/tools/3d-analyst-toolbox/how-kriging-works.htm)
749
750 Fural, Ş., Kükreler, S., Cürebal, İ. (2020). Geographical information systems based ecological risk
751 analysis of metal accumulation in sediments of İkizcetepeler Dam Lake (Turkey). *Ecological*
752 *Indicators*, 119. <https://doi.org/10.1016/j.ecolind.2020.106784>.
753
754 Fural, Ş., Kükreler, S., Cürebal, İ., & Aykır, D. (2021). Spatial distribution, environmental risk
755 assessment, and source identification of potentially toxic metals in Atikhisar dam, Turkey.
756 *Environmental Monitoring and Assessment*. 193, [https://doi.org/10.1007/s10661-021-09062-](https://doi.org/10.1007/s10661-021-09062-6)
757 [6](https://doi.org/10.1007/s10661-021-09062-6).
758
759 Feng H, Jiang H, Gao W, Weinstein M P, Zhang Q, Zhang W, Yu L, Yuan D and Tau J. (2011). Metal
760 contamination in sediments of the western Bohai Bay and adjacent estuaries, China. *Journal of*
761 *Environmental Management*, 92, 1185–97. <https://doi.org/10.1016/j.jenvman.2010.11.020>.
762
763 Gao, L.; Wang, Z.; Shan, J.; Chen, J.; Tang, C.; Yi, M.; Zhao, X. (2016). Distribution characteristics
764 and sources of trace metals in sediment cores from a trans-boundary watercourse: An example
765 from the Shima River, Pearl River Delta. *Ecotoxicol. Environ. Saf.* 134, 186–195.
766 <https://doi.org/10.1016/j.ecoenv.2016.08.020>.
767
768 Gaudette, H.E., Flight, W.R., Toner, L., Folger, D.W. (1974). An inexpensive titration method for the
769 determination of organic carbon in recent sediments. *Journal of Sedimentary Research* 44,
770 249–253. <https://doi.org/10.1306/74D729D7-2B21-11D7-8648000102C1865D>.
771
772 Gülsever, G., Arslan, Ö.Ç. (2019). Current status of heavy metal pollution in İzmir inner bay
773 sediments. 2nd International Agriculture, Environment and Health Congress Full Text
774 Abstract Book, 1769-1776.
775
776 Hakanson, L. (1980). An ecological risk index for aquatic pollution control: A sedimentological
777 approach. *Water Research*, 8, 975-1001.
778
779 Hasan A.B., Kabir S., Reza A.H.M., Zaman M.N., Ahsan A., Rashid M. (2013). Enrichment factor
780 and geo-accumulation index of trace metals in sediments of the ship breaking area of Sitakund
781 Upazilla (Bhatiary–Kumira), Chittagong, Bangladesh. *Journal of Geochemical Exploration*,
782 125, 130–137.
783
784 Kaya, H., Erginal, G., Çakır, Ç., Gazioğlu, C., Erginal, A. (2017). Ecological risk evaluation of
785 sediment core samples, Lake Tortum (Erzurum, NE Turkey) using environmental indices.
786 *International Journal of Environment and Geoinformatics*, 4, 227-239.
787 <https://doi.org/10.30897/ijegeo.348826>.
788
789 Konaş, A., Kucuksezgin, F., Altay, O., Uluturhan, E., 2004. Monitoring of eutrophication and nutrient
790 limitation in the İzmir Bay (Turkey) before and after Wastewater Treatment Plant.
791 *Environment International*, 29, 1057–1062. [https://doi.org/10.1016/S0160-4120\(03\)00098-9](https://doi.org/10.1016/S0160-4120(03)00098-9)
792
793 Kükreler, S., Erginal, A. E., Kılıç, Ş., Bay, Ö., Akarsu, T., & Öztura, E. (2020). Ecological risk
794 assesment of surface sediments of Çardak Lagoon along a human disturbance gradient.
795 *Environ Monit Asses*, 192. <https://doi.org/10.1007/s10661-020-08336-9>.
796
797 Li, X., Liu, L., Wang, Y., Luo, G., Chen, X., Yang, X., et al. (2012). Integrated assessment of heavy
798 metal contamination in sediments from a coastal industrial basin, NE China. *PLoS ONE*, 7(6),
799 1–10. <https://doi.org/10.1371/journal.pone.0039690>.

- 800 Li, Y., Qu, X., Zhang, M., Peng, W., Yu, Y., Gao, B., 2018. Anthropogenic Impact and Ecological
801 Risk Assessment of Thallium and Cobalt in Poyang Lake Using the Geochemical Baseline.
802 Water 10, 1703. <https://doi.org/10.3390/w10111703>.
803
- 804 Liu, J. et al. (2017). Occurrence and risk assessment of heavy metals in sediments of the Xiangjiang
805 River, China. *Environ. Sci. Pollut. Res.Int.* 24, 2711. <https://doi.org/10.1007/s11356-016-8044-8>.
806
807
- 808 Looi L.J., Aris A.Z., Yusoff F., Mohd N and Haris I.H. (2019). Application of enrichment factor,
809 geoaccumulation index, and ecological risk index in assessing the elemental pollution status of
810 surface sediments. *Environ Geochem Health*, 41,27–42 <https://doi.org/10.1007/s10653-018-0149-1>.
811
812
- 813 Macdonald, D.D., Carr, R.S., Calder, F.D. (1997). Development and evaluation of sediment quality
814 guidelines for Florida coastal waters. *Oceanographic Literature Review*, 6, 638.
815
- 816 MacDonald, D.D., Ingersoll, C.G., Berger, T.A. (2000). Development and Evaluation of Consensus-
817 Based Sediment Quality Guidelines for Freshwater Ecosystems. *Arch. Environ. Contam.*
818 *Toxicol.* 39, 20–31. <https://doi.org/10.1007/s002440010075>.
819
- 820 Martin, D.F., 1972. *Marine Chemistry: Theory and Applications*, First U.S. Edition. ed. Marcel
821 Dekker Inc, New York, NY.
822
- 823 MGM, (2021). (General Directorate of Meteorology) <https://izmir.mgm.gov.tr/>.
- 824 MTA, (2021). [http:// earth sciences.mta.gov.tr/mainpage.aspx](http://earth.sciences.mta.gov.tr/mainpage.aspx).
- 825 Niu, Y. et al. (2015). Spatial evaluation of heavy metals concentrations in the surface sediment of
826 Taihu Lake. *Int. J. Environ. Res. Public Health*, 12, 15028–15039.
- 827 Özkan, E.Y. (2012). “A new assessment of heavy metal contaminations in an Europhicated Bay
828 (Inner İzmir Bay, Turkey)” *Turkish Journal of Fisheries and Aquatic Sciences*, 12, 135-147.
- 829 Özkan E.Y. and Büyükişık B. (2012). "Geochemical and statistical approach for assessing heavy metal
830 accumulation in the Southern Black Sea Sediments" *Ecology*, 21, 11-24.
- 831 Jahan, S., & Strezov, V. (2018). Comparison of pollution indices for the assessment of heavy metals in
832 the sediments of seaports of NSW, Australia. *Marine Pollution Bulletin*, 128, 298-306.
833 <https://doi.org/10.1016/j.marpolbul.2018.01.036>.
- 834 Jeong, H., Choi, Y. J., Lim, J., Shim, J. W., Kim, Y. O., & Ra, K. (2020). Characterization of the
835 contribution of road deposited sediments to the contamination of the close marine
836 environment with trace metals: Case of the port city of Busan (South Korea). *Marine Pollution*
837 *Bulletin*, 161, <https://doi.org/111717>. 10.1016/j.marpolbul.2020.111717.
- 838 Ji, K.; Kim, J.; Lee, M.; Park, S.; Kwon, H.J.; Cheong, H.K.; Jang, J.Y.; Kim, D.S.; Yu, S.; Kim,
839 Y.W.; Lee K.W.; Yang S.O; (2013). Assessment of exposure to heavy metals and health risks
840 among residents near abandoned metal mines in Goseong, Korea. *Environ. Pollut.* 178, 322–
841 328. <https://doi.org/10.1016/j.envpol.2013.03.031>.
- 842 Merhaby, D., Ouddane, B., Net, S., & Halvani, J. (2018). Assessment of trace metals contamination in
843 surficial sediments along Lebanese Coastal Zone. *Marine Pollution Bulletin*, 113, 881-890.
844 <https://doi.org/10.1016/j.marpolbul.2018.06.031>.

- 845 Muhammad, S.; Shah, M.T.; Khan, S. (2011). Heavy metal concentrations in soil and wild plants
846 growing around Pb-Zn sulfide terrain in the Kohistan region, northern Pakistan. *Microchem. J.*
847 99, 67–75. <https://doi.org/10.1016/j.microc.2011.03.012>.
- 848 Müller, G. (1996). Index of geoaccumulation in sediments of the Rhine River. *Geo Journal*, 2, 108 -
849 118.
- 850 Nowrouzi M. and Pourkhabbaz A. (2014). Application of geoaccumulation index and enrichment
851 factor for assessing metal contamination in the sediments of Hara Biosphere Reserve, Iran.
852 *Chemical Speciation and Bioavailability*, 26, 99-105,
853 <https://doi.org/10.3184/095422914X13951584546986>.
- 854 Oliveira, T. S., Xavier, D., Santos, L. D., França, E. J., Sanders, C. J., Passos, T. U., & Barcellos, R. L.
855 (2020). Geochemical background indicators within a tropical estuarine system influenced by a
856 port-industrial complex. *Marine Pollution Bulletin*, 161, <https://doi.org/111794>.
857 10.1016/j.marpolbul.2020.111794.
- 858 Özkan, E.Y., Kocatas, A., Büyükişık, B., (2008). Nutrient dynamics between sediment and overlying
859 water in the inner part of İzmir Bay, Eastern Aegean. *Environ. Monit. Assess.* 143, 313–325.
860 <https://doi.org/10.1007/s10661-007-9984-8>.
- 861 Özkan, E. Y., Büyükişık, H. B., Konaş, A., & Türkdoğan, M. (2017). A survey of metal
862 concentrations in marine sediment cores in the vicinity of an old mercury-mining area in
863 Karaburun, Aegean Sea. *Environ. Sci. Pollut. Res.*, 24, 13823–13836.
- 864 Panagos, A., Papadopoulos, N., Alexandropoulou, S., Synetos, S., & Varnavas, S. (1989). Geochemical
865 study of sediments from deposits. *Marine Geology*, 110, 93–114. doi:10.1016/0025-
866 3227(93)90108-8.
- 867 Phillips DJH, Rainbow P.S. (1993) *Biomonitoring of aquatic trace contaminants*. London Chapman
868 and Hall.
- 869 Palas, S., (2020) Investigation of heavy metal accumulation in Late Quaternary-Contemporary surface
870 sediments of Aliğa Bay, M.T.A. *Natural Resources and Economy Bulletin*, 29, 29-48.
- 871 Roberts, D.A., Birchenough, S.N., Lewis, C., Sanders, M.B., Bolam, T., Sheahan, D. (2013). Ocean
872 acidification increases the toxicity of contaminated sediments. *Global Change Biology* 19,
873 340–351. <https://doi.org/10.1111/gcb.12048>.
- 874 Rainbow PS (1992) The significance of accumulated heavy metal concentrations in marine organisms.
875 In: Miskiewicz AG (ed) *Assessment of the distribution, impacts and bioaccumulation of*
876 *contaminants in aquatic environments*, Proceedings of a bioaccumulation Workshop. Water
877 Board and Australian Marine Science Association Inc., Sydney.
- 878 Rumisha, C., Elskens, M., Leermakers, M., & Kochzius, M. (2012). Trace metal pollution and its
879 influence on the community structure of soft bottom molluscs in intertidal areas of the Dar es
880 Salaam coast, Tanzania. *Marine Pollution Bulletin*, 521-531.
881 <https://doi.org/10.1016/j.marpolbul.2011.12.025>.
- 882 Rodríguez-Espinosa, P.F., Shruti, V.C., Jonathan, M.P., Martinez-Tavera, E., 2018. Metal
883 concentrations and their potential ecological risks in fluvial sediments of Atoyac River basin,

- 884 Central Mexico: Volcanic and anthropogenic influences. *Ecotoxicology and Environmental*
885 *Safety* 148, 1020–1033. <https://doi.org/10.1016/j.ecoenv.2017.11.068>.
- 886 Strickland, J., Parsons, T., 1972. *A Practical Handbook of Seawater Analysis*.
- 887 Schiff, K.C. and Weisberg, S.B. (1999) Iron as a reference element for determining trace metal
888 enrichment in Southern California coast shelf sediments. *Mar. Environ. Res.*, 48, 161–176.
- 889 Siddiquee, N.A., Ahmed, M.K., Quddus, M.M.A., Parween, S., Islam, M.H. (2006). Trace metal
890 concentration in sediments of Chittagong ship breaking area. *The Journal of Noami*. 23, 23–
891 30.
- 892 Singovszka, E. and Balintova M. (2019). Enrichment Factor and Geo-Accumulation Index of Trace
893 Metals in Sediments in the River Hornad, Slovakia. *IOP Conf. Series: Earth and*
894 *Environmental Science* 222, <https://doi.org/10.1088/1755-1315/222/1/012023>.
- 895 Sunlu, F.S., Sunlu, U., Büyükışık, B., Kükrer, S., Uncumusaoglu, A., 2012. Nutrient and chlorophyll -
896 a trends after wastewater treatment plant in İzmir Bay (Eastern Aegean Sea). *Journal of*
897 *Animal and Veterinary Advances* 11, 113–123. <https://doi.org/10.3923/javaa.2012.113.123>.
- 898 Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii.
899 *Environmental Geology* 39, 611–627. <https://doi.org/10.1007/s002540050473>.
- 900 Sun, Z.; Mou, X.; Tong, C.; Wang, C.; Xie, Z.; Song, H.; Sun, W.; Lv, Y. (2015). Spatial variations
901 and bioaccumulation of heavy metals in intertidal zone of the Yellow River estuary, China.
902 *Catena*, 126, 43–52. <http://dx.doi.org/10.1016/j.catena.2014.10.037>.
- 903 Tang, W., Shan, B., Zhang, H., Zhang, W., Zhao, Y., Ding, Y., et al. (2014). Heavy metal
904 contamination in the surface sediments of representative limnetic ecosystems in eastern China.
905 *Scientific Reports*, 4, 1–7. <https://doi.org/10.1038/srep07152>.
- 906 Tunca, E., Aydın, M. & Şahin, Ü.A. (2018). An ecological risk investigation of marine sediment from
907 the northern Mediterranean coasts (Aegean Sea) using multiple methods of pollution
908 determination. *Environ. Sci. Pollut. Res.* 25, 7487–7503. [https://doi.org/10.1007/s11356-017-](https://doi.org/10.1007/s11356-017-0984-0)
909 [0984-0](https://doi.org/10.1007/s11356-017-0984-0).
- 910 Varol, M. & Şen, B. (2012). Assessment of nutrient and heavy metal contamination in surface water
911 and sediments of the upper Tigris River, Turkey. *Catena*, 92, 1-10.
912 <https://doi.org/10.1016/j.catena.2011.11.011>.
- 913 Viard, B., Pihan, F., Promeprat, S., & Pihan, J.-C. (2004). Integrated assessment of heavy metal (Pb,
914 Zn, Cd) highway pollution: bioaccumulation in soil, Gramineae and land snails.
915 *Chemosphere*, 55, 1349-1359.
- 916 Varnavas, S. P. (1989). Metal Pollution of the Kalloni Bay, Lesvos Greece. *Proceedings of the*
917 *conference“ Environmen-tal Science and Technology”*, Lesvos, Greece, 211–220.
- 918 Williams J.A. and Antoine J. (2020). Evaluation of the elemental pollution status of Jamaican surface
919 sediments using enrichment factor, geoaccumulation index, ecological risk and potential
920 ecological risk index. *Marine Pollution Bulletin*, 157.
921 <https://doi.org/10.1016/j.marpolbul.2020.111288>.

- 922 Xiao, R.; Bai, J.; Lu, Q.; Zhao, Q.; Gao, Z.; Wen, X.; Liu, X. (2015). Fractionation, transfer, and
923 ecological risks of heavy metals in riparian and ditch wetlands across a 100-year
924 chronosequence of reclamation in an estuary of China. *The Science of the Total Environment*.
925 517, 66–75. <https://doi.org/10.1016/j.scitotenv.2015.02.052>.
- 926 Xu, F. et al. (2017). Assessment of heavy metal contamination in urban river sediments in the
927 Jiaozhou Bay catchment, Qingdao, China. *Catena*, 150, 9–16.
928 <https://doi.org/10.1016/j.catena.2016.11.004>.
- 929 Yang, J. et al. (2014). Sediment quality assessment for heavy metal contamination in the Dongzhai
930 Harbor (Hainan Island, China) with pollution indice approach. *The Open Chemical*
931 *Engineering Journal*, 8, 32–37.
- 932 Zhang, G., Bai, J., Zhao, Q., & et al. (2016). Heavy metals in wetland soils along a wetland-forming
933 chronosequence in the Yellow River Delta of China: Levels, sources and toxic risks.
934 *Ecological Indicators*. 69, 331–339. <https://doi.org/10.1016/j.ecolind.2016.04.042>.
- 935
- 936
- 937