#### **RESEARCH ARTICLE**



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

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#### Abstract

This study aims to investigate the ecological risk level of potentially toxic elements (PTEs) in İzmir Inner Gulf. Samples were taken from 16 stations selected in the southern littoral zone of the gulf for four seasons (winter, spring, summer, and autumn). Multi-element, total organic carbon, chlorophyll-*a*, biogenic silica and carbonate analyses were carried out. To determine contamination level and ecological risks, some indices (enrichment factor, modified hazard quotient and potential risk analysis, toxic risk index, etc.) were calculated. Mo and Pb show significant anthropogenic enrichment in the inner gulf. These are followed by Cu, Cd, and Zn with moderate accumulation. Risk assessment indices point out that Ni, Cr, and Cd have a serious potential to create risk for ecosystem, and these are followed by As, Hg, Pb, Zn, and Cu. According to the spatial distribution, land use maps, and factor analysis, the Cd, Zn, and Cr increases are localized at the mouth of the Poligon Stream. Pb and Cu accumulate at the mouth of four large streams feeding the eastern part of the gulf. Pb and Cu enrichment is associated with traffic and industrial discharges. While one of the sources of Hg is anthropogenic, another source is eutrophication resulting from benthic and planktonic diatom blooms. While Fe and Mn are added to the gulf via rivers as a result of rock and soil erosion, another source is sediment. Cr, As, and Ni come from anthropogenic and lithogenic sources and immobilized in sediment.  $CO_3^{-2}$  source is marine (biogenic) and dilutes other immobilized PTEs. It is understood that the peripheral stations rich in allochthonous organic carbon and the stations close to the central area rich in autochthonous organic carbon contribute to the carbon source in question.

Keywords Potential toxic elements  $\cdot$  Regional ecological risk assessment  $\cdot$  Environmental degradation  $\cdot$  İzmir Inner Gulf  $\cdot$  Source identification

### Introduction

The marine environment is one of the world's most valuable yet understudied areas (Williams and Antoine 2020). As a result of increased urbanization and rapid industrialization,

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potential toxic elements (PTEs) are becoming more common in aquatic environments due to their durability, toxicity, and ability to enter the food chain (Bastami, et al. 2014; Xiao et al. 2015; Ahamad et al. 2020). In the food chain, these PTEs may be bioaccumulated and biomagnified (Gu et al. 2021).

Analyses of water, sediments, and biomonitoring organisms can be used to determine the relative PTE pollution in aquatic environments (Phillips and Rainbow 1993; Atalar et al. 2013). PTEs released into aquatic environments can be trapped on suspended materials and transported into the sediment (Schiff and Weisberg 1999; Nowrouzi and Pourkhabbaz 2014; Bat et al. 2018; Bat and Özkan 2019). Effective pollution management and clean up solutions are essential for significant progress in coastal and marine biodiversity conservation. Quantitative assessment of PTEs and accurate identification of the polluting sources are required for the development of such strategies (Jafarabadi et al. 2021).

Sediments which are released into the overlying water by natural and anthropogenic processes such as bioturbation and dredging are an appropriate indication of marine ecosystem health and can represent the level of water pollution. Sediments are commonly thought of as trace PTE scavengers because of their propensity to transfer and store trace PTEs (Looi et al. 2019). Organic and inorganic matters are found in the sediments of rivers, estuaries, oceans, and other water supply systems (Siddiquee et al. 2006; Hasan et al. 2013). They are linked to hydrological connectivity, vegetation features, water quality, land use, and mineral type, in addition to acting as a reservoir for contaminants such as PTEs (Li et al. 2018; Ahamad et al. 2020). Both natural and man-made components created or derived from the environment usually end up in sediments (Singovszka and Balintova, 2019). PTEs from contaminated sediments can adversely affect water quality and aquatic life (Liu et al. 2017; Li et al. 2018; Looi et al. 2019). In the food chain, these PTEs may be bioaccumulated and biomagnified (Sun et al. 2015; Gu et al. 2021). PTEs in sediments come from either natural sources like atmospheric precipitation, ore deposits, geological weathering, storms, wind bioturbation, and wave-induced bedrock weathering or anthropogenic sources such as mining, shipping, industrial emission, smelting, fuel generation, electroplating, sludge discharge, energy transmission, dense urban areas, wastewater irrigation, and agricultural activities (Altın et al. 2009; Muhammad et al. 2011; Sun et al. 2015; Maurya and Kumari 2021). As a result of their toxicity, bioaccumulation, non-degradability, and vast sources, as well as their persistence in the aquatic environment, PTEs have piqued the interest of researchers (Gao et al. 2016).

PTEs, unlike other contaminants, do not biodegrade and are subject to a worldwide ecological cycle in which natural waters play a key role (Siddiquee et al. 2006). PTEs can be found in low concentrations (nanograms to micrograms in the liter range) in natural aquatic ecosystems (Atalar et al. 2013; Singovszka and Balintova 2019). However, serious biological consequences can occur when PTE concentrations reach a certain extent (Lu et al. 2019). Among the pollutants, PTEs are usually non-biodegradable and toxic to living aquatic organisms and humans although some of them (e.g., Cr, Cu, Ni, Mn, Zn) play an important role in fundamental metabolic functions in living organisms (Dang et al. 2021). In recent years, high PTE contamination levels have become a source of growing concern regarding environmental pollution as a result of PTEs toxicity and its buildup in aquatic habitats (Hasan et al. 2013). As a result, PTE contaminations are serious environmental problem attracting growing attention due to their potential to endanger human and ecosystem health (Amin et al. 2009; Özkan and Büyükışık 2012; Tang et al. 2014; Kaya et al. 2017; Kükrer et al. 2020; Fural et al. 2021). PTE pollutants present in sediments have been demonstrated to pose a risk to marine organisms in nearfuture ocean acidification conditions, according to studies (Roberts et al. 2013; Williams and Antoine 2020). Sediment quality guidelines (SQGs), enrichment factor (EF), ecological risk index (mRI), potential ecological risk index (PERI), modified hazard quotient (mHQ), ecological contamination index (ECI), and toxic risk index (TRI) are common indices used to determine the degree of PTEs contaminations in sediments (Singovszka and Balintova 2019).

İzmir inner gulf has been under the pressure of pollution for many years. To solve this problem in 2002, a treatment plant and Big Channel Project were put into operation. For this reason, it was expected that the waste inflows to the inner gulf would cease or decrease after 2002. In this study, the effects of the treatment plant and Big Channel Project on PTEs contaminations in the inner gulf were investigated.

The main objectives of the current study are (1) to investigate the extent and degree of PTE distributions and concentrations in the sediment of İzmir Inner Gulf, (2) to reveal the extent to which the sediment is anthropogenically contaminated by using EF values, and (3) to evaluate the risk indices (mRI, PERI, mHQ, ECI, and TRI) using GIS. This study is also expected to assist in the development of regional sediment quality guidelines (SQGs) using the background levels of pollutants.

### **Material and method**

#### Study area

There are many gulfs with interesting hydrographic and sedimentological features extending in the east-west direction on the coastal zone of the Anatolian peninsula facing the Aegean Sea. While some of these gulfs maintain their natural state, some are under anthropogenic pressure. İzmir Gulf is open to the anthropogenic effects of settlements, industry, transportation networks, and agricultural activities (Fig. 1). The water exchange capacity of the Aegean Sea and the İzmir Gulf, which is a semiclosed feature, is limited. This increases the likelihood of ecological risks created by PTEs discharging into the gulf. The inner gulf is a point where many streams discharge, mainly the mouth of old Gediz, Bostanlı, Bayraklı, Manda, Arap, Melez, Bornova, Poligon, and Ilica. These streams have carried urban and industrial wastes into the inner gulf for many years.

Major industrial activities in the region are food processing, beverage manufacturing and bottling, tanneries, oil, soap and paint production, chemical industries, paper and pulp mills, textile industries, metalworking, and timber processing (Kontaş et al. 2004). Apart from these, the inner gulf was exposed to receiving domestic wastes for a long



Fig. 1 Location map of İzmir Inner Gulf showing 16 sampling stations

time and has gained a eutrophic character. The streams were planned to carry only rain water, thanks to the wastewater treatment plant (Big Channel Project), which was put into operation at full capacity in 2002. This study examined the effect of the Big Channel Project on the cleansing process of the inner gulf.

The annual total rainfall in İzmir is 710.5 mm. İzmir receives 382.6 mm of precipitation in winter, 153.3 mm in spring, 21.7 mm in summer, and 152.9 mm in autumn (MGM 2021). Accordingly, almost half of the annual rainfall occurs in the winter season. The wet season in İzmir is as follows: winter > spring > autumn > summer.

The study area is bordered by the mouth of Çakalburnu Dalyan Stream in the west and Bornova Stream in the east, where the Poligon, Melez, Manda, Arap and Bornova streams, which form the southern shore of the İzmir Inner Gulf, are discharged (Fig. 1).

#### Sampling and analytical methods

Samples were taken from 16 stations selected in the southern littoral zone of the İzmir Inner Gulf for four seasons (winter, spring, summer, autumn) in 2015. Surface sediment samples were taken with a Van Veen Grab. They were then placed in plastic bags and transported to the laboratory in ice boxes. Wet samples were used for Chl-*a* analysis. After the sediment

samples were extracted with 90% acetone, they were measured spectrophotometrically (Strickland and Parsons 1972). Samples for total organic carbon (TOC), biogenic silica (BSi),  $CO_3^{-2}$ , and elemental analyses were dried in a drying oven and pulverized by pounding in a porcelain mortar. TOC analyses were performed by the Walkley–Black method, which is performed by oxidation of organic matter with  $K_2Cr_2O_7$  (Gaudette et al. 1974).

 $\text{CO}_3^{-2}$  analyses were carried out by the gasometric method based on the measurement of the partial pressure of the CO<sub>2</sub> gas released from the reaction of CO<sub>3</sub><sup>-2</sup> with 10% HCl, according to Martin (1972). BSi measurements were performed with the method recommended by (De Master 1981). PTEs analysis were performed at Bureau Veritas Laboratory (Canada) using the ICP-MS method. Standard reference material, duplicate, and blind sample reading methods were used for quality control of elemental analysis. Recovery values of PTE measurements vary between 83 and 114%.

# Contamination level and ecological risk assessment methods

#### **Contamination level of sediments**

Enrichment factor (EF) is found by the ratio of the current PTE concentration to the background concentration. EF is

calculated by the following formula (Acevedo-Figueroa et al. 2006; Zhang et al. 2007; Brady et al. 2015):

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

Here,  $C_i$  is the PTE concentration measured in the sediment,  $C_{ref}$  is the concentration of the reference PTE selected for normalization in the sediment sample,  $B_i$  is the regional background value of the PTE, and  $B_{ref}$  is the background value of the reference PTE for normalization. Ti was used as the reference PTE because it is a lithophile PTE that is far from anthropogenic effects. Background data from a study conducted in the outer part of İzmir Gulf were used in the ecological risk index calculations. The background values of the PTEs as mg/kg are Fe (9950), Mn (221), Cr (167), Ni (41.10), Zn (32), As (14), Pb (6.35), Cu (5.80), Hg (1.67), Mo (0.30), and Cd (0.05) (Özkan et al. 2017). EF results were evaluated according to Sutherland (2000): EF < 2, minimal or no enrichment; EF = 2-5, moderate enrichment; EF = 5-20, significant enrichment, EF = 20-40, very high enrichment; and EF > 40, extremely high enrichment.

# Modified ecological risk (mRI) and potential ecological risk index (PERI)

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

$$mRI = EF_i \times Tr_i \tag{2}$$

$$PERI = \sum_{i=1}^{n} mRI$$
(3)

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

## Modified hazard quotient (mHQ) and ecological contamination index (ECI)

The mRI and PERI are indices that are based on the amount of PTE enrichments in sediment. Apart from these frequently used indices, there are also indices created using threshold values to determine the effects of PTEs contents in the sediment on the 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):

$$mHQ = \left[C_i \left(\frac{1}{TEL} + \frac{1}{PEL} + \frac{1}{SEL}\right)\right]^{1/2}$$
(4)

Here,  $C_i$  refers to the measured PTE 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:  $0.5 \le mHQ < 1.0$  very low severity of contamination,  $1.0 \le mHQ < 1.5$  low severity of contamination,  $2.0 \le mHQ < 2.0$  moderate severity of contamination,  $2.0 \le mHQ < 3.0$  high severity of contamination,  $3.0 \le mHQ < 3.5$  very high severity of contamination, and mHQ > 3.5 extreme severity of contamination (Benson et al. 2018).

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:

$$ECI = B_n \sum_{i=1}^n m H Q_i$$
(5)

Here,  $B_n$  is the inverse of the eigenvalue obtained from the principal component analysis for PTEs only with respect to multiplication. ECI findings are evaluated in the following manner: ECI < 2 uncontaminated,  $2 \le \text{ECI} < 3$ uncontaminated to slightly contaminated,  $3 \le \text{ECI} < 4$ slightly to moderately contaminated,  $4 \le \text{ECI} < 5$  moderately contaminated,  $5 \le \text{ECI} < 6$  considerably to highly contaminated,  $6 \le \text{ECI} < 7$  highly contaminated, and ECI > 7 extremely contaminated (Benson et al. 2018). ECI and mHQ give satisfactory results in revealing the extent of pollution, site-specific status, and cumulative contamination effects by PTEs in aquatic ecosystems. In addition, the indices of ECI and mHQ, which are analytical methods used in regional ecological risk studies, for the first time in İzmir Inner Gulf, which is a hot spot in the Eastern Aegean Sea, constitute a new approach.

#### Toxic risk index (TRI)

TRI is another index used to determine the ecotoxicological effects of PTEs (Zhang et al. 2016). The following formula was used to determine the toxic risk index (TRI<sub>i</sub>) of each PTE in the study. Here,  $C_i$  refers to the measured concentration of the PTE, TEL refers to the "threshold effect level," and PEL refers to the "probable effect level" (MacDonald et al. 1997).

$$TRI_{i} = \sqrt{\frac{((C_{i}/TEL)^{2} + (C_{i}/PEL)^{2})}{2}}$$
(6)

The TRI value, which represents the toxic risk of the area, is obtained by summing the  $TRI_i$  values calculated for each PTE:

$$TRI = \sum_{i=1}^{n} TRI_i \tag{7}$$

The following scale is used in the interpretation of TRI values: TRI  $\leq$  5 no toxic risk, 5 < TRI  $\leq$  10 low toxic risk, 10 < TRI  $\leq$  15 moderate toxic risk, 15 < TRI  $\leq$  20 considerable toxic risk, and TRI > 20 very high toxic risk.

#### Spatial and multivariate statistical analyses

Spatial analyses were performed in Arc-Map 10.7 software using the kriging interpolation method. This method is an interpolation method that estimates the optimum values of the data at other points using the data of the nearby points and is calculated in the following manner:

$$N_{p} = \sum_{i=1}^{n} Pi \times Ni$$
(8)

In the formula, N refers to the number of sampling points, Ni refers to the geoid undulation values of the points used in the calculation of  $N_p$ ,  $N_p$  refers to the undulation value to be calculated, and Pi refers to each Ni value used in the calculation of N (ESRI 2021).

Factor analysis, Spearman's rank correlation test and cluster analysis were performed to identify the source and transport processes of the PTEs and other variables used in the study. Anova test was applied to determine seasonal differences between variables. Statgraphics Centurion XVI was used for all statistical analyses.

#### **Results and discussion**

#### Spatial and seasonal change of variables

Spatial and seasonal distribution maps of PTEs are presented in Figs. 2 and 3. Fe is one of the most abundant PTEs in the sediments (Ustaoğlu and Islam 2020). As it accumulates in the offshore Bornova Stream in the eastern zone in summer and winter, it reaches high concentrations in the middle part of the study area in spring and autumn. Distribution maps of Cd indicate that Cd is localized in the southern coastal zone of the gulf. It is thought that this is caused by the domestic wastes carried by the Poligon Stream and the agricultural area to the west of the stream (Fig. 1). While Cr shows a more-or-less homogeneous distribution in winter and spring, it is concentrated in the south coastal zone in autumn and summer. It is seen that the Poligon and Bornova streams have an increased Cr concentration in winter. It is observed that Cu accumulation increases in the southern coastal zone in all four seasons. Fe is found in higher concentrations in winter and autumn, and lower in the rest of the year. It is thought that the increases are due to the eroded material carried to the gulf due to precipitation.

Winter and spring distributions appear to be more regular. Hg is seasonally localized in different regions. In this context, it is considered that there are different input points. Significant accumulation was detected at the mouth of Bornova Stream in winter and Poligon Stream in spring and autumn. Mn is an essential PTE for flora and fauna. It can be added to the ecosystem by the dissolution of minerals, as well as from anthropogenic activities (Shil and Singh 2019; Ustaoğlu and Islam 2020). While Mn showed a nearly homogeneous distribution in the study area in the spring, it increased its concentration in the middle parts of the gulf in other seasons. Ni distribution did not show significant seasonal differences. It was determined that it mainly accumulates in the middle part of the gulf and reaches its lowest levels at the mouths of the eastern streams. It is seen that the southern coastal zone, the harbor area, and the eastern stream mouths are the accumulation areas for Pb. While the distribution is more regular in winter, high values are localized in other months. Zn increases its accumulation in the southern coastal zone and at the mouth of the Poligon Stream. The seasonal minimum, maximum, and mean concentrations of PTEs are presented in supplementary Table S1.

TOC, Chl-*a*, and BSi concentrations were found to be higher in the southern coastal zone. Since these three variables are associated with primary production processes, their concentrations increased and covered a larger area during the warm seasons.  $CO_3^{-2}$  reached high



Fig. 2 Spatial and seasonal change of PTEs concentrations (part 1)



Fig. 3 Spatial and seasonal change of PTEs concentrations (part 2)

concentrations at the mouth of the Arap, Melez, Manda, and Bornova streams in winter, summer, and autumn (Fig. 4). At first, it was thought that high  $CO_3^{-2}$  concentration at this point might be related to the sedimentation of Miocene lacustrine  $CO_3^{-2}$  in the Arap Stream and Melez Stream basins (MTA 2021). Similarly, the source of the  $CO_3^{-2}$  in the mouth of the Poligon Stream in the spring might be related to the Upper Senonian clastic  $CO_3^{-2}$  rocks in the stream basin (MTA 2021). However, the results of the correlation test and factor analysis indicate a negative relationship between  $CO_3^{-2}$  and terrestrial Ni and Cr. In this respect, when an overall evaluation was made, it was concluded that the source of  $CO_3^{-2}$  is not rocks but is of biogenic origin. There are no geological formations that can be a source of  $CO_3^{-2}$  apart from the sources mentioned above. In this case, the  $CO_3^{-2}$  concentration is expected



**Fig. 4** Spatial and seasonal change of TOC, Chl-a, CO<sub>3</sub><sup>-2</sup>, and BSi

to reach its maximum concentration only in the specified river mouths. However, the maximum concentrations identified in ST 11 (8.33%) and ST 16 (9.67%) were not related to stream inputs. This supports the hypothesis that the source of  $CO_3^{-2}$  is biogenic.

The average PTE concentrations of the four seasons in the inner gulf of İzmir and the PTE concentrations of some of the gulfs in the Aegean Sea in respect of the TEL (threshold effect level) PEL (probable effect level) and SEL (significant effect level) were examined. According to the findings, As concentration was lower than that of Ayvalık Gulf and Edremit Gulf but higher than Aliağa Gulf. The average As concentration detected in the inner gulf of İzmir exceeds the TEL and PEL values. As in Ayvalık Gulf and Edremit Gulf, it has been moderately significantly contaminated due to urbanization and industrialization. As is responsible for most of the ecological risk in Ayvalık Gulf (Tunca et al. 2018). Because the Edremit and Ayvalık gulfs are under the pressure of urbanization and industry like İzmir Gulf, the Cd concentration is lower than that of Ayvalık Gulf, Astakos Gulf, and Kalloni Gulf; and the TEL, PEL, and SEL are higher than that of Edremit Gulf. Cr concentration is higher than TEL, PEL, and SEL and all gulfs except Astakos Gulf. Because Cr enrichment was not detected in İzmir Gulf, the possible source of Cr is lithological. In the study of Gülsever and Arslan (2019), the Cr concentration was determined above the TEL and PEL values. Mn concentration is higher than all gulfs except Astakos and Kalloni gulfs. Mn is defined as a diagenetic PTE in the gulfs of Astakos and Kalloni (Panagos et al. 1989; Varvanas 1989). Cu, Fe, Ni, Pb, Zn, and Hg concentrations were higher than all comparative gulfs. In the İzmir Inner Gulf, Cu and Zn are moderately

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Location	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	Reference	
İzmir Inner G. (Turkey)	23.07	0.45	114.28	64.49	32,500	0.51	487	86.64	79.36	219.00	This Study	
İzmir Inner G. (Turkey)		0.34	100.62	59.50	28,383	0.35	420		62.27	188.44	Gülsever and Arslan 2019	
Aliağa G. (Turkey)	20.60		78.60	16.70	22,000		212	28.80	34.80	55.80	Palas, 2020	
Ayvalık G. (Turkey)	Ayvalık G. (Turkey) 36.73 0.47		23.24	8.92	8725		178	41.42	14.78	60.73	Tunca et al. 2018	
Edremit G. (Turkey)	35.50	0.23	29.10	5.05	20,819		202	56.09	9.36	43.04	Tunca et al. 2018	
Astakos G. (Greece)		3.25	166.00	23.00			687		28.00	89.00	Panagos et al. 1989	
Kalloni G. (Greece)		3.20		48.00			910		96.00	103.00	Varnavas 1989	
TEL	5.90	0.60	37.30	35.70		0.17		18.00	35.00	123.00	MacDonald et al. 2000	
PEL	17.00	3.53	90.00	197.00		0.49		36.00	91.30	315.00	MacDonald et al. 2000	
SEL	33.00	10.00	110.00	110.00		2.00		75.00	250.00	820.00	MacDonald et al. 2000	

Table 1 Comparison of PTEs concentrations (mg/kg) in some gulfs of the Aegean Sea

enriched and other PTEs are low. This shows that Cu and Zn in the inner gulf are exposed to more anthropogenic effects than the compared gulfs. Cu, Pb, and Zn exceed the TEL value. Ni exceeds the TEL, PEL, and SEL values. When the PTE concentrations were compared with the study conducted in İzmir Inner Gulf in 2019, a decrease was observed in all values (Table 1). The probable reason is that the sampling points of the studies are in different locations.

In an earlier study conducted in the inner gulf of İzmir, the minimum and maximum concentrations of PTEs in mg/kg were as follows: Hg 0.40–0.99, Cd 0.15–0.82, Pb 68–103, Cr 140–281, Cu 37–79, Zn 110–311, Ni 93–146, and Mn 243–328 (Küçüksezgin 2001). In the current study, the minimum and maximum concentrations of PTEs in mg/kg are as follows: Hg 0.20–0.93, Cd 0.16–0.92, Pb 38.50–141.75, Cr 78.50–217.75, Cu 31.25–97.50, Zn 103.00–356.80, Ni 44.00–122.12, and Mn 293.25–1032.30. According to the findings, a decreasing trend was detected in all other PTEs except for the minimum and maximum values of Ni and the maximum values of Cu and Pb.

#### **Evaluation of PTE contaminations**

The PTEs were listed as follows according to the general average EF 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) > As (0.71) > Cr (0.39) > Hg (0.14). Accordingly, Mo and Pb were significantly enriched, while Cu, Cd, and Zn were moderately enriched. Other PTEs were classified as "minimal or no enrichment" (Figs. 5 and 6). The seasonal minimum, maximum, and mean values of EF are presented in supplementary Table S2.

The study area can be divided into four areas in terms of PTEs accumulations. The first area is the eastern streams area (ESA), which is in the eastern part of the gulf and where four large streams are discharged. Timber, textiles, paper, food, tanning, and PTEs processing factories operate in this region. In addition, the International İzmir Port is also in

this region. The second important accumulation zone is the Alsancak region (AR). Shipping and ferry traffic is heavy in this area. The third zone is the southern coastal zone (SCZ). This area is adjacent to the highway, lengthwise. The last important zone is the mouth of the Poligon Stream (MPS), located in the south. As, Ni, and Pb showed enrichment in ESA. As and Ni showed low enrichment and Pb showed moderate to significant enrichment.

While As and Ni accumulation increased in ESA in the spring and summer months, Pb is enriched in this region throughout the year, except winter. As and Ni showed low enrichment, while Pb showed moderate to significant enrichment. Atmospheric deposition is described as the primary input pathway of Pb (Dang et al. 2021). Therefore, the possible source of the winter enrichment of Pb is the ferry traffic in AR, and the source of the enrichment in ESA in other seasons is industrial-domestic wastes and the port. Pb is an important anthropogenic pollutant in port areas (Chen et al. 2020; Jeong et al. 2020). Cu, Fe, and Mn concentrations are predominantly concentrated in AR and ESA. The enrichment ranges from moderate significant for Cu and low significant for Fe and Mn. Cu is enriched in summer and winter, Fe in winter and spring, Mn in winter, spring and autumn in AR, and other seasons in ESA. The likely source of Cu enrichment in AR is the ferry traffic. The Manda Stream, Arap Stream, and Melez Stream pass through regions where industry and urbanization are the most intense. In this case, the reason for the enrichment in ESA may be the discharge of domestic and industrial wastes.

The fact that Cu is affected by anthropogenic activities taking place in port regions has been identified in busy ports in various countries of the world (Jahan and Strezov 2018; Chen et al. 2020; Jeong et al. 2020). Fe did not show a significant accumulation in other seasons, except for the significant level of enrichment in AR in the spring. The only source for such unnatural accumulation around this area is the port. The possible source of enrichment here may be discharged from ships. Spatial analyses showed that Mn was enriched



Fig. 5 Spatial and seasonal changes of EFs (part 1)

in winter and spring with anthropogenic effects originating from the port. Discharges from ships, maintenance, and shipping activities in ports can be a source of Mn (Oliveira et al. 2020). Cd, Cr, and Mo enrichment were localized in SCZ and MPS. Low-moderate enrichment for Cd, low for Cr, and moderate-very high enrichment for Mo were determined in the study area. These PTEs also showed a relatively higher accumulation in MPS in winter and spring. In summer and autumn, their enrichment widened across the SCZ. The possible source of Cd is the Poligon Stream,



Fig. 6 Spatial and seasonal changes of EFs (part 2)

where domestic waste and sewage discharge has been carried out for many years (Merhaby et al. 2018). Ports and transportation networks are other important anthropogenic sources of Cd (Jeong et al. 2020). Accordingly, the possible source of high EF values around AR (as part of SCZ) is the port, and the source of the high accumulation detected along SCZ is the highway. This is because transportation networks can affect Cd, Pb, and Zn concentrations up to 320 m away (Viard et al. 2004).

The agricultural area to the west of Poligon Stream is also considered as another source (Ustaoğlu 2020). Chromium is found in many minerals and is widely distributed in rocks and soils. Waste water, atmospheric deposition, and fertilizers are other sources (Quinton and Catt 2007). However, there is no anthropogenic enrichment in İzmir Gulf. According to the spatial analysis, Poligon Stream discharges Mo, which has a significant ecological effect. Mo is an important pollutant of sediment and undersea fauna in coastal areas (Rumisha et al. 2012). Hg does not pose an ecological risk hazard due to enrichment, but domestic and industrial wastes could arrive at ESA in the spring, and a small anthropogenic effect was experienced as a result of the port in other seasons. Hg is an important pollutant in port areas (Jahan and Strezov 2018; Chen et al. 2020). The Hg increases seen in SCZ, including AR, are insignificant. Zn is enriched at the lower limits of the significant level in autumn and enriched moderately in other seasons. Zn showed lowsignificant enrichment in the study area. Spatial analyses show that Zn was enriched in spring and summer in MPS. Zn is a major pollutant that can result from domestic waste and sewage (Merhaby et al. 2018). Poligon Stream is an area where domestic waste and sewage have been discharged for many years. In addition, the agricultural area near the MPS could also be a source of Zn (Ke et al. 2017; Dang et al. 2021). A possible reason for the enrichment in ESA is the port and the streams passing through the industrial area. Zn is an PTE that is frequently encountered in port areas and can easily be absorbed into the underwater fauna (Beneditto et al. 2019).

# Ecological and ecotoxicological risk assessment of PTEs

Minimum, maximum, and mean values of the mHQ are present in supplementary data in Table S3. According to the average data, the mHQ index is ranked as Ni (2.87) > Cr (2.65)>As (2.42)>Hg (2.03)>Pb (1.83)>Zn (1.63)>Cu (1.63) > Cd (0.93). Accordingly, a high level of risk was identified for Ni and Cr; a significant level of risk for As and Hg; a medium level of risk for Pb, Zn, and Cu; and a very low level of risk was identified for Cd. Spatial analyses show that the minimum mHQ values were concentrated in ESA in winter (Fig. 7). It is believed that this is caused by the high flow rates into the inner gulf from streams in the winter months, when the maximum precipitation falls, slowing down the sedimentation and distributing the transported PTEs within the inner gulf. Limited water input facilitates the precipitation of PTEs (Islam et al. 2014). Heavy rainfall carries pollutants and particles away from the river mouth. In İzmir Gulf, the flow rate of the streams increases significantly, even in short-term precipitation. The As-induced risk level in the study area varies between medium and high. According to the distribution maps, the risk of As increases in spring and autumn and covers a large part of the study area. The risk starts from ESA (especially Bornova Stream) in winter and spreads to the middle parts of the gulf, while in summer it is localized in MPS. As toxicity has the feature of inactivating about 200 enzymes, primarily cellular energy pathways and DNA synthesis/repair (Ratnaike 2003). While the mHQ values of Cd indicate a minor-medium range, the Cr values were found in the medium-very high range. It has been determined that the risk from Cd and Cr widens in winter and spring and decreases in other seasons. This can be attributed to the increase in these PTEs loading the gulf in winter by precipitation.

On the risk map, it is seen that the risk originates from MPS. Except for summer, the risk level of Cu starts from MPS and spreads throughout the SCZ. In the summer, AR draws attention as the area where the risk is concentrated.

The risk level ranges from very low-significant. Cr is known for its carcinogenic and mutagenic effects. It is noteworthy that the level of risk is high (Bazrafshan et al. 2016). Cd is the cause of many chronic and acute diseases. Although it is found in very low concentrations in nature, its level can be increased by human action. The most important human activities that increase Cd levels are fertilizers, pesticides, and mining activities (Islam et al. 2015; Bazrafshan et al. 2016). The mHQ level of Ni is in the medium-extremely high range. While the risk of Ni is localized in the middle part of the gulf in summer and winter months, it expands toward the SCZ in other months. Skin allergies, lung fibrosis, and kidney and cardiovascular system poisoning are among the effects of Ni (Denkhaus and Salnikow 2002). Ecological risks originating from Hg vary in the low-high range throughout the year. Risks are concentrated in the SCZ in the spring and autumn. ESA in winter and AR in summer are the regions where the risk is concentrated. Hg can cause neurological, nephrological, immunological, cardiac, motor, reproductive, and genetic disorders (Zahir et al. 2005). The risks from Pb are distributed between low and very high. The seasonal and spatial distributions of Pb risks vary. Risks concentrated in the SCZ and ESA in the winter are distributed over most of the study area, while in the spring, they are concentrated in the AR and MPS, and in the summer and autumn in the SCZ and ESA. Pb is highly toxic to the skeletal and nervous system (Bazrafshan et al. 2016). Zn has a very low-significant level of risk. The main source of Zn-induced risk emerges in MPS and spreads from there to the gulf, primarily to the SCZ. Zn and Cu can be toxic to the ecosystem above threshold levels (Bazrafshan et al. 2016).

In the ecological risk analyses, indices working with different principles are discussed. While mHQ and mRI indices were used in the individual evaluation of PTEs, PERI, ECI, and TRI indices were used in the integrated risk assessment of PTEs. The mHQ index is calculated using the threshold values obtained from ecotoxicological assays on certain benthic organisms such as TEL, PEL, SEL. mRI uses the EF value and the toxic risk coefficients attributed to PTEs. When the results of the two indices were compared, mRI gave a result in parallel with the EF values and determined a significant risk for the Cd. On the other hand, mHQ, highlighted Ni, Cr, As, and Hg, which have low EF values and are thought to come from natural sources. This shows that the mHQ index provides an advantage in determining the risks of PTEs exceeding certain toxicological limits, even if the source is natural. In integrated risk determination, PERI refers to the sum of individual risks (mRI) based on EF. The focus here is on the enrichment level of the PTEs. Due to the use of data obtained from PCA/FA in the ECI index, it gives area/resource specific results. The TRI index is based on results from TEL/PEL-based ecotoxicological studies. As a result, when these three integrated indexes are compared, it



Fig. 7 Spatial and seasonal changes of mHQ

is seen that the risk findings of ECI and TRI are at a higher level, while the PERI values are lower. PERI is based on anthropogenic effect. Area-specific results obtained from ECI provide an important advantage. Minimum, maximum, and mean values of the ECI are presented in supplementary data in Table S3. ECI values were found in the range of 3.80–7.11 in the whole study area, and the average was calculated as 5.68. The minimum value was found in ESA in winter, while the maximum value was found in SCZ in autumn. Accordingly, the degree of contamination varies between slightly to moderately extremely. Seasonal averages varied between 5.46 and 5.82. Accordingly, the contamination level is considerably to highly contaminated. In this context, it was determined that ECI values did not show significant differences between seasons. ECI values were higher in ESA in winter, MPS, and SCZ in spring and autumn, and AR in summer.

Minimum, maximum, and mean values of the mRI, PERI, and TRI are presented in supplementary data in Table S4. The sequence of the four-season average data of mRI is: Cd (114.79) > Pb (27.97) > Cu (24.29) > As (7.09) > Hg (5.64) > Ni (4.45) > Zn (2.92) > Mn (1.03) > Cr (0.78). Accordingly, while Cd created significant ecological risks in all seasons throughout the inner gulf, other PTEs did not create ecological risks in any season. Since MPS is the main source of Cd in the gulf, its potential ecological risk is also higher in this area. However, in the summer and spring, it expands the risk area towards SCZ and AR. The risk of Cd rises to a high level in the autumn. Although the average potential ecological risk values of Cu and Pb indicate low risk, the maximum risk levels increase to moderate. Ecological risk values of Cu intensify in two main locations: AR and



Fig. 8 Spatial and seasonal changes of mRI (part 1)

ESA. Ecological risks of Pb were predominantly identified in the ESA. In winter, the risky area shifts to the AR. Even the maximum values of Zn, Ni, Mn, As, Cr, and Hg do not exceed the low risk threshold (Fig. 8). The PERI average for four seasons was 193.02. Accordingly, a moderate potential ecological risk was found to exist in the inner gulf; with a range of 95.45–373.47. This indicates that the integrated risk of all PTEs ranges from low

![](_page_14_Figure_3.jpeg)

Fig. 9 Spatial and seasonal changes of mRI, PERI, TRI, and ECI (part 2)

to significant. Seasonal averages are between 184.06 and 210.33, indicating moderate potential ecological risk. It is understood that there are no significant differences in PERI values between seasons. However, the regions where ecological risks are localized show seasonal differences. While PERI values were higher in MPS in winter and spring, they increased in SCZ in the other two seasons (Fig. 9).

According to average values, the TRI value was 16.64 in winter, 15.04 in spring, 17.92 in summer, and 17.85 in autumn. Accordingly, a significant toxic risk exists in all seasons. The order of responsibility of the PTEs from TRI is Ni > Cr > As > Hg > Pb > Zn > Cu > Cd. MPS emerges as an important source in terms of TRI-based risk values. That the risk increases in ESA in winter and in AR in summer is remarkable. The season when high risks cover a larger area is spring.

Although previous studies have shown that total PTEs concentrations are sufficient to determine the overall pollution level, more comprehensive studies are needed to determine the mobility and bioavailability of PTEs (Kang et al. 2017; Liu et al. 2018). The seasonal minimum, maximum, and mean values of the ecological risk indices are presented in supplementary Table S2.

# Multivariate statistical analyses and source identification

Correlation test and principal component analysis reduce a large number of variables to a few components, making it easier to identify possible sources of PTEs (Dang et al. 2021). Four factors with an eigenvalue > 1 were identified for factor analysis. These factors explained 79.59% of the total variance. The first factor explained 38.44% of the variance and consisted of TOC, Mo, Cu, Pb, Zn, Cd, Cr, and Hg. This factor represented the anthropogenic effect. Mo, Cu, Pb, Zn, and Cd are PTEs of anthropogenic origin, which are in the moderate-significant class according to EF. It is also included in the second factor with a weight close to its load in the first factor. This indicates that Cr has mixed resources. Hg is of a low enrichment value; it is also present in Factor 3 with a weight close to its load value in Factor 1. While one of the sources of Hg is anthropogenic, another source is eutrophication (benthic and planktonic diatom blooms).

According to the spatial distribution and land use maps, the Cd, Zn, and Cr increases are localized at the mouth of the Poligon Stream. In addition to the wastewater carried by the stream, it is thought that the agricultural area located just west of the stream contributed to this. Pb and Cu accumulate at the mouth of four large streams feeding the eastern part of the gulf. These streams have carried the wastes of the industrial zone of the city for many years. In addition, this area is the junction point of city traffic. Pb and Cu enrichment is associated with traffic and industrial discharges. TOC, on the other hand, is related to eutrophication, which is one of the most important problems of the İzmir Inner Gulf. Cr is the only PTE in this factor with a low enrichment value. The second factor explained 19.04% of the total variance and consisted of Ni, Fe, As, Cr (positive load), and  $CO_3^{-2}$  (negative load). Factor 2 represents the lithogenic sources as well as the accumulation of Fe in the surface sediment due to the mobilization of Fe in the sediment. On the other hand, the contribution of  $CO_3^{-2}$ , with a marine origin, has a negative effect on this factor.

Fe loading (factor 2 loading value: 0.67) and Mn are not included in this factor (factor 2 loading value: 0.00), which can be explained by the fact that the sediment's overlying water is oxygenated and the sediment has reduced conditions along the column (Matthiesen 1998). The fact that the oxidation of reduced Mn takes a longer time than Fe is explained by the immobilization of Fe by oxidation on the sediment surface and Mn passes into the water column without being oxidized.

The factor 3 explained 15.24% of the total variance and consisted of Chl-*a*, BSi, and Hg. This factor represented primary production. It consisted of Chl-*a* and BSi accumulated in the sediment, as well as Hg. The participation of Hg in this factor may be related to the transport of algae from water to sediment, depending on the uptake.

The fourth and the final factor 4 explained 6.87% of the total variance and consisted of Fe and Mn. This factor also represented rock erosion, similar to factor 2. However, the presence of these two PTEs in a different factor may be due to differences in the transport processes (Table 2).

Based on the correlation test, TOC had a positive but weak relationship with Mo, Cu, Pb, Zn, Cd and Cr. The role of TOC in transporting these PTEs appeared to be low.

Table 2 Factor analysis

	Factor 1	Factor 2	Factor 3	Factor 4
TOC	0.50	-0.01	0.10	-0.14
$CO_3^{-2}$	-0.03	-0.60	0.29	0.10
Мо	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
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
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

 $CO_3^{-2}$  had a weak negative relationship with Mo, Ni, Fe, and Cr. Accordingly,  $CO_3^{-2}$  is believed to have no function in the distributions of PTEs. Cu, Pb, Zn, Cd, and Mo with anthropogenic enrichment had strong positive correlations with each other. These PTEs are thought to share source and transport processes. Apart from these PTEs, Mo had a relationship with Ni, Fe, As, Cr, and Hg, but its relationship was weak with other PTEs, except Cr, Ni, Mn, Fe, and As, which displayed a strong relationship with each other and a relatively weak relationship with Cr. The low enrichment values of these PTEs and the relationships between them showed that they were transported from natural sources to the inner gulf by common transportation processes. Although Hg is an PTE that does not show enrichment, it had a weak correlation with Mo, Cd, and Cu of anthropogenic origin, having a strong correlation with Pb and weak correlation with As, which are naturally sourced PTEs. This may relate to a similarity in the transportation processes rather than a common source. Chl-a, which represents primary productivity, had a positive weak relationship with Mn and Pb. Similarly, BSi showed a weak positive relationship with Pb. This indicates that phytoplankton play a partial role in the transport of lead to the sediment. The 0.99 correlation between BSi and Chl-a indicated that the contribution of diatoms to the concentration of Chl-a is important, and that the diatoms controlled the Chl-a concentrations. The absence of a statistically significant correlation between these two parameters (BSi and Chl-a) representing primary production and TOC suggests that some of the carbon source may be allochthonous (Table 3). It is understood that the peripheral stations rich in allochthonous organic carbon and the stations close to the central area rich in autochthonous organic carbon contribute to the carbon source in question.

Two important clusters are noteworthy according to the dendrogram obtained from cluster analysis. One of them is the cluster representing the anthropogenic contribution among Mo, Cu, Zn, Cr, and Cd, and the other is the cluster representing the natural processes between Ni, As, Fe, and Mn. These two clusters are also compatible with the factor analysis results. The high affinity between Chl-*a* and BSi was also consistent with the results of factor analysis and the correlation test. Although there was a relationship between Hg and Pb, the distance of these two PTEs was great. A similar result was encountered in the correlation test, and a high correlation was found between the two PTEs (Fig. 10). This similarity is thought to be based on common transport processes. TOC and  $CO_3^{-2}$  did not seem to play an important role in the transport and distribution of PTEs.

One-way ANOVA was performed at 95% confidence interval to identify whether there was a difference between seasonal concentrations for each of the 15 variables measured in the study. While there was a significant difference between the seasons in the concentrations of  $CO_3^{-2}$ , Cu, Chl-a, and BSi, no significant difference was found for the other PTEs. A multiple range test (LSD) was performed to detect the seasons which created a difference. Accordingly, the  $CO_3^{-2}$  concentration varied in the spring but had similar levels in the other three seasons. Cu concentration showed a significant difference between winter-summer, winterautumn, and spring-summer. From this point of view, it can be argued that there is a difference between dry seasons and humid seasons in terms of precipitation. Considering that it is a lithophile PTE and is carried to the inner gulf by erosion, this difference between rainy and dry seasons is significant. Chl-a and BSi concentrations showed statistically significant differences between winter-spring and winter-summer.

Table 3 Correlation test

	TOC	CO <sub>3</sub> <sup>-2</sup>	Мо	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Hg	Chl-a
TOC														
$CO_{3}^{-2}$	-0.05													
Мо	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								
Mn	-0.21	-0.04	-0.08	-0.03	0.16	-0.07	0.62							
Fe	-0.13	-0.39	0.25	0.00	-0.04	0.14	0.85	0.72						
As	-0.01	-0.13	0.39	0.26	0,34	0.28	0.75	0.60	0.67					
Cd	0.36	-0.16	0.70	0.65	0.50	0.75	0.21	-0.08	0.17	0.27				
Cr	0.33	-0.36	0.85	0.57	0.42	0.79	0.49	0.08	0.34	0.46	0.65			
Hg	0.23	0.19	0.33	0.55	0.80	0.38	0.09	0.18	-0.04	0.32	0.45	0.35		
Chl-a	0.12	0.18	-0.17	0.11	0.43	-0.09	0.01	0.25	-0.04	0.19	0.05	-0.06	0.60	
BSi	0.14	0.20	-0.19	0.11	0.45	-0.10	-0.01	0.25	-0.06	0.17	0.04	-0.08	0.60	0.99

![](_page_17_Figure_1.jpeg)

![](_page_17_Figure_2.jpeg)

This may be due to the fact that abiotic factors such as light and temperature that affect primary production stimulate the increase in plant biome with the arrival of summer.

### Conclusion

İzmir Gulf has been exposed to the pressure of domestic, industrial, and agricultural pollutants for a long time. In 2002, the domestic waste of the city started to be treated with the Big Channel Project. According to the spatial accumulation of the pollutants, four areas were determined in the gulf. These are the ESA with industrial polluting streams and a port, the AR with heavy ferry traffic, the SCZ by the highway, and the MPS at the Poligon Creek mouth. In four different regions, seasonal PTE levels and contamination status in sediment samples were evaluated using both existing pollution indices and new ecological risk indices. There are previously published publications about the PTE content of the sediment in the region. In this study, evaluations were made with GIS as a new concept and by applying sourcebased indices, such as mHQ and ECI, which have come into use relatively recently. Accordingly, Mo and Pb show significant anthropogenic enrichment in the inner gulf. These are followed by Cu, Cd, and Zn with moderate accumulation. It is understood that high/extreme risks from PTE continue in this study. While mHQ and mRI indices are used in the individual evaluation of PTEs, PERI, ECI, and TRI indices were used in the integrated risk assessment of PTEs. The mHQ index using individual PTEs and threshold values for specific biological populations such as TEL, PEL, and SEL provides information on the severity of environmental contamination. When the results of the two indices were compared, mRI gave a parallel result to the EF values, indicating a significant potential ecological risk for the Cd. The ecological contamination index (ECI) is an aggregated index representing overall contamination and associated ecological risks based on the contribution of all hazardous PTEs in an aquatic ecosystem. The spatial distribution and severity of sediment contamination by PTEs are in descending order, based on the proposed indices modified hazard quotient (mHQ), and ecological contamination index, (ECI): Ni > Cr > As > Hg > Pb > Zn > Cu > Cd. High risk was determined for Ni and Cr, significant risk for As and Hg, and moderate risk and very low risk for Pb, Zn, and Cu. The lowest risk level was determined for Cd. The results of the integrated assessment for all PTEs point to serious risks. The mHQ and mRI sequences of each PTEs are different: Cd>Pb>Cu> As > Hg > Ni > Zn > Cr for mRI. The discrepancy between mHQ and mRI can be explained by different mechanisms for these indices. In this study, ecological risk assessment was made according to total PTEs. In future studies, the determination of the chemical fractions of PTEs (depending on carbonate, Fe-Mn oxides, organic matter and sulfides) in the sediment will reveal more valid results in terms of PTEs bioavailability. Thus, the lack of studies on chemical fractions in İzmir Gulf will be eliminated. In addition, there is a need to study emerging pollutants such as hormones, nanomaterials, microplastics, food additives, mutagenic, and pharmaceutical wastes in the İzmir Inner Gulf, where domestic, industrial, and agricultural wastes coexist.

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### Declarations

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