

# THE ROLE OF ORGANIC AND INORGANIC SUBSTANCES IN SEDIMENT POLLUTION IN THE MARMARA SEA BETWEEN GEMLIK (BURSA) AND BANDIRMA (BALIKESIR) AND THEIR EFFECT ON FORAMINIFERA

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**Abstract.** This study aims to evaluate the relationship between organic and inorganic substances in the recently observed pollution in the Sea of Marmara. The heavy metal analysis results of the sediments taken from the sea were interpreted by quality assessment methods. Polluted spots are the sea areas adjacent to the Gemlik and Bandırma locations and the areas where wastewater is discharged into the sea. Organic matter and elemental analyses of marine waters taken from streams (Nilüfer Çayı and Gönen Çayı) which are thought to carry pollution loads into the sea and from the points where they are poured into the sea revealed that their concentrations are very high. Analysis results of drilling and gravity core samples taken from the study area show that organic materials accumulate more in the sediments of the current period than in the old periods. In the current period, the primary sources of pollution in the Sea of Marmara are domestic and industrial wastewater discharged directly or indirectly into the sea. Secondary sources are ship traffic and agricultural activities. In addition, we observed that the main causes of eutrophication and mucilage, which are observed frequently in the Marmara Sea, are organic matter and heavy metal pollution. Morphological changes are frequently observed in foraminifera members located in locations where heavy metals are concentrated.

**Keywords:** *pollution index, contamination, bioindicator, marine pollution, morphological change*

## Introduction

All over the world, seas are polluted directly and/or indirectly by human activities. When it comes to marine pollution, only plastic, metal, paper, and cardboard wastes (sea litter) on the sea surface come to mind. But the biggest invisible dangers are non-biodegradable inorganic and organic wastes. The origin of heavy metals and other pollutants in the seas can be either natural or artificial. In the geological structure of the southern coast of the Marmara Sea, there are mineral deposits such as Pb (lead), Zn (zinc), Cu (Copper), Mo (molybdenum), As (arsenic), mineralization zones, and various mafic and ultramafic rocks with a high level of minerals such as Ni (nickel), Co (Cobalt) and Cr (Chrome) (Pehlivan, 2017). The exploitation of mineral deposits, weathering of rocks, and elemental pollution from thermal waters are considered natural source pollution. Industrial wastewater, leachate of solid wastes, heavy metals mixed with sea water as a result of maritime transport and agricultural activities, and atmospheric transports are anthropogenic pollutions. Heavy metals that cannot be chemically and biologically

degraded in seawater sink to the bottom and are incorporated into marine sediments. The accumulation process of heavy metals and other toxic elements in the marine environment can be elucidated by the systematic analysis of preserved seafloor sediments and marine current sediments from the surface to the bottom, which has formed since the beginning of the Holocene. Another pollutant occurring in marine environments is organic substances. Carbon and nitrogen, the main components of organic matter, can have characteristics of the surface, subsurface flows, and deposition processes, including anthropogenic activities in the natural system (Zetsche et al., 2011; Souza et al., 2017). Stable isotopes such as carbon (C) and nitrogen (N) can be used to evaluate geochemical processes in the environment and detect anthropogenic impact (Jacob, 2011). Phosphorus pollution from domestic wastewater to the marine environment is also a serious type of pollution. Phosphorus and other pollutants in wastewater must be removed in order not to pollute the sea. However, the methods used in today's treatment plants are not sufficient for phosphorus removal. For this, some biological and chemical methods have been developed. However, each method has some specific effects on phosphorus removal from wastewater (Dursun and Oktaç, 2005). Various studies have been carried out in the previous years regarding the study area (Çağatay et al., 1996; Balkıs and Çağatay, 2001; Ünlü and Alpar, 2006; Sari, 2008; Mülayim et al., 2011). In most of these studies, only recent marine sediments were used for heavy metal and organic matter analysis. In the present study, the records of the anthropogenic period and before were examined by comparing the surface sediments with the deep-sea sediments.

Various indices (Enrichment Factor, Pollution Index, Pollution Loading Index, Geological Accumulation index, Ecological Accumulation Index) are used to distinguish between natural and anthropogenic pollution accumulating in marine environments. Thanks to these indices, it is possible to comment on the origin of pollution. Thanks to the use of indices in this study, it was possible to compare the anthropogenic period and before. By examining the geological features of the South Marmara drainage basin, the potential of heavy metals and other pollutants that can accumulate in the marine environment was investigated. The Pollution Index (Yümün, 2017) method was applied to the samples obtained from the study area. Also, the pollution map of the region was drawn with the Kriging method.

Gemlik Bay, which is one of the parts of the study area, is a semi-closed depression with the deepest point of 113 m (Artüz, 2002; Alpar and Yaltırak, 2002; Meriç et al., 2005; Uğur et al., 2021). According to many studies, while the average slope is 0.3 degrees in the Southern Shelf of the Marmara Sea, it is about 1 degree in the Gulf of Gemlik (Alpar and Yaltırak, 2002). Nilüfer Stream, Karsak Stream, Kocaman Stream, and Kemalpaşa River are streams flowing into Gemlik Bay. Gemlik and its surroundings are located in the Western Pontide tectonic unit (Sakarya Continent) (Şengör and Yılmaz, 1981; Yılmaz et al., 1995) or in the tectonic area called Sakarya Zone (Okay et al., 1999). The stratigraphic units in the region are listed from bottom to top as metamorphic rocks of the Sakarya continent, Eocene sediments and volcanic, Eocene-Oligocene sediments, Neogene sediments, alluvium, and recent swamp deposits. Metamorphic rocks are the cornerstone of Gemlik Bay.

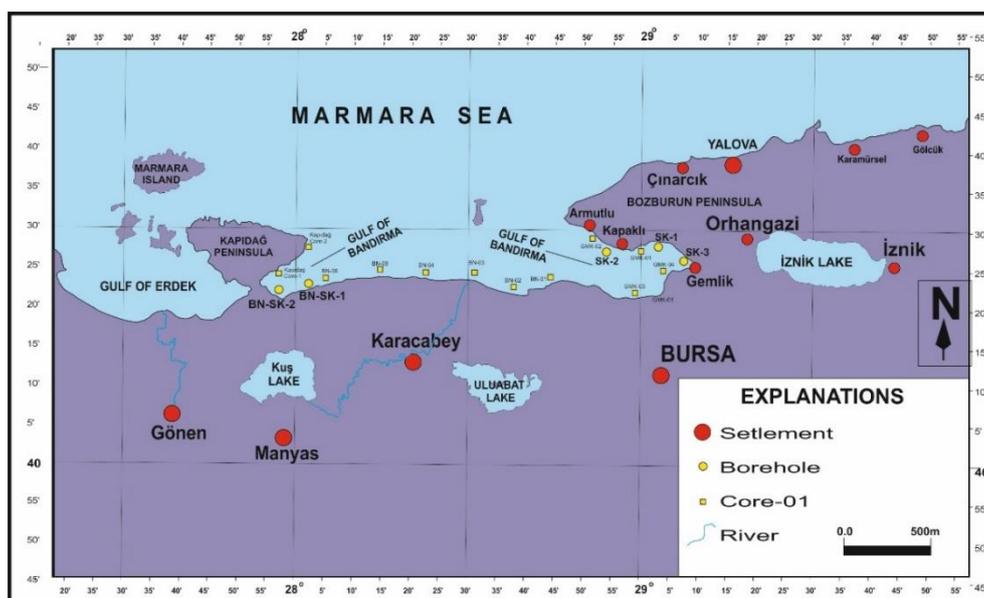
Bandırma Bay, another part of the study area, is located in the south of the Marmara Sea. Morphologically, it is surrounded by rock units consisting of uplifts in the south and east. The gulf has a semi-bay morphology, formed by the sea coming ashore. In the region, it is seen that the basement or old rocks represent the high areas, while the younger units form the lowest areas. Bandırma Bay generally has a low coastal morphology. The

region is not rich in freshwater resources. Eğirdere is the longest river in Bandırma, and Gönen Stream has the highest flow rate, which is one of the most polluting sources of the Marmara Sea due to the domestic and industrial wastes it carries (Balkıs and Çağatay, 2001; Çağatay et al., 2006).

## Materials and Methods

### *Sampling and Laboratory Analysis*

A total of four drilling core samples were taken, three from Gemlik Bay and one from Bandırma. In addition, gravity core samples were taken from twelve locations from Gemlik Bay to Bandırma Bay. Analyzes were made by taking 25 samples from the Gemlik drilling and 35 samples from the Bandırma drillings. However, the average values of the analysis results of the drilling samples were used. Moreover, seawater samples were taken from five locations, and freshwater samples from two streams flowing into the Marmara Sea (*Figure 1*). Organic matter and heavy metal analyzes of all sediment and water samples were made. The physical properties of the water samples were measured.



*Figure 1. Location map of sediment samples*

The samples taken were defined in terms of stratigraphy, color, sedimentary structure, and organic matter in the laboratory environment. The sediment sampling for geochemical analysis was done according to the methods used by Yümün (2017), Kam and Önce (2016), and Yümün and Önce (2017). In this model, a sample of 15 grams was taken from the sediment core and surface samples for every ten cm or macro-facies change. For heavy metal analysis, the samples were placed in aluminum containers and left to dry in an oven at 50 °C for about 4 hours. The dried samples were pounded in a mortar and sieved through a 250-micron sieve. As a result of sieving, the coarse particles were separated, and the remaining samples were placed in ziplock bags and made ready for geochemical analysis. Sediment samples were dissolved for analysis. Twelve ml of

HNO<sub>3</sub> and 4 ml of HCl were added to the samples in combustion tubes for melting. Then, it was heated for 1 hour at 98 °C and 1.5 hours at 200 °C. The prepared acidic mixture varies according to the type of analysis to be performed and the analysis method. After the tubes are cooled, their caps are opened in a fume hood and filled with ultrapure water up to 50 ml. Then, it is filtered using filter papers. The prepared samples are placed in the measurement unit of the ICP-OES device and readings are made for 21 heavy metals (Dinçer and Dökmeci, 2006; Kaçar and İnal, 2008; Yümün, 2017; Dökmeci et al., 2019). Results are obtained in mg/L. These analyzes were carried out in Tekirdağ Namık Kemal University Scientific Research Laboratory. For organic matter analysis, approximately 200 g samples were taken from the levels sampled for heavy metal analysis. Samples were stored in the dark. TOC-L series analyzer (Model SSM 5000 A) was used for total organic carbon analysis. TC, TOC, and IC measurements were made with this device. Total nitrogen measurements were carried out in order to determine the C/N ratio in the samples employing Vapodest VAP 20s model device. The results are given as a percentage value (Doğanay, 2014; Dinçer et al., 2019). In physical analysis, EcoSense DO200A Model Portable Oxygen Meter, Trans Instruments pH meter HP3040, Portable pH/ORP/mV Meter, Electrical Conductivity Meter, ZAG Instruments Atc Model portable salinity meter, Multitermeometer capacity portable heat meter (-50 - +150 °C) were used.

Current and Holocene sediment depths in boreholes are given in parentheses (Gemlik SK-1 (12 m-22 m), Gemlik SK-2 (9 m-18 m), Gemlik SK-3 (11-20 m), Bandırma Sk-1 (10-20 m), Bandırma SK-2 (11 m-20 m)). The first depths given represent the current sediments and the second depths represent the Holocene period. The Holocene epoch represents 10 thousand years.

### ***Sediment Quality Assessment Methods***

Numerical measurement methods are based on the calculation of environmental quality indices (sediment quality indices). These methods allow joint and easy interpretation of environmental quality analysis data. There are many indices and methods used to determine the effect of anthropogenic wastes discharged into marine environments. These methods are Enrichment Factor (EF), Contamination Factor (Cf), Pollution Loading Index (PLI), Geological Accumulation Index (I-geo), Ecological Risk Index (Er), and Pollution Index (PI).

For the evaluation of elemental concentrations of seafloor sediments, average shale metal concentrations are used as they best represent the upper level of the earth's crust in the absence of anthropogenic pollution (Taylor and McLennan, 1995; Algan et al., 2004; Pekey et al., 2004; Pehlivan, 2017). In *Table 1*, heavy metal contents of some geological reference rocks suggested by Turekian and Wedepohl (1961) and Krauskoph (1985) are given.

## **Result and Discussion**

### ***Sedimentological Findings***

Sedimentological characteristics of borehole and core samples are given in *Table 1*. The samples taken by the gravity core method are generally blackish gray and sandy gray colored, consisting of high water, fine sandy silt, and brown-gray sandy clay layers. These grains of sand carried from land to the sea are the products of degradation and fragmentation of mafic and ultra-mafic rock assemblages on land. The white, yellowish-

white quartz grains in the sand grains are derived from metamorphic rocks protruding on the coast. Metamorphic, mafic, and ultramafic rocks are suitable for the enrichment of chromium, iron, lead, and zinc. The cause of heavy metal pollution in locations where there is no anthropogenic pollution can be geological formations in the terrestrial area. Among the sediments defined in *Table 2*, dark-colored sediments contain more heavy metals, while light-colored ones have quartz density.

**Table 1.** Heavy metal concentrations of some geological reference rocks (Turekian et al., 1961; Krauskopf et al., 1985)

Elements	Unit	Earth Crust	Shale	Sandstone	Limestone	Ultrabasics	Basalt	Deep Sea Clays
Fe	%	5.00	4.70	0.98	0.38	9.40	8.60	6.50
Zr	ppm	165.00	180.00	19.00	-	45.00	140.00	150.00
Cr	ppm	100.00	90.00	35.00	11.00	1600.00	170.00	90.00
Mn	ppm	950.00	850.00	50.00	1100.00	1620.00	1500.00	6700.00
Ni	ppm	75.00	70.00	2.00	20.00	2000.00	130.00	225.00
Cu	ppm	55.00	45.00	5.00	4.00	10.00	87.00	250.00
Zn	ppm	70.00	95.00	16.00	20.00	50.00	105.00	165.00
Cd	ppm	0.10	0.30	-	-	-	0.20	0.40
Pb	ppm	13.00	20.00	7.00	9.00	1.00	6.00	80.00
As	ppm	1.80	13.00	1.00	1.00	1.00	2.00	13.00
V	ppm	135.00	130.00	20.00	20.00	40.00	250.00	120.00
Sb	ppm	0.20	1.50	-	0.20	0.10	0.20	1.00

## Contamination Analysis of Sediment Samples

### Geochemical Analyses of Sediment Samples

Sediment samples were subjected to toxic element analysis using the ICP-OES instrument, and the analysis results are given in *Table 3 and Table 4*.

Although arsenic concentration was high in Gemlik gravity core samples (As: 6.48-7.76 ppm) and Bandırma gravity core samples (As: 23.08-20.42 ppm), we did not detect it in other locations. While high concentrations of Zn, B, Cd, Cu, Pb, and Sb were discovered in both Gemlik and Bandırma samples, only a very minor concentration of Hg was recorded in Bandırma samples. The concentration values of the sediment samples Zn (68-78 ppm), As (0), B (37.80-46.68 ppm), Cd (0), Co (15.06-19.43 ppm), Cr (100.1-129.1), Cu (35.62-43.48 ppm), Ni (95.63-128.48 ppm), Pb (0), Pt (0), Sb (0), Hg (0) are higher between Bandırma and Gemlik than the values of crust and shale (Turekian and Wedepohl, 1961; Krauskopf, 1985). However, these results are lower than the element concentrations of the Gemlik and Bandırma coastal sediment samples.

It is noteworthy that the elements are in high concentrations (Zn, As, B, Cd, Co, Cr, Cu, Ni, Pb, Pt, Sb, Hg) in the Gemlik gravity core samples, whereas the concentrations are low in the drilling samples. This shows that the gravity core samples represent a more recent period than the drilling samples. Also, it suggests that the current period is more polluted than before. Sulfur (S: 450.50-5744.20 ppm), Phosphorus (P: 365.20-184 ppm), and Potassium (K: 10293.5-22947.0 ppm) concentrations are very high in Gemlik Bay samples compared to both drilling samples and gravity core samples taken from other locations. It is seen that the concentrations of Al, Ca, Fe, K, Na, Mg, and Mn are close to each other in all locations. Whether toxic elements would cause environmental pollution was evaluated by analytical methods.

**Table 2.** Sedimentological definitions in the samples of the study area

Sample Location	Coordinate		Sea Water Depth (m)	Sedimentological identification
	Y	X		
GMK BH-1	666900.67	4480394.26	27,00 m	Blackish gray, sandy clay (27.00-31.50m), Gray colored, high water content and fine sandy silt (31.50-33.00m), Brown-gray sandy clay (33.00-39.80m)
GMK BH-2	677320.64	4480754.23	35,60 m	Blackish gray, clayey, fine sand (35.60-38.00m), Blackish gray, medium sandy and silty clay (38.00-40.00m), Greenish gray, mollusc shell and clay-cemented, sandy silt and silty clay ( 40.00-48.90m)
GMK BH-3	681148.61	4478831.64	6,00 m	Blackish gray, medium sandy and silty clay (6.00-9.00 m) containing mollusc shells, Blackish gray, clayey and sandy gravel (18.00 m) End of drilling (9.00-21.00 m)
GMK Cor-1	661623.85	4479718.77	81 m	Dark gray, high water content (Sludge), Fine Sand, silty clay (70,00m)
GMK Cor-2	651912.48	4483984.87	75 m	Dark gray colored, high water content, fine silt and sandy clay (70 m)
GMK Cor-3	664528.00	4470879.79	98 m	Gray colored, high water content, fine sand silty clay (100 m)
GMK Cor-4	681409.62	4477623.62	20 m	Dark gray colored, mollusc shell, fine sand interbedded, silty clay
BANDIRMA BH-1 Avarage Value	577531.35	4470752.94	25 m	Gray colored, mollusc shell, pebbly sand interbedded, silty clay
Kapıdağ Cor-1	588116.00	4480897.76	48 m	Light gray colored silty clay and sandy silty clay
Kapıdağ Cor-2	587032.00	4478671.00	38 m	Light gray fine sandy clay and silty clay
GMK-BN-1	643203.00	4473520.10	46 m	Gray, fine sand, silty clay
GMK-BN-2	637228.00	4472805.00	48 m	Dark gray fine silt and sandy clay
GMK-BN-3	632614.00	4474145.00	52 m	Gray, clayey fine sand, silty clay
GMK-BN-4	625987.00	4476241.00	26 m	Dark gray fine silty clay and fine sandy clay
GMK-BN-5	609048.00	4477657.00	44 m	Dark gray clayey silt and sandy silt
GMK-BN-6	595672.00	4473341.00	43 m	Light gray colored fine sandy clay and silty clay

GMK BH 1, 2 and 3 show the Gemlik drillings numbered 1, 2 and 3.; BANDIRMA BH-1 Avarage Value: show the Bandırma drilling numbered 1.; GMK Cor-1-3: shows the Gemlik Core Samples 1-3; GMK-BN-1-6: shows the Bandırma-Gemlik Between Core Samples 1-6; Kapıdağ Cor 1-2: shows the Kapıdağ Core Samples 1-2

**Table 3.** Average results of ICP-OES analysis for Zn, As, B, Cd, Co, Cr, Cu, Ni, Pb, Pt, Sb, Hg elements

Sample Location	Coordinate		Sea Water Depth (m)	Sedimentological identification
	Y	X		
GMK BH-1	666900.67	4480394.26	27,00 m	Blackish gray, sandy clay (27.00-31.50m), Gray colored, high water content and fine sandy silt (31.50-33.00m), Brown-gray sandy clay (33.00-39.80m)
GMK BH-2	677320.64	4480754.23	35,60 m	Blackish gray, clayey, fine sand (35.60-38.00m), Blackish gray, medium sandy and silty clay (38.00-40.00m), Greenish gray, mollusc shell and clay-cemented, sandy silt and silty clay ( 40.00-48.90m)
GMK BH-3	681148.61	4478831.64	6,00 m	Blackish gray, medium sandy and silty clay (6.00-9.00 m) containing mollusc shells, Blackish gray, clayey and sandy gravel (18.00 m) End of drilling (9.00-21.00 m)
GMK Cor-1	661623.85	4479718.77	81 m	Dark gray, high water content (Sludge), Fine Sand, silty clay (70,00m)
GMK Cor-2	651912.48	4483984.87	75 m	Dark gray colored, high water content, fine silt and sandy clay (70 m)
GMK Cor-3	664528.00	4470879.79	98 m	Gray colored, high water content, fine sand silty clay (100 m)
GMK Cor-4	681409.62	4477623.62	20 m	Dark gray colored, mollusc shell, fine sand interbedded, silty clay
BANDIRMA BH-1 Average Value	577531.35	4470752.94	25 m	Gray colored, mollusc shell, pebbly sand interbedded, silty clay
Kapıdağ Cor-1	588116.00	4480897.76	48 m	Light gray colored silty clay and sandy silty clay
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GMK-BN-4	625987.00	4476241.00	26 m	Dark gray fine silty clay and fine sandy clay
GMK-BN-5	609048.00	4477657.00	44 m	Dark gray clayey silt and sandy silt
GMK-BN-6	595672.00	4473341.00	43 m	Light gray colored fine sandy clay and silty clay

**Table 4.** Average results of ICP-OES analysis for Al, Ca, Fe, K, Na, Mg, Mn, P, and S elements

TOXIC ELEMENTS	Zn	As	B	Cd	Co	Cr	Cu	Ni	Pb	Pt	Sb	Hg
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
<b>LOD VALUE</b>	<0,001	0,01-0,1	0,001-0,01	<0,001	<0,001	0,001-0,01	0,001-0,01	0,001-0,01	0,01-0,1	0,001-0,01	0,01-0,1	0,01-0,1
<b>SAMPLE LOCATION</b>	<0,001	0,01-0,1	0,001-0,01	<0,001	<0,001	0,001-0,01	0,001-0,01	0,001-0,01	0,01-0,1	0,001-0,01	0,01-0,1	0,01-0,1
GMK/COR-1 Average value	250,9	6,66	65,04	3,98	20,74	84,28	45,00	129,5	13,26	3,49	1,60	0,61
GMK/COR-2 Average value	168,5	7,13	69,54	1,58	18,80	77,27	45,62	109,1	16,34	1,14	1,38	0,65
GMK/ COR-3 Average value	121,5	7,76	82,14	0,57	22,32	103,2	50,60	142,6	16,88	0,00	1,77	0,00
GMK/ COR-4 Average value	101,3	6,48	44,60	1,64	18,38	55,82	49,49	83,46	11,73	1,19	1,02	0,00
GMK BH-1 Average value	163,65	0	37,20	5,35	14,19	46,82	39,31	63,60	0	0	0	0
GMK BH-2 Average value	134,16	0	24,64	5,89	13,74	12,48	38,13	12,25	0	0	0	0
GMK BH-3 Average value	169,52	0	20,87	6,77	17,22	63,90	36,72	53,09	0	0	0	0
BANDIRMA BH-1 Average value	55,22	0	13,31	3,72	8,89	42,21	18,29	34,43	0	0	0	0
GMK-BN/1 Average value	68,78	0	37,80	0	15,81	100,1	40,82	95,63	0	0	0	0
GMK-BN/2 Average value	75,60	0	44,83	0	19,43	129,1	35,62	128,48	0	0	0	0
GMK-BN/3 Average value	80,32	0	46,68	0	15,48	103,0	36,70	122,76	0	0	0	0
GMK-BN/4 Average value	70,98	0	44,08	0	15,13	106,3	41,12	116,80	0	0	0	0
GMK-BN/5 Average value	76,72	0	45,20	0	15,06	111,7	43,48	115,74	0	0	0	0
GMK-BN/6 Average value	69,60	0	46,38	0	16,01	105,2	37,75	119,20	0	0	0	0
KAPIDAĞ COR-1 Average value	90.4	23.08	36.12	0	84.12	89.60	25.47	222.83	0	0	2.23	0
KAPIDAĞ COR-2 Average value	95.2	20.42	40.54	0	89.17	95.10	28.32	237.12	0	0	3.94	0
** MARMARA DENİZİ Average value	79,9	16,53	36,3	1,7	24,50	47,9	22,1	56,5	12,94	0,99	2,17	1,73

### *Enrichment Factor (EF) Calculations*

The Enrichment Factor (EF) was calculated using equation (1) defined by Buat-Menard and Chessele (1979) (Table 5).

$$EF = \frac{\left(\frac{[M]}{[N]}\right)_{sample}}{\left(\frac{[M]}{[N]}\right)_{background}} \quad (\text{Eq.1})$$

where,

[M]<sub>sample</sub> : Metal M concentration for the studied sample

[M]<sub>background</sub> : Regional background value for M

[N]<sub>sample</sub> : Concentration of normalization element for each metal sample

[N]<sub>background</sub> : Value of normalization element in the background.

While calculating the enrichment factor, iron (Fe) was used as the normalization element. Since mafic and ultramafic rocks are mixed into the sea in Gemlik Bay (Algan et al., 2004), Albania (Prohic and Juracic, 1989), and Iskenderun Bay (Ergin et al., 1996), Fe element was used as a normalization element, which generated successful results in the analysis (Herut and Sandler, 2006). The calculated EF value of less than 1 (EF<1) indicates crustal origin. EF value between 1-3 indicates less enrichment, between 3-5 indicates possible crustal origin (very enriched), and EF>5 indicates no crustal origin. Also, heavy metal enrichment is of anthropogenic origin (Zhang, 1999; Halstead et al., 2000; Reiman and Caritat, 2005; Galuszka et al., 2014).

Mn enrichment results indicate that Gemlik Core-4 (3.9) and Kapıdağ Core-1 (4.0) samples exhibit anthropogenic origin. Also, Co pollution exhibits anthropogenic origin in Kapıdağ Core-22 (5.5). In GMLK SK-2, Zn pollution is also present (3.22 ppm). Ni enrichment is noticed at GMK-BN/2 (3.2 ppm), GMK-BN/3 (3.23 ppm), GMK-BN/4 (3.49), GMK-BN/5 (3.5 ppm), GMK-BN/6 (3.6 ppm), Kapıdağ COR-1 (3.6 ppm), Kapıdağ COR-2 (4.0 ppm) locations. It can be thought that these pollutions are mostly caused by industry, maritime transport, and agricultural activities.

### *Contamination Factor (Cfi) Calculations*

The Contamination Factor defined by Hakanson (1980) was calculated by Equation (2) given below (Table 6). If the calculated Contamination Factor (**Cfi**) is <1, there is little contamination in the inspection area. **Cfi** value between 1 and 3 indicates moderate contamination, 3-6 indicates significant contamination, and >6 indicates very high contamination.

$$Cf_i = C_i/C_{ni} \quad (\text{Eq.2})$$

where,

C<sub>i</sub>: Element concentration measured in sediment,

C<sub>ni</sub>: Pre-industrial reference value for the element.

According to the contamination coefficient calculations, it is seen that there is very high contamination in GMK BH-2 (Cf Cd: 19.99) and GMK BH-3 (Cf Cd: 22.6) samples. We think that the pollution seen in the Gemlik region is caused by ship transportation and agricultural spraying. Mn (5.8), Ni (3.9), and Co (4.4) pollution were detected in Kapıdağ-1 sample, and Ni (4.2) and Co (4.7) pollution in Kapıdağ-2 sample. These pollutions in the Kapıdağ region are also caused by sea transportation and agricultural spraying.

**Table 5.** Krauskoph (1985) shale values (\*) of the samples and Enrichment Factor values calculated according to Marmara Sea Mean values (\*\*)

Toxic Element	GMLK COR-1	GMLK COR-2	GMLK COR-3	GMLK COR-4	GMLK BH-1	GMLK BH-2	GMLK BH-3	BANDIRMA BH-2								
	*	**	*	**	*	**	*	**								
EF <sub>Mn</sub>	1,4	1,97	0,89	1,24	1,2	1,6	3,9	0,72	0,96	1,3	0,87	1,2	0,74	1,0	0,72	1,0
EF <sub>Co</sub>	1,4	0,60	1,33	0,58	1,4	0,6	1,2	1,2	1,25	0,5	1,2	0,5	1,15	0,5	1,2	0,5
EF <sub>Ni</sub>	2,32	1,62	2,1	1,46	2,5	1,7	1,5	1,2	1,5	1,0	0,36	0,2	0,96	0,7	1,2	0,8
EF <sub>Cu</sub>	1,25	1,5	1,36	1,40	1,4	1,6	1,4	0,98	1,46	1,7	1,42	1,6	1,01	1,2	0,98	1,1
EF <sub>Zn</sub>	3,31	1,87	2,38	1,59	1,5	1,0	1,3	1,4	2,87	1,9	3,22	1,6	2,26	1,5	1,4	0,9
EF <sub>Cr</sub>	1,17	1,25	1,15	0,12	1,4	1,5	0,8	1,2	0,88	0,9	0,28	0,2	0,9	0,9	1,2	1,2
EF <sub>Cd</sub>	16,65	1,66	7,1	0,70	2,3	0,2	6,8	-	29,75	2,9	32,9	3,3	28,6	2,9	-	3,0
EF <sub>As</sub>	0,64	0,29	0,74	0,3	0,7	0,33	0,6	0,28	-	-	-	-	-	-	-	-

Toxic Element	GMK-BN/1	GMK-BN/2	GMK-BN/3	GMK-BN/4	GMK-BN/5	GMK-BN/6	KAPIDAĞ COR-1	KAPIDAĞ COR-2								
	*	**	*	**	*	**	*	**								
EF <sub>Mn</sub>	0,9	1,2	0,82	1,1	0,8	1,2	0,73	1,0	0,7	0,98	0,74	1,0	2,8	4,0	0,7	0,9
EF <sub>Co</sub>	1,5	0,7	1,8	0,8	1,5	0,7	1,7	0,7	1,7	0,7	1,8	0,8	5,4	2,3	5,5	2,4
EF <sub>Ni</sub>	2,5	1,8	3,2	2,2	3,23	2,3	3,49	2,4	3,5	2,4	3,6	2,5	3,6	2,7	4,0	2,8
EF <sub>Cu</sub>	1,7	1,9	1,36	1,6	1,5	1,7	1,9	0,9	2,0	2,3	1,8	2,0	0,69	0,8	0,6	0,9
EF <sub>Zn</sub>	1,4	0,9	1,4	0,9	1,6	1,0	1,56	1,0	1,7	1,1	1,5	1,0	1,15	0,8	1,18	0,8
EF <sub>Cr</sub>	2,1	2,2	2,5	2,6	2,1	2,2	2,47	2,6	2,6	2,8	2,5	2,6	1,2	1,3	1,2	1,3
EF <sub>Cd</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
EF <sub>As</sub>	-	-	-	-	-	-	-	-	-	-	-	-	2,15	0,96	1,9	0,82

**Table 6.** Contamination Factor values calculated according to Krauskoph (1985) shale values (\*) and Average values (\*\*) of the Marmara Sea samples

Sample Location	C <sub>f</sub> Mn		C <sub>f</sub> Fe		C <sub>f</sub> Ni		C <sub>f</sub> Cu		C <sub>f</sub> Zn		C <sub>f</sub> Co		C <sub>f</sub> As		C <sub>f</sub> Cr		C <sub>f</sub> Cd	
	*	**	*	**	*	**	*	**	*	**	*	**	*	**	*	**	*	**
GMK Cor-1	1,1	2,8	0,8	1,4	1,8	2,3	1,0	2,0	2,6	3,1	1,1	0,8	0,5	0,4	0,9	1,8	13,3	2,3
GMK Cor-2	0,7	1,6	0,7	1,3	1,6	1,9	1,0	2,1	1,8	2,1	0,9	0,8	0,6	0,4	0,9	1,6	5,3	0,9
GMK Cor-3	1,0	2,4	0,8	1,5	2,1	2,5	1,1	2,3	1,3	1,5	1,2	0,9	0,6	0,5	1,2	2,2	1,9	0,3
GMK Cor-4	3,1	7,7	0,8	1,4	1,2	1,5	1,1	2,2	1,1	1,3	1,0	0,8	0,5	0,4	0,6	1,2	5,5	1,0
GMK BH-1	0,6	1,4	0,6	1,4	0,9	1,1	0,9	1,8	1,7	2,0	0,7	0,6	-	-	0,5	1,0	17,8	3,1
GMK BH-2	0,5	1,3	0,6	1,1	0,2	0,2	0,8	1,7	1,9	1,7	0,7	0,6	-	-	0,2	0,3	19,9	3,5
GMK BH-3	0,6	1,5	0,8	1,1	0,8	0,9	0,8	1,7	1,8	2,1	0,9	0,7	-	-	0,7	1,3	22,6	4,0
Bandırma BH-2	0,3	0,7	0,4	0,7	0,5	0,6	0,4	0,8	0,6	0,7	0,2	0,4	-	-	0,5	0,9	-	3,7
GMK-BN/1	0,5	1,2	0,5	1,0	1,4	1,7	0,9	1,8	0,7	0,9	0,8	0,6	-	-	1,1	2,1	-	-
GMK-BN/2	0,5	1,2	0,6	1,0	1,8	2,3	0,8	1,6	0,8	0,9	1,0	0,8	-	-	1,4	2,7	-	-
GMK-BN/3	0,5	1,1	0,5	1,0	1,8	2,2	0,8	1,7	0,9	1,0	0,8	0,6	-	-	1,1	2,2	-	-
GMK-BN/4	0,4	0,9	0,5	0,8	1,7	2,1	0,9	1,9	0,7	0,9	0,8	0,6	-	-	1,2	2,2	-	-
GMK-BN/5	0,3	0,8	0,5	0,8	1,7	2,0	1,2	2,0	0,8	0,9	0,7	0,6	-	-	1,2	2,3	-	-
GMK-BN/6	0,4	0,9	0,5	0,8	1,7	2,1	1,2	1,7	0,7	0,9	0,8	0,7	-	-	1,2	2,2	-	-
Kapıdağ-1	2,3	5,8	0,8	1,5	3,2	3,9	1,0	1,2	1,0	1,1	4,4	3,4	1,8	1,4	1,0	1,9	-	-
Kapıdağ-2	0,6	1,5	0,9	1,5	3,4	4,2	1,1	1,3	1,0	1,2	4,7	3,6	1,6	1,2	1,1	2,0	-	-

### Pollution Loading Index (PLI) Calculations

The pollution loading index (PLI) defined by Tomlinson et al. (1980) was also calculated in this study (Table 7). PLI calculations are calculated using the Contamination factor (*Cfi*) values revealed by Hakanson (1980). Pollution loading index values are obtained using Equation 3.

$$PLI = (Cf_1 \times Cf_2 \times Cf_3 \times \dots \times Cf_n)^{1/n} \quad (\text{Eq.3})$$

The Pollution Loading Index (PLI) value of < 0 indicates that the environment is not contaminated, 0-1 indicates that the environment has started to become contaminated, and >1 shows a contaminated environment.

**Table 7.** Pollution Loading Index Values calculated according to Krauskopf (1985) shale values (\*), and the average values of the Marmara Sea samples (\*\*)

Sample Location	PLI		Sample Location	PLI	
	*	**		*	**
GMK Cor-1	1,12	1,9	GMK-BN/2	0,77	1,4
GMK Cor-2	0,98	1,4	GMK-BN/3	0,74	1,3
GMK Cor-3	1,1	1,4	GMK-BN/4	0,68	1,2
GMK Cor-4	1,14	1,6	GMK-BN/5	0,67	1,2
GMK BH-1	1,15	1,4	GMK-BN/6	0,68	1,2
GMK BH-2	0,84	0,92	Bandırma BH-2	0,45	0,8
GMK BH-3	1,3	1,5	Kapıdağ-Cor 1	1,6	2,2
GMK- BN/1	0,70	1,3	Kapıdağ-Cor 2	1,4	1,9

When the Pollution Loading Index (PLI) results are compared with the shale values of Krauskopf (1985), moderate and high contamination is observed in all locations. According to the averages of the Marmara Sea, there are high levels of pollution in all locations. Although these values show the presence of pollution in the Sea of Marmara, they also show that it is less polluted than the world average.

### Ecological Risk Index (Er) Calculations

The method used in the calculations of the Ecological Risk Index (Hakanson, 1980) depends on the sensitivity and efficiency of the aquatic environment. It is calculated by Equation (4) given below, depending on the heavy metal accumulation in the sediments and the toxicity of the elements (Table 8).

$$R_i = \sum E_r^i$$

$$E_r^i = T_r^i C_f^i \quad (\text{Eq.4})$$

$$C_f^i = C_0^i / C_n^i$$

The evaluation intervals suggested by Hakanson (1980) were used to comment on the toxic effects of metals.

**Table 8.** Ecological risk index values calculated according to shale values of Krauskoph (1985) (\*) and average values of Marmara Sea samples (\*\*)

Sample Location	E <sub>r</sub> Mn		E <sub>r</sub> Ni		E <sub>r</sub> Cu		E <sub>r</sub> Zn		E <sub>r</sub> As	
	*	**	*	**	*	**	*	**	*	**
GMK Cor-1	1,1	2,8	9,0	11,5	5,0	10,0	2,7	3,1	5	4
GMK Cor-2	0,7	1,6	8,0	9,5	5,0	10,5	1,8	1,6	6	4,3
GMK Cor-3	1,0	2,4	10,5	12,5	5,6	11,5	1,3	1,5	6	4,7
GMK Cor-4	3,1	7,7	5,9	7,5	5,5	11,0	1,1	1,3	5	3,9
GMK BH-1	0,6	1,4	4,5	5,5	4,5	9,0	1,7	2,0	-	-
GMK BH-2	0,5	1,3	1,0	1,0	4,0	8,5	1,9	1,7	-	-
GMK BH-3	0,6	1,5	4,0	4,5	4,0	8,5	1,8	2,1	-	-
Bandırma BH-2	0,3	0,7	2,5	3,0	2,0	4,0	0,5	0,7	-	-
GMK- BN/1	0,5	1,2	9,0	8,5	4,5	9,0	0,7	0,9	-	-
GMK-BN/2	0,5	1,2	9,2	11,5	4,0	8,0	0,8	0,9	-	-
GMK-BN/3	0,5	1,1	8,8	11,0	4,1	8,5	0,9	1,0	-	-
GMK-BN/4	0,4	0,9	8,3	10,5	4,6	9,5	0,7	0,9	-	-
GMK-BN/5	0,3	0,8	8,3	10,0	4,9	10,0	0,8	0,9	-	-
GMK-BN/6	0,4	0,9	8,5	10,5	4,2	8,5	0,7	0,9	-	-
Kapıdağ Cor-1	2,3	5,8	15,9	19,5	2,9	6,0	1,0	1,1	18	13,9
Kapıdağ Cor-2	0,6	1,5	17	21,0	3,2	6,5	1,0	1,2	16	12,3

The Ecological Risk Index ( $E_r$ ) is evaluated as follows.  $E_r^i < 40$  low potential ecological risks,  $40 \leq E_r^i < 80$  moderate potential ecological risks,  $80 \leq E_r^i < 160$  significant potential ecological risks,  $160 \leq E_r^i < 320$  high potential ecological risks,  $E_r^i \geq 320$  very high potential ecological risks.  $E_r^i$  refers to ecological risk calculated for each measured metal element, and  $T_r^i$  is a toxic response factor for metal elements. The toxic reaction factors of Cu, Zn, As, Ni, Mn, and Pb are 5, 1, 10, 5, 1, and 5, respectively.  $C_f^i$  is the pollution factor for the metal element (i). (Pejman et al., 2015).

Although pollution was detected according to all methods, Ecological Risk Index ( $E_r$ ) Calculations revealed no pollution. This method can be used in pollution analysis for many regions. Based on this method, the low potential risk of the Marmara Sea values suggests that the Marmara Sea is cleaner than other seas. However, the presence of signs of pollution in all other methods indicates that the Sea of Marmara is at a critical threshold.

#### *Pollution Index (PI) Calculations*

The Pollution Index (PI), developed by Yümün (2017), is the empirical value obtained by dividing the average of the measurement values by the number of measurements. It is calculated using *Equation 5*. The Pollution Index was applied by Yümün (2017) for West Marmara and gave good results in terms of determining the pollution locations. Therefore, it was applied to the Southeast Marmara Sea in the present study.

$$PI = [(MV_1/MV_{ort}) + (MV_2/MV_{ort}) + \dots + (MV_n/MV_{ort})] / n \quad (\text{Eq.5})$$

The parameters used in the equation are described as follows;

PI: Pollution Index (Unitless), MV1: Heavy metal measurement value (ppm), MV<sub>ort</sub>: Heavy metal measurement value average (ppm), n: Measured heavy metal number.

This correlation provides a more realistic approach in terms of using local data as "background value" compared to other pollution analysis methods. For this purpose, the average values for the Marmara Sea were calculated by using the geochemical analysis outcomes obtained by Yümün (2017), Yümün et al. (2021), and Yümün and Kam (2017), and these values were used in the study. The average values calculated for this study can be used as "background values" in all pollution analysis studies regarding the Marmara Sea. The obtained PI values of <0.75 denote a clean environment, 0.75-1 beginning of pollution, 1-1,2 polluted environment, and >1.2 very polluted environments (*Table 9 and Figure 2*).

According to the Pollution Index (PI) Calculations, it is seen that pollution is high in all locations other than the Bandırma Core-1 sample. Especially in the Gemlik region, the pollution is at a very high level. Necessary precautions should be taken to ensure that pollution will not become dangerous for public and environmental health. The reason why there is not much pollution in the Core-1 sample is that this region is outside the gulf. Because there is no settlement close to this location and it is an area far from ship traffic.

#### *Geological Accumulation Index (I-geo) Calculations*

The Geological Accumulation Index (I-geo) was defined by Muller (1969). While calculating this index, the world average shale values calculated by Turekian et al. (1961), Krauskopf et al. (1985), and Abraham and Parker (2008) were used as background values (*Tables 10, 11*). *Equation 6* given below is used in the calculations of the Geological Accumulation Index (I-geo).

$$I\text{-geo} = (\log_2 C_n) / (1.5 * B_n) \quad (\text{Eq.6})$$

where,

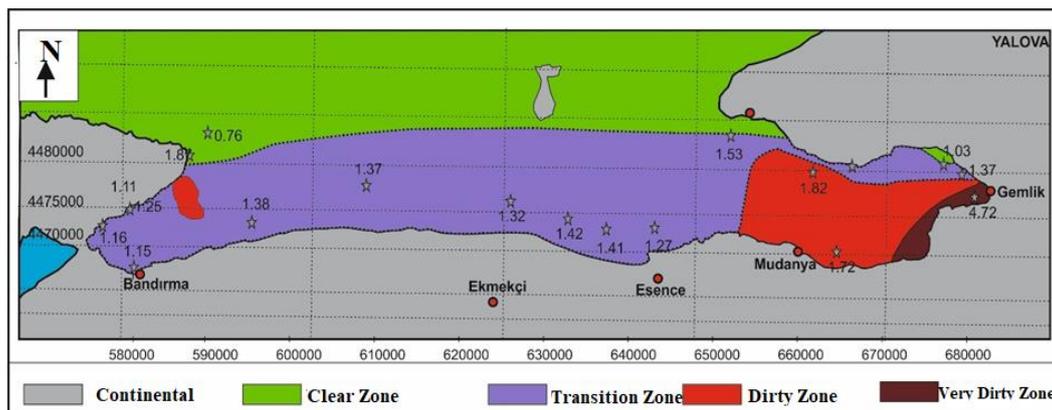
Cn: The metal concentration measured in the sediment sample,

Bn: Geochemical background (shale) value of metal concentration,

1.5: It is the background correlation factor, and 7 different pollution classes of the Igeo value are defined.

**Table 9.** Pollution Index values calculated according to the Marmara Sea mean values (\*\*)  
of the samples

SAMPLE LOCATIONS	PI	SAMPLE LOCATIONS	PI
GMK/ COR -1	1.82	GMK-BN/2	1.41
GMK/ COR -2	1.53	GMK-BN/3	1.42
GMK/ COR -3	1.72	GMK-BN/4	1.32
GMK/COR-4	4.72	GMK-BN/5	1.37
GMK BH-1	1.48	GMK-BN/6	1.38
GMK BH-2	1.03	Bandırma BH-2	1.16
GMK BH-3	1.37	Bandırma Cor-1	0.76
GMK-BN/1	1.27	Bandırma Cor-2	1.87



**Figure 2.** Pollution Map prepared by Kriging Method using Pollution Index values of the study area (The obtained PI values of <0.75 denote a clean environment, 0.75-1 beginning of pollution, 1-1,2 polluted environment, and >1.2 very polluted environments (Table 9 and Figure 2))

**Table 10.** Sediment quality classification of I-geo value

I geo category	Value	Sediment Quality
0	$I_{geo} \leq 1$	No pollution
1	$0 < I_{geo} < 1$	Less pollution
2	$1 < I_{geo} < 2$	Orta derecede kirlilik
3	$2 < I_{geo} < 3$	Kirlenmiş
4	$3 < I_{geo} < 4$	Önemli derecede kirlilik
5	$4 < I_{geo} < 5$	Çok fazla kirlilik
6	$I_{geo} \geq 5$	Aşırı derecede kirlilik

**Table 11.** The geological accumulation index calculated according to the shale values of Krauskoph (1985) (\*), and average values of Marmara Sea samples (\*\*) (measurement accuracy  $\pm 0.05$ )

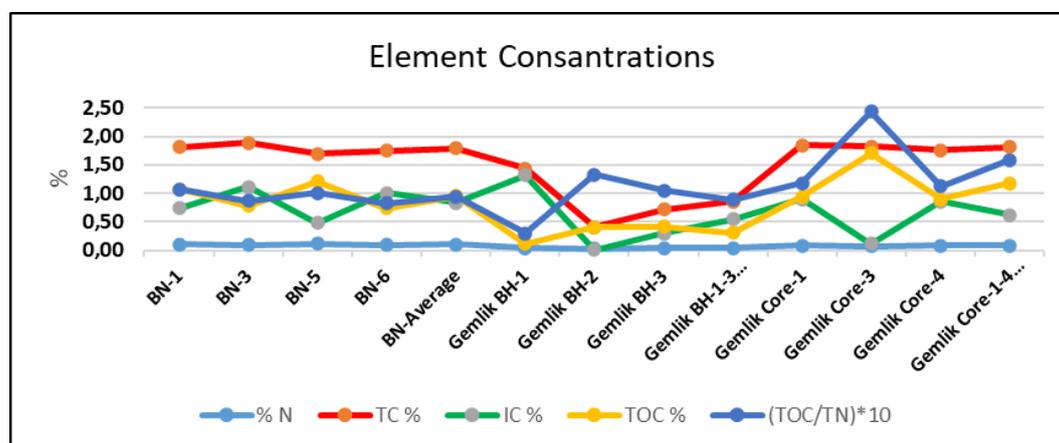
LOCATIONS AND SAMPLES	(Igeo) Fe		(Igeo) Ni		(Igeo) Zn		(Igeo) Cd		(Igeo) Co		(Igeo)Cr		(Igeo)Cu		(Igeo)Mn	
	(10 <sup>-5</sup> )*	(10 <sup>-5</sup> )**	*	**	*	**	*	**	*	**	*	**	*	**	*	**
GMK COR-1	15	26	0,05	0,06	0,04	0,05	3,1	0,5	0,1	0,08	0,03	0,06	0,06	0,11	0,005	0,01
GMK COR-2	15	26	0,05	0,06	0,04	0,04	1,0	0,2	0,1	0,08	0,03	0,06	0,06	0,1	0,005	0,01
GMK COR-3	15	26	0,05	0,06	0,04	0,04	1,2	-0,2	0,1	0,08	0,03	0,06	0,06	0,1	0,005	0,01
GMK COR-4	0,1	26	0,04	0,05	0,03	0,04	1,1	0,2	0,1	0,08	0,03	0,06	0,06	0,1	0,006	0,02
GMK BH-1	15	26	0,04	0,05	0,04	0,04	3,7	0,7	0,09	0,07	0,03	0,05	0,05	0,1	0,005	0,01
GMK BH-2	15	26	0,02	0,03	0,03	0,05	3,9	0,7	0,09	0,07	0,02	0,04	0,05	0,1	0,004	0,01
GMK BH-3	15	26	0,04	0,05	0,04	0,04	4,3	0,8	0,01	0,08	0,03	0,06	0,05	0,1	0,004	0,01
GMK-BN/1	14	26	0,04	0,05	0,03	0,04	-	-	0,01	0,08	0,03	0,06	0,06	0,1	0,005	0,01
GMK-BN/2	15	26	0,05	0,06	0,03	0,04	-	-	0,1	0,08	0,04	0,07	0,05	0,1	0,005	0,01
GMK-BN/3	15	26	0,05	0,06	0,03	0,04	-	-	0,01	0,07	0,03	0,06	0,05	0,1	0,005	0,01
GMK-BN/4	14	26	0,05	0,06	0,03	0,04	-	-	0,01	0,07	0,04	0,06	0,06	0,1	0,005	0,01
GMK-BN/5	14	26	0,05	0,06	0,03	0,04	-	-	0,01	0,07	0,03	0,07	0,06	0,1	0,004	0,01
GMK-BN/6	14	26	0,05	0,06	0,03	0,04	-	-	0,13	0,04	0,04	0,06	0,05	0,1	0,004	0,01
BND BH-2	14	26	0,03	0,05	0,03	0,04	0,5	0,5	0,08	0,08	0,03	0,06	0,04	0,1	0,004	0,01
Kapıdağ Cor-1	15	26	0,05	0,06	0,03	0,04	-	-	0,2	0,06	0,03	0,06	0,05	0,1	0,006	0,01
Kapıdağ Cor-2	15	26	0,05	0,06	0,03	0,04	-	-	0,16	0,06	0,04	0,06	0,05	0,1	0,005	0,01

### Total Organic Carbon, Organic Carbon, Inorganic Carbon, Total Nitrogen Analysis Results

The total organic carbon, total carbon, total inorganic carbon, and total nitrogen analysis results of the samples are given in *Table 12* and *Figure 3*. We determined that the average total carbon (TC: 0.86), inorganic carbon (IC: 0.54), and total organic carbon value (TOC: 0.31) in the drilling samples of the Gemlik Region were low. On the contrary, average total carbon (TC: 1.79), inorganic carbon (IC: 0.62), and total organic carbon value (TOC: 1.18) were found to be high in the Bandırma Region gravity core samples. The average total carbon (TC: 1.81), inorganic carbon (IC: 0.84), and total organic carbon (TOC: 0.95) values were found to be the highest in the Gemlik Region gravity core samples. The total nitrogen value in the Marmara Sea was found to be low in the Gemlik BH 1-3 drilling samples (0.003-0.004%), high in Gemlik gravity core samples (0.07-0.08%), and the highest value was determined in the Bandırma gravity core samples (0.09%-0.12%).

**Table 12.** Total organic carbon, total carbon, total inorganic carbon and total nitrogen analysis values of 10 samples taken from Gemlik and Bandırma regions (Avr: Average)

Samples	% N	TC %	IC %	TOC %	(TOC/TN)/10	TOC/TN
BN-1	0.10	1.81	0.74	<b>1.07</b>	1.07	10.70
BN-3	0.09	1.89	1.11	<b>0.78</b>	0.87	8.70
BN-5	0.12	1.69	0.48	<b>1.21</b>	1.01	10.10
BN-6	0.09	1.75	1.01	0.74	0.82	8.20
BN-Average	<b>0.10</b>	<b>1.79</b>	<b>0.84</b>	<b>0.95</b>	<b>0.94</b>	<b>9.43</b>
Gemlik BH-1	0.04	1.44	1.32	0.12	0.30	3.00
Gemlik BH-2	0.03	0.41	0.01	0.40	1.33	13.30
Gemlik BH-3	0.04	0.72	0.30	0.42	1.05	10.50
Gemlik BH-1-3 (Avr)	<b>0.04</b>	<b>0.86</b>	<b>0.54</b>	<b>0.31</b>	<b>0.89</b>	<b>8.93</b>
Gemlik Core-1	0.08	1.84	0.90	0.94	1.18	11.75
Gemlik Core-3	0.07	1.82	0.11	1.71	2.44	24.40
Gemlik Core-4	0.08	1.76	0.86	0.90	1.13	11.30
Gemlik Core-1-4 (Avr)	<b>0.08</b>	<b>1.81</b>	<b>0.62</b>	<b>1.18</b>	<b>1.58</b>	<b>15.82</b>



**Figure 3.** Total organic carbon, total carbon, total inorganic carbon, and total nitrogen analysis values of 10 samples taken from Gemlik and Bandırma region

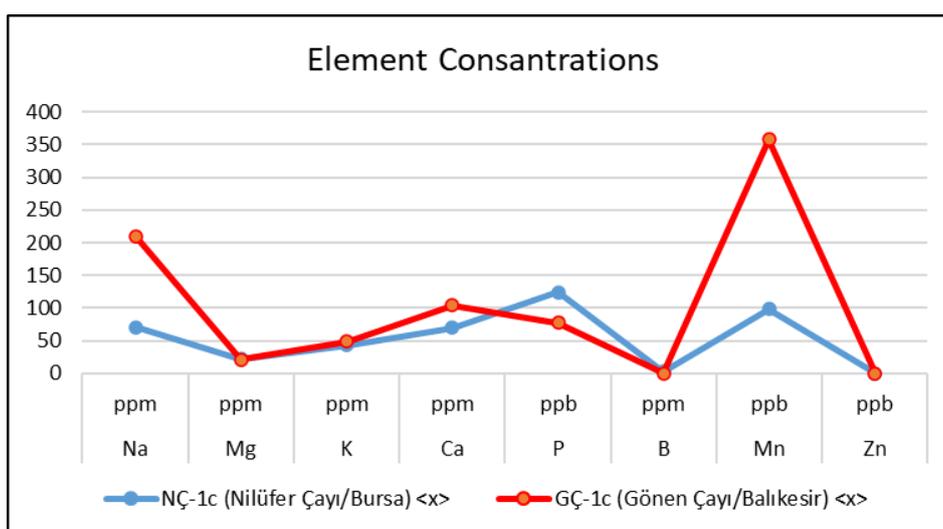
Drilling samples represent deeper than the seabed, while gravity core samples represent current sediments on the seafloor. This shows that the current period sediments are more polluted than the old periods. The results show the polluting effects of wastewater discharged into the Marmara Sea because of ship traffic and agricultural activities.

### *Evaluation of Pollution Caused by Streams Spilled into the Sea*

Water samples were taken from the streams pouring into the Gemlik and Bandırma Bays [NC-1c (Nilüfer Stream/Bursa), GC-1c (Gönen Stream/Balıkesir)], and geo-chemical analyzes of water samples were made. The analyzed elements are Na, Mg, K, Ca, P, Fe, Cu, B, Mn, Zn, Al, As, Pb, Cd, Hg, Mo, Co, Cr, Sb, Bi, and Ni (Table 13). Although Phosphorus (P) values are high in both stream samples, it is noteworthy that Mn, Ca, and Na values are higher in Gönen Stream compared to Nilüfer Stream. The reason for this may be that industrial establishments in Gönen (Balıkesir) produce wastes rich in P and Mn. However, it is seen that Nilüfer Stream is richer in terms of Boron (B) and Phosphorus (P) elements (Figure 4).

**Table 13.** Geochemical analyzes of stream samples poured into the study area

Sample	Type	Na	Mg	K	Ca	P	B	Mn	Zn
		ppm	ppm	ppm	ppm	ppb	ppm	ppb	ppb
NÇ-1c (Nilüfer Stream /Bursa)	1	<b>69.58</b>	22.28	43.56	68.76	<b>126.37</b>	2.90	94.82	0
	2	<b>71.57</b>	20.94	43.18	70.40	<b>121.60</b>	2.87	101.90	0
	<x>	<b>70.57</b>	21.61	43.37	69.58	<b>123.98</b>	2.88	98.36	0
GÇ-1c (Gönen Stream/Balıkesir)	1	<b>210.67</b>	20.96	48.22	103.16	<b>54.80</b>	0.13	340.68	0
	2	<b>210.12</b>	20.07	48.49	104.06	<b>100.11</b>	0.13	375.71	0
	<x>	<b>210.40</b>	20.51	48.36	103.61	<b>77.45</b>	0.13	358.20	0
Limit Values		<b>250.00</b>	-	-	-	<b>35</b>	500	-	5



**Figure 4.** Geochemical analysis graph of the stream samples poured into the study area

In both cases, we observed that the marine environment is polluted as a result of the discharge of industrial wastes into the sea by rivers. According to these results, the wastes of the industrial establishments operating in Bursa and Balıkesir should be controlled, and the wastewater should not be discharged into the streams or the sea without treatment. Otherwise, irreversible pollution in the Sea of Marmara and mass extinctions may occur in the creatures living in the sea. In order to examine the pollution caused by the rivers in the sea, seawater samples were taken from the points where the rivers spill. Fe, Cu, Al, As, Pb, Cd, Hg, Mo, Co, Cr, Sb, Bi, Ni element concentrations in GMK-1b, KRŞ-1b, BND-2c, BND-1b and MŞÇ-1b locations could not be measured because they were below the measurement limit. But, the concentration values of Na, Mg, K, Ca, P, B, Mn, and Zn elements were above the measurement limits, therefore the measurement could be achieved (*Tables 13 and 14*).

It is seen that the elemental concentrations of the Gemlik (GMK-1b) sample are very different from the elemental concentrations of the Kurşunlu (KRŞ-1b), Bandırma (BND-1b, and BND-2c) and Misakça (MŞÇ-1b) samples. Industrial activities in and around Gemlik, and ship traffic in the gulf have caused high concentrations of phosphorus (P: 696.46-713.60 ppm) and manganese (Mn: 128.74-145.17 ppm). Phosphorus (P: 139.16-230.50 ppm) concentration is also high in Bandırma (BND-2c) samples. Domestic and industrial wastes that cause phosphorus, nitrogen, and manganese increase are carried to the sea by rivers and promote serious pollution in the sea. The mucilage problem, which started in the Sea of Marmara in recent years, still continues on the sea floor and threatens marine life. Nutrients transported by wastewater discharged to the sea cause an overabundance of plant assets in the sea, such as algae.

### ***Foraminiferal Assemblages Detected in the Study Area and the Effect of Environmental Pollution on Foraminifers***

A rich foraminiferal assemblage (*Adelosina cliarensis*, *Adelosina duthersi*, *Adelosina mediterraneensis*, *Ammonia compacta*, *Ammonia tepida*, *Ammonia parkinsoniana*, *Anomalinoidea rubiginosus*, *Biloculinella labiata*, *Brizalina spathulata*, *Bulimina aculeata*, *Cornispira foliaca*, *Criboelphidium poeyanum*, *Cycloforina contorta*, *Cycloforina villafrance*, *Dentalina subsoluta*, *Dentalina wimani*, *Elphidium complanatum*, *Elphidium crispum*, *Epinoides concameramatus*, *Lachenella sp.*, *Lagena leavis*, *Lobatula lobatula*, *Masilina secans*, *Melonis pompilioides*, *Miliolinella subrotunda*, *Quinqueloculina jugosa*, *Quinqueloculina seminula*, *Planorbulina mediterraneensis*, *Pygro inornata*, *Rectovigerina phlegeri*, *Rosalina brady*, *Spiroloculina angulosa*, *Spiroloculina excavata*, *Textularia bocki*) was determined from the drilling and core samples taken from the study area. As a result of the identification of the obtained foraminifers, we determined that there are 25 genera and 33 species of foraminifera (*Table 15, Plate 1 and Plate 2*). Although the foraminiferal shells obtained from the Bandırma-Gemlik intercalation sediments (*Plate 1, 1-a, b and 2-a,b: Quinqueloculina seminula* BN 2-7 and BN 2-8) are in natural color and texture, the foraminiferal shells obtained from the Gemlik samples (*Plate-1, 3-a,b: Quinqueloculina stalkerii* Gemlik Core 5-1) are darkened in color and texturally deformed. Again, the color change of the foraminifer is high in species obtained from the Gemlik region (*Plate 2, 1-a,b: Ammonia compacta* Gemlik Core 4-3), and moderate in the species found in the Bandırma region (*Plate 2, 2-a,b: Ammonia compacta* Bandırma-1 30.70-30.80), and there is no color change in the foraminiferal species found between Bandırma and Gemlik (*Plate 2, 3-a,b: Ammonia parkinsoniana* BN Core 6-2) (*Figure 5*).

**Table 14.** Geochemical analyzes of seawater and streams flowing into the sea from the study area

Sample	Type	Na	Mg	K	Ca	P	B	Mn	Zn
		ppm	ppm	ppm	ppm	ppb	ppm	ppb	ppb
GMK-1b (Gemlik/Bursa)	1	1696.84	233.71	124.27	172.78	696.46	0.83	145.17	0
	2	1692.05	230.69	128.03	171.93	713.60	0.83	128.74	0
	<Average Value>	1694.45	232.20	126.15	172.36	705.03	0.83	136.95	0
KRŞ-1b (Kuruşunlu/Bursa)	1	6424.02	888.11	346.97	321.70	0.00	3.20	56.71	0
	2	6415.98	879.63	409.58	334.31	0.00	3.20	66.74	0
	<Average Value>	6420.00	883.87	378.28	328.01	0.00	3.20	61.72	0
BND-2c (Bandırma/Balıkesir)	1	6444.65	878.56	416.95	325.32	139.16	3.16	65.70	0
	2	6751.51	845.38	414.53	330.73	230.50	3.18	70.03	0
	<Average Value>	6598.08	861.97	415.74	328.03	184.83	3.17	67.87	0
BND-1b (Bandırma/Balıkesir)	1	6582.91	836.96	407.93	322.91	0.00	3.14	65.55	0
	2	6581.22	870.75	410.11	326.95	0.00	3.25	66.81	0
	<Average Value>	6582.07	853.86	409.02	324.93	0.00	3.20	66.18	0
MSC- 1b (Misakça/Balıkesir)	1	6494.51	865.81	407.36	329.21	0.00	3.10	100.16	0
	2	6601.44	857.07	410.47	325.11	0.00	3.15	101.64	0
	<Average Value>	6547.98	861.44	408.92	327.16	0.00	3.13	100.90	0
Limit Values		<b>250.00</b>	-	-	-	<b>35</b>	500	-	5

**Table 15.** Foraminiferal assemblage determined from sounding and core samples taken from the study area

Sample Number	<i>Adelosina cliarensis</i>	<i>Adelosina duthersi</i>	<i>Adelosina mediterraneensis</i>	<i>Ammonia compacta</i>	<i>Ammonia tepida</i>	<i>Ammonia parkinsoniana</i>	<i>Anomalinoideis rubiginosus</i>	<i>Biloculinella labiata</i>	<i>Brizalina spathulata</i>	<i>Bulinina aculeata</i>	<i>Cornispira foliata</i>	<i>Criboelphidium poeyanum</i>	<i>Cycloforina contorta</i>	<i>Cycloforina villafrance</i>	<i>Dentalina subsoluta</i>	<i>Dentalina wimani</i>	<i>Elphidium complanatum</i>
Gemlik Core-1	-	-	-	29	2	-	-	-	-	-	-	-	2	2	-	-	-
Gemlik Core-2	1	-	-	33	4	2	-	-	-	-	-	-	1	1	-	-	2
Gemlik Core-3	10	-	-	1	5	2	-	-	-	-	-	-	6	2	-	-	1
Gemlik Core-4	1	-	-	85	1	11	-	-	-	-	-	-	1	-	-	-	13
Bandırma Core-1	1	1	-	55	-	2	3	-	-	-	-	-	-	2	-	-	1
Bandırma Core-2	2	1	-	43	-	1	-	-	-	-	-	-	-	1	-	-	1
BN Core-1	4	-	-	56	2	-	-	1	-	-	-	-	-	-	-	-	-
BN Core-2	-	-	1	26	5	-	-	2	-	-	-	-	-	-	-	-	9
BN Core-3	-	-	-	14	-	-	4	1	-	-	-	-	-	-	-	-	-
BN Core-4	2	-	-	38	4	2	-	-	-	-	-	-	-	-	-	-	10
BN Core-5	-	-	-	18	3	-	-	2	-	1	-	-	-	-	-	-	-
BN Core-6	-	-	-	42	2	-	-	-	34	14	-	-	-	-	-	1	-
Gemlik BH-1	3	-	-	4	3	2	-	-	-	-	-	4	5	-	-	-	3
Gemlik BH-2	-	-	-	59	20	5	-	-	-	-	-	6	8	-	-	-	35

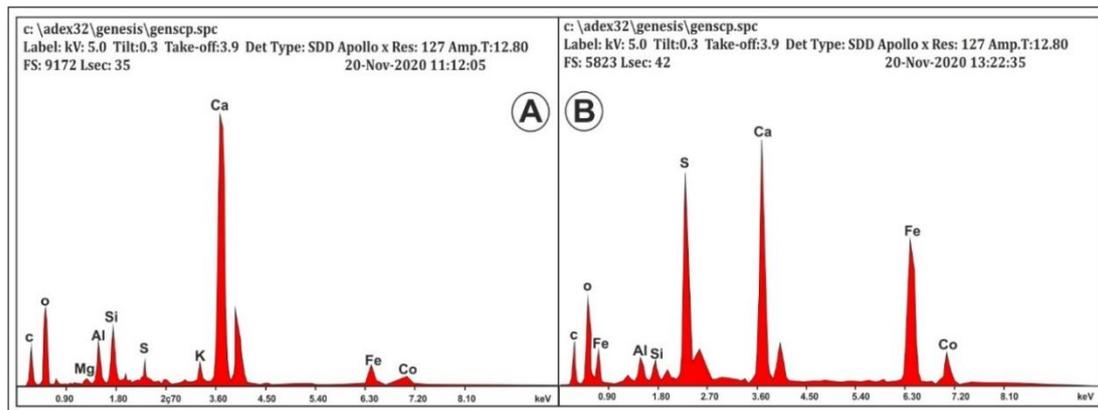
Sample Number	<i>Elphidium crispum</i>	<i>Epinoideis concameratus</i>	<i>Lachenella sp.</i>	<i>Lagena leavis</i>	<i>Lobatula lobatula</i>	<i>Masilina secans</i>	<i>Melonis pompilioides</i>	<i>Miliolinella subrotunda</i>	<i>Quinqueloculina jugosa</i>	<i>Quinqueloculina seminula</i>	<i>Planorbulina mediterraneensis</i>	<i>Pygro inornata</i>	<i>Rectovigerina phlegeri</i>	<i>Rosalina brady</i>	<i>Spiroloculina angulosa</i>	<i>Spiroloculina excavata</i>	<i>Textularia bocki</i>
Gemlik Core-1	4	-	-	-	-	-	-	-	2	12	2	-	-	-	-	-	-
Gemlik Core-2	12	-	-	-	2	-	-	2	1	11	-	-	-	-	-	-	-
Gemlik Core-3	2	-	-	-	2	-	-	1	3	1	7	-	-	-	-	-	-
Gemlik Core-4	95	-	-	-	7	-	-	2	1	25	1	-	-	-	-	-	-
Bandırma Core-1	13	-	-	-	3	-	-	1	-	4	2	-	-	-	-	-	-
Bandırma Core-2	20	-	-	-	2	-	-	1	-	8	3	-	-	-	-	-	-
BN Core-1	3	-	-	-	8	-	11	-	-	35	3	7	-	-	2	5	23
BN Core-2	7	4	-	-	3	-	-	-	-	11	5	-	-	-	1	2	9
BN Core-3	9	2	1	-	4	-	7	-	-	14	1	-	-	6	5	2	23
BN Core-4	11	-	-	1	5	-	1	-	-	11	-	-	-	-	-	-	2
BN Core-5	2	2	-	-	4	-	3	2	-	5	-	-	-	-	-	-	-
BN Core-6	9	13	-	2	5	1	11	5	-	38	4	3	6	-	-	-	11
Gemlik BH-1	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gemlik BH-2	85	-	-	-	5	-	-	-	-	4	-	-	-	-	-	-	-



**Plate 1.** 1 a,b: *Quinqueloculina seminula* BN 2-7; 2 a, b: *Quinqueloculina seminula* BN 2-8; 3 a, b: *Quinqueloculina stalkerii* Gemlik Core 5-1; 4 a, b: *Quinqueloculina stalkerii* Gemlik Core 4-3; 5 a, b: *Pseudotriloculina laevigata* Gemlik Core 5-2; 6 a, b: *Pseudotriloculina laevigata* Gemlik Core 5-3; 7 a, b: *Massilina guelteriana* Gemlik Core 5-3; 8 a, b: *Miliolinella elongata* K.5 30.70-30.80; 9 a, b: *Adelosina cliarensis* BN 4-1; 10 a, b: *Biloculinella labiata* BN 2-8; 11: *Textularia bocki* K.7 30.50-30.60; 12: *Dentalina subsolata* BN 3-8; 13: *Bulimina aculeata* BN 6-1; 14: *Lagena laevis* BN 6-1; 15: *Spiroloculina excavata* BN 3-9; 16: *Spiroloculina angulosa* BN 3-5; 17: *Brizalina spathulata* BN 6-3; 18: *Rectovigerina phlegeri* BN 6-1; 19: *Textularia globulosa* BN 3-9. (Scala unit is mm)



**Plate 2.** 1 a, b: *Ammonia compacta* Gemlik Core 4; 2 a,b: *Ammonia compacta* Bandırma-1 30.70-30.80; 3 a, b: *Ammonia parkinsoniana* BN Core 6-2; 4 a, b: *Ammonia parkinsoniana* BN 3-1; 5 a, b: *Rosalina bradyi* Bandırma -6A 35.10-35.20; 6 a, b: *Anamalinoides rubiginosus* BN 5-1; 7 a, b: *Anamalinoides rubiginosus* Bandırma 2-6; 8: *Melonis pomplioides* BN 2-4; 9 a, b: *Criboelphidium poeyonum* Gemlik Core 6-2; 10 a, b: *Eponides concameratus* BN 6-1; 11 a, b: *Lobatula lobatula* BN 5-9; 12: *Elphidium crispum* BN 5-8; 13: *Elphidium crispum* Gemlik Core 3-1; 14 a, b: *Planorbulina mediterraneensis* BN 2-5. (Scala unit is mm)



**Figure 5.** Surface element analysis with a Scanning Electron Microscope (SEM). A: *Ammonia compacta* (Plate 2 1a-b, (Gemlik Core-4), B: *Anamalinoides rubiginosus* (Plate 7 a, b, Bandırma Core-2)

In geochemical analysis, we determined that the Marmara Sea is very polluted in the regions close to the Gemlik and Bandırma settlements, and there is almost no pollution in the Bandırma-Gemlik Buffer Zone. Both geochemical analyzes and paleontological studies prove the high level of contamination in Gemlik and Bandırma. Color changes and morphological alterations are observed in foraminiferal shells affected by these contaminations (Plate 1 and 2).

## Discussion and Conclusion

In this study, surface and deep-sea sediments of the study area were investigated in terms of heavy metal accumulation for the first time. Sediment evaluation indices were used to interpret heavy metal analysis results. Depending on these indices, we investigated whether the pollution was anthropogenic or of natural origin. In the calculation of these indices, both the mean values of the Marmara Sea obtained from previous studies (Yümün, 2017) and the shale values (Krouskoph, 1985) were used as background values. The use of local values allowed more realistic calculations for the study area.

The Enrichment Factors (EF) was calculated using equation defined by Buat-Menard and Chessele (1979). Especially, cadmium enrichment (EF<sub>cd</sub>) is greater than 5 in four surface samples taken from the Gemlik region, which shows that the contamination is definitely not of crustal origin and the enrichment is anthropogenic. The enrichment in metals such as Ni and Zn is at the initial level, and the enrichment factor (EF<sub>x</sub>) of other elements is less than 5, which indicates there is no enrichment. The enrichment of Cd, Ni, and Zn in the Gemlik region may be due to the increasing industrialization and the uncontrolled use of fertilizers and pesticides in olive cultivation. The Co enrichment in Core-1 of the samples taken from Kapıdağ region is >5 and it is not of crustal origin. Mn and Ni enrichment in Kapıdağ Core-1 and Core-2 is between 3-5 and can be attributed to possible crustal origin. In the samples taken between Bandırma and Gemlik, the enrichment values are below 5, but a moderate enrichment is observed in the Ni values. Since this enrichment is between 3-5, it can be argued that it is the crustal origin. Enrichment Factor values are below 5 in six surface samples taken from the region between Gemlik and Bandırma. Considering this result, it is seen that the enrichment

values are lower in these areas where there is no or less settlement, no industry, and fewer agricultural activities.

Secondly, the Contamination Factor defined by Hakanson (1980) was used for pollution evaluation. In the contamination factor (*C<sub>fi</sub>*) calculations, Cd contamination values in Gemlik and Bandırma samples are  $C_{fCd} > 6$ , indicating very high contamination. In parallel with the enrichment factor, the contamination value is very high in locations where settlements, industry, and agricultural activities are intense. In the intermediate zones, the contamination values are medium or low. Especially the *C<sub>fMn</sub>* value was calculated to be very high in GMK core-4, which is located in the Gemlik residential area. Except for the samples taken between Gemlik and Bandırma, the pollution load index was calculated as  $> 1$  and the environment were evaluated as very dirty.

As the third index, Pollution Loading Index (PLI) Calculations defined by Hakanson (1980) was used for pollution evaluation. The low values in the calculations of the geological accumulation index indicate that the pollution in the environment is not of natural origin but depends on other factors. It remains true that pollution loads in this region arise from residential, industrial, and agricultural wastes.

Finally, the Pollution Index (PI) defined by Yümün (2017) was used as the Pollution Assessment Method. Pollution Index (PI) calculation results revealed  $PI < 1$  in Kapıdağ core-1 location and  $PI > 1$  in all other locations. Locations with a PI value of  $> 1$  correspond to regions where settlements, industry, and agricultural activities are intense. The results in the intermediate region, which were found to be moderately dirty or clean compared to other methods, were found to be dirty in this method. The reason is the polluted waters spilling into the sea and mineralization on the coast. It should not be forgotten that it has a secondary effect on agricultural activities. Using the obtained Pollution Index values, the PI map was prepared with the Kriging Method. This map is an important data source in terms of being a document showing the pollution status of the region. In the analysis results of total organic carbon, total carbon, total inorganic carbon, and total nitrogen of ten samples, the values were mostly obtained as  $< 1$ . Locations with high organic matter rates are especially clayey and silty anaerobic environments. In terms of elemental analysis, we observed that these locations were heavily polluted. In a conclusion, the Enrichment Factor (EF), Contamination Factor (*C<sub>fi</sub>*), Pollution Loading Index (PLI), Geological Accumulation Index (I-geo), Ecological Risk Index (Er) and Pollution Index (PI) values show anthropogenic pollution in areas where settlements, ports and agricultural activities are intense.

It was concluded that Foraminifer individuals obtained from Gemlik and Bandırma locations were affected by environmental pollution. A decrease in the number of foraminifer individuals and morphological disorders were observed in the shell structures of the individuals obtained. Color changes and morphological changes are observed in foraminiferal shells affected by these contaminations (*Plates 1 and 2*). Surface element analysis was performed on individuals with changes in their shell structure such as deformation and color change, and their pollution values were analyzed. Here, too, it has been observed that living life is damaged a lot in locations where polluting elements are concentrated.

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