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Research Article

Spatial and Temporal Assessment of Heavy Metal Contamination in the Black Sea Surface Waters

Hakan Atabay[1*], Ertuğrul Aslan[1], İbrahim Tan[1], Leyla Gamze Tolun[1], Nuray Çağlar[2]

[1]TUBITAK-Marmara Research Center, TUBITAK Marmara Research Center - Climate and Life Sciences Vice Presidency - Marine Research and Technologies Research Group, Kocaeli, Türkiye
[2]Istanbul University, Institute of Marine Sciences and Management, Department of Chemical Oceanography, Istanbul, Türkiye

* Corresponding author: H. Atabay
E-mail: hakan.atabay@tubitak.gov.tr

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Abstract

This study presents a comprehensive spatial and temporal analysis of heavy metal contamination in the surface sea waters of the Black Sea. A total of 382 samples were collected from 56 sampling stations across seven sampling periods and subsequently analysed. The concentration levels, spatial and temporal distribution, contamination degree, and correlations with environmental parameters for eight heavy metals (Cu, Zn, As, Ni, Cr, Pb, Cd, and Co) were examined. The findings revealed that heavy metal contamination was mainly observed in areas influenced by rivers with high industrial discharges and agricultural activities, regions affected by deep sea discharges, and locations associated with port operations.

In the Black Sea, unfavourable land conditions have led to the discharge of untreated domestic and industrial waste water, mainly through deep sea outfalls. In addition, the siting of industrial facilities in coastal areas and riverine discharges contribute to localised water pollution problems. Heavy metal concentrations were found in the following order: Cu>Zn>As>Ni>Cr>Pb>Cd>Co. Heavy metal concentrations were generally higher in winter than in summer. Copper concentrations exceeded Türkiye's seawater quality standards during the winter seasons. Based on contamination factor (CF) values, 57.3% of the measurements indicated low contamination, 7.6% moderate, 8.9% considerable, and 26.2% very high levels of copper contamination. The CF values for As and Cd at stations influenced by the Samsun deep sea discharge occasionally reached considerable and high levels. The contamination factor (CF) values for all other heavy metals measured along the Black Sea coast were <1, indicating low levels of contamination.

Keywords: Black Sea, Sea Water, Heavy Metal, Contamination Factor, Contamination Degree

Introduction

Over the past two decades, there has been a notable increase in interest surrounding trace elements in seawater (Riley and Chaster, 1983). Toxic trace elements, including lead, mercury, arsenic, and cadmium, are present in trace quantities in coastal marine ecosystems. However, it is important to acknowledge that the natural cycles are also influenced by anthropogenic sources of metals (Gardner and Ravenscroft, 1996). In particular, anthropogenic activities such as industrial processes and agricultural practices contribute significantly larger amounts of these substances to the marine environment (Caetano et al., 2022). It has long been established that the Black Sea, a semi-enclosed inland sea, is susceptible to the effects of anthropogenic activities. (Sur et al., 2004; Alkan et al., 2015). Geochemical studies have demonstrated that the Black Sea coast of Türkiye has also been subjected to these pressures, resulting in an elevated level of heavy metals accumulated in the sediment. (Algan et a., 1999; Alkan et al., 2015; Sarı et al., 2018).

Legal legislation at Regional and European level, with the agreement of member states, is crutial for controlling the pressures resulting from anthropogenic activities in the seas and protecting their ecosystems. The Marine Strategy Framework Directive (MSFD) (2008/56/EC) establishes a framework for the development of marine strategies. The aim is to improve the quality of the marine environment in European seas. In particular, one of the MSFD descriptors of "good environmental status (GES)" of the marine environment emphasizes that contaminant levels, including those of metals, do not result in adverse effects on marine ecosystems (Descriptor D8). The monitoring of contaminants under D8 is closely linked to environmental pollution assessments under the Water Framework Directive (WFD) (2000/60/EC). Thresholds for contaminants identified under the Water Framework Directive (WFD) have been set based on the Environmental Quality Standards (EQS) set out in Directive 2013/39/EU, with the aim of protecting pelagic organisms in the water column. The information on background levels of metals in water matrix is also important and need to be taken account in assessment of possible effects on aquatic organisms.

A review of the literature on metal concentrations in aquatic environments reveals that the highest accumulation occurs in bottom sediments (Kruopiene, 2007; Brils 2008; Kubryakov, 2011; Ozkan and Buyukisik, 2012). While threshold values for water matrices have been established, research focusing on metal levels in water matrices remains limited. Furthermore, data on background levels are lacking (Tueros et al., 2008). In general, metal concentrations are reported below the detection limits of conventional analytical techniques, which are inherently limited in their ability to detect lower concentrations.

In a few of the studies conducted in the Black Sea region, contaminants, including metals, were monitored in accordance with MSFD requirements. These include EU-supported projects such as MISIS and the recent ANEMONE (Moncheva and Boichenco 2014; Oros, 2020; Lazar 2021). Studies carried out in coastal area of Türkiye were limited in spatial and temporal scale (Balkis and Aksu, 2012; Balkis et al., 2012; Çoban et al., 2009; Baltas et al., 2017; Elderwish et al., 2018; Karabayir et al., 2020).

The findings from a three-year monitoring project conducted between 2014 and 2016 reveal that the Sakarya River in the western Black Sea basin and the Yeşilırmak River in the eastern Black Sea basin significantly contribute to the pollution of the Black Sea ecosystem (MoEU-DGEIAPI and TUBITAK-MRC, 2016; Menteş, et al., 2019).

This study examines the heavy metal pollution levels in surface seawater along Türkiye's Black Sea coast. It focuses on three key areas: (1) their spatial and seasonal variations, (2) the sources of the pollution, and (3) the correlations between these pollutants and the physicochemical factors in the seawater. Furthermore, the results may be employed as a point of reference for the evaluation of prospective trends in heavy metal concentrations in seawater.

Materials and Methods

Study area

The Black Sea is a semi-enclosed inland sea with a surface area of approximately 4.2×105 km² and a maximum depth of 2,200 meters, located between Türkiye, Bulgaria, Romania, Ukraine, Russia, and Georgia. The Black Sea has its only connection to the oceans through the Istanbul Strait, linking it to the Mediterranean Sea via the Sea of Marmara. The mean depth of the north-western Black Sea coast is approximately 50 metres. In contrast to the north-western region, the depth rises abruptly, resulting in the continental shelf being reached with a steep slope. In the Black Sea, a permanent halocline layer exists between depths of 150 and 200 metres, separating the upper layer waters, which are oxygen-rich, from the bottom waters, which are characterised by the presence of hydrogen sulphide.

The region faces considerable environmental challenges as a result of the pollutant loads from domestic, industrial and riverine sources in coastal countries, including Türkiye. The most significant inputs are pollutants and nutrients originating from the Danube, Dniester, and Dnieper rivers located in the northwest of the Black Sea. On Türkiye's coasts, there are issues caused by pollutants carried by the Kızılırmak, Yeşilırmak, Sakarya, and Filyos rivers, which have the highest annual flow rates (Tan et al., 2023). Although small- to medium-sized industrial facilities dominate in the Black Sea basins, their wastewater exerts pressure on the rivers. Large-scale industrial facilities, on the other hand, have been established in coastal districts. In the Black Sea region, major industrial facilities include the Zonguldak Coal Enterprises, Ereğli Iron and Steel Works, Samsun Copper and Fertilizer Industries, and Artvin Hopa Copper Operations. Additionally, due to unfavorable land conditions around the Black Sea, domestic wastewater is mostly discharged through deep-sea outfalls.

Türkiye's Black Sea coast stretches 1,695 kilometers, reaching from the Bulgarian border in the west to the Georgian border in the east (Bakan and Büyükgüngör 2000; Altas and Büyükgüngör 2007). In order to evaluate the impact of marine activities, surface seawater samples were collected during the winter and summer seasons from 2021 to 2024 along the Black Sea coastline of Türkiye, encompassing all provinces from İğneada to Hopa. Sampling was conducted at 56 stations situated at varying distances from the shore, ranging from approximately 180 metres to 25 kilometres, with depths between 8 and 1,010 metres. Sampling stations were designated to include areas affected by various pressures, less impacted areas, and reference stations.

Sampling, sample preparation and analysis

Due to the very low concentrations of heavy metals in seawater (especially at open sea stations), great care must be taken during sampling and analysis to avoid contamination by cross-contamination or the loss of analytes. Therefore, the most crucial step in seawater sampling is to establish appropriate sampling and pretreatment protocols. In particular, precise measurement of heavy metal analyses in seawater requires appropriate analytical equipment and personnel with specific expertise in these analyses. The samples were collected using the R/V TÜBİTAK Marmara vessel, and the research expedition lasted about two weeks. Physical measurements were conducted utilising a Sea-Bird SBE 25Plus CTD device, equipped with an SBE 27 pH sensor and an SBE 32C rosette system, comprising 12 sampling bottles, each with an 8-litre capacity. In addition to the physical measurements of temperature, salinity, and pH, analyses for dissolved oxygen (SM 4500 B:2005), chlorophyll-a (SM 10200 H), and heavy metals were also conducted. The analysis of chlorophyll-a was conducted using a Shimadzu UV-VIS Spectrophotometer (UV-1900i), while the analysis of dissolved oxygen was performed with the aid of a Metrohm automatic titrator.

In order to ensure the accuracy of heavy metal analysis, it is essential that all samples are collected using materials and equipment that prevent contamination. The use of plastic or Teflon materials is recommended as a means of preventing contamination. Water samples are obtained from the surface layer, at a depth of one metre below the surface. Seawater is subsequently transferred from Niskin bottles into plastic containers, preserved with nitric acid, and stored in a refrigerator at a temperature of 4–8 °C until further laboratory analysis is conducted. Metal analyses are carried out directly on unfiltered seawater samples that have been acidified to pH 2 with ultrapure nitric acid. Heavy metals, such as As, Cd, Co, Cr, Cu, Ni, Pb and Zn, were determined by inductively coupled plasma mass spectrometry (ICP-MS) (NexION 300). Measurements were made using the standard methods given by SM. 3030 E. Nitric Acid Digestion (2023).

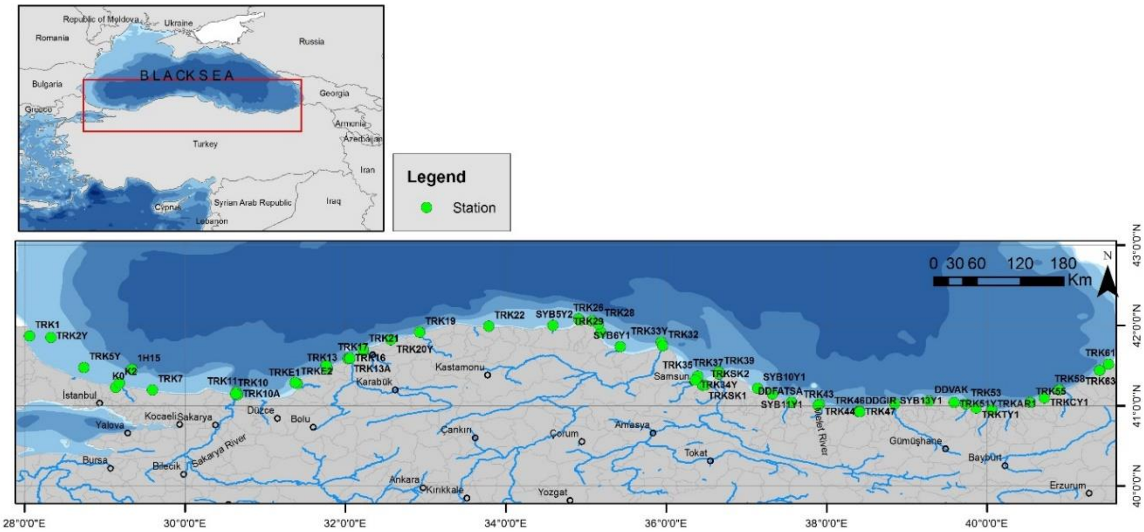


Fig. 1. The map illustrates the spatial distribution of sampling locations in the Black Sea.

In this study, the CF and contamination degree (CD) were applied for the assessment of seawater quality (Hakanson, 1980; Wang et al., 2018). The CF indicates the pollution level of a single heavy metal, while the CD represents the pollution level of total heavy metals in the environment.

$$CF = \frac{\text{Cheavy metal}}{\text{Cbackground}}$$

$$CD = \sum_{i=1}^{n} CF$$

where Cheavy metal is the concentration of the heavy metal, and Cbackground is the corresponding background in the study area. Environmental quality standards were used as reference values for background concentrations. The Environmental Quality Standards (EQS) established by Türkiye for seawater are presented in Table 1.

A comprehensive analysis of all physicochemical parameters and dissolved heavy metal concentrations was conducted. To assess the statistical reliability of the data, normality and homogeneity were verified using the Kolmogorov-Smirnov and Levene tests, respectively. For variables that did not meet the assumptions of normality and homogeneity, the non-parametric Kruskal-Wallis test (K-W) was utilized. The strength and direction of potential correlations among variables were determined using Spearman correlation analysis. Principal component analysis (PCA) was used to identify potential contaminant sources. SPSS 26.0 was used for statistical analysis.

Table 1. The Environmental Quality Standards (EQS (µg/l)) for seawater set by Türkiye (YSKY, 2023)

Arsenic (CAS 7440-38-2)	Cadmium and its compounds (CAS 7440-43-9)	Chromium (CAS 7440-47-3)	Cobalt (CAS 7440-48-4)	Copper (CAS 7440-50-8)	Lead and its compounds (CAS 7439-92-1)	Nickel and its compounds (CAS 7440-02-0)	Zinc (CAS 7440-66-6)
AMC: 10.0	AMC: 0.20	AMC: 4.20	AMC: 0.30	AMC: 1.30	AMC: 1.3	AMC: 8.6	AMC: 5.33
MAC-EQS*: 20.0	MAC-EQS: ≤ 0.45 (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)	MAC-EQS: 88.0	MAC-EQS: 2.60	MAC-EQS: 5.70	MAC-EQS: 14.0	MAC-EQS: 34.0	MAC-EQS: 76.00

** Annual mean concentration (AMC)*
***Maximum allowable concentration (MAC-EQS)*

Quality control

To ensure the reliability of the collected data, several quality control measures were rigorously implemented throughout the study (UNEP/MEDWG.509/26). The ICP-MS was calibrated daily before each series of analyses using standard solutions of the relevant metals. Blank measurements were performed during the analysis to monitor contamination originating from reagents and equipment. All samples were analysed in triplicate to assess within-sample variability. The certified reference material (UME CRM 1206) for seawater was also analysed to verify the accuracy of the results. The interlaboratory test (Quasimeme AQ3 round 2018.2) was participated and successful results were obtained.

Results

A total of 56 sampling stations were selected in the Black Sea (Fig.1) for the study. Seven sampling expeditions were conducted between 2021 and 2024, four in July and three in February. The minimum, maximum, and average values of temperature, salinity, pH, Secchi disk depth, dissolved oxygen, and chlorophyll-a concentrations measured at all sampling stations during the summer and winter seasons from 2021 to 2024 are given in Table 2.

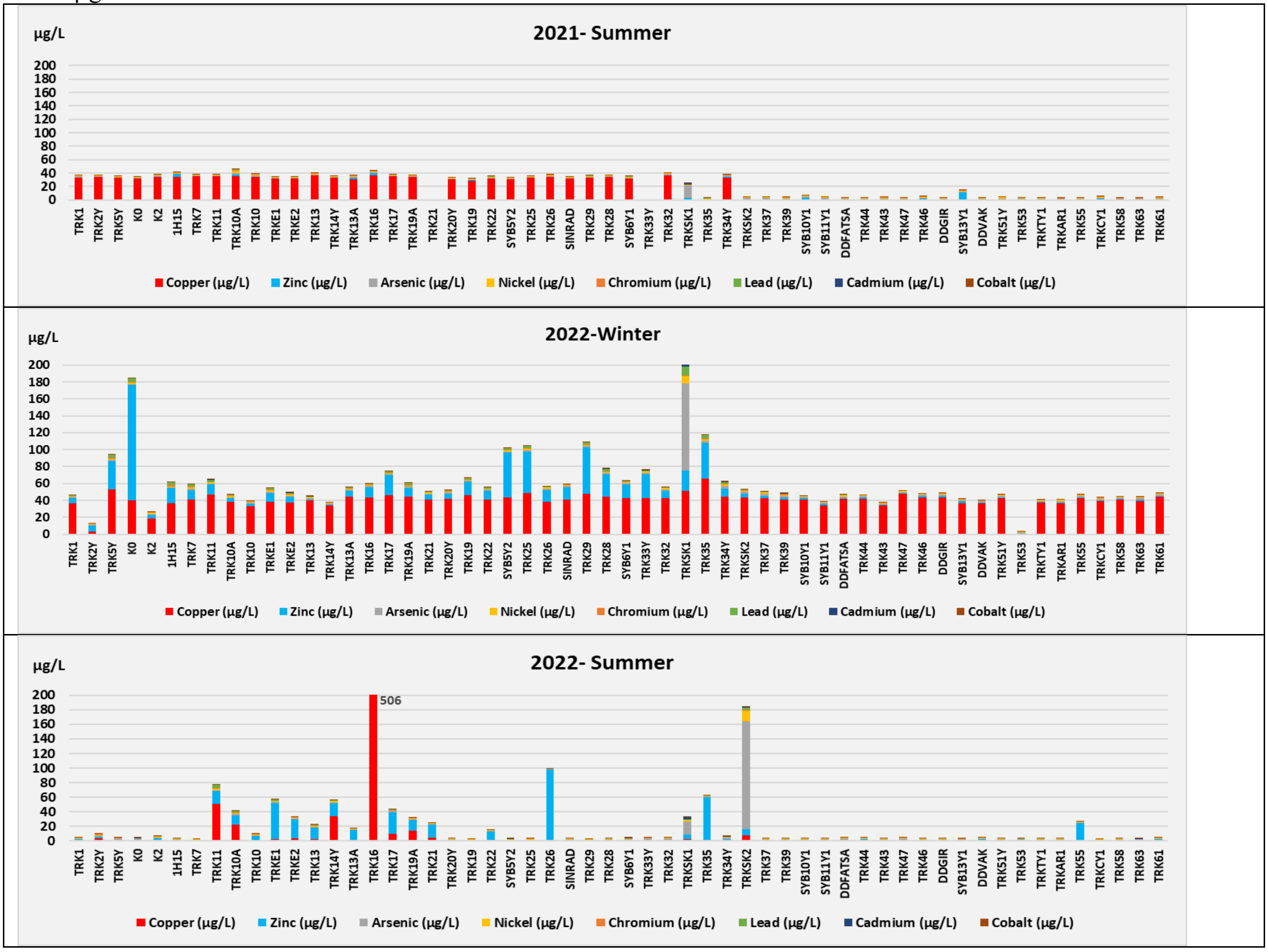
Table 2. Summary of summer and winter seasons and spatial changes of physicochemical parameters in Black Sea seawater.

Year/ Season	Concentration	Temperature (°C)	Salinity (PSU)	pH	DO (mg/L)	CHL-a (µg/L)	Secchi Disk Depth (m)
2021 Summer	N	57	57	57	57	57	47
	Range	23.15-26.40	13.96-18.45	8.24-8.56	6.74-8.40	<0.05-9.46	0.50-12.50
	Mean±std	24.7±0.74	17.68±0.98	8.32±0.05	7.59±0.35	1.19±1.69	5.06±2.70
2022 Winter	N	56	56	56	56	56	52
	Range	7.19-9.73	14.59-18.67	8.17-8.39	8.69-10.84	0.32-7.59	0.20-11.00
	Mean±std	8.61±0.61	18.08±0.69	8.29±0.04	9.65±0.47	2.04±1.48	4.69±2.68
2022 Summer	N	56	56	56	56	56	52
	Range	22.82-26.19	17.54-18.59	8.09-8.32	5.80-8.40	0.20-7.24	1.50-13.00
	Mean±std	24.80±0.75	18.25±0.22	8.28±0.03	7.23±0.57	0.87±1.06	5.87±2.59
2023 Winter	N	56	56	56	56	56	51
	Range	7.39-9.91	15.68-18.67	8.10-8.39	7.88-10.05	0.21-3.24	0.20-11.00
	Mean±std	9.05±0.56	18.13±0.56	8.26±0.05	9.45±0.39	1.32±0.79	4.54±2.41
2023 Summer	N	54	54	54	54	53	51
	Range	23.39-28.15	14.83-18.52	8.29-8.45	6.01-9.17	0.15-1.83	2.00-14.40
	Mean±std	25.87±1.44	17.80±0.60	8.38±0.04	7.63±0.52	0.57±0.38	7.50±2.28
2024 Winter	N	52	52	52	53	53	44
	Range	8.22-11.54	16.37-18.73	8.18-8.35	8.62-10.82	0.59-4.53	0.50-13.00
	Mean±std	10.03±0.93	18.35±0.50	8.30±0.03	9.79±0.51	1.45±0.85	6.72±2.37
2024 Summer	N	56	56	54	55	53	52
	Range	24.06-27.97	16.12-18.84	8.25-8.37	6.63-7.97	0.08-4.83	0.50-13.00
	Mean±std	26.49±0.86	17.83±0.52	8.32±0.03	7.32±0.28	0.56±0.67	6.96±2.53

Table 3. Heavy metal concentrations in the surface waters of the Black Sea.

Year/ Season	Concentration	As (µg/L)	Cd (µg/L)	Co (µg/L)	Cr (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
2021 Summer	N	55	55	55	55	55	55	55	55
	Range	0.91-18.02	0.01-1.69	0.05-0.59	0.18-1.84	0.03-36.90	0.77-3.48	0.02-0.49	0.08-11.20
	Mean±std	1.86±2.25	0.10±0.26	0.09±0.08	0.33±0.24	18.21±16.81	1.13±0.37	0.06±0.09	0.77±1.75
2022 Winter	N	56	56	56	56	56	56	56	56
	Range	1.09-102.88	0.03-7.61	0.04-0.59	0.14-1.56	0.62-65.52	0.73-8.76	0.02-10.27	0.24-136.33
	Mean±std	3.40±13.54	0.21±1.01	0.11±0.08	0.51±0.33	40.04±9.56	1.35±1.04	1.22±1.66	12.84±21.60
2022 Summer	N	56	56	56	56	56	56	56	56
	Range	0.70-147.72	0.01-3.51	0.04-0.95	0.09-1.89	0.33-450.54	0.58-15.00	0.02-3.78	0.08-96.75
	Mean±std	4.31±19.63	0.14±0.52	0.08±0.12	0.29±0.34	13.79±62.70	1.23±1.90	0.33±0.76	9.05±17.85
2023 Winter	N	56	56	56	56	54	56	56	56
	Range	0.73-26.97	0.02-11.22	0.06-1.56	0.15-53.35	10.37-200.35	0.67-55.48	0.02-5.97	0.08-66.67
	Mean±std	2.32±4.48	0.34±1.58	0.15±0.21	2.59±7.18	38.59±31.61	2.68±7.27	0.67±1.21	5.12±11.64
2023 Summer	N	54	54	54	54	54	54	54	54
	Range	0,89-2.89	0.02-0.43	0.06-0.36	0.11-1.15	0,03-10,06	0.63-1.59	0.02-0.78	0.08-25.61
	Mean±std	1.33±0.35	0.06±0.07	0.10±0.04	0.31±0.16	0.66±1.57	0.99±0.18	0.08±0.14	5.16±4.56
2024 Winter	N	53	53	53	53	53	53	53	53
	Range	0.30-9.61	0.01-1.37	0.01-0.32	0.07-5.20	0.76-23.52	0.23-3.50	0.31-4.92	5.25-74.18
	Mean±std	1.50±1.26	0.10±0.19	0.08±0.04	0.99±0.92	5.12±4.13	1.24±0.57	1.73±1.04	33.97±16.00
20214 Summer	N	55	55	55	55	55	55	55	55
	Range	0.38-1.85	0.01-0.11	0.01-0.08	0.06-0.41	0.13-2.35	0.28-1.29	0.02-0.22	0.08-11.99
	Mean±std	1.28±0.27	0.07±0.02	0.05±0.01	0.19±0.06	0.56±0.37	0.91±0.20	0.03±0.04	1.28±1.88

During the summer sampling periods, surface seawater temperatures ranged 22.89-28.15°C, while during the winter sampling periods they ranged 7.19-11.54°C. Throughout the sampling periods, salinity ranged 13.96-18.84 and pH 8.09-8.56. The low salinity values correspond to the areas of transitional water which are influenced by the input from the river. In the surface seawater, dissolved oxygen (DO), chlorophyll-a (Chl-a) and Secchi disk depth ranged 5.80-9.17 mg/L, <0.05-9.46 µg/L and 0.50-14.40 m, respectively, during the summer period. In the winter period these values ranged 7.88-10.84 mg/L for DO, 0.21-3.24 µg/L for Chl-a and 0.20-13.00 m for Secchi disk depth. The lowest chlorophyll-a values were recorded at the stations located in the open sea waters of the western Black Sea, far away from any anthropogenic pressure (1H15, TRK5Y). The highest chlorophyll-a values were recorded during the winter season at the stations located near the Sakarya River (TRK10A, TRK11) and the Yeşilırmak River (TRK37), the Samsun deep sea discharge station (TRKSK1) and the Samsun Terme station (SYB10Y1). The lowest Secchi disk values were found at stations influenced by river inputs during the weeks with rainfall. The concentrations of metals present in the seawater samples have been summarised in Table 3. The findings demonstrate that the concentrations of different metals, including As, Cd, Co, Cr, Cu, Ni, Pb and Zn, were within the range of 0.30-147.72 µg/L, 0.01-11.22 µg/L, 0.01–1.56 µg/L, 0.06–53.35 µg/L, 0.03–450.54 µg/L, 0.23-55.48 µg/L, <0.02-10.27 µg/L and <0.08-136.33 µg/L, respectively. It is evident that spatial variations in measurement results are caused by differences in activities within the region. Furthermore, the spatial variability of naturally occurring pollutants must be taken into account. The concentrations of heavy metals were found in the following order Cu > Zn > As > Ni > Cr > Pb > Cd > Co (Table 3, Fig.2). In general, it was observed that the concentrations of heavy metals were higher in the winter than in the summer. Copper was found to have higher concentrations than other heavy metals throughout the Turkish Black Sea coastline during the winter seasons of 2022 and 2023. Similarly, Zinc showed higher concentrations in the western and central Black Sea in winter 2023 and throughout the Black Sea in winter 2024 (Fig.2). The spatial distribution of Cu and Zn suggests contributions from rivers in the Black Sea and from a variety of other coastal sources. The highest arsenic concentrations were found at stations TRKSK1 and TRKSK2 near the deep-sea discharge area in Samsun. Nickel was generally detected in low concentrations. During the seven sampling periods between 2021 and 2024, elevated levels were recorded only once, in the winter of 2023, at the TRKE2 station in Ereğli (TRKE2: 55,47 µg/L). In the other six sampling periods monitored in Ereğli, an average concentration of 1.28 µg/L was recorded. Similar results were obtained over all seven sampling periods at TRKE1, which is located close to TRKE2 (mean 1.21 µg/L). The TRKE2 station was followed by other stations affected by deep sea discharges, including Samsun (TRKSK1: 8.76 µg/L and 6.47 µg/L in the winters of 2022 and 2023, respectively, and TRKSK2: 14.99 µg/L in the summer of 2022) and Vakfıkebir (DDVAK: 6.05 µg/L in the winter of 2023). The highest chromium concentrations, similar to those of nickel, were found at the TRKE2 station in the winter of 2023 (53.35 µg/L), followed by the DDVAK station (12.73 µg/L) and the TRK13 station in Zonguldak (7.98 µg/L) during the same period. In other monitoring periods, chromium concentrations below 1.00 µg/L were detected at these stations (Fig.3). Lead (Pb) originates mainly from industrial discharges, vehicle exhaust and oil leaks from boats (Mathivanan ve Rajaram, 2013; Maria et al. 2004). The highest concentration of Pb was measured only once, at the TRKSK1 station, in the winter of 2022. In the Black Sea, the concentrations of Pb and Co have shown low levels (Fig.3), with a relatively narrow range of variability and a even distribution throughout the study area. The concentrations of cadmium were notably high at the TRKSK1 and TRKSK2 stations, indicating the influence of the deep sea discharges. In addition, once elevated cadmium concentration was measured near the mouths of the Filyos River (TRK16: 1.02 µg/L in the summer of 2021) and the Yeşilırmak River (TRK37: 1.17 µg/L in the winter of 2023).



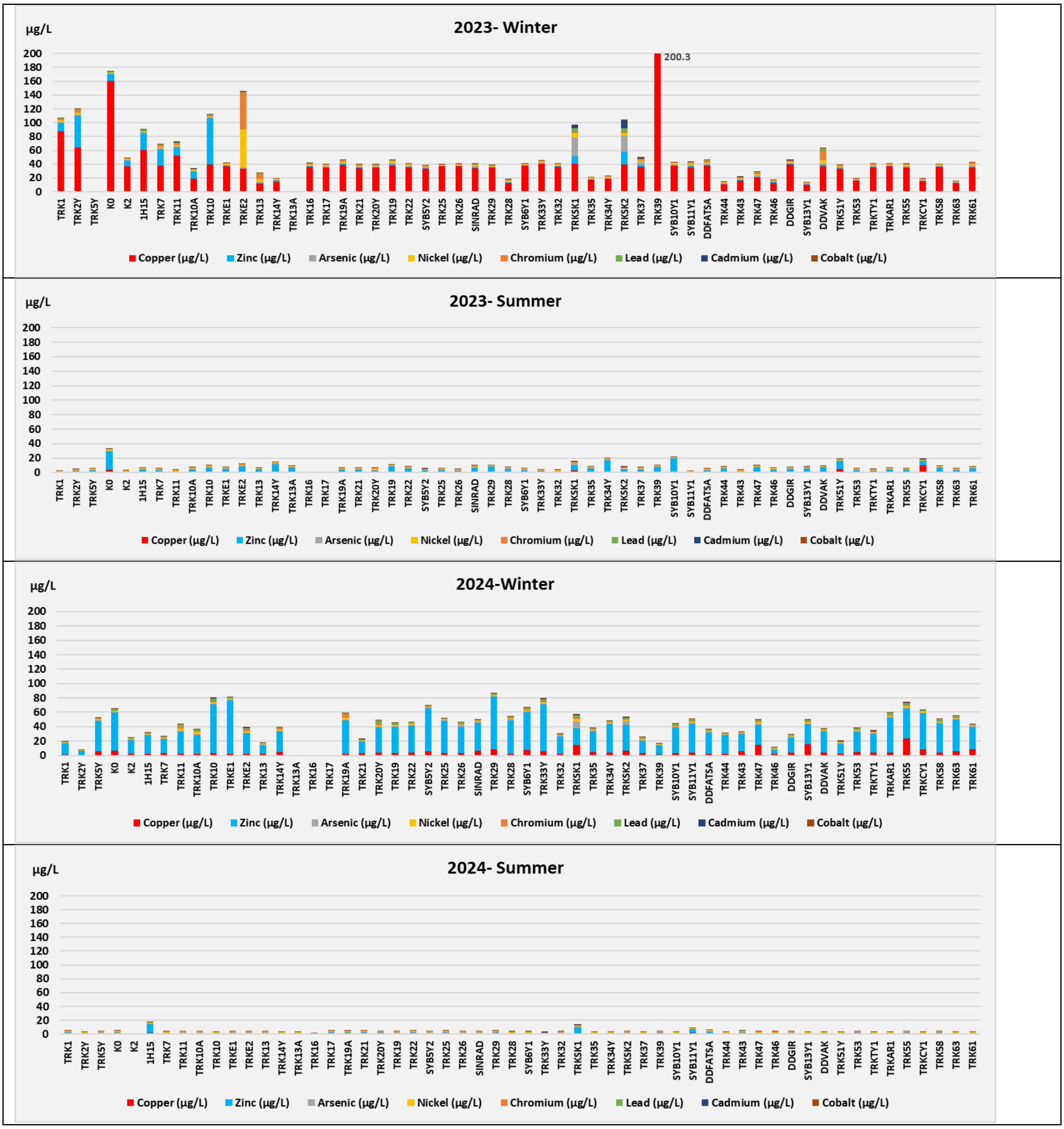
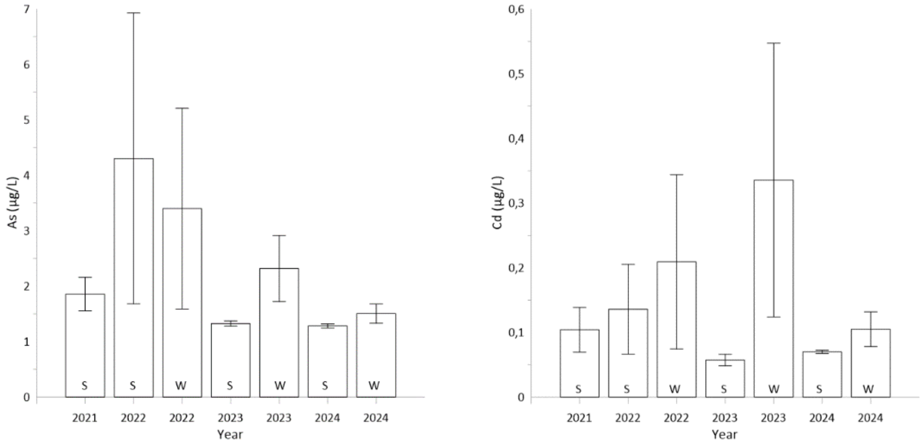


Fig. 2. Spatial and temporal variations of heavy metals in the surface seawater in the Black Sea



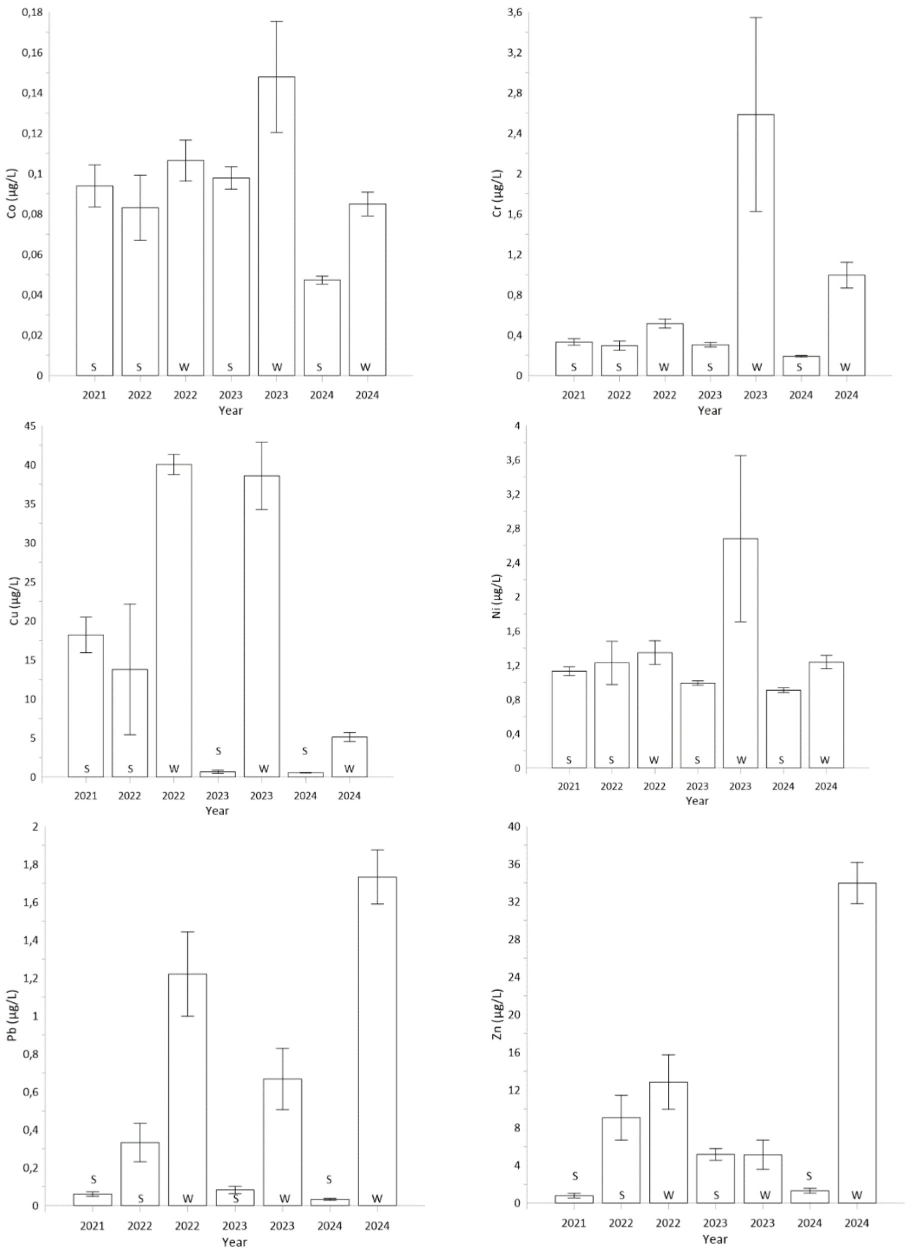


Fig. 3. Seasonal variations of the concentration of heavy metals in the surface sea water of the Black Sea coast of Türkiye. Error bars indicate standard errors. (S: Summer; W: Winter)

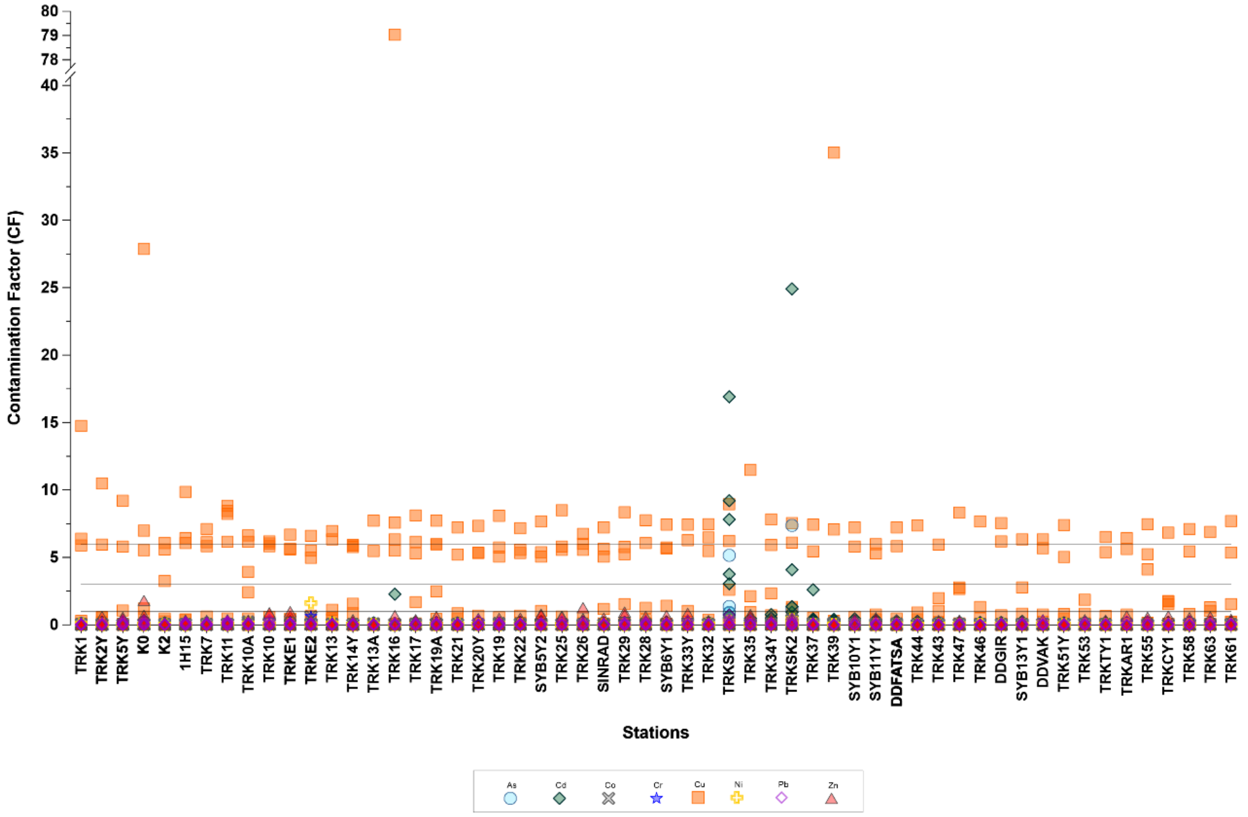
Table 4. Rates of heavy metals exceeding Türkiye's Environmental Quality Standards (MAC-EQS) in 382 samples collected from 56 stations between 2021 and 2024.

	Cu	Zn	As	Ni	Cr	Pb	Cd	Co
Number of samples (N) which exceed the MAC-EQS for heavy metals	163	2	4	1	0	0	10	0
%	42.78	0.52	1.05	0.26	0.00	0.00	2.62	0.00
MAC-EQS (µg/L) (YSKY, 2023)	5.70	76.00	20.00	34.00	88.00	14.00	0.45	2.60
CF	0.01-79.04	0.00-1.79	0.01-7.39	0.01-1.63	0.00-0.61	0.00-0.73	0.02-24.93	0.00-0.60
CD	0.08-80.08 (all heavy metals) 0.05-27.00 (except Cu)							

Discussion and Conclusion

Heavy metal concentrations in the Black Sea were assessed according to the Seawater Quality Standards of Türkiye (YSKY, 2023) (Table 4). In general, based on the total number of sea water samples analysed along the Black Sea coast of Türkiye, 42.78% of the samples exceeded the established MAC-EQS value for Cu; about 2.62%, 1.05%, 0.52% and 0.26% exceeded that for Cd, As, Zn and Ni respectively. Cr, Pb and Co showed low concentrations, these metals remained without any contribution.

The concentrations of the heavy metals in seven periods (4 in summer and 3 in winter) were used for the calculation of the CFs and CDs (Table 4). The heavy metal contamination levels were assessed on the basis of the CF and CD value standards (Table 4, Fig.4 and Fig.5). The CF values of Cu, Zn, As, Ni, Cr, Pb, Cd and Co have ranges of 0.01-79.04, 0.00-1.79, 0.01-7.39, 0.01-1.63, 0.00-0.61, 0.00-0.73, 0.02-24.93 and 0.00-0.60, respectively. CF values exceeding 1 signify metal enrichment in the sea water relative to established Environmental Quality Standards (Udayakumar et al., 2011). This result demonstrates the high contamination pressure of Cu in the Black Sea. The concentrations of Cu exceeded Türkiye seawater quality standard in winter seasons. According to the CF values, 57.3% of the measurement results were classified as having low, 7.6% as moderate, 8.9% as considerable, and 26.2% as very high levels of copper contamination. Due to the high CF values for copper, Figure 5 has been created alongside Figure 4 to provide a clearer understanding of the distribution of other heavy metals. The CF values for As and Cd at stations TRKSK1 and TRKSK2, which are influenced by the Samsun deep sea discharge, were observed to occasionally reach considerable and high levels (Fig.5). The CF values of Pb, Cr, Ni, Cd and Co were all <1 in the surface sea waters of the study area. Two different results were obtained in the CD calculations: one including all metals and the other excluding copper results (Table 4, Fig.4 and Fig.5). When all metal results were included, the CD values ranged from 0.08 to 80.08. When copper was excluded, the CD values ranged from 0.05 to 27.00. The CD values were 66.0% at low and 30.9% at moderate contamination levels when all metals were included. However, when copper was excluded, the CD values were (98.7%) at low contamination levels.



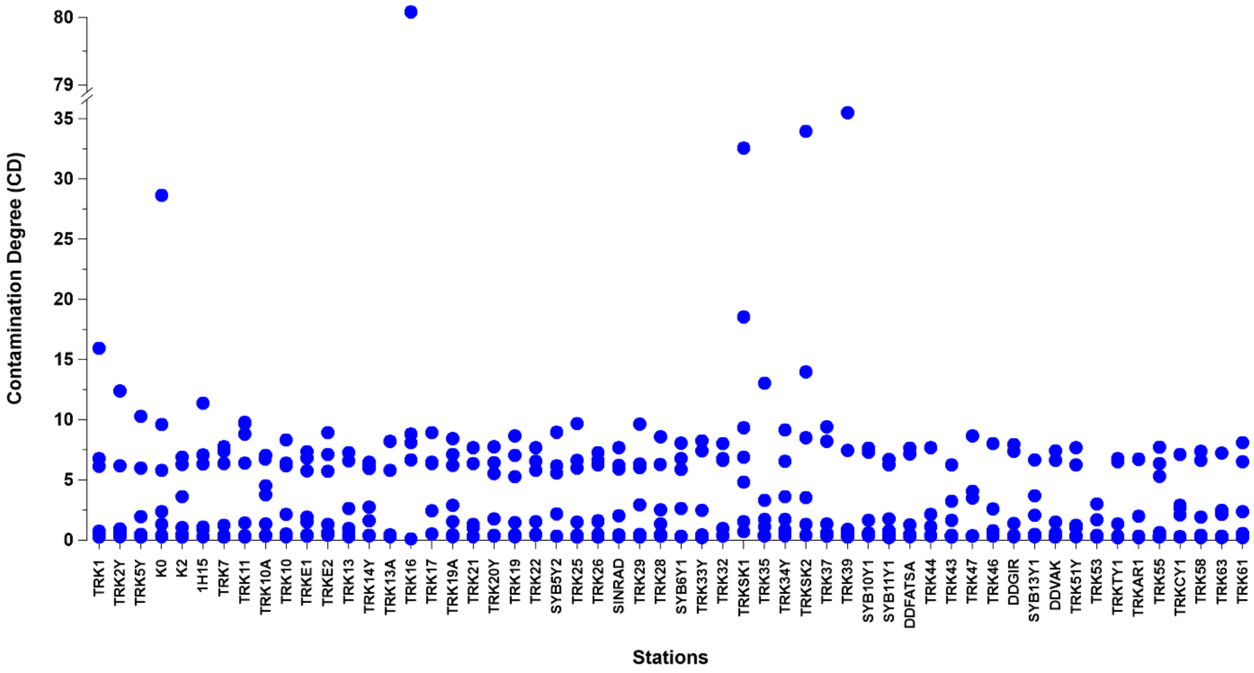
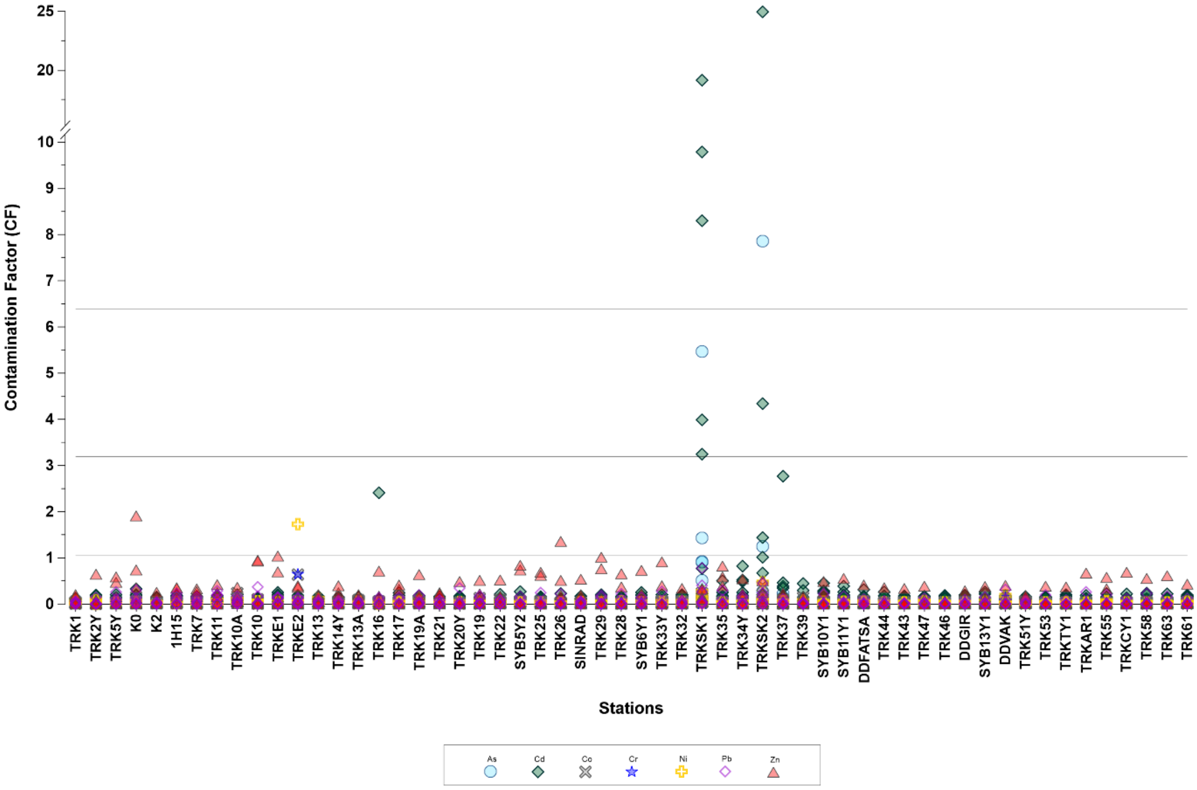


Fig. 4. Contamination Factor (CF) and Contamination Degree (CD) for heavy metals in the Black Sea



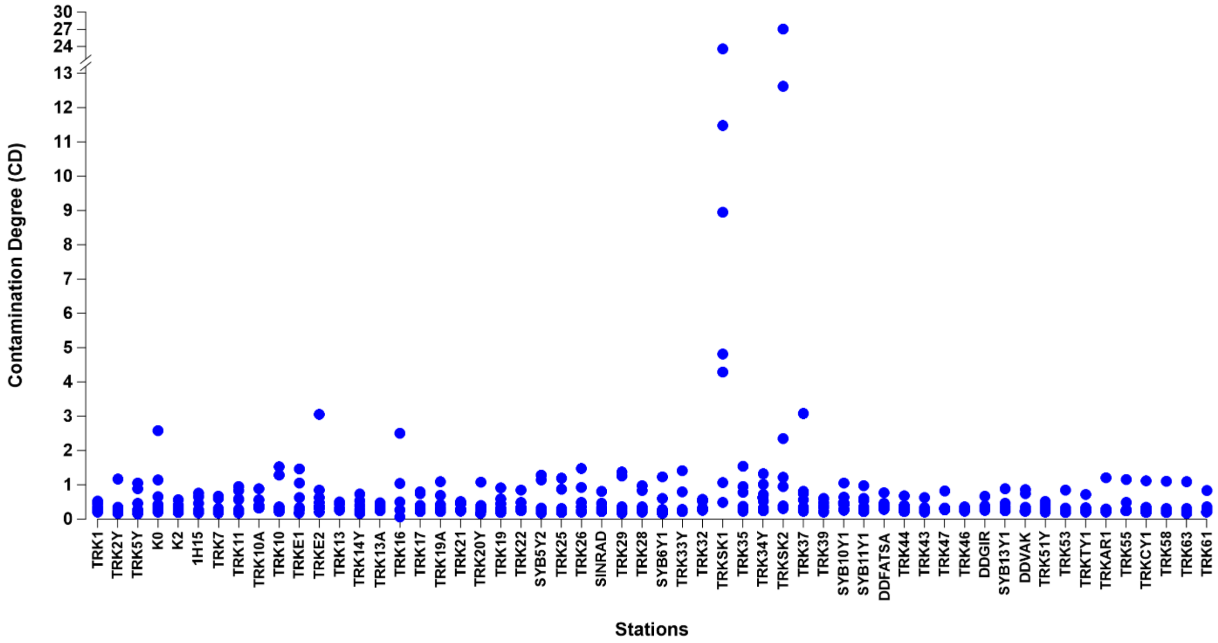
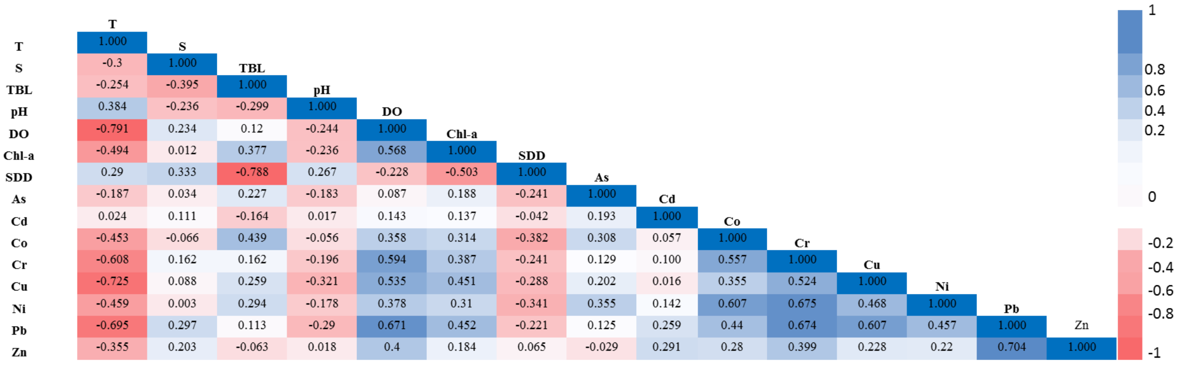


Fig. 5. Contamination Factor (CF) and Contamination Degree (CD) for heavy metals other than copper in the Black Sea

The strength and direction of the relationships between dissolved heavy metal concentrations and physicochemical parameters are shown in Table 5, as indicated by the correlation coefficients. Concentrations of all heavy metals, except for Cd, showed a significant negative correlation with temperature. In particular, Cu, Cr, and Pb exhibited a strong negative relationship with temperature, which corresponding to higher concentrations in winter compared to summer. No correlations were observed between salinity and any of the metals. A relationship might have been established if the sampling points, particularly those near river inputs, had been located within transitional waters. The negative correlation between dissolved oxygen and temperature resulted in a positive correlation between dissolved oxygen and metal concentrations. Metals also showed a positive correlation with chlorophyll-a, especially Cu and Pb. The seasonal variation of copper concentrations, an essential nutrient for phytoplankton growth and metabolic processes, may also be influenced by phytoplankton activity. No dissolved metals were correlated with turbidity or Secchi disk depth. The correlation analysis among the metals revealed that Zn exhibited a positive relationship only with Pb, which represented the strongest correlation among the metals. Additionally, Pb, Cr, Cu, Ni, and Co were positively correlated with each other. These metals are commonly associated with activities such as the manufacturing of chemical fertilisers and nitrogen compounds, manufacturing of iron and steel products and ferroalloys, copper production, and operations in urban waste water. No correlation was found between Cd and any other metal (Table 5).

Tablo 5. Spearman's rank correlation matrix for dissolved heavy metal concentrations and seawater physicochemical parameters



	T	S	TBL	pH	DO	Chl-a	SDD	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
T	1.000														
S	-0.3	1.000													
TBL	-0.254	-0.395	1.000												
pH	0.384	-0.236	-0.299	1.000											
DO	-0.791	0.234	0.12	-0.244	1.000										
Chl-a	-0.494	0.012	0.377	-0.236	0.568	1.000									
SDD	0.29	0.333	-0.788	0.267	-0.228	-0.503	1.000								
As	-0.187	0.034	0.227	-0.183	0.087	0.188	-0.241	1.000							
Cd	0.024	0.111	-0.164	0.017	0.143	0.137	-0.042	0.193	1.000						
Co	-0.453	-0.066	0.439	-0.056	0.358	0.314	-0.382	0.308	0.057	1.000					
Cr	-0.608	0.162	0.162	-0.196	0.594	0.387	-0.241	0.129	0.100	0.557	1.000				
Cu	-0.725	0.088	0.259	-0.321	0.535	0.451	-0.288	0.202	0.016	0.355	0.524	1.000			
Ni	-0.459	0.003	0.294	-0.178	0.378	0.31	-0.341	0.355	0.142	0.607	0.675	0.468	1.000		
Pb	-0.695	0.297	0.113	-0.29	0.671	0.452	-0.221	0.125	0.259	0.44	0.674	0.607	0.457	1.000	
Zn	-0.355	0.203	-0.063	0.018	0.4	0.184	0.065	-0.029	0.291	0.28	0.399	0.228	0.22	0.704	1.000

The potential sources and interrelationships of dissolved heavy metals in surface waters were further analyzed using Principal Component Analysis (PCA) and annual monitoring data. The correlation between metals was assessed prior to PCA (Tablo 5), with Cu and Zn metals omitted from the evaluation. PCA sampling adequacy was calculated with the Kaiser-Meyer-Olkin (KMO) test. The KMO statistical value was 0.585, which is a satisfactory PCA value. These values collectively explain 79.73% of the total variance in dissolved heavy metals. PC1 and PC2, respectively, accounted for 51.17% and 28.558% of the total variance (Table 6).

Co, Cr and Ni mainly contribute to PC1. Ni, Cr, and Co originate from various anthropogenic sources, including the iron and steel industry, the inorganic chemical industry, and landfill leachate. Co, Ni, and Cr are commonly utilized in the coating industry, primarily to prevent corrosion of products and enhance their durability (Díaz-de-Alba et al., 2021). Cd, As, Pb and Co primarily contribute to PC2. The metals contributing to PC2 primarily originate from the fertilizer and copper industries (Altas and Büyükgüngör 2007; Ustaoğlu et al., 2024).

Tablo 6. Result of the first two PCs for dissolved heavy metals

	PC1	PC2
Ni	0.980	
Cr	0.962	
Co	0.860	0.391
Cd		0.848
As		0.810
Pb		0.755

The present study focuses on the spatial distribution of surface metal concentrations along the Black Sea. The results demonstrate that the four coastal regions, Sakarya and Ereğli in the western Black Sea, Samsun in the central Black Sea, and between Trabzon and Hopa in the east Black Sea, differ significantly from other coastal areas in terms of metal pollution. Additionally, the results of the principal component analysis (PCA) indicate a clustering of metal sectors from the PCA1 and PCA2 groups within these geographical areas.

In the risk assessment of metals, the reference values given in the Türkiye regulations for priority pollutants were used. However, the current thresholds, particularly for copper, do not adequately characterise the Black Sea. It is recommended that long-term seasonal monitoring be carried out in order to revise the thresholds for heavy metals in seawater. The results of the heavy metals in the sea water obtained in areas where there is no pressure can be used as reference values in future studies.

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