Regional Studies in Marine Science 50 (2022) 102169

Contents lists available at ScienceDirect

Regional Studies in Marine Science

journal homepage: www.elsevier.com/locate/rsma

Investigation of spatial and seasonal variation of water quality along the mid-Black Sea coast (from Sinop to Ordu) of Turkey, by multivariate statistical techniques

Sevde Üstün Odabaşı [a,*], Zeynep Ceylan [b], İlknur Şentürk [c], Feryal Akbal [a], Gülfem Bakan [a], Hanife Büyükgüngör [a]

[a] Engineering Faculty, Environmental Engineering Department, Ondokuz Mayis University, Samsun, 55200, Turkey
[b] Engineering Faculty, Industrial Engineering Department, Samsun University, Samsun, 55420, Turkey
[c] Engineering Faculty, Environmental Engineering Department, Sivas Cumhuriyet University, Sivas, 58140, Turkey

ARTICLE INFO

Article history:
Received 7 September 2021
Received in revised form 6 January 2022
Accepted 6 January 2022
Available online 13 January 2022

Keywords:
Black Sea
Monitoring
Heavy metals
Statistical analysis
Physicochemical parameters

ABSTRACT

The Black Sea is a closed basin surrounded by six countries and is the last spill point for the rivers from different watersheds. Due to these discharges from surrounding countries, the Black Sea is exposed to high and moderate pollution levels. Therefore, monitoring water quality changes in the mid-Black Sea coastal area is necessary to develop pollution control strategies. This study aims to examine the temporal and spatial changes of seawater quality along the mid-Black Sea coast of Samsun, Turkey. The samples were collected from 13 monitoring stations from the three distances in four seasons in 2013. The samples were analyzed for 22 parameters: nitrate-nitrogen (NO_3-N), ammonium-nitrogen (NH_4-N), phenol, methylene blue active substances (MBAS), total carbon (TC), total inorganic carbon (TIC), total organic carbon (TOC), iron (Fe), aluminum (Al), manganese (Mn), chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), pH, temperature (T), dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS) and salinity. Multivariate statistical techniques (Principal component analysis (PCA), factor analysis (FA), and cluster analysis (CA)) were applied to analyze seawater quality variations. Factor analysis of seawater chemical variables was found to be eight factors in total. These eight factors account for 79.13%, 82.27%, 78.60%, and 78.69% of the total variances in winter, spring, summer, and fall, respectively. Cluster analysis classified the monitoring sites into two groups based on similarities of seawater characteristics.

1. Introduction

The Black Sea is a semi-enclosed sea highly exposed to anthropogenic effects due to the great catchment area and isolated nature (UNEP, 2018). The catchment area of the Black Sea is very large, with a total surface area of 2 million km^2, which is about five times the surface area of the Black Sea. Pollution carried from the provinces bordering the Black Sea constitutes a significant burden. In addition, the uneven distribution of the population living on the Black Sea coast is another factor affecting pollutant concentrations (EEA, 2015). Anthropogenic pollutants such as organic matter, nutrients, agricultural and industrial pollutants, and toxic wastes from towns, cities, farms, and factories flow into the Black Sea (Akbal et al., 2011a; Arici and Bat, 2017; Baltas et al., 2017; Şimşek et al., 2021; Topcuoğlu et al., 2003; Üstün Odabaşı et al., 2018). Considering that about 90% of seawater is naturally anoxic, the Black Sea is highly susceptible to anthropogenic effects (Altaş and Büyükgüngör, 2007). The strong density stratification inhibits vertical mixing, and the deep waters are not ventilated by lateral currents, leading the Black Sea towards a point of no return (Bat et al., 2018). For this reason, it is important and necessary to conduct seawater quality monitoring studies to prevent seawater pollution and to obtain information about the current situation.

Samsun, which has a population of approximately 1.2 million, is one of the important cities that carry pollution to the Black Sea. The 1355 km long Kızılı rmak River with a catchment area of 78,180 km^2 flows into the Black Sea from Samsun's Bafra district, while the 418 km long Yeşilırmak River with a 36,100 km^2 basin area flows into the Black Sea from the Çarşamba district of Samsun (Büyükgüngör et al., 2014). Although these two major rivers carry a significant amount of anthropogenic

---

* Corresponding author.
E-mail addresses: sevde.ustun@omu.edu.tr (S. Üstün Odabaşı), zeynep.ceylan@samsun.edu.tr (Z. Ceylan), ilknursenturk@cumhuriyet.edu.tr (İ. Şentürk), fakbal@omu.edu.tr (F. Akbal), gbakan@omu.edu.tr (G. Bakan), hbuyukg@omu.edu.tr (H. Büyükgüngör).

https://doi.org/10.1016/j.rsma.2022.102169

waste, data on the pollution status of Samsun and its surrounding coasts (seawater) are rare and need to be investigated. The only way to obtain information about the current state of seawater and coastal waters is to conduct research in which temporal and spatial changes are monitored with regular monitoring programs. Since such studies will provide important data on the current pollution loads and their sources, it will be ensured that the authorities take steps to solve the problem.

Multivariate statistical analyzes allow for easier interpretation of data by helping to identify the main factors of variances of a system. In this way, it is aimed to reduce the number of variables by simplifying while preserving the original data (Ouyang et al., 2006; Shrestha and Kazama, 2007). Principal component analysis (PCA), factor analysis (FA), cluster analysis (CA), and discriminant analysis (DA) are frequently used to identify pollution sources in the temporal and spatial monitoring of seawater quality (Su et al., 2011; Zhou et al., 2007). Multivariate statistical methods were used to interpret the analysis results, to identify and evaluate the potential risks of the pollution source to the Black Sea.

In this study, the mid-Black Sea region was chosen as the target region (Samsun, Ordu, Sinop provinces), and it was aimed to define the seasonal and spatial changes of seawater in the coastline of this region. The effect of pollution caused by domestic, agricultural, and industrial discharges has been monitored by sampling from selected points. In addition, statistical interpretation of the data was made in order to reveal the pollution situation. This study, in which the pollution situation in the Black Sea is analyzed, contains significant findings for researchers and decision-makers.

2. Material and methods

2.1. Monitoring area

Fig. 1 demonstrates the location of 13 sampling stations chosen for monitoring seawater quality of the mid-Black Sea coast of Turkey. The main locations are Sinop, Yakakent, Bafra (Kızılırmak), Engiz, Kurupelit, Atakum, Samsun Harbour, Tekkeköy (Organized Industrial Zone (OIZ)), Çarşamba (Yeşilırmak), Terme, Ünye, Fatsa, and Ordu. Samples were taken and analyzed in winter (January), spring (April), summer (July), and autumn (November) season in 2013 from three distances; short distance 0.310 miles (0.5 km), mid-distance 3 miles (4.8 km), and long-distance 20 miles (32.1 km) were selected to understand the distribution of pollutants. The locations of sampling points are given in Table 1 according to latitude and longitude, which were taken with the help of GPS.

2.2. Sample collection and analytical methods

Seawater samples were taken from almost 1-meter depth with the help of the Nansen bottle. 5 L polyethylene bottles were used to collect seawater samples. Bottles were pre-washed with water sample at the collection point. Sample bottles were kept in ice boxes while being transported to the laboratory. For the metal analysis, the samples brought to the laboratory were filtered using a membrane filter with the pore size of 45 μm and transferred to 100 ml brown glass bottles, previously washed with 10% nitric acid, and dried at 40 °C. These bottles were then kept in the refrigerator at 4 °C until analysis. Dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS), salinity, pH, and temperature (T) were measured in situ using a field multi-probe (Consort C335). Water quality parameters such as ammonium-nitrogen (NH_4–N), nitrate-nitrogen (NO_3–N), methylene blue active substances (MBAS), and phenol were measured by using UV/VIS spectrometer (PG T70). Total carbon (TC), total organic carbon (TOC) and total inorganic carbon (TIC) in seawater samples were analyzed on the same day with Apollo 9000 TOC Analyzer. Metals Iron (Fe), aluminum (Al), manganese (Mn), chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb) were analyzed with ICP-OES (Perkin Elmer Optima 4300DV). LGC standard Nass-6 reference material was used for ICP-OES measurements.

2.3. Data analysis and multivariate statistical methods

Among the multivariate statistical techniques PCA, FA and CA techniques were used to calculate the data set of seawater quality. The SPSS 13.0 software package was used for the multivariate statistical calculations. PCA is a statistical technique used in the interpretation of multivariate, complex and non-directly interpretable data. (Hsu et al., 2016). Its goal is extracting important information from data summarizing patterns in multivariate data set, and reducing numbers of variables in analyses (Jafarzadegan et al., 2019; Syms, 2019). Here, we used PCA to define the correlation and impact factors of water quality parameters with metals. FA tries to extract a lower dimensional linear structure from the data set. FA is a method of collecting many variables under several headings. PCA/FA were done on the correlation matrix of reorganized data. CA is a techniques that are used to classify objects or cases into related groups called clusters (Akbal et al., 2011b). CA helps in interpreting the data and indicates the contaminant patterns (Akbal et al., 2011b; Arora, 2014). CA was used to determine the relationship between the sampling points.

3. Result and discussion

3.1. Characterization of seawater

The mean, maximum, minimum, and standard deviation values of 22 parameters examined in seawater are shown in Table 2.

The pH value of seawater samples is between 6.5–8.5. The highest EC values were measured at Kurupelit and Samsun Harbor stations (30 μS/cm). It has been determined that there was no significant difference between sampling stations for these parameters, and the obtained results were compatible with the literature (Bat et al., 2019; Akbal et al., 2011b; Baltas et al., 2017; Gokkus and Berber, 2019). In addition, it was determined that both pH (6.5–8.5) and EC (<300 μS/cm) values were in accordance with the reference values defined in the Surface Water Quality Regulation (SWQR) of Turkey. When the lowest and highest values of TC, TIC, and TOC concentrations were examined, they were detected in the range of 33.340–53.440, 30.470–50.170, and 2.226–4.554 mg/L, respectively. In a similar study conducted between 2007 and 2008, TOC analyses were performed on seawater samples taken from Atakum and Kurupelit stations. In the study, TOC analysis results were found as 2.9719 and 2.7892 mg/L for Atakum and Kurupelit stations, respectively (Bakan et al., 2014). In the present study, TOC values of Atakum and Kurupelit stations were found to be 2.795 and 2.855 mg/L, respectively. According to the similar results of both studies, the TOC value in seawater remained constant, and it is thought that it was not exposed to any organic pollution. Nitrogen-related pollution in seawater was investigated with NH_4–N and NO_3–N parameters, and the highest values of these parameters were measured at the Samsun Harbor sampling point as 0.954 and 2.391 mg/L, respectively. The NH_4–N parameter in Samsun Harbor is in the medium-class water quality class according to SWQR, while the NO_3–N parameter is in the very good water quality class (SWQR, 2016). According to the US Environmental Protection Agency (EPA) standard, the maximum allowable concentration is 0.02 mg/L for NO_3–N and between 0.02–0.4 mg/L for NH_4–N for the organisms living in seawater

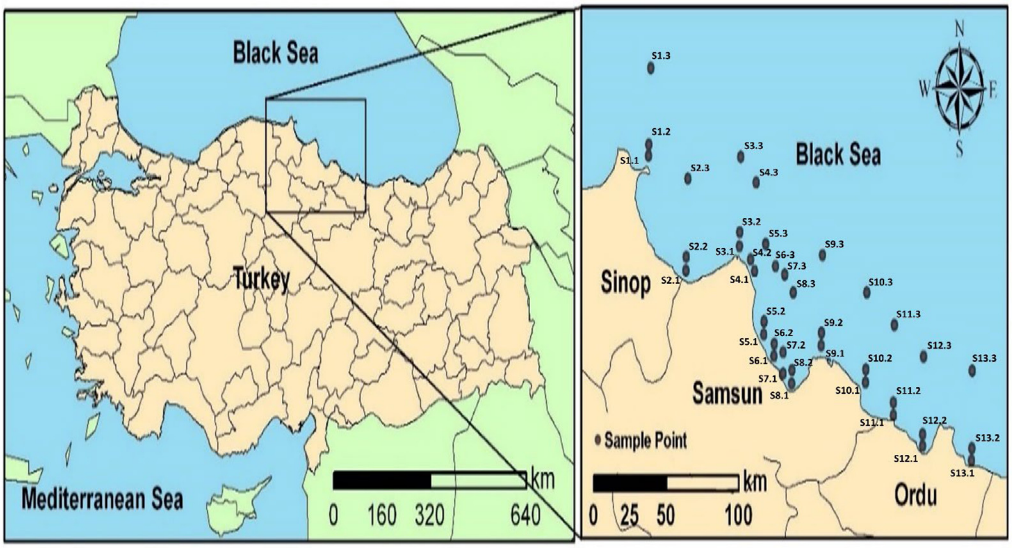

Fig. 1. Location of sampling stations at three distances (Bakan et al., 2017).

Table 1
Distances, codes, latitude, and longitude of sampling stations.

Sampling stations	No		Distance	Latitude–Longitude
Sinop	S1	(1)	0.310 miles	42° 02′ 58″ N – 035° 11′ 23″ E
		(2)	3 miles	42° 05′ 24″ N – 035° 11′ 23″ E
		(3)	20 miles	42° 22′ 12″ N – 035° 11′ 23″ E
Yakakent	S2	(1)	0.310 miles	41° 38′ 18″ N – 035° 31′ 24″ E
		(2)	3 miles	41° 41′ 24″ N – 035° 31′ 24″ E
		(3)	20 miles	41° 58′ 30″ N – 035° 31′ 24″ E
Bafra (Kızılırmak)	S3	(1)	0.310 miles	41° 44′ 32″ N – 035° 57′ 50″ E
		(2)	3 miles	41° 47′ 35″ N – 035° 57′ 50″ E
		(3)	20 miles	42° 04′ 35″ N – 035° 57′ 50″ E
Engiz	S4	(1)	0.310 miles	41° 39′ 10″ N – 036° 05′ 30″ E
		(2)	3 miles	41° 41′ 40″ N – 036° 03′ 30″ E
		(3)	20 miles	41° 58′ 40″ N – 036° 05′ 30″ E
Kurupelit	S5	(1)	0.310 miles	41° 25′ 30″ N – 036° 10′ 45″ E
		(2)	3 miles	41° 28′ 15″ N – 036° 10′ 45″ E
		(3)	20 miles	41° 45′ 15″ N – 036° 10′ 45″ E
Atakum	S6	(1)	0.310 miles	41° 20′ 45″ N – 036° 16′ 00″ E
		(2)	3 miles	41° 23′ 30″ N – 036° 16′ 00″ E
		(3)	20 miles	41° 40′ 30″ N – 036° 16′ 00″ E
Samsun Harbor	S7	(1)	0.310 miles	41° 21′ 45″ N – 036° 20′ 30″ E
		(2)	3 miles	41° 21′ 45″ N – 036° 20′ 30″ E
		(3)	20 miles	41° 38′ 45″ N – 036° 20′ 30″ E
Tekkeköy (OIZ)	S8	(1)	0.310 miles	41° 15′ 00″ N – 036° 25′ 00″ E
		(2)	3 miles	41° 18′ 00″ N – 036° 25′ 00″ E
		(3)	20 miles	41° 35′ 00″ N – 036° 25′ 00″ E
Çarşamba (Yeşilırmak)	S9	(1)	0.310 miles	41° 23′ 40″ N – 036° 39′ 15″ E
		(2)	3 miles	41° 26′ 30″N – 036° 39′ 15″ E
		(3)	20 miles	41° 43′ 30″ N – 036° 39′ 15″ E
Terme	S10	(1)	0.310 miles	41° 16′ 00″ N – 037° 01′ 30″ E
		(2)	3 miles	41° 18′ 45″ N – 037° 01′ 30″ E
		(3)	20 miles	41° 35′ 45″ N – 037° 01′ 30″ E
Ünye	S11	(1)	0.310 miles	41° 09′ 00″ N – 037° 15′ 25″ E
		(2)	3 miles	41° 11′ 50″ N – 037° 15′ 25″ E
		(3)	20 miles	41° 28′ 50″ N – 037° 15′ 25″ E
Fatsa	S12	(1)	0.310 miles	41° 02′ 25″ N – 037° 30′ 00″ E
		(2)	3 miles	41° 05′ 00″ N – 037° 30′ 00″ E
		(3)	20 miles	41° 22′ 00″ N – 037° 30′ 00″ E
Ordu	S13	(1)	0.310 miles	40° 59′ 30″ N – 037° 54′ 15″ E
		(2)	3 miles	41° 02′ 15″ N – 037° 54′ 15″ E
		(3)	20 miles	41° 19′ 15″ N – 037° 54′ 15″ E

(U.S. EPA, 2022). NO_3–N concentrations in surface waters are normally low (0–18 mg/L), but NO_3–N pollution is increased as a result of agricultural runoff, dumping wastes, or contamination with human or animal wastes. The results of the study show

Table 2
Statistical summary of the concentrations of 22 parameters studied in mid-Black Sea water.

		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13
NH_4–N (mg/L)	Mean	0.031	0.034	0.049	0.034	0.179	0.096	0.111	0.031	0.043	0.209	0.050	0.052	0.067
	Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.020	0.000	0.000	0.000
	Max	0.167	0.185	0.506	0.260	0.940	0.718	0.954	0.100	0.206	0.954	0.170	0.226	0.162
	SD	0.056	0.055	0.144	0.077	0.294	0.206	0.271	0.035	0.061	0.317	0.059	0.069	0.054
NO_3–N (mg/L)	Mean	0.101	0.033	0.000	0.000	0.006	0.009	0.256	0.001	0.161	0.024	0.022	0.156	0.059
	Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Max	1.091	0.276	0.000	0.000	0.069	0.112	2.391	0.006	0.885	0.291	0.260	1.023	0.635
	SD	0.313	0.080	0.000	0.000	0.020	0.032	0.686	0.002	0.306	0.084	0.075	0.300	0.183
Phenol (mg/L)	Mean	0.156	0.186	0.192	0.032	0.163	0.064	0.358	0.100	0.173	0.221	0.088	0.074	0.085
	Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Max	0.886	0.507	1.068	0.253	0.611	0.259	1.006	0.388	0.472	1.386	0.598	0.283	0.342
	SD	0.279	0.164	0.309	0.073	0.182	0.094	0.400	0.145	0.180	0.411	0.178	0.108	0.126
MBAS (mg/L)	Mean	0.830	0.791	0.828	1.186	0.908	0.833	0.785	0.517	0.627	0.813	0.745	0.649	0.767
	Min	0.480	0.410	0.300	0.610	0.460	0.277	0.270	0.148	0.223	0.510	0.340	0.380	0.520
	Max	1.220	1.140	1.820	1.750	1.360	1.820	1.280	1.280	1.410	1.170	1.260	1.220	1.400
	SD	0.202	0.233	0.621	0.349	0.292	0.489	0.389	0.444	0.489	0.183	0.286	0.221	0.264
TC (mg/L)	Mean	40.130	39.227	39.698	40.500	40.780	40.310	41.870	45.370	44.510	43.440	42.350	43.770	42.650
	Min	33.340	33.436	36.525	35.710	36.950	35.400	36.180	38.220	37.290	34.420	34.590	36.860	34.610
	Max	46.100	44.782	49.665	50.190	50.190	50.710	51.180	51.250	50.580	52.840	53.440	51.240	50.690
	SD	3.520	3.062	3.462	3.700	3.840	3.930	5.440	4.980	5.380	5.940	6.960	4.830	4.980
TOC (mg/L)	Mean	2.944	2.773	3.128	2.717	2.855	2.795	2.802	2.894	2.992	2.913	2.815	3.109	2.771
	Min	2.560	2.307	2.375	2.477	2.513	2.226	2.344	2.486	2.590	2.364	2.355	2.406	2.353
	Max	3.713	3.318	4.024	3.694	3.671	3.657	3.382	3.708	3.573	3.611	3.316	4.554	3.470
	SD	0.378	0.337	0.546	0.337	0.406	0.407	0.294	0.375	0.294	0.388	0.309	0.620	0.299
TIC (mg/L)	Mean	37.060	36.218	36.490	37.425	37.970	37.410	39.810	42.570	41.510	40.610	39.740	40.510	39.840
	Min	30.470	31.037	33.380	33.222	34.470	32.500	33.660	34.510	33.730	32.060	32.630	34.300	32.260
	Max	43.540	41.206	46.690	43.245	47.660	48.380	47.900	48.240	47.920	49.610	50.170	47.940	47.860
	SD	3.630	2.797	3.500	2.784	3.960	4.040	5.790	5.050	5.500	5.570	6.690	4.590	4.800
Fe (mg/L)	Mean	0.220	0.406	0.079	0.159	0.068	0.133	0.098	0.134	0.141	0.093	0.135	0.082	0.140
	Min	0.031	0.013	0.024	0.032	0.017	0.000	0.000	0.012	0.032	0.031	0.023	0.018	0.000
	Max	1.580	1.410	0.160	0.300	0.180	0.340	0.190	0.440	0.480	0.171	0.610	0.170	0.780
	SD	0.431	0.435	0.047	0.096	0.044	0.100	0.059	0.156	0.126	0.054	0.163	0.043	0.207
Al (mg/L)	Mean	0.206	0.505	0.140	0.183	0.150	0.190	0.137	5.200	0.158	0.294	0.123	0.152	0.427
	Min	0.015	0.030	0.067	0.036	0.045	0.053	0.023	0.020	0.027	0.051	0.034	0.063	0.035
	Max	1.080	1.410	0.340	0.310	0.350	0.350	0.320	61.000	0.352	1.180	0.240	0.530	3.200
Mn (μg/L)	Mean	7.250	4.770	7.580	10.270	2.673	7.360	16.000	6.620	11.250	6.200	8.760	5.750	4.587
	Min	0.000	0.000	0.000	2.100	0.000	0.000	0.000	0.000	0.000	1.500	0.000	0.000	0.000
	Max	31.000	19.000	53.000	44.000	7.800	68.000	153.000	27.000	55.000	23.000	50.000	24.000	9.400
	SD	9.300	5.410	14.460	12.000	2.845	19.170	43.200	8.130	14.970	6.160	13.910	7.460	2.918
Cr (μg/L)	Mean	14.640	10.700	10.060	35.900	31.000	15.500	35.300	20.170	48.200	13.530	10.280	9.380	18.220
	Min	3.400	3.300	0.000	3.200	3.700	2.400	1.700	0.000	2.000	0.000	0.000	0.000	0.000
	Max	50.000	20.000	30.000	203.000	182.000	33.000	186.000	88.000	305.000	45.000	30.000	35.000	77.000
	SD	13.050	5.210	9.360	56.700	56.500	9.580	60.100	23.040	83.400	12.980	10.500	9.540	21.610
Ni (μg/L)	Mean	6.340	5.950	5.760	6.250	4.710	5.520	4.610	24.000	6.870	12.840	8.620	6.600	6.800
	Min	1.500	0.000	0.000	1.800	0.000	0.000	0.000	0.000	0.000	2.050	0.000	1.600	0.000
	Max	15.000	20.700	17.000	18.000	11.600	18.000	11.400	221.000	24.000	44.000	27.900	30.000	26.000
	SD	4.810	6.770	5.350	4.900	2.662	4.960	3.850	62.300	7.390	14.780	9.600	7.700	7.750
Cu (μg/L)	Mean	34.600	12.640	55.400	36.700	49.200	20.610	11.330	18.970	10.860	23.040	19.180	17.830	19.790
	Min	2.100	0.000	0.000	3.100	0.000	0.000	0.000	0.000	3.800	5.200	6.200	5.400	4.200
	Max	198.000	24.000	287.000	250.000	475.000	96.000	35.000	55.000	24.000	109.000	81.000	36.000	53.000
	SD	53.500	8.130	102.400	71.300	134.300	29.030	11.230	19.930	6.150	28.580	21.110	10.900	15.710
Zn (μg/L)	Mean	42.350	30.790	36.420	47.790	41.600	44.770	34.930	54.000	51.830	113.800	87.100	46.580	54.000
	Min	11.300	8.900	19.000	18.000	8.000	14.000	14.000	19.200	24.000	17.000	13.000	19.000	8.500
	Max	75.000	66.400	87.000	90.000	158.000	76.000	70.000	255.000	97.000	537.000	616.000	101.000	186.000
	SD	22.140	15.510	19.050	23.250	39.200	19.490	16.230	64.400	27.500	150.600	167.500	24.620	49.700
Cd (μg/L)	Mean	0.330	0.016	0.142	0.370	0.693	0.572	0.310	0.168	0.311	0.369	2.040	0.642	0.112
	Min	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Max	2.570	0.190	0.930	3.900	7.310	6.160	3.270	1.230	1.820	2.900	24.000	5.900	1.010
	SD	0.738	0.055	0.309	1.117	2.104	1.763	0.936	0.404	0.601	0.862	6.920	1.678	0.298
Pb (μg/L)	Mean	23.890	11.790	94.600	80.900	69.600	52.900	14.080	19.640	13.030	19.550	38.100	24.600	20.220
	Min	0.000	0.000	0.000	0.000	0.900	0.000	0.000	0.000	2.300	0.000	4.800	4.500	0.000
	Max	69.000	21.000	893.000	720.000	704.000	455.000	65.000	60.140	30.000	84.000	306.000	101.000	102.000
	SD	22.880	7.890	253.000	204.000	200.400	129.700	19.860	24.030	7.840	23.980	85.100	26.180	27.370
pH	Mean	8.212	8.200	8.186	8.245	8.300	8.296	8.272	8.277	8.262	8.241	8.216	8.253	8.231
	Min	7.840	7.850	7.080	7.900	8.010	7.950	8.020	7.970	7.980	7.820	7.900	7.870	7.810
	Max	8.540	8.530	8.520	8.530	8.540	8.510	8.430	8.480	8.450	8.490	8.370	8.530	8.440
	SD	0.241	0.225	0.399	0.231	0.192	0.209	0.155	0.184	0.161	0.237	0.164	0.194	0.210

(*continued on next page*)

Table 2 (*continued*).

		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13
T (C°)	Mean	17.440	17.250	17.430	17.530	17.770	17.810	17.630	17.270	17.380	16.850	17.390	15.530	15.430
	Min	12.700	12.400	12.800	13.100	12.700	12.800	12.400	11.800	12.300	12.400	12.700	10.500	10.400
	Max	24.900	25.000	25.200	25.700	26.200	26.500	25.500	26.100	25.900	25.700	26.500	24.400	24.600
	SD	4.970	5.120	5.180	5.000	5.370	5.350	4.950	5.370	5.100	5.220	5.340	5.420	5.460
DO (mg/L)	Mean	8.560	8.635	9.002	8.943	9.056	9.489	9.282	9.746	9.610	9.288	9.320	9.095	9.103
	Min	7.390	7.390	7.660	7.660	7.880	7.960	8.340	8.350	8.460	8.310	8.330	8.050	7.730
	Max	9.300	9.270	10.030	10.080	10.150	10.690	11.050	11.370	11.460	10.170	10.080	10.020	10.200
	SD	0.762	0.708	0.868	0.811	0.783	0.999	1.062	1.156	1.067	0.613	0.620	0.670	0.830
EC (mS/cm)	Mean	28.575	28.667	29.108	29.067	29.242	28.942	29.017	28.400	28.267	28.133	28.383	28.192	28.575
	Min	27.100	27.800	28.100	28.300	28.300	27.700	27.500	25.500	22.900	24.700	27.600	27.400	27.300
	Max	29.500	29.700	29.700	29.900	30.000	29.700	30.000	29.700	29.800	29.400	29.400	28.800	29.300
	SD	0.753	0.697	0.478	0.568	0.552	0.610	0.765	1.046	1.848	1.271	0.642	0.491	0.637
Salinity (‰)	Mean	17.634	17.705	18.025	18.048	18.072	17.856	18.017	17.538	17.397	17.628	17.537	16.556	17.658
	Min	16.630	17.120	17.310	17.480	17.540	17.090	17.240	15.570	13.620	16.660	16.970	7.310	16.790
	Max	18.230	18.350	18.390	18.520	18.610	18.320	18.570	18.410	18.480	18.220	18.200	17.790	18.130
	SD	0.506	0.445	0.349	0.375	0.353	0.347	0.402	0.708	1.283	0.490	0.426	2.930	0.422
TDS (g/L)	Mean	17.063	17.134	17.446	17.472	17.489	17.256	17.433	16.955	16.822	17.047	16.962	16.000	17.065
	Min	16.080	16.550	16.750	16.910	16.910	16.470	16.710	15.030	13.110	16.110	16.410	6.990	16.210
	Max	17.670	17.780	17.800	17.930	18.020	17.760	17.980	17.820	17.890	17.630	17.630	17.230	17.540
	SD	0.503	0.454	0.334	0.364	0.350	0.357	0.388	0.694	1.267	0.489	0.428	2.855	0.415

that the NO_3–N and NH_4–N values are not too high according to the regulations. However, in the study conducted by Akbal et al. (2011b), NO_3–N values for Kurupelit and Atakum stations were determined as 0.3400 and 0.2975 mg/L, respectively. When these results are compared with the NO_3–N values measured at the same stations in the present study, it is seen that the NO_3–N values of the previous study are quite high. The reason for this may be that the region was seriously polluted as a result of agricultural activities at that time. For phenol, there is no limit value in the SWQR and EPA standards, but there are values for phenol derivatives. In the present study, the phenol concentration in the Kurupelit station was determined as 0.163 mg/L. However, in a previous study, the phenol concentration at the Kurupelit sampling point was 0.0518 mg/L (Akbal et al., 2011a). When the results are evaluated, it is seen that there is an increase in phenol pollution for this station. The main sources of phenol pollution are natural sources as well as domestic, industrial, and agricultural activities (Anku et al., 2017). It is thought that the reason for this increase may be the discharge of domestic and agricultural wastes. In addition, surfactant concentrations in seawater were investigated, and the highest surfactant (*Methylene Blue Active Substances*) (MBAS) concentration was measured at the Engiz station (1750 mg/L). According to the European Community (EC) standards, the water quality criteria for surfactants is 0.2 mg/L (European Communities, 1989). In the literature, it has been reported that surfactants consume the DO in the water during their decomposition in the aquatic environment and therefore cause sudden oxygen depletion of organisms living in the aquatic environment. Again, Balcıoğlu (2014) stated in the study that the presence of surfactants above 0.1 mg/L in seawater might cause toxic effects for aquatic organisms. In the present study, the surfactant values were found to be above the limit values determined by the EC standard, and indicating that the lives of aquatic organisms are in danger. When the DO values were examined after the surfactants, the DO values for all stations were found to be suitable for I. class water quality value (>6 mg/L) according to SWQR (2016). In the present study, organic pollution, as well as heavy metal pollution, was investigated. Akbal et al. (2011b) stated in the previous research that heavy metal pollution carried to the Black Sea via rivers is high. However, primary heavy metal pollution is thought to originate from industrial activities. Accordingly, Tekkeköy station, which is one of the sampling points in the study, is located in Samsun organized industrial zone (OIZ), and it has been determined that the heavy metal concentrations of the samples taken from this station are generally higher. The highest Al and Ni concentrations were detected at Tekkeköy station. The Al concentration was 61 mg/L and the Ni concentration was 305 mg/L. When the value is compared with the standards, the limit value for Al is 22 μg/L and the limit value for nickel is 24 μg/L according to SWQR (2016). As for the EPA standard, there is no limit value for Al, but the acute exposure limit for Ni is 74 μg/L and the chronic toxicity limit is 8.2 μg/L (U.S. EPA, U.S, 2022b). Ni concentration is 20 μg/L according to EC standard (European Communities, 2007). According to the standards, Al and Ni concentrations have been measured quite above the limit values. In the study conducted in 2000–2001, the Ni concentration in seawater taken from the Tekkeköy sampling point was measured as 0.027 mg/L (27 μg/L) (Altaş and Büyükgüngör, 2007). A similar Ni concentration (24 μg/L) was determined in the present study. When the results of both studies are compared, the presence of metal processing factories in the organized industrial zone indicates that industrial pollution in this region has continued for many years. In the same study, Ni concentration was determined as 0.006 mg/L (6 μg/L) in the samples taken from Çarşamba (Yeşilırmak) station (Altaş and Büyükgüngör, 2007). In the present study, the Ni concentration for the same station was measured as 6.870 μg/L. The similarity of the results of the study shows that these regions have been exposed to continuous Ni pollution over the years. When Cu pollution was examined in previous studies, it was noted that in a study conducted in 2007–2008, the Cu concentration of seawater samples taken from Atakum station was determined as 0.0258 mg/L (25.8 μg/L) (Akbal et al., 2011b). In the present study, the Cu concentration of the sample taken from the Atakum station was measured as 20.610 μg/L. It is noteworthy that the results of both studies were similar, and it was also determined that both SWQR and EPA standards exceeded the limit values. When the mean values of Mn and Cr measurements were evaluated according to SWQR and EPA, it was determined that the limit values of the standards were not exceeded for all sampling points. However, when the Al measurements were evaluated, the limit values of the SWQR and EPA standard were exceeded at all sampling points. In the measurement results of Fe metal, it was determined that the maximum limit values of the standards were exceeded at the other stations, except for five stations (Bafra, Kurupelit, Samsun Harbour, Terme, and Fatsa). The water quality parameters of SWQR, EPA and EC standards are compiled in Table 3.

The level of pollution in the Black Sea has been studied by many researchers (Akbal et al., 2011a; Altaş and Büyükgüngör, 2007; Arici and Bat, 2017; Çevik et al., 2008; Gokkus and Berber,

Table 3
Water quality criteria for aquatic life (U.S. EPA, 2022; U.S. EPA, U.S, 2022b, Turkey SWQR, EC standard).

Pollutant	EPA Saltwater (acute) (μg/L)	EPA Saltwater (chronic) (μg/L)	Turkey SWQR I class (Very good) (mg/L)	Turkey SWQR III class (Medium) (mg/L)	EC Standard (μg/L)
NH_4–N	–	–	<0.2	>1	–
NO_3–N	20	–	<3	>10	–
MBAS	–	–			≤200
DO	–	–	>8	<6	–
pH	–	6.5–8.5	6–9	6–9	–
Metals	EPA Saltwater (acute) (μg/L)	EPA Saltwater (chronic) (μg/L)	Turkey SWQR Saltwater Minimum (μg/L)	Turkey SWQR Saltwater Maximum (μg/L)	EC Standard (μg/L)
Fe	–	–	36	101	–
Al	–	–	2.2	22	–
Cr	1.1	50	4.2	88	–
Ni	74	8.2	8.6	34	20
Cu	4.8	3.1	1.3	5.7	–
Zn	90	81	5.33	76	–
Cd	33	7.9	0.2	1.5	0.2
Pb	140	5.6	1.3	14	7.2
Mn	–	–	<100	>500	–

2019). The present study and previous studies at the mid-Black Sea coast are compiled in Table 4. In a study conducted on the Black Sea coast of the Sevastopol region of Russia, it was determined that the Cu (17.4 μg/L) and Cd (0.69 μg/L) measurement values were similar to the values in the present study (Niemiec et al., 2015). Again, It has been determined that the Cd measurements (0.28; 0.32–0.64 μg/L) in the previous studies (2017 and 2019) in the Sinop region and the measurements in the present study are similar to each other. When Cd values were compared with the SWQR, EPA, and EC standards, it was determined that the limit values for SWQR (1.5 μg/L) and EPA (7.9 μg/L) were not exceeded, but the limit values for EC (0.2 μg/L) were exceeded for some stations. However, the concentrations reported by Altaş and Büyükgüngör (2007) for the same region were found to be quite high (16–37 μg/L), and it is seen that the limit values were exceeded. For Pb, it was determined that the measurement results (14 μg/L) obtained in the study of Altaş and Büyükgüngör (2007) and the measurement results in the present study were similar. The similarity of the study results suggested that the Samsun Harbor station might have been exposed to Pb pollution for a long time. In addition, when the Pb results were interpreted for water quality standards, it was found that the limit values for SWQR, EPA, and EC standards were exceeded at all sampling points in the present study. However, when the mean values of Zn measurements were evaluated according to SWQR and EPA, it was determined that standards' limit values were not exceeded for all sampling points. When the Zn measurement results in the study by Coban et al. (2009) were compared with the present study, it was found that the results were similar. Nevertheless, in the study by Arici and Bat (2017), it is seen in Table 4 that the Zn measurement results are pretty high compared to the present study.

3.2. *Evaluation of seawater quality parameters*

Both natural processes and anthropogenic inputs can cause changes in seawater quality. These pollutions can damage human health and the aquatic environment due to spreading from a point or non-point sources. It was aimed to interpret the data in a simpler way by using PCA/FA analysis for the evaluation of seawater quality. PCA provides an alternative perspective to determine the distribution and quality of pollution in seawater. Accordingly, Table 5 is summarized the seawater quality correlation matrix obtained from PCA. It can be seen from Table 5 that there is a strong correlation between TC and TIC in winter (0.989) and in autumn (0.966). This is because carbon is present in these waters in the form of TIC. It was also found that DO and temperature were negatively correlated in autumn (−0.657). Wu et al. (2009) reported in their study that the solubility of oxygen in water increases, as the temperature decreases. In the previous studies it was also reported that temperature has a negative correlation with dissolved oxygen, which is due to the fact that cold water has a higher dissolved oxygen saturation than hot water (Hamzah et al., 2016; Said et al., 2004; Yap et al., 2011). In the spring, high correlations were found between salinity and EC (0.996) and TDS and EC (0.997). The relationship between TDS and EC is a function of dissolved cations and anions in water, and the relationship between them is not linear because the mobility of ionic species is variable. These correlations were determined in the autumn season as 0.987 and 0.989, respectively. However, it was observed that there was a low correlation between these parameters in winter and summer. The relationship between TDS and EC is a function of dissolved cations and anions in water, and the relationship between them is not linear because the mobility of ionic species is variable (Thirumalini and Joseph, 2009). When the seasonal changes of metals in seawater were examined; for aluminum and iron metals, moderate correlations were observed in autumn (0.620) and spring (0.620), and weaker correlations were observed in summer (0.384) compared to spring and autumn. It is considered that the transport of industrial discharges to the Black Sea via rivers is high due to the high rainfall in the spring in the Mid-Black Sea region of Turkey. In the study Bat et al. (2010) stated that the pollution load carried from the Kızılırmak and Yeşilırmak rivers is much higher than the other rivers pouring into the Black Sea. Similarly, in a study conducted in India, it was reported that heavy metal concentrations in the water in the river system increased during rainy periods (Jain and Sharma, 2001). It is seen that there is a strong correlation between zinc and nickel metals in the spring (0.764) and summer (0.891) seasons, and a weaker correlation in the autumn (0.342) season. The presence of Zn and Ni in seawater is thought to be due to industrial discharges. In the study of the Bakan and Büyükgüngör (2000), industries in the Black Sea region were compiled and possible wastes from the Mid-Black Sea region (especially Samsun) were listed as non-ferrous metal industry and iron and steel industry. It is considered that this pollution is intense in the spring and summer, and there is diluted in the autumn.

Another metal pollution is seen to be caused by Cu and Pb. It has been determined that Cu and Pb have moderate correlations in winter (0.683) and autumn (0.607) seasons and high

Table 4
Pollutant parameters observed in some of the previous studies held for mid-Black Sea waters.

Sampling points	Concentration of metals				References
	Cd (μg/L)	Pb (μg/L)	Cu (μg/L)	Zn (μg/L)	
Sinop	0.330	23.890	34.600	42.350	Present Study
	0.28	1.28	1.43	174.00	Bat et al. (2019)
	0.32–0.64	1.23–6.61	1.39–17.56	181.00–508.00	Arici and Bat (2017)
	16.00–27.00	0–10.00	67.00–90.00	14.00–269.00	Altaş and Büyükgüngör (2007)
Bafra (Kızılırmak)	0.142	94.600	55.400	36.420	Present Study
	2.00–3.00	0–83.00	33.00–65.00	0–11.00	Altaş and Büyükgüngör (2007)
Kurupelit	0.693	69.600	49.200	41.600	Present Study
	5.00	1080.5	12.3	–	Akbal et al. (2011a)
Atakum	0.572	52.900	20.610	44.770	Present Study
	2.30	1089.3	25.80	–	Akbal et al. (2011a)
Samsun Harbor	0.310	14.080	11.330	34.930	Present Study
	11.00–12.00	0–14.00	58.00–82.00	40.00–190.00	Altaş and Büyükgüngör (2007)
Tekkeköy (OIZ)	0.168	19.640	18.970	54.000	Present Study
	13.00–14.00	34.00–102.00	4.00–65.00	0-56.00	Altaş and Büyükgüngör (2007)
Ordu	0.112	20.220	19.790	54.000	Present Study
	8.00–13.00	55.00–82.00	70.00–112.00	0–4.00	Altaş and Büyükgüngör (2007)
Zonguldak	0.29–1.71	5.19–8.02	2.84–7.73	11.4–54.2	Coban et al. (2009)
İnebolu	nd	nd	nd	0.0051	Gokkus and Berber (2019)
Bartın	nd	nd	nd	0.0044	Gokkus and Berber (2019)
Giresun	–	7.92	8.98	4.30	Baltas et al. (2017)
Trabzon	–	6.24	9.53	4.61	Baltas et al. (2017)
Rize	–	5.14	9.05	4.40	Baltas et al. (2017)
Artvin	–	5.50	9.13	4.24	Baltas et al. (2017)
Rize (Inner of Harbor)	nd	29.00	7.50	207.50	Çevik et al. (2008)
Rize (out of Harbor)	nd	nd	nd	12.00	Çevik et al. (2008)
Çamburnu	3.00	nd	19.50	6.50	Çevik et al. (2008)
Çayeli	nd	17.50	9.00	6.00	Çevik et al. (2008)
Hopa	nd	39.00	20.50	81.50	Çevik et al. (2008)

nd:non-detected.

correlations in spring (0.870) and summer (0.883) seasons. Heavy metals, such as Cu, Zn and Fe, do not cause a sizeable toxic effect at low concentrations, as they are necessary for the continuity of activities in the living environment. On the other hand, heavy metals such as Pb, Hg and, Cd do not function in the living body and can cause toxic effects even at low concentrations. In addition, the accumulation of heavy metals in living organisms and their inclusion in the food chain are among the most important problems (Serafim et al., 2012). The presence of metals in seawater is important because it can negatively affect processes such as absorption and desorption (Hung et al., 2001). In most studies conducted by researchers in different areas, it has been reported that metal pollution in seawater is caused by surface flows and anthropogenic activities (Liu et al., 2020; Shrestha et al., 2008; Su et al., 2011; Üstün Odabaşı et al., 2018; Wu et al., 2009; Zhao et al., 2012).

Factor analysis was implemented to normalized data sets (22 variables). When factor analysis of seawater chemical variables was performed seasonally, eight factors were found that accounted for 79.13%, 82.27%, and 78.60% of the total variance for winter, spring, and summer. For the autumn factor analysis of seawater chemical variables, seven factors that constitute 78.69% of the total variance of the data set were produced. Table 6 summarizes the rotated factor loads for all seasons, the variance clarified by each factor, and the cumulative variance. The remaining parts of the total variance for these seasons are only small percentages and had very low and negligible correlation coefficients.

For the winter season, Factor 1 constitutes 17.061% of the total variance with strong positive SAL, TDS loadings and strong negative loadings of TOC and Mn. This factor is linked to the mineral parameters. Factor 2 constitutes 15.217% of the total variance with strong positive TC and TIC loadings. This factor indicates the carbon related group. Factor 3 constitutes 12.321% of the total variance with strong positive Ni, Pb and pH loadings. This factor indicates the group of toxic metals. Ni correlates strongly with Pb (r = 0.768), which may recommend the same sources. Factor 4 constitutes 9.205% of the total variance with strong positive phenol, Cr and DO loadings. This factor represents effects from anthropogenic sources. Factor 5, strong positive NO_3–N and Cd loadings constitute 7.771% of the total variance. This factor represents nutrient-related resources. Factor 6 constitutes 6.602% of the total variance with strong positive Fe. This factor is belonged to common sources of natural processes of dissolution of geological soil components. Factor 7 accounts for 5.983% of the total variance with strong negative temperature. This factor represents physical change. Factor 8 constitutes 5.153% of the total variance with strong positive EC. This factor indicates natural inputs.

For the spring season, Factor 1 constitutes 23.667% of the total variance, representing the strong positive group of toxic metals. Cd (r = 0.964) and Pb (r = 0.947) are strongly associated, suggesting the same sources. Factor 2 constitutes 16.741% of the total variance with positive EC, SAL loadings. This factor is associated with mineral parameters. Factor 3 constitutes 10.418% of the total variance with strong positive TC and TIC loadings. This factor indicates the carbon-related group. Factor 4 is positively associated with Fe and Al metals and constitutes 8.068% of the total variance. Fe metal (r = 0.829) and Al (r = 0.805) have a strong correlation; this factor is belonged to the soil. It is thought that the natural processes of dissolution of geological soil components are related to common sources. Factor 5 constitutes 7.750% of the total variance with strong positive TOC and Ni loadings. This factor represents anthropogenic effects. Factor 6 is associated with the negative temperature parameter with 5.910% of the total variance. This factor is related to physical parameters. Factor 7 constitutes 4.996% of the total variance with positive Cr metal loading. This factor is associated with industrial discharges. Factor 8, on the other hand, constitutes 4.727% of the total variance with strong positive NO_3–N loading. This factor is associated with the nutrient group and is related to agricultural flows.

For the summer season, Factor 1 constitutes 17.687% of the total variance with strong positive Cr, Ni, and Zn metal loading. This factor is associated with industrial resources. Several industrial plants are located in the region, and it is thought that the origin

Table 5
Correlation matrix for seawater chemistry of mid-Black Sea.

Winter

	NH$_4$-N	NO$_3$-N	Phenol	MBAS	TC	TOC	TIC	Fe	Al	Mn	Cr	Ni	Cu	Zn	Cd	Pb	pH	T	DO	EC	SAL	TDS
NH$_4$-N	1																					
NO$_3$-N	−0.086	1																				
Phenol	−0.157	−0.013	1																			
MBAS	−0.262	−0.278	0.280	1																		
TC	−0.253	0.236	0.183	**0.421****	1																	
TOC	0.091	0.119	−0.021	0.004	0.100	1																
TIC	−0.249	0.238	0.186	**0.407***	**0.989****	0.056	1															
Fe	−0.217	−0.052	−0.094	0.100	−0.056	−0.096	−0.065	1														
Al	−0.180	−0.090	−0.040	0.051	−0.137	−0.237	−0.139	0.283	1													
Mn	0.039	0.078	−0.115	−0.206	−0.120	**0.407***	−0.143	−0.018	**0.368***	1												
Cr	−0.037	0.093	**0.462****	0.246	0.164	**0.339***	0.157	−0.085	−0.050	−0.008	1											
Ni	−0.155	0.067	−0.008	0.041	0.156	−0.041	0.177	−0.125	−0.163	0.056	−0.163	1										
Cu	−0.052	−0.079	0.164	0.135	0.023	−0.074	−0.022	−0.054	−0.100	−0.080	−0.141	**0.612****	1									
Zn	0.260	0.084	−0.131	−0.106	0.081	0.179	0.093	−0.140	−0.195	0.261	−0.037	0.299	−0.093	1								
Cd	−0.098	**0.777****	0.052	−0.001	0.297	0.021	0.308	0.086	−0.047	0.108	0.134	0.223	−0.061	**0.386***	1							
Pb	−0.300	0.114	0.243	0.204	**0.365***	−0.112	**0.353***	−0.042	−0.249	−0.174	−0.030	**0.595****	**0.683****	−0.028	0.170	1						
pH	−0.150	0.000	−0.140	0.076	0.179	0.059	0.188	0.011	0.013	−0.006	0.100	**−0.451****	**−0.728****	−0.012	0.002	−0.303	1					
T °C	−0.068	−0.117	0.220	0.013	0.002	0.138	−0.043	−0.088	−0.069	0.146	−0.002	**−0.321***	0.026	−0.175	**−0.343***	−0.074	−0.051	1				
DO	−0.143	0.183	**0.511****	0.296	**0.418****	0.188	**0.456****	−0.266	−0.197	−0.130	**0.488****	0.100	−0.193	−0.011	0.300	0.047	0.112	−0.176	1			
EC	0.022	−0.188	−0.052	0.128	−0.078	0.007	−0.111	0.094	−0.149	0.000	−0.020	0.062	0.176	−0.023	−0.019	0.314	0.096	−0.048	−0.201	1		
SAL	−0.070	−0.167	0.142	0.288	−0.035	**−0.581****	−0.019	0.114	0.011	**−0.538****	0.098	−0.043	0.092	−0.204	0.035	0.238	0.034	−0.167	0.035	**0.400***	1	
TDS	−0.070	−0.168	0.138	0.289	−0.035	**−0.581****	−0.019	0.115	0.008	**−0.538****	0.097	−0.045	0.089	−0.203	0.033	0.237	0.039	−0.164	0.029	**0.403***	**1.000****	1

Spring

	NH$_4$-N	NO$_3$-N	Phenol	MBAS	TC	TOC	TIC	Fe	Al	Mn	Cr	Ni	Cu	Zn	Cd	Pb	pH	T	DO	EC	SAL	TDS
NH$_4$-N	1																					
NO$_3$-N	−0.004	1																				
Phenol	0.031	0.215	1																			
MBAS	0.053	0.011	0.271	1																		
TC	−0.293	−0.107	**0.403***	0.102	1																	
TOC	−0.059	−0.186	0.090	−0.194	−0.079	1																
TIC	−0.274	−0.008	**0.393***	0.146	0.967**	−0.201	1															
Fe	−0.095	0.060	−0.121	−0.019	0.142	−0.010	0.145	1														
Al	0.028	0.094	0.033	−0.024	0.217	−0.085	0.224	**0.620****	1													
Mn	−0.167	−0.094	−0.227	0.033	−0.066	−0.090	−0.088	0.256	0.044	1												
Cr	0.043	−0.037	−0.209	0.126	−0.121	−0.128	−0.098	0.108	0.197	0.214	1											
Ni	−0.073	−0.111	−0.159	0.098	0.124	**0.516****	0.071	0.090	0.043	0.146	0.076	1										
Cu	−0.130	−0.005	−0.016	0.055	0.193	0.072	0.201	**0.398***	0.191	**0.414****	0.068	0.289	1									
Zn	−0.118	−0.112	−0.122	0.132	0.142	**0.344***	0.110	0.139	0.101	0.328*	0.046	**0.764****	**0.661****	1								
Cd	−0.094	−0.077	−0.085	0.055	0.038	0.045	0.041	0.160	−0.042	**0.446****	0.024	0.223	**0.871****	**0.716****	1							
Pb	−0.111	−0.068	−0.074	0.091	0.140	0.043	0.141	0.252	0.205	**0.400***	0.084	0.313	**0.870****	**0.804****	**0.921****	1						
pH	0.049	-.0399*	**−0.337***	−0.048	**−0.533****	0.004	**−0.537****	−0.300	−0.234	0.076	−0.110	−0.127	−0.070	0.100	0.250	0.144	1					
T °C	−0.218	0.057	**−0.318***	−0.207	0.068	−0.146	0.109	−0.178	−0.042	0.091	−0.026	0.045	0.253	0.273	**0.342***	**0.338***	0.235	1				
DO	−0.126	−0.135	−0.242	−0.192	−0.173	0.098	−0.198	−0.239	−0.190	0.204	0.012	0.101	0.021	0.228	0.164	0.143	**0.338***	**0.337***	1			
EC	0.269	−0.086	−0.156	0.233	**−0.430****	−0.125	**−0.383***	−0.249	−0.216	−0.019	0.196	−0.215	**−0.344***	−0.240	−0.179	−0.245	**0.346***	0.082	−0.209	1		
SAL	0.267	−0.087	−0.155	0.251	**−0.424****	−0.136	**−0.378***	−0.244	−0.212	−0.012	0.183	−0.224	**−0.352***	−0.239	−0.184	−0.247	**0.339***	0.079	−0.208	**0.996****	1	
TDS	0.269	−0.085	−0.149	0.254	**−0.424****	−0.133	−0.377*	−0.247	−0.213	−0.018	0.182	−0.223	**−0.350***	−0.239	−0.183	−0.247	**0.339***	0.076	−0.221	**0.997****	**1.000****	1

(*continued on next page*)

Table 5 (*continued*).

Summer

	NH_4-N	NO_3-N	Phenol	MBAS	TC	TOC	TIC	Fe	Al	Mn	Cr	Ni	Cu	Zn	Cd	Pb	pH	T	DO	EC	SAL	TDS
NH_4-N	1																					
NO_3-N	−0.026	1																				
Phenol	0.041	−0.066	1																			
MBAS	−0.102	−0.056	−0.219	1																		
TC	0.278	0.202	−0.161	−0.073	1																	
TOC	0.015	0.285	−0.004	−0.294	0.225	1																
TIC	0.284	0.070	−0.149	0.003	**0.943****	−0.052	1															
Fe	−0.131	−0.034	−0.033	−0.007	0.237	0.104	0.233	1														
Al	−0.094	−0.046	−0.122	−0.109	0.245	−0.008	0.259	**0.384***	1													
Mn	−0.129	0.005	−0.168	0.127	−0.223	0.004	−0.195	**0.340***	0.066	1												
Cr	0.068	0.021	−0.192	−0.099	−0.049	0.062	−0.023	**0.393***	0.033	**0.451****	1											
Ni	−0.018	−0.019	−0.092	−0.237	−0.175	0.225	−0.222	**0.347***	−0.038	**0.329***	**0.870****	1										
Cu	−0.062	0.074	−0.119	−0.055	−0.228	−0.148	−0.193	−0.047	−0.047	−0.031	−0.053	−0.037	1									
Zn	−0.042	0.008	−0.169	−0.139	−0.225	0.086	−0.236	**0.363***	−0.002	**0.538****	**0.893****	**0.891****	0.084	1								
Cd	0.035	0.067	−0.177	0.015	−0.180	−0.112	−0.135	−0.142	−0.069	−0.033	−0.045	−0.011	**0.730****	0.041	1							
Pb	−0.073	0.015	−0.075	−0.025	−0.211	−0.015	−0.204	−0.038	−0.065	−0.046	−0.155	−0.094	**0.883****	0.000	**0.665****	1						
pH	0.237	0.058	−**0.319***	0.005	0.107	−0.101	0.142	−0.004	0.009	0.018	0.089	0.075	0.289	0.110	0.223	0.294	1					
T °C	0.308	0.010	−0.239	−0.120	0.069	0.093	0.055	0.097	0.219	0.150	0.100	0.138	−0.001	0.156	0.090	0.100	0.113	1				
DO	**0.445****	0.018	0.057	−**0.409****	0.158	−0.032	0.167	0.053	0.136	0.107	0.183	0.199	−0.158	0.166	−0.145	−0.187	0.250	**0.485****	1			
EC	−**0.338***	0.014	0.004	−0.032	−0.165	−0.017	−0.178	−0.104	−0.072	−0.060	−0.126	−0.085	0.077	−0.058	0.069	0.060	−0.131	−0.084	−**0.427****	1		
SAL	−0.035	−0.141	−0.129	−0.046	−0.128	−0.123	−0.107	−0.117	−0.169	−0.227	−0.118	−0.110	0.018	−0.139	−0.053	−0.063	−0.083	−**0.331***	−**0.379***	**0.366***	1	
TDS	−0.044	−0.141	−0.132	−0.037	−0.151	−0.120	−0.132	−0.098	−0.164	−0.227	−0.128	−0.116	0.035	−0.142	−0.049	−0.044	−0.093	−**0.325***	−**0.388***	**0.364***	**0.998****	1

Autumn

	NH_4-N	NO_3-N	Phenol	MBAS	TC	TOC	TIC	Fe	Al	Mn	Cr	Ni	Cu	Zn	Cd	Pb	pH	T	DO	EC	SAL	TDS
NH_4-N	1																					
NO_3-N	0.142	1																				
Phenol	−0.016	0.117	1																			
MBAS	−0.040	−0.188	−0.260	1																		
TC	**0.481****	0.189	−0.033	−0.212	1																	
TOC	0.039	−0.036	−**0.379***	0.183	0.081	1																
TIC	**0.450****	0.176	0.160	−0.263	**0.966****	−0.069	1															
Fe	−0.131	−0.088	0.096	0.167	−0.084	0.041	−0.035	1														
Al	−0.018	−0.006	0.000	0.009	−0.100	−0.009	−0.064	**0.620****	1													
Mn	0.055	−0.045	0.085	−0.085	0.169	0.039	0.161	0.338*	0.256	1												
Cr	−**0.407***	−0.124	0.044	−0.021	−**0.473****	0.080	−**0.481****	**0.355***	0.100	−0.044	1											
Ni	−0.138	−0.140	−0.068	0.150	−**0.339***	−0.096	−0.326*	0.175	0.156	−0.020	0.297	1										
Cu	**0.365***	−0.027	−0.051	0.159	**0.335***	−0.025	0.333**	0.226	0.131	−0.250	−0.145	0.254	1									
Zn	0.189	−0.040	0.054	0.068	0.104	−0.034	0.129	**0.611****	**0.501****	0.160	0.215	**0.342***	**0.397***	1								
Cd	−0.097	−0.049	**0.743****	−0.215	−0.106	−**0.408****	0.151	0.219	0.150	−0.010	−0.020	0.020	−0.010	0.099	1							
Pb	**0.482****	0.115	0.009	0.043	**0.652****	0.092	0.621**	0.206	0.313	0.214	−**0.444****	−0.072	**0.607****	**0.417****	−0.094	1						
pH	0.029	−0.047	0.182	−0.126	−0.058	−0.067	0-.038	−0.094	−0.287	−0.346*	0.282	−0.008	0.114	0.024	0.078	−0.256	1					
T °C	−**0.563****	0.080	0.196	−0.054	−**0.557****	−0.034	−**0.524****	0.126	0.014	0.074	**0.433****	0.141	−**0.596****	−0.094	0.113	−**0.567****	0.074	1				
DO	**0.391***	−0.136	−0.197	0.031	**0.541****	0.218	**0.480****	−0.127	−0.102	−0.188	−**0.354***	−0.257	**0.582****	−0.015	−0.200	**0.493****	0.180	−**0.657****	1			
EC	−0.016	0.041	0.158	0.203	0.035	−0.122	0.060	0.059	−0.061	−0.088	0.198	0.045	0.284	−0.133	0.073	−0.002	0.289	0.049	0.245	1		
SAL	−0.017	0.009	0.171	0.249	−0.007	−0.130	0.021	0.060	−0.054	−0.108	0.205	0.021	0.265	−0.154	0.083	−0.020	0.294	0.046	0.241	**0.987****	1	
TDS	−0.034	0.021	0.173	0.239	−0.013	−0.126	0.016	0.067	−0.051	−0.100	0.213	0.030	0.258	−0.151	0.086	−0.026	0.298	0.071	0.229	**0.989****	**0.998****	1

*Correlation is significant at the 0.05 level (2-tailed). $p < 0.05$.

**Correlation is significant at the 0.01 level (2-tailed). $p < 0.01$.

Table 6
Rotated factor correlation coefficients for each season.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8
Winter								
NH_4-N	−0.063	−0.453	−0.115	−0.051	−0.137	−0.499	0.301	−0.026
NO_3-N	−0.100	0.102	−0.003	0.036	**0.945**	−0.038	0.005	−0.105
Phenol	0.109	0.104	0.220	**0.762**	−0.004	−0.011	−0.259	−0.087
MBAS	0.174	0.539	0.055	0.374	−0.406	0.213	0.055	0.180
TC	−0.038	**0.928**	0.014	0.114	0.124	−0.074	0.026	−0.030
TOC	**−0.773**	0.054	−0.100	0.264	0.021	−0.214	−0.027	0.241
TIC	−0.001	**0.929**	−0.002	0.117	0.130	−0.082	0.069	−0.078
Fe	0.081	−0.003	−0.075	−0.154	0.069	0.651	−0.051	0.202
Al	−0.040	−0.152	−0.084	0.007	−0.129	**0.825**	0.070	−0.250
Mn	**−0.767**	−0.181	0.004	0.002	0.045	0.325	0.141	0.093
Cr	−0.068	0.030	−0.162	**0.841**	0.065	−0.033	0.004	0.129
Ni	−0.060	0.211	**0.768**	−0.092	0.058	−0.058	0.408	0.008
Cu	0.056	−0.002	0.932	−0.031	−0.090	−0.024	−0.105	0.118
Zn	−0.316	0.030	0.021	−0.084	0.099	−0.252	0.670	0.097
Cd	−0.003	0.192	0.042	0.159	**0.809**	0.103	0.411	0.067
Pb	0.183	0.402	**0.715**	0.008	0.151	−0.059	−0.073	0.326
pH	0.023	0.298	**−0.808**	−0.062	0.003	0.028	0.019	0.191
T °C	−0.252	−0.017	−0.029	0.027	−0.142	−0.113	**−0.760**	0.051
DO	0.046	0.382	−0.086	**0.704**	0.128	−0.196	0.171	−0.234
EC	0.161	−0.056	0.077	−0.050	−0.081	−0.002	0.030	**0.898**
SAL	**0.887**	−0.028	0.014	0.156	−0.053	0.091	0.062	0.326
TDS	**0.886**	−0.027	0.010	0.151	−0.055	0.090	0.060	0.331
Eigenvalues	3.753	3.348	2.711	2.025	1.710	1.452	1.316	1.134
% Total variance	17.061	15.217	12.321	9.205	7.771	6.602	5.983	5.153
Cumulative %variance	17.061	32.278	44.599	53.804	61.575	68.177	74.160	79.313
Spring								
NH4-N	−0.042	0.268	−0.425	0.152	−0.009	0.299	−0.230	0.056
NO3-N	−0.017	−0.073	−0.083	0.029	−0.133	0.009	−0.032	**0.951**
Phenol	−0.026	−0.117	0.329	−0.113	−0.071	0.642	−0.354	0.224
MBAS	0.181	0.342	0.228	−0.151	−0.018	0.637	0.268	0.034
TC	0.058	−0.238	**0.921**	0.133	0.017	0.106	−0.110	−0.061
TOC	−0.020	−0.141	−0.181	−0.034	**0.809**	0.036	−0.224	−0.133
TIC	0.077	0.181	**0.932**	0.136	−0.070	0.094	−0.095	0.032
Fe	0.194	−0.194	0.003	**0.829**	−0.009	0.028	0.177	−0.014
Al	0.065	−0.102	0.127	**0.805**	−0.019	−0.064	0.081	0.055
Mn	0.456	−0.085	−0.106	0.029	−0.101	−0.023	0.594	−0.142
Cr	−0.023	0.196	−0.027	0.176	0.045	0.007	**0.756**	0.076
Ni	0.246	−0.081	0.116	0.004	**0.877**	−0.026	0.188	0.013
Cu	**0.883**	−0.202	0.088	0.219	0.070	0.006	0.053	0.047
Zn	**0.750**	−0.074	0.100	−0.027	0.577	−0.074	0.115	−0.033
Cd	**0.964**	−0.075	−0.041	−0.050	0.012	−0.049	0.016	−0.060
Pb	**0.947**	−0.093	0.064	0.107	0.094	−0.069	0.056	−0.034
pH	0.229	0.249	−0.474	−0.332	−0.136	−0.254	−0.114	−0.516
T °C	0.368	0.197	0.237	−0.218	−0.075	**−0.765**	−0.055	0.143
DO	0.117	−0.356	−0.184	−0.508	0.041	−0.395	0.248	−0.154
EC	−0.137	**0.941**	−0.205	−0.097	−0.085	−0.005	0.067	−0.058
SAL	−0.137	0.941	−0.198	−0.097	−0.095	0.003	0.070	−0.061
TDS	−0.137	0.944	−0.198	−0.096	−0.092	0.010	0.063	−0.058
Eigenvalues	5.207	3.683	2.292	1.775	1.705	1.300	1.099	1.040
% Total variance	23.667	16.741	10.418	8.068	7.750	5.910	4.996	4.727
Cumulative %variance	23.667	40.408	50.826	58.894	66.644	72.554	77.550	82.277
Summer								
NH_4-N	−0.024	−0.010	−0.022	0.336	0.676	−0.328	−0.102	−0.002
NO_3-N	−0.019	0.077	−0.155	0.140	−0.091	−0.175	**0.711**	0.150
Phenol	−0.150	−0.140	−0.198	−0.138	−0.077	−0.101	−0.082	**−0.827**
MBAS	−0.143	−0.086	−0.234	0.021	−0.498	−0.224	−0.342	0.567
TC	−0.138	−0.156	−0.059	**0.886**	0.097	0.172	0.254	0.068
TOC	0.117	−0.100	−0.022	0.022	0.042	0.056	**0.798**	−0.133
TIC	−0.142	−0.125	−0.064	**0.903**	0.090	0.175	−0.001	0.094
Fe	0.503	−0.039	−0.093	0.320	−0.198	0.555	−0.065	−0.060
Al	−0.015	−0.029	−0.098	0.194	0.070	**0.812**	−0.079	0.043
Mn	0.531	−0.089	−0.292	−0.265	−0.103	0.167	−0.074	0.323
Cr	**0.940**	−0.063	−0.039	0.061	0.067	−0.018	0.009	0.075
Ni	**0.919**	−0.021	0.002	−0.113	0.128	−0.015	0.129	−0.077
Cu	0.012	**0.948**	0.039	−0.077	−0.062	0.005	−0.037	−0.016
Zn	**0.944**	0.063	−0.058	−0.155	0.065	0.024	0.039	0.067
Cd	−0.028	**0.835**	−0.027	−0.083	0.005	−0.061	0.008	0.108
Pb	−0.079	**0.919**	−0.042	−0.118	−0.050	0.049	0.021	−0.016
pH	0.125	0.422	−0.033	0.279	0.322	−0.167	−0.099	0.331

(*continued on next page*)

Table 6 (*continued*).

T °C	0.019	0.044	−0.230	−0.172	0.661	0.368	0.127	0.346
DO	0.147	−0.133	−0.325	0.088	**0.800**	0.064	−0.058	−0.104
EC	−0.136	0.046	0.495	−0.322	−0.273	0.212	0.216	0.088
SAL	−0.060	−0.046	**0.948**	−0.013	−0.113	−0.119	−0.127	0.025
TDS	−0.064	−0.033	**0.944**	−0.031	−0.122	−0.106	−0.129	0.025
Eigenvalues	3.891	3.205	2.707	1.906	1.694	1.528	1.263	1.099
% Total variance	17.687	14.568	12.304	8.664	7.699	6.947	5.741	4.995
Cumulative %variance	17.687	32.255	44.599	53.233	60.922	67.868	73.610	78.605
Autumn								
NH_4-N	0.688	−0.053	−0.025	−0.029	0.046	0.000	0.174	
NO_3-N	0.073	0.040	−0.057	0.014	−0.030	−0.031	**0.933**	
Phenol	−0.053	0.125	0.087	**0.825**	−0.180	0.144	0.079	
MBAS	−0.053	0.335	0.053	−0.326	0.373	−0.416	−0.301	
TC	**0.818**	0.001	−0.002	−0.042	−0.412	0.030	0.176	
TOC	0.019	−0.067	0.096	**−0.724**	−0.235	0.102	−0.102	
TIC	**0.798**	0.012	0.025	0.202	−0.408	0.033	0.143	
Fe	−0.081	0.104	**0.884**	0.044	−0.034	−0.012	−0.119	
Al	−0.003	−0.040	**0.751**	0.053	0.051	−0.242	0.015	
Mn	−0.043	−0.051	0.446	0.008	−0.554	−0.392	0.012	
Cr	−0.593	0.191	0.377	−0.133	0.083	0.487	−0.029	
Ni	−0.203	0.002	0.322	0.026	**0.773**	−0.009	0.009	
Cu	0.687	0.254	0.258	−0.014	0.487	0.138	−0.083	
Zn	0.221	−0.168	**0.803**	0.046	0.261	0.171	0.039	
Cd	−0.058	0.024	0.139	**0.878**	−0.057	0.057	−0.143	
Pb	**0.797**	0.007	0.370	−0.046	−0.032	−0.226	0.095	
pH	−0.020	0.231	−0.147	0.084	0.084	**0.829**	−0.056	
T °C	**−0.833**	0.067	0.084	0.092	−0.131	0.057	0.200	
DO	**0.752**	0.239	−0.139	−0.242	−0.047	0.196	−0.280	
EC	0.035	**0.980**	−0.012	0.068	0.020	0.093	0.034	
SAL	0.015	**0.987**	−0.028	0.075	0.031	0.077	−0.010	
TDS	0.000	**0.988**	−0.019	0.075	0.026	0.083	0.005	
Eigenvalues	4.693	3.545	2.855	2.391	1.556	1.203	1.070	
% Total variance	21.330	16.116	12.977	10.866	7.073	5.469	4.866	
Cumulative %variance	21.330	37.445	50.422	61.288	68.361	73.830	78.696	

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

of pollution is industrial activities. Factor 2 exhibits the positive toxic metals group and constitutes 14.568% of the total variance. Cu (r = 0.948) are strongly associated with Pb (r = 0.919) and Cd (r = 0.835) suggesting the same sources. Factor 3 constitutes 12.304% of the total variance with strong positive SAL and TDS loadings. This factor indicates the mineral-related group. Factor 4 represents 8.664% of the total variance with strong TC (r = 0.886) and TIC (r = 0.903) loadings. This factor indicates the carbon-related group. Factor 5 is associated with strong positive DO, accounting for 7.699% of the total variance. This factor represents natural inputs. Factor 6 is strongly associated with Al (r = 0.812) and moderately associated with Fe (r = 0.555), accounting for 6.947% of the total variance. This factor is associated with the common sources of natural processes of dissolution of geological soil components. Factor 7 constitutes 5.741% of the total variance with strong positive NO_3–N and TOC loadings. This factor is belonged to the nutrient group and is related to agricultural runoffs. Factor 8 constitutes 4.995% of the total variance with strong negative phenol loading. This factor is thought to be associated with anthropogenic pollution.

For the autumn season, Factor 1 represents 21.330% of the total variance, with strong positive TC, TIC, Pb, and DO associate with strong negative temperature loadings. This factor indicates the organic-related group. Factor 2 constitutes 16.116% of the total variance with strong positive EC, SAL, and TDS loadings. This factor indicates the mineral-related group. Factor 3 constitutes 12.977% of the total variance with strong positive Fe (r = 0.884), Al (r = 0.751) and Zn (r = 0.803) metals. This factor is associated with the common sources of natural processes of dissolution of geological soil constituents. Factor 4 accounts for 10.866% of the total variance with strong positive phenol and Cd (r = 0.878) and strong negative TOC. This factor represents anthropogenic effects. Factor 5 constitutes 7.033% of the total variance with strong positive Ni (r = 0.773) metal loading. This factor is associated with industrial resources. Factor 6 is strongly associated with positive pH, accounting for 5.469% of the total variance. This factor is associated with natural inputs. Factor 7 constitutes 4.866% of the total variance with strong positive NO_3-N loading. This factor represents the nutrient group and is related to agricultural flows.

In this study, seawater quality parameters with absolute correlation coefficient >90% were accepted as important for seasonal and spatial variation of seawater. The major water quality parameters that can be used to assess the seasonal variations of the water quality are shown in Table 7. This Table is compiled considering the correlation coefficients more significant than 90%.

In winter, carbon-related parameters (TC and TIC) and nutrient-related parameters (NO_3–N) are important parameters that contribute to water quality changes. All of these parameters were positively correlated in water quality variation in winter. Carbon-related parameters (TC and TIC) may be commented as describing impacts from natural inputs, while inorganic nutrients may be commented as representing impacts from anthropogenic inputs (Table 7).

In the spring, carbon-related parameters (TIC), nutrient-related parameters (NO_3–N), mineral-related parameters (EC, SAL) as well as toxic metals-related parameters (Cd, Pb) are important parameters that contribute to variations of the water quality. All of these parameters are positively correlated with each other. The parameters related to inorganic carbon represent effects from natural inputs. Inorganic nutrients may be commented as representing influences from anthropogenic inputs. Mineral-related parameters (EC, SAL) can be related to common sources of natural dissolution processes of geological soil components. Cd correlates strongly with Pb (r = 0.921), which may suggest the same sources (Table 5). It can be interpreted as the toxic metal-related parameters represent the effects of the discharge of industrial wastewater.

Table 7
The most important quality parameters determined in seawater for each seasons.

Season	Highly correlated parameter
Winter	TC, TIC, NO_3–N
Spring	TIC, NO_3–N, Cd, Pb, EC, SAL
Summer	TIC, Cr, Ni, Zn, Cu, Pb, SAL, TDS
Autumn	NO_3–N, EC, SAL, TDS

The correlation factor of these parameters is greater than 90%.

In the summer, carbon-related parameters (TIC), mineral-based parameters (SAL, TDS), and toxic metals-related parameters (Cr, Ni, Zn, Cu, Pb) are important parameters that change water quality. All of these parameters are positively correlated with each other. Carbon-related parameters (TIC) can be interpreted as representing impacts from natural inputs. Mineral-related parameters (SAL, TDS) can be related to common sources of natural processes of dissolution of geological soil components. In the group of toxic metals, Cr is strongly associated with Zn ($r = 0.893$) and Ni ($r = 0.870$), which may recommend the same sources (Table 6). On the other hand, Pb is strongly related to Cu ($r = 0.833$). It can be interpreted as the toxic metal-related parameters represent the effects of the discharge of industrial wastewater.

In the autumn, nutrient-related parameters (NO_3–N) and mineral-based parameters (EC, SAL, TDS) are important parameters that contribute to variations in water quality. All of these parameters were positively correlated in water quality variation in autumn. Inorganic nutrients may be commented as representing impacts from anthropogenic inputs. In addition, mineral-related parameters (EC, SAL) can be associated with common sources of natural processes of dissolution of geological soil components.

As a result of seasonal analysis, it is seen that salinity and electrical conductivity have a strong correlation. Therefore, salinity and EC data in Table 7 reveal to be the most important variables that generally contribute to mid-Black Seawater quality. High salinity is considered normal due to the natural structure of seawater. On the other hand, heavy metals (Cd, Pb, Cr, Ni, Zn, and Pb) are seen to show strong positive loading in spring and summer. It is thought that the discharges of industrial activities may cause metal pollution. As shown from Table 7, NO_3–N shows a strong positive association in winter, spring, and summer. It has been observed that NO_3–N, which is an inorganic nutrient, generally has a strong correlation value. It is thought that NO_3–N may enter rivers due to discharges from agricultural areas. Also, It is believed that the TIC value of the carbon group is generally strongly correlated due to biological activities and decomposition in seawater (Koziorowska et al., 2017).

3.3. Cluster analysis

CA was applied to identify related groups in the sampling site. CA was calculated using the Ward method's relation to the square of the Euclidean distance as a measure of similarity (Akbal et al., 2011a). Two statistically significant clusters have been created for seawater stations, and the dendrograms in these two clusters are given in Fig. 2. Cluster 1 corresponds to stations S1, S2, S8, S9, S10, S11, S12, and S13. These stations are described by the highest Ni and Zn metal values attributable to industrial wastewater discharges. Cluster 2 corresponds to stations S3, S4, S5, S6, and S7. NH_4–N, MBAS, Cr, Pb, Cu and SAL, EC, TDS values attributed to their industrial discharges and solid waste disposal activities characterize these stations.

4. Conclusions

This study investigated the temporal and spatial changes of seawater quality along the mid-Black Sea coast of Samsun, Turkey. The obtained results were evaluated using PCA/FA and CA multiple statistical techniques. First of all, as a result of the investigated seawater characterization, NO_3–N and NH_4–N from agricultural runoff, as well as heavy metals from industrial discharges, were determined as important quality parameters. These results were then evaluated by statistical analysis. The most important parameters affecting the seawater quality are; as the TC, TIC, and NO_3–N in the winter, the TIC, NO_3–N, Cd, Pb, EC, and SAL in the spring, the TIC, Cr, Ni, Zn, Cu, Pb, EC, SAL, and TDS in the summer, and finally, the NO_3–N, EC, SAL, and TDS were detected in the autumn. As for the PCA assessment, it was determined that heavy metals had a strong correlation in spring and summer. In spring; the Pb and Cd, and in summer; the Pb, Cr, Ni, Zn, and Cu heavy metals showed a strong correlation (>0.90). In addition, NO_3–N, another important water quality parameter, showed a strong correlation in spring and autumn. (>0.90). On the other hand, according to the factor analysis, it was determined that the parameters affecting the seawater quality were related to toxic metals (industrial wastewater), nutrients (anthropogenic sources), natural inputs and dissolved salts (dissolution and degradation process). Finally, the sample areas in the cluster analysis results were grouped into two groups.

As a result, it was seen that the parameter that is important for one season is not important for another season. Therefore, it is necessary to examine the seawater quality seasonally and temporally. In addition, the reliability of the results obtained with statistical analyses was increased. It is predicted that Cd, Pb, Cr, Ni, Zn, and Cu metal values are caused by industrial discharge, NO_3–N values are caused by currents from agricultural areas, and finally TIC values are anthropogenic effects in seawater.

CRediT authorship contribution statement

Sevde Üstün Odabaşı: Conceptualization, Methodology, Writing – original draft. **Zeynep Ceylan:** Software, Formal analysis. **İlknur Şentürk:** Investigation, Writing – review & editing. **Feryal Akbal:** Visualization, Writing – review & editing. **Gülfem Bakan:** Writing – review & editing. **Hanife Büyükgüngör:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

This research has been funded by Ondokuz Mayis University, Turkey (Project No. ÇEV.1901. 13.001).

Consent for publication

Both authors and the funding agency and the university where the analysis was done have the consent for publication and have no objections.

Data availability

All data produced or analyzed during this study is included in this article.

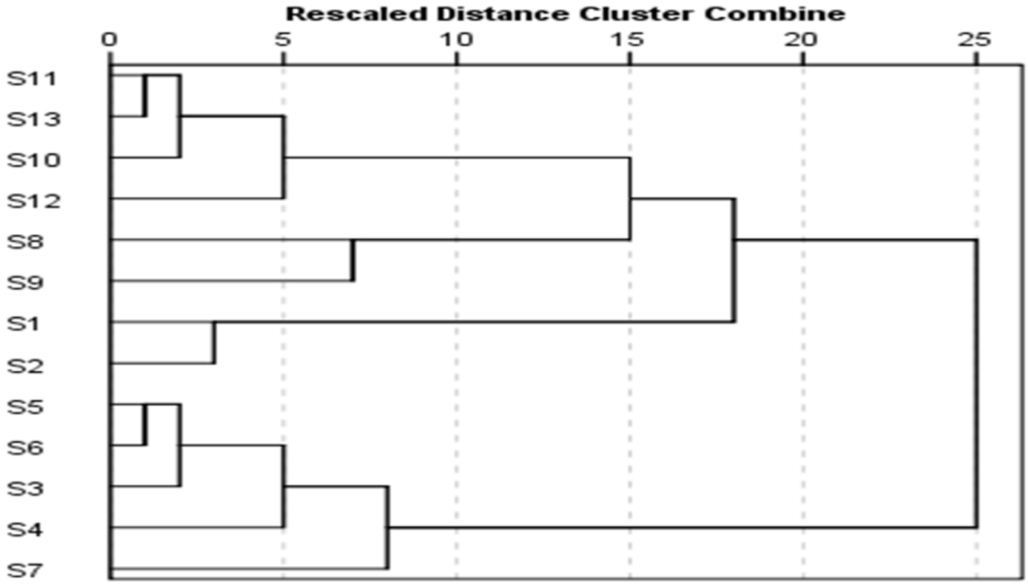

Fig. 2. Dendrogram of clustering of sampling sites in the mid-Black Sea.

References

Akbal, F., Gürel, L., Bahadir, T., Güler, I., Bakan, G., Büyükgüngör, H., 2011a. Multivariate statistical techniques for the assessment of surface water quality at the mid-Black Sea coast of Turkey. Water Air Soil Pollut. 216, 21–37. http://dx.doi.org/10.1007/s11270-010-0511-0.

Akbal, F., Gürel, L., Bahadir, T., Güler, I., Bakan, G., Büyükgüngör, H., 2011b. Water and sediment quality assessment in the mid-Black Sea coast of Turkey using multivariate statistical techniques. Environ. Earth Sci. 64, 1387–1395. http://dx.doi.org/10.1007/s12665-011-0963-6.

Altaş, L., Büyükgüngör, H., 2007. Heavy metal pollution in the Black Sea shore and offshore of Turkey. Environ. Geol. 52, 469–476. http://dx.doi.org/10.1007/s00254-006-0480-1.

Anku, W.W., Mamo, M.A., Govender, P.P., 2017. Phenolic compounds in water: Sources, reactivity, toxicity and treatment methods. In: Phenolic Compd. - Nat. Sources, Importance Appl.. http://dx.doi.org/10.5772/66927.

Arici, E., Bat, L., 2017. Assessment of elemental uptakes by Ulva (Chlorophyta) species collected from Sinop coasts of the Black Sea. Pakistan J. Mar. Sci. 26, 1–13.

Arora, Amarpreet Singh, 2014. Use of cluster analysis-a data mining tool for improved water quality monitoring of River Satluj. Int. J. Adv. Comput. Sci. Appl. 6, 63–69.

Bakan, G., Büyükgüngör, H., 2000. The Black Sea. Mar. Pollut. Bull. 41, 24–43. http://dx.doi.org/10.1016/S0025-326X(00)00100-4.

Bakan, Gulfem, Büyükgüngör, H., Bakan, Gülfem, Akbal, F., 2014. Land-based pollution monitoring and assessment of Black Sea Region 987–975.

Bakan, G., Şişman, A., Akbal, F., Büyükgüngör, H., 2017. Environmental pollution assessment of the Black Sea Coast of Turkey based on GIS-mapping techniques. PONTE Int. Sci. Res. J. 73, 185–198. http://dx.doi.org/10.21506/j.ponte.2017.6.13.

Balcıoğlu, E.B., 2014. A preliminary research on anionic detergent pollution of coastal surface water from various regions of Marmara Sea. Afyon Kocatepe Univ. J. Sci. Eng. 14, 39–44. http://dx.doi.org/10.5578/fmbd.7917.

Baltas, H., Sirin, M., Dalgic, G., Bayrak, E.Y., Akdeniz, A., 2017. Assessment of metal concentrations (Cu, Zn, and Pb) in seawater, sediment and biota samples in the coastal area of Eastern Black Sea, Turkey. Mar. Pollut. Bull. 122, 475–482. http://dx.doi.org/10.1016/j.marpolbul.2017.06.059.

Bat, Levent, Şahin, Fatih, Öztekin, A., 2019. Assessment of Heavy Metals Pollution in Water and Sediments and Polychaetes in Sinop Shores of The Black Sea Assessment of Heavy Metals Pollution in Water and Sediments and Polychaetes in Sinop Shores of The Black Sea. 22, 806–816.

Bat, L., Gökkurt, O., Sezgin, M., Üstün, F., Sahin, F., 2010. Evaluation of the Black Sea land based sources of pollution the coastal region of Turkey. Open Mar. Biol. J. 3, 112–124. http://dx.doi.org/10.2174/1874450800903010112.

Bat, L., Öztekin, A., Şahin, F., Arıcı, E., Özsandıkçı, U., 2018. An overview of the Black Sea pollution in Turkey. MedFAR 1, 67–86, Bat al..

Büyükgüngör, H., Bakan, G., Akbal, F., 2014. Land-based pollution monitoring and assessment of Black Sea Region 987–975.

Çevik, U., Damla, N., Kobya, A.I., Bulut, V.N., Duran, C., Dalgic, G., Bozaci, R., 2008. Assessment of metal element concentrations in mussel (M. Galloprovincialis) in Eastern Black Sea, Turkey. J. Hazard. Mater. 160, 396–401. http://dx.doi.org/10.1016/j.jhazmat.2008.03.010.

Coban, B., Balkıs, N., Aksu, A., 2009. Heavy metal levels in sea water and sediments of Zonguldak, Turkey. J. Black Sea Mediterr. Environ. 15, 23–32.

Şimşek, A., Sancak, Ş., Bakan, G., 2021. Monitoring of heavy metal pollution in water and sediments at the mid-Black Sea Region by using passive sampling method diffusive gradients in thin films. Turk. J. Agric. Food Sci. Technol. 9, 1076–1086. http://dx.doi.org/10.24925/turjaf.v9i6.1076-1086.4217.

EEA, 2015. European Environment Agency (EEA) [WWW Document]. URL https://www.eea.europa.eu/soer/2015/countries/black-sea.

European Communities, 1989. S.I. No. 294/1989 - European Communities (Quality of Surface Water Intended For The Abstraction of Drinking Water) Regulations, 1989. [WWW Document]. URL http://www.irishstatutebook.ie/eli/1989/si/294/made/en/print#.

European Communities, 2007. Water environmental quality standards. In: CONCAWE Review.

Gokkus, K., Berber, S., 2019. Heavy metal pollution in Inebolu and Bartin Ports, Black Sea, Turkey. Indian J. Geo-Mar. Sci. 48, 1600–1608.

Hamzah, F.M., Jaafar, O., Jani, W.N.F.A., Abdullah, S.M.S., 2016. Multivariate analysis of physical and chemical parameters of marine water quality in the straits of Johor, Malaysia. J. Environ. Sci. Technol. 9, 427–436. http://dx.doi.org/10.3923/jest.2016.427.436.

Hsu, L.C., Huang, C.Y., Chuang, Y.H., Chen, H.W., Chan, Y.T., Teah, H.Y., Chen, T.Y., Chang, C.F., Liu, Y.T., Tzou, Y.M., 2016. Accumulation of heavy metals and trace elements in fluvial sediments received effluents from traditional and semiconductor industries. Sci. Rep. 6, 1–12. http://dx.doi.org/10.1038/srep34250.

Hung, T.-C., Meng, P.-J., Han, B.-C., Chuang, A., Huang, C.-C., 2001. Trace metals in different species of mollusca, water and sediments from Taiwan coastal area. Chemosphere 44, 833–841. http://dx.doi.org/10.1016/S0045-6535(00)00491-4.

Jafarzadegan, M., Safi-Esfahani, F., Beheshti, Z., 2019. Combining hierarchical clustering approaches using the PCA method. Expert Syst. Appl. 137, 1–10. http://dx.doi.org/10.1016/j.eswa.2019.06.064.

Jain, C.K., Sharma, M.K., 2001. Distribution of trace metals in the Hindon River system. Indian J. Hydrol. 253, 81–90. http://dx.doi.org/10.1016/S0022-1694(01)00484-X.

Koziorowska, K., Kuliński, K., Pempkowiak, J., 2017. Distribution and origin of inorganic and organic carbon in the sediments of Kongsfjorden, Northwest Spitsbergen. Eur. Arct. Cont. Shelf Res. 150, 27–35. http://dx.doi.org/10.1016/j.csr.2017.08.023.

Liu, L., Dong, Y., Kong, M., Zhou, J., Zhao, H., Tang, Z., Zhang, M., Wang, Z., 2020. Insights into the long-term pollution trends and sources contributions in Lake Taihu, China using multi-statistic analyses models. Chemosphere 242, 125272. http://dx.doi.org/10.1016/j.chemosphere.2019.125272.

Niemiec, M., Wiśniowska-Kielian, B., Arasimowicz, M., Kuzminowa, N., 2015. Assessment of the Black Sea ecosystem pollution with copper and cadmium in selected bays of Sevastopol region. J. Ecol. Eng. 16, 119–127. http://dx.doi.org/10.12911/22998993/60467.

Ouyang, Y., Nkedi-Kizza, P., Wu, Q.T., Shinde, D., Huang, C.H., 2006. Assessment of seasonal variations in surface water quality. Water Res. 40, 3800–3810. http://dx.doi.org/10.1016/j.watres.2006.08.030.

Said, A., Stevens, D.K., Sehlke, G., 2004. An innovative index for evaluating water quality in streams. Environ. Manage. 34, 406–414. http://dx.doi.org/10.1007/s00267-004-0210-y.

Serafim, A., Company, R., Lopes, B., Rosa, J., Cavaco, A., Castela, G., Castela, E., Olea, N., Bebianno, M.J., 2012. Assessment of essential and nonessential metals and different metal exposure biomarkers in the human placenta in a population from the south of Portugal. J. Toxicol. Environ. Health A 75, 867–877. http://dx.doi.org/10.1080/15287394.2012.690704.

Shrestha, S., Kazama, F., 2007. Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan. Environ. Model. Softw. 22, 464–475. http://dx.doi.org/10.1016/j.envsoft.2006.02.001.

Shrestha, S., Kazama, F., Nakamura, T., 2008. Use of principal component analysis, factor analysis and discriminant analysis to evaluate spatial and temporal variations in water quality of the Mekong river. J. Hydroinformatics 10, 43–56. http://dx.doi.org/10.2166/hydro.2008.008.

Su, S., Li, D., Zhang, Q., Xiao, R., Huang, F., Wu, J., 2011. Temporal trend and source apportionment of water pollution in different functional zones of Qiantang River, China. Water Res. 45, 1781–1795. http://dx.doi.org/10.1016/j.watres.2010.11.030.

SWQR, 2016. Turkey's ministry of forestry and water affairs surface water quality regulations.

Syms, C., 2019. In: Fath, B.B.T.-E. of E. (Ed.), Principal Components Analysis, second ed. Elsevier, Oxford, pp. 566–573. http://dx.doi.org/10.1016/B978-0-12-409548-9.11152-2.

Thirumalini, S., Joseph, K., 2009. Correlation between electrical conductivity and total dissolved solids in natural waters. Malays. J. Sci. 28, 55–61. http://dx.doi.org/10.22452/mjs.vol28no1.7.

Topcuoğlu, S., Ergül, H.A., Baysal, A., Ölmez, E., Kut, D., 2003. Determination of radionuclide and heavy metal concentrations in biota and sediment samples from pazar and rize stations in the eastern Black Sea. Fresenius Environ. Bull. 12, 695–699.

UNEP, 2018. United Nations Environment Programme (UNEP) [WWW Document]. URL https://www.unep.org/explore-topics/oceans-seas/what-we-do/working-regional-seas/regional-seas-programmes/black-sea.

U.S. EPA, 2022. US Environmental Protection Agency, Water: Monitoring & Assessment. https://archive.epa.gov/water/archive/web/html/vms57.html (accessed 18 January 2022).

U.S. EPA, U.S, 2022b. Environmental Protection Agency Report an Environmental Violation. https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table (accessed 18 January 2022).

Üstün Odabaşı, S., Şentürk, I., Maryam, B., Akbal, F., Bakan, G., Büyükgüngör, H., 2018. Temporal variation of mercury in Turkish Black Sea waters and associated risk assessment. Glob. Nest J. 20, 345–354.

Wu, M.L., Wang, Y.S., Sun, C.C., Wang, H., Dong, J. De, Han, S.H., 2009. Identification of anthropogenic effects and seasonality on water quality in Daya Bay, South China Sea. J. Environ. Manag. 90, 3082–3090. http://dx.doi.org/10.1016/j.jenvman.2009.04.017.

Yap, C.K., Chee, M.W., Shamarina, S., Edward, F.B., Chew, W., Tan, S.G., 2011. Assessment of surface water quality in the Malaysian coastal waters by using multivariate analyses. Sains Malays. 40, 1053–1064.

Zhao, Y., Xia, X.H., Yang, Z.F., Wang, F., 2012. Assessment of water quality in Baiyangdian lake using multivariate statistical techniques. Proc. Environ. Sci. 13, 1213–1226. http://dx.doi.org/10.1016/j.proenv.2012.01.115.

Zhou, F., Guo, H. Cheng, Liu, Y., Hao, Z. Jia, 2007. Identification and spatial patterns of coastal water pollution sources based on GIS and chemometric approach. J. Environ. Sci. 19, 805–810. http://dx.doi.org/10.1016/S1001-0742(07)60135-1.