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Correlation between water quality and pollution parameters in the surface waters of the coastal areas of the Sea of Marmara, Türkiye

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Abstract

The coastal areas of the Marmara Sea are exposed to many pollution sources and pollutants. In addition to these sources, freshwater sources such as rivers and streams flow into this inland sea and cause serious stress. In this study, physicochemical parameters such as dissolved oxygen (DO), pH, salinity (S) and temperature (T) measured in surface water samples taken from the coastal area of the Marmara Sea, which is under the influence of intense pollution. In addition, nutrients such as nitrite+nitrate (NO2-+ NO3-), total nitrogen (TN), dissolved inorganic phosphorus (o- PO43-), total phosphorus (TP) and pollution parameters such as anionic surfactant (AS), total petroleum hydrocarbons (TPH) were also analyzed and their correlations with each other were evaluated. Furthermore, the concentrations of particulate organic matter (POC) in water samples and total organic carbon (TOC) in coastal sediments were also determined. Accordingly, DO and pH values were found to be high at the stations where water circulation was active, and these results were similar to chlorophyll-a values. In addition, when the water quality parameters were evaluated according to the continental surface water quality criteria, it was determined that the surface waters of the coastal area of the Marmara Sea were in the middle-class water quality in terms of TN and TP. The highest values of TPH and AS among the stations were found in Poyrazköy station. The high TOC values detected in the sediments of stations such as Erdek, Başiskele and Büyükkumla indicate the presence of a significant organic load. The findings of this study can shed light and provide the basis for long-term studies to make a complete assessment of water quality in these areas.

Keywords Sea of Marmara • nutrients • TPH • anionic surfactant



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Introduction

Sources of pollution are mostly human activities. Examples include untreated discharges of used domestic and industrial wastewater, runoff from agricultural areas, dust and other wastes carried by wind and floods. As a result of domestic and industrial wastewater discharged at a much higher rate than the seas can handle, algal blooms called eutrophication are observed. Eutrophication is a form of biological pollution that can have detrimental effects, leading to the degradation of aquatic ecosystems. The degradation of aquatic ecosystems is a serious threat to both economic stability and environmental health (Damar et al., 2021; Achman et al., 1993).

Pollution sources are categorized into three main types: direct wastewater discharge, surface runoff from contaminated areas, and atmospheric pollution. Pollution itself is divided into two types: point pollution and diffuse pollution. Point pollution refers to localized pollution that is easy to identify and trace. Wastewater discharged directly into the sea through sewage is an example of this. Point pollution is more prevalent in developed countries (Gazioğlu, 2018; Powley et al., 2016; Peavy et al., 1985).

The transport of pollutants from urban areas, agricultural lands via irrigation and rainfall, surface runoff from ports and construction sites, and floods introduces carbon, nitrogen, phosphorus, and other nutrient-rich particles into surface water bodies. These nutrient inputs contribute to eutrophication, a process characterized by the excessive proliferation of pollution-indicator species and naturally occurring microorganisms. In eutrophic environments, biological processes accelerate, leading to a rapid increase in consumer organisms, which in turn alters the chemical and physical properties of the aquatic ecosystem. Such disruptions can destabilize the food web, potentially causing the decline of plankton-feeding aquatic species and rendering the changes irreversible without intervention. Eutrophication, primarily driven by nitrogen and phosphorus enrichment from human activities-including urbanization, industrialization, agriculture, and animal husbandryfundamentally disrupts ecological equilibrium. It leads to shifts in N/P/Si ratios, excessive organic matter production, permanent alterations in planktonic communities, reduced bio-optical properties of seawater, oxygen depletion in bottom waters, and long-term changes in macro-benthic assemblages. The primary driver of eutrophication is the introduction of nutrient-laden wastewater into aquatic ecosystems through surface runoff or direct discharge, originating from both domestic and industrial sources.

The Sea of Marmara exhibits unique environmental conditions. First, its large surface area can make it vulnerable to atmospheric deposition. The second important point is that there are important industrial zones in the northern and southern basins surrounding it. Most of the wastewater of these organized industries is discharged into this inland sea or the rivers reaching it without treatment processes. Of the wastewater discharged into the Sea of Marmara, 8.3% is industrial wastewater and 91.7% is domestic/urban wastewater. Of these, 51.3% is discharged by deep-sea discharge and 46% is discharged after advanced biological treatment processes (TÜBİTAK, 2021). This causes excessive pollution of the Sea of Marmara. Since the Sea of Marmara is located between the Mediterranean and the Black Sea and has a continuous current system, pollutants can be transported over long distances. The third point is that the Sea of Marmara has a large volume and the hydraulic residence time of water in this sea is long. As a result, pollutants can persist in this environment for extended periods (Aksu et al., 2024; Balcioğlu, 2024; Atabay et al., 2024; Korkmaz et al., 2024; Yücel et al., 2024; Taşdemir, 2002).

The Sea of Marmara has been acting as a receiving environment where pollutants can be discharged for years. Pollution in the Sea of Marmara is not limited to the Istanbul Strait, Izmit Bay and Gemlik Bay. This sea is exposed to pollution from discharges of domestic and industrial wastewater, agricultural activities, ship wastewater and atmospheric deposition (Taşdemir and Payan, 2000; Solmaz et al., 2000).

Total petroleum hydrocarbons (TPH) can enter marine ecosystems in a variety of ways, including shipwrecks, oil spills from leaks during fuel loading and unloading operations, chronic pollution from industrial activities, urban runoff and natural seepage from underwater oil reservoirs (Gong et al., 2014; Nazir et al., 2008). The presence of TPH in the marine environment poses a significant ecological risk. Damage to marine organisms is defined as physical asphyxiation, direct toxicity or biological growth and bioaccumulation processes (Wei et al., 2022; Bao et al., 2021; Kapsdis et al., 2021; Foshtami et al., 2019). It has also been reported that the main causes of pollution in the Turkish Seas are oil transportation, ship traffic, atmospheric deposition and industrial discharges (Güven et al., 2008).

Detergents contain anionic surfactants such as various linear alkalibenzene sulfonates (LAS), which are important pollutants for aquatic life. LAS are the most widely used anionic surfactants in the formulation of detergents in developed and developing countries around the world, and due to their widespread use, they are often found in



wastewater and marine receiving environments (Gonzalez-Mazo et al., 1999). These substances mostly originate from cleaning activities and are found extensively in domestic and industrial wastewater. Detergents decompose by biochemical reactions in the receiving environment where they ultimately reach, reducing the dissolved oxygen in the environment and making the environment anoxic. Detergents also contain oxygen-depleting substances that can seriously harm fish and marine animals (Lewis, 1991; Cserhati et al., 2002).

In this study, water quality parameters in water samples taken from the coasts of the Sea of Marmara, which is under the influence of a serious pollution load, were examined. Concentrations of water parameters such as $NO_2^{-+}NO_3^{-}$, total nitrogen (TN), $o-PO_4^{3-}$, total phosphorus (TP), chlorophyll-a (Chl-a), suspended solids, anionic surfactant (AS), total petroleum hydrocarbons (TPH), particulate organic carbon (POC), particulate organic nitrogen (PON), total suspended solids (TSS) and total organic carbon (TOC) in the sediment were determined and basic physicochemical parameters were evaluated and discussed.

Materials and Methods

The shallow threshold depths of the Istanbul Strait and Çanakkale Strait and the difference in salinity of the waters of Mediterranean and Black Sea origin create a two-layered water column and current system in the Straits and the Sea of Marmara and prevent the effective circulation of the lower water. At the bottom, the more saline water of Mediterranean origin (38.5 ‰) flows into the Black Sea, while at the top, the less saline water of Black Sea origin (18 ‰) flows into the Mediterranean Sea (Ünlüata et al., 1990). Due to the mixing and diffusion events in the Straits and the Sea of Marmara, the boundary (halocline) between these two water masses, which reach approximately 36 ‰ and 22 ‰ salinity in the Sea of Marmara, is located at approximately 25 m.

In this study, sampling was carried out along the entire coast of the Sea of Marmara, including the Straits. The sampling points were selected based on their relatively easy accessibility to the seaside, and some of them are inhabited (Figure 1). Sampling was carried out between 08 - 15 April 2024.

Water and sediment sampling in coastal areas

Water sampling was carried out from 20 different stations along the coast of the Sea of Marmara from the surface. Water samples were taken in 100 ml white polyethylene bottles that were washed with HCl and rinsed with distilled water. For chlorophyll-a, water samples were taken in 1 L white polyethylene bottles and filtered through 0.45 μ m GF/C filter paper. For suspended solids and POC, water samples were taken in 1 L white polyethylene bottles similar to those used for chlorophyll-*a* and filtered with filter papers dried at 90°C for 1 hour, using GF/C filter paper for suspended solids and GF/F filter paper for (POC). The filter papers were wrapped in aluminum foil and stored in deep freezer (-18°C) until analysis. Water samples for anionic surfactant and total petroleum hydrocarbons were taken in 1 L brown glass bottles and 10 ml of dichloromethane (DCM) was added to the samples to protect them from bacterial decomposition. Coastal area sediment samples were taken in glass jars by diving or grab. Nutrient bottles, brown glass bottles and jars were brought to the laboratory under cold chain (+4°C). Nutrient bottles and sediment samples were kept in deep freezer (-18°C) until analysis, while water samples in brown glass bottles were kept in cold environment and analyzed as soon as possible.

Physicochemical data sampling

Dissolved oxygen, pH, temperature and salinity values of the water were measured in situ with AQUAREAD (Aquaprobe-AP-700) multiparameter device. Dissolved oxygen values (mg/L) were also calibrated by Winkler method (Winkler, 1888).

Nutrient analysis, Chl-a and TSS determination

 $NO_2^{-+} NO_3^{--}$ analysis is based on 90-95% reduction of the analyzed nitrate to nitrite by passing it through a cadmium granule column. Under acidic conditions, nitrite ions form a pink diazo compound in the presence of sulfanilamide and N-naphthylethylene diamine hydrochloride. Light absorption is measured at 550 nm wavelength of the photometer. For the determination of total nitrogen, basic persulfate oxidation method was applied (Grasshoff et al., 1983). With this method, total nitrogen contained in 50 ml of seawater sample to which 5 ml of oxidation reagent containing potassium persulfate buffered with boric acid-NaOH mixture is added is converted into inorganic form by applying constant temperature (115°C) for 2 hours in autoclave. At the end of the oxidation, the pH is checked to see if the value is close to 8.0. Following this process, the total nitrogen content of the samples is determined by applying the $NO_2^- + NO_3^-$ determination method (APHA, 2000; Grasshoff et al., 1983).

The analysis of orthophosphate in seawater is based on the reaction with ammonium molybdate to form complex heterepoly acid. This acid is reduced by ascorbic acid to form a blue colored complex. The light absorption of this complex is measured at 880 nm wavelength of the photometer and the concentration is calculated. The basic persulfate oxidation method was applied for the determination of total phosphate (Grasshoff et al., 1983). With this method, total phosphate contained in 50 ml of seawater sample



Figure 1. Sampling points (1-Florya, 2- Marmara Ereğli, 3-Tekirdağ, 4- Şarköy, 5- Gelibolu, 6- Burhanlı Köyü, 7- Bigalı, 8- Kumkale, 9- Kepez, 10- Çardak, 11- Kemer, 12- Erdek, 13- Turan Köyü, 14- Yenice, 15- Kurşunlu, 16- Büyükkumla, 17- Yalova, 18- Karamürsel, 19- Başiskele, 20- Poyrazköy)

to which 5 ml of oxidation reagent containing potassium persulfate buffered with boric acid-NaOH mixture is added is converted into inorganic form by applying constant temperature (115°C) for 2 hours in autoclave. As a result of oxidation, the pH values of the samples whose pH decreased to 4-5 are increased to 7.5-8. Following this process, the total phosphate content of the samples is determined by applying orthophosphate determination method in UV-Vis spectrophotometer (Shimadzu UV-1800 Spectrophotometer) (APHA, 2000; Grasshoff et al., 1983).

For Chl-*a* analysis, 1 L water samples were filtered through Whatmann GF/C papers and calculated by measuring their absorbance at different wavelengths in UV spectrophotometer after extraction with acetone (APHA, 2000).

In addition, TSS were determined in the water samples taken from the stations within the scope of the research. For this purpose, water samples taken in a certain volume (ml) were filtered through GF/C paper whose weight was previously noted (initial weight). The filter papers were dried in an oven set at 105°C for 1 hour and then allowed to cool in a desiccator. The cooled filter papers were weighed (final weight). TSS calculation was made according to the formula below (APHA, 2005).

TSS (mg/L) = (final weight (A) - initial weight (B))x1000/V

Determination of AS and TPH

The method used for the determination of anionic detergents is the spectrophotometric measurement of the salt formed by the reaction of methylene blue with anionic surfactants by dissolving in chloroform (APHA, 1995). Methylene blue was added to a certain volume of buffered water samples and extracted with chloroform. The chloroform, after being shaken with the washing solution, was adjusted to 100 mL with pure chloroform and measured by UV at a wavelength of 652 nm.

For TPH determination, a certain volume of water sample was extracted with DCM and after evaporation, the residue was dissolved in hexane and the extract was passed through a clarifier. The final volume was then adjusted to 1 ml and the samples were measured by fluorescence spectroscopy (UVF) (Jasco FP- 6300) (Kelly et al., 2000). Concentrations were calculated using the standard curve equation based on chrysene (μ g/L).

TOC Analysis

The analysis was carried out on samples dried at 105 °C and ground in an agate mortar according to the Walkey-Blake method (Loring and Rantala, 1992; Gaudatte et al., 1974). This method involves oxidation of organic matter with potassium dichromate and titration of excess dichromate with ferrous ammonium sulfate under diphenylamine indicator.

FTIR and POC Analysis

After filtering the water samples for POC, the filter papers were stored in the deep freezer. Then, they were removed, dried in an oven at 90°C for 1 hour, reweighed, and recorded. Then, chemical characterization of the organic carbon content in the papers was carried out using FTIR (Fourier Transform Infrared Spectroscopy) (PerkinElmer). Finally, POC concentrations were determined titrimetrically according to the Walkey-Blake



method (Loring and Rantala, 1992; Gaudatte et al., 1974) using paper plates.

Results

Physicochemical Results

In the study, physicochemical parameters such as temperature, salinity, dissolved oxygen (DO), and pH were measured in surface water samples taken from 20 different points in the coastal area of the Sea of Marmara.

Salinity values ranged from 18.08‰ to 23.93‰, with a mean of 20.85 \pm 1.40‰, while temperature values ranged from 17.4°C to 20.0°C, with a mean of 18.59 \pm 0.73°C. Relatively high salinity values were found in the Çanakkale Strait due to its proximity to Mediterranean waters.

DO values were measured between 6.97 - 10.57 mg/L with a mean of $9.12 \pm 0.84 \text{ mg/L}$ and pH values were measured between 8.01 - 8.36 with a mean of 8.21 ± 0.10 (Table 1). In general, it is seen that DO and pH values are compatible. The highest DO values were found at Kepez and Yalova stations, which is thought to be due to the higher circulation at these points (Figure 2).

Nutrient Results

Within the scope of the study, $NO_2^-+NO_3^-$, TN, $o-PO_4^{3-}$, TP, Chl*a* values of coastal area surface water were also determined.

NO₂⁻⁺NO₃⁻ contents were found in the range of 15.14- 16.59 μ M with a mean of 15.58 ± 0.37 μ M, while TN values were found in the range of 160- 442.53 μ M with a mean of 307.49 ± 77.06 μ M. The highest NO₂⁻⁺NO₃⁻ was found at Erdek station and the lowest values were found at Marmara Ereğli, Tekirdağ, Poyrazköy stations. The highest TN concentration was found at Kepez station and the lowest value was found at Şarköy station. Chl-*a* values were found in the range of 0.61- 2.49 with a mean of 1.88 ± 0.39 μ g/L. Moreover, since pH values

were similar to DO and Chl-*a* concentrations except Marmara Ereğlisi, Poyrazköy and Karamürsel stations, it is thought that high pH values are related to primary production (Figure 3).

Table 1. Physicochemical parameters by stations

Station No	Stations	DO (mg/L)	рН	Temperature (°C)	Salinity (‰)
1	Florya	8.9	8.24	19.10	19.87
2	M. Ereğli	8.26	8.06	18.5	19.35
3	Tekirdağ	8.21	8.18	18.8	20.98
4	Şarköy	9.67	8.36	17.7	21.12
5	Gelibolu	8.51	8.21	17.9	21.74
6	Burhanlı	9.69	8.3	18	21.96
7	Bigalı	9.08	8.31	17.4	22.76
8	Kumkale	8.99	8,22	19.4	23.93
9	Kepez	10.57	8,34	20	22.32
10	Çardak	8.44	8.21	18.50	21.29
11	Kemer	9.1	8.29	19.9	21.67
12	Erdek	9.77	8.25	19.2	21
13	Turan	9.05	8.2	18.7	21.3
14	Yenice	8.79	8.3	19.40	21.73
15	Kurşunlu	9.99	8,27	17.80	19.05
16	Büyükkumla	8.39	8,12	18.30	20.11
17	Yalova	10.36	8,18	17.70	19.74
18	Karamürsel	9.8	8.03	18.20	19.32
19	Başiskele	9.89	8.16	18.40	19.66
20	Poyrazköy	6.97	8.01	18.9	18.08

In o-PO₄³⁻ values, the highest concentration of 34.42 μ M was found at Burhanlı station and the lowest value was found at Kepez station. o-PO₄³⁻ concentrations were found in the range of 4.42- 34.42 μ M with an average of 14.69 ± 6.53 μ M. TP values were found in the range of 19.94- 42.69 μ M with an average of 31.17 ± 7.18 μ M. The highest TP value was detected at Başiskele



Figure 2. DO and pH values by stations



Figure 3. NO2-+NO3-, TN and Chl-a concentrations by stations

station in Izmit Bay and the lowest concentration was detected at Büyükkumla station.

In the upper layer of the Black Sea, nutrient content increases in certain months due to the input of runoff materials from non-point sources (Okuş et al., 2002a). In addition, nutrients enter the upper layer as a result of the mixing of sewage contaminated substrates in the southern part of the Istanbul strait (Okuş et al., 2002b).

In addition, Tuğrul et al. (2002) reported that NO_2+NO_3-N and PO_4-P concentrations were lowest in summer and early fall and increased significantly in early winter. In this study, there is no seasonal assessment, but when the stations along the coasts are evaluated in general, especially the high values in $o-PO_4^{3-}$ and TP indicate terrestrial anthropogenic inputs (Figure 4).

Although *o*-PO₄³⁻ values were close to each other across the stations, relatively low values among inorganic phosphate values were found in the stations in the Çanakkale Strait. Especially towards the east of the Sea of Marmara, inorganic phosphate values were found to be high. In other words, as we approach the Black Sea, the surface waters are characteristic of the Black Sea origin waters. High values suggest anthropogenic inputs from point and diffuse sources. Furthermore, based on the continental surface water quality criteria (Official Gazette, 2021), the surface waters in the coastal area of the Sea of Marmara were classified as medium quality in terms of total nitrogen (TN) and total phosphorus (TP).



Figure 4. o-PO₄³⁻, TP and AS concentrations by stations

Inorganic nitrogen and phosphorus ratios in seawater

The composition of seawater is generally known as the Redfield ratio of 106:16:1 (atomic weight) for carbon, nitrogen and phosphorus (Redfield et al., 1963). Naturally, many situations fall outside these generalizations. For example, phosphorus in the eutrophic zone cycle faster than nitrogen. For this reason, low concentrations of phosphorus can be found while nitrogen is absent. During phytoplankton proliferation, the nutrients in the water are used at these rates. It is possible to determine how much of the nitrogen, phosphorus and carbon compounds entering the receiving environment will play a role in phytoplankton development and thus prevent eutrophication problems by determining the limiting nutrient element. Although there is no exact threshold for determining the limiting nutrient in aquatic environments, the N/P ratio provides guidance: when N/P = 5, both nitrogen and phosphorus are limiting; when N/P<5, nitrogen is the limiting nutrient, indicating a nitrogen-controlled system; and when N/P > 16, phosphorus is the limiting nutrient, indicating a phosphorus-controlled system (Coveney and Wetzel, 1995).

N/P ratios vary between 0.4 and 3.6 in all stations. (Figure 5). Although the highest ratio was found at Kepez station, nitrogen is the limiting element at all stations in the study, since the value in question is N/P<5.

As part of the Wastewater Master Plan prepared by the Istanbul Water-Wastewater and Sewerage Administration (ISKI) between 1993 and 1999, anthropogenic (urban and industrial) inputs to the Sea of Marmara were controlled through deep sea discharges at Yenikapı, Üsküdar, Baltalimanı, Küçüksu, Küçükçekmece, Kadıköy, Ataköy, Paşabahçe, and Paşaköy (Okuş et al., 2008). However, the deep discharges planned to be sent to the Black Sea with waters originating from the Mediterranean Sea caused unwanted back inputs to the Sea of Marmara, especially during periods when southerly winds prevailed. In addition, after the mucilage incident in 2021, "The Sea of Marmara and Islands" was declared as -Special Environmental Protection Area- and it was aimed to reduce these inputs with the 22-item Action Plan put into practice with the circular of the Ministry of Environment, Urbanization and Climate Change dated 07.06.2021 and numbered 2021/12 (MMU, 2021).

AS and TPH Results

In addition to physicochemical and nutrient parameters, AS and TPH concentrations of pollutant parameters were also analyzed throughout the sampling stations.

AS values of seawater ranged between $5.05 - 66.77 \ \mu g/L$. The lowest concentration was detected at Yenice station and the highest value was detected at Poyrazköy station. The fact that the highest value was found in Poyrazköy station can be explained by the fact that this station is both close to the Black Sea and affected by the currents coming from there, and that it is affected by the discharges due to the settlement and tourism activities near the station. In addition, the fact that the station is located in an area closed to circulation also explains the reason for the high concentration.

There are studies on AS pollution in the coastal area in the seas of our country. Apart from the Sea of Marmara, AS concentrations examined in the Gulf of Izmir varied between 0.032-0.232 mg/L. In the study, it was revealed that Melez River carries a high amount of AS load to the gulf (Yılmaz et al., 2006). In addition, in a study examining detergent concentrations on the coasts of Giresun province in the Black Sea, these values were reported in the range of 0.887- 1.987 mg/L (Polat and Akkan, 2016). In another study conducted



Figure 5. N/P ratios according to stations

in Gökçeada in the North Aegean, surfactant values were determined between 0.020 - 0.051 mg/L (Balcıoğlu, 2019a).

In studies conducted in the Sea of Marmara, the detergent concentration was reported as 0.243 mg/L in 2004 (Güven and Çoban, 2013), while it was 0.042 mg/L in the Istanbul Strait and 0.059 mg/L in the Çanakkale Strait (Güven et al., 2008). Similarly, in 2005, the concentration in the Çanakkale strait was 0.035 mg/L (Güven et al., 2008; 2006), in 2012 it was 0.048 mg/L (Balcıoğlu, 2014a). In 2013 it was 0.067 mg/L in the Çanakkale Strait, 0.077 mg/L in the Istanbul Strait and 0.073 mg/L in the Sea of Marmara (Balcıoğlu, 2014b).

In this study, AS concentrations in water samples taken from the coasts of the Çanakkale Strait were determined in the range of 0.012 - 0.021 mg/L with a mean value of 0.018 ± 0.003 mg/L. It is noteworthy that the values found both in the Sea of Marmara and in the Çanakkale Strait and Istanbul coasts are relatively lower than the values reported in previous studies (Balcıoğlu, 2014a; Balcıoğlu, 2014b; Güven et al., 2008; Güven and Çoban, 2013; Balcıoğlu, 2015; Balcıoğlu, 2019b). It is thought that the measures to gradually reduce the use of phosphate in detergents, as stated in the action plan put into practice in 2021, have an impact on this situation.

Detergents are completely synthetic and are not formed by natural processes in any way. Therefore, there is no limit value for the amounts of these pollutants in the sea, which is the last environment they reach. However, according to the limit values recommended by the World Health Organization, detergent values that can be determined in drinking water should not be above 0.2 mg/L (Anonymous, 2007). In addition, in the classification of "Quality of Inland Water Resources" in the Official Gazette dated 2012 and numbered 28483, the detergent value should be maximum 0.05 mg/L for the water to be of first class quality (Official Gazette, 2012). In the 2006 dated and 26048 numbered Official Gazette, according to the table of quality criteria to be provided for waters used for swimming and recreation purposes, this value should be at a level (\leq 0.3 mg/L) that will not cause permanent foam formation (Official Gazette, 2006). In addition, in the water quality criteria applied in the European Union, the recommended surfactant value is \leq 0.3 mg/L and the limit value is accepted as "no permanent foam formation". Since the highest AS value of 66.77 μ g/L (0.067 mg/L) detected in the water samples taken within the scope of this study is above the recommended value in the swimming water quality regulation and the water quality criteria applied in the EU, it is understood that the water is not in first class water quality.

Since the Sea of Marmara is exposed to intense oil pollution due to its location, population density and coasts of cities with industrial activities, studies on the determination of oil pollution are also quite numerous. Especially in studies conducted after accidents, high levels of pollution have been reported. For example, Güven et al. (2004) revealed that 25 tons of oil was spilled into the sea in the M/V GOTIA ship accident and that this accident was the source of oil pollution in the water by fingerprint analysis. The same researcher determined the highest TPH amounts as 29.55 μ g/L in the Istanbul Strait and 42.96 μ g/L in the Çanakkale Strait in a study conducted in the waters of the Turkish Straits and emphasized that the values they found were far above the international acceptable limit values (Güven et al., 2008).

Another study conducted in the Sea of Marmara was carried out by Balcıoğlu (2013) in the Turkish Straits System, and the TPH concentrations in the surface waters taken from 17 different coastal points in February 2013 were found to be 2.71 mg/L in the Istanbul Strait according to the krizen standard. Balcıoğlu (2019c) also examined the TPH concentrations in the surface waters of the Prince Islands and found TPH concentrations in the ranges of 2-6.6 μ g/L in Kınalıada, 2.3- 6.7 μ g/L in Heybeliada, 2.2- 6.8 μ g/L in Burgazada and 3.7 - 7.2 μ g/ L in Büyükada.

TPH values of coastal area surface water ranged from 2.64 μ g/L to 333.09 μ g/L across all stations (Figure 6). The lowest concentration was found in Turan Village. The low value can be attributed to Turan Village's location at the highest point of the Erdek peninsula, with a small population due to its isolation from urban influences and the impact of moving water circulation. The remarkably high TPH value at the Poyrazköy station is thought to be related to the fact that the samples were taken from a shore with low circulation and close to boats and from a point of the Istanbul Strait near to the Black Sea, similar to AS. In addition to studies reporting oil pollution in the Black Sea (Balcıoğlu et al., 2018; Balkıs et al., 2011; Readman et al., 2002; Üstün-Kurnaz and Büyükgüngör, 2007; Ünlü and Alpar, 2009), research has also shown that the Black Sea is polluted by petroleum hydrocarbons from rivers (Balcıoğlu, 2018; Güven and Çoban, 2012; Balcıoğlu and Öztürk, 2009).

The absorbances of samples prepared for TPH measurement were also tested in UV fluorescence (UVF) across different wavelength ranges based on ring numbers. This approach was necessary because aromatic hydrocarbon values in the water environment fall below the detection limits of HPLC, making them unmeasurable. Instead, the method developed by Ehrhardt and Burns (1999) was used. Using the absorbance values obtained, the percentage distribution of ringed hydrocarbons was calculated by ring number, allowing for the assessment of potential sources of anthropogenic TPH pollution. The wavelength ranges were set as follows: 280–300 nm for single-ring compounds, 300–375 nm for two rings, 325–375 nm for three to four rings, and 400–475 nm for five rings.

Hydrophobicity and water solubility significantly affect the presence of PAHs in the environment as in all other pollutants. PAHs with 2, 3-4 rings are more likely to be found in water than other PAHs due to their relatively high solubility and volatility. Unsubstituted hydrocarbons containing mostly 4-6 aromatic rings are usually formed during incomplete combustion of organic matter (Readman et al., 2002). Among the PAH rings, low-ring compounds can be degraded very quickly and cannot be detected in the environment. Since the durability of PAH compounds increases with the number of rings, the presence of high-ring PAHs in the environment indicates long-standing contamination. 1-ring PAHs represent benzene, 2-ring PAHs represent compounds such as naphthalene, acenaphthalene, acenaphthene, fluorene. Since low-ring compounds such as these are not stable and break down quickly in the environment, the fact that they are determined

in the water environment indicates a fresh pollution input. 3-4 rings represent thermodynamically stable PAHs such as phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b+k)fluoranthene, and 5 rings represent PAHs such as benzo(a)pyrene, dibenzo(a,h)anthracene. As seen in Figure 7, the percentage of PAH rings in the graph shows that the ratios of 3-4 and 5-ring compounds are significantly higher than the ratios of 1- and 2-ring compounds, indicating that there is a long-standing pollution in the environment.

The TPH findings of the surface waters taken in the study were evaluated by comparing with the limit values specified in different regulations. According to United Nations Environment Programme (UNEP) (1989), the limit value for TPH is 1.5 μ g/L, according to Food and Agriculture Organization of the United Nations (FAO) (1982) it is 2.5 μ g/L and according to Water Pollution Control Regulation (WPCR) (2022) it is 3 μ g/L. The values found in most of the 20 stations where



Figure 7. Percentages of PAH rings by station



water samples were taken within the scope of our study (Figure 7) are above the limit values determined by these authorities. These results reveal that the surface waters of the coastal areas of the Sea of Marmara are severely polluted with TPH. This coincides with the ongoing pollution findings with the presence of 3-4 and 5-ring compounds as seen in the PAH ring numbers graph. The low DO value at this station with high pollution is thought to be the result of this situation. High TPH levels throughout the coastal areas of the Sea of Marmara may cause harmful effects on marine organisms and ecosystems. Petroleum hydrocarbons are toxic to a wide range of marine organisms including fish, invertebrates and phytoplankton. Pollution can lead to bioaccumulation and biomagnification of hydrocarbons in the food chain, potentially affecting the entire ecosystem. This can disrupt ecological processes, reduce biodiversity and affect the long-term sustainability of marine resources related to fisheries. Due to the above mentioned impacts, the assessment of TPH levels in the coastal area is crucial for effective environmental management and protection. Monitoring TPH levels can help identify pollution sources and develop targeted mitigation strategies. It also enables the evaluation of the effectiveness of existing regulations and policies to prevent and reduce hydrocarbon pollution. Detailed long-term monitoring programs can provide valuable data for adaptive management approaches of the ecosystem of the Sea of Marmara.

TSS, TDS, POC, PON in water and TOC in sediment

The distribution of particulate organic matter in seawater is influenced by terrestrial (natural-mineralogical and anthropogenic) inputs and biological activities. Water samples from these stations were analyzed for suspended solids and total dissolved solids. POC analyses were performed to identify carbon origins, followed by FT-IR (Fourier Transform Infrared Spectroscopy) chemical characterization of the collected filter paper samples.

In this study, the lowest total dissolved solids (TDS) concentrations ranged from 10.16 to 23.6 mg/L, with an average of 18.46 \pm 2.39 mg/L. TSS values ranged from 12.3 to 55.4 mg/L, with an average of 34.3 \pm 11.21 mg/L. (Figure 8).

POC and PON concentrations of the water were found in the range of 0.86- 10.25 mg/L with a mean of 5.42 \pm 2.89 and 0.07- 0.85 mg/L with a mean of 0.45 \pm 0.24 mg/L, respectively (Figure 9). TSS and POC values were similar in all stations except Şarköy, Kumkale, Yalova and Poyrazköy stations.

The distribution of organic carbon in marine environments is a crucial parameter to measure, as it offers valuable insights into sedimentary depositional environments, water column dynamics, and pollutants retained within the sediment. Generally, the concentration of organic matter increases with decreasing grain size. Therefore, the clay fraction of the sediment contains more organic matter than the sand fraction. Factors such as primary production and the amount of oxygen in the water column, the permeability of the sediment, the chemistry and microbiology of the pore water, and the physical and mineralogical properties of the sediment material play a role in the accumulation of organic matter (Folger, 1972). Most of the organic matter in sediments is composed of different components such as humic and fulvic acids and residual organic matter. Residual organic matter (bitumen and kerogen) depends on the mineral structure of the sediment. Clay minerals can absorb 50-60% of the organic matter formed by the decomposition of phytoplankton (Bordovsky, 1965).

The average organic carbon (C_{org}) content of the Sea of Marmara sediments is between 0.04% and 6.21% (Çağatay et al., 2000; Algan et al., 2004). In this study, TOC values ranged between 0.1- 2.4% with a mean value of 1.42 ± 0.61% (Figure 10).







Figure 9. POC and PON values of water samples by stations

Low values indicate the presence and/or abundance of carbonate material.

Characterization of Particulate Organic Matter

FT-IR is a type of spectroscopy that measures changes in bond vibrational energies. In fact, FT-IR is a chemical instrumental method that uses an empirical mathematical formulation to measure the wavenumber versus the infrared intensity of light with respect to the functional group with which it interacts. The infrared region of the electromagnetic light spectrum is between 14000 cm⁻¹ and 10 cm⁻¹ and consists of three main regions: near-wavelength infrared (NIR; 4000~14000 cm⁻¹), mid-wavelength infrared (MIR; 400~4000 cm⁻¹) and far-wavelength infrared (FIR; 4~400 cm⁻¹). IR rays are absorbed by the vibrational motions of the molecule. With this method, molecular bonding in organic structures can be characterized and qualitative analyses such as the state of bonds in the

structure, bonding sites and whether the structure is aromatic or aliphatic can be performed.

In this context, when FT-IR spectra of POC filters representing particulate organic matter were analyzed, common peaks were determined at low rates in all samples. The peak detected at 3350-3450 cm⁻¹ indicates the presence of the OH functional group originating from carbohydrates, proteins or polyphenols, the peak at 1730-1700 cm⁻¹ indicates the presence of the fatty acid-derived group, the peak at 1540 cm⁻¹ indicates the presence of the presence of the group originating from the amide structure containing C-N and the peak at 875 cm⁻¹ indicates the presence of the carbonate-derived group. Again, C-O carbohydrate peaks at 1080 cm⁻¹ and Si-O-Si peaks at 1020 cm⁻¹ are present at high rates in all sample spectra (Figure 11). Silicate peaks suggest the presence of clayey material of terrestrial origin and/or diatoms.



Figure 10. Percentages of TOC in sediment samples by station



Figure 11. FT-IR graph of Erdek and Florya stations

Conclusion

The Sea of Marmara, which forms the Turkish Straits System together with the Istanbul and Canakkale Straits, is an inland sea exposed to various pollution sources due to its location. In addition to industrial and domestic wastewater discharges, agricultural runoffs, and maritime activities, the coastal areas, particularly the southern shelf, also receive river inputs, further contributing to nutrient and pollutant loads. As an international waterway, the TSS serves as a biological corridor for different species, making the preservation of its ecological balance crucial. To ensure the sustainability of the Sea of Marmara's ecosystem, it is essential to regulate discharge limits from both point and diffuse sources, encourage the use of phosphate-free detergents, implement good agricultural practices to reduce nutrient inputs, and conduct regular biodegradability tests on detergents and cleaning products. Moreover, the sea is under significant threat from oil pollution due to ports, shipyards, intensive maritime transportation, and potential accidents resulting from the physical structure of the straits. Therefore, inspections and penal sanctions should be strengthened to efficiently prevent ship-borne pollution. These measures, alongside regular environmental monitoring programs, are vital for maintaining and improving water quality, and the findings of this research may serve as a foundation for long-term studies and conservation efforts.

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