CHARACTERISATION OF FLOATING MICROPLASTIC IN ROMANIAN COASTAL WATERS, WESTERN BLACK SEA

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Abstract. Microplastic pollution has developed as a significant environmental challenge, particularly in marine ecosystems such as the Black Sea, where its impact over the ecosystem and on the biodiversity is concerning. This study focuses on the visual characterization and distribution of microplastics in the Romanian coastal waters of the western Black Sea, using samples collected in March 2024, from five key locations: Sulina, Sf. Gheorghe, Mamaia, Constanța, and Eforie. A total of 2526 microplastic particles were identified, with an average concentration of 3.07 particles per cubic meter. The microplastics were described based on their morphology, color, and size. Fibers were the most common type, followed by fragments, while the other appeared in smaller quantities. The most predominant color was black, particularly in areas near Mamaia and Sf. Gheorghe. Blue and red particles were also observed, but not as frequent as the black ones. The size distribution analysis showed that 1553 particles were smaller than 1 mm, while 973 exceeded 1 mm, indicating that there is a significant plastic degradation in the marine environment. Spectral analysis indicated that the predominant polymer types were polyethylene and polypropylene. Those are commonly used in packaging, fishing gears and industrial application. This research provides insights into the types, distribution, and possible sources of microplastics in the Black Sea, contributing to strategies for mitigating marine pollution in this region.

Key words: microplastics; Black Sea; Danube; pollution

1. INTRODUCTION

The dominance of microplastic pollution has emerged as a critical environmental issue, drawing substantial attention from the scientific community worldwide (Hu *et al.,* 2019). Microplastics, defined as plastic particles less than 5 mm in diameter, have been detected across various ecosystems, including marine environments (Ahmad *et al.,* 2020). Their persistence, ability to transport pollutants, and impact on marine life make them a significant subject of study. Recent research has underscored the severity of microplastic contamination in the Black Sea, a semi-enclosed body of water bordered by Bulgaria, Georgia, Romania, Russia, Turkey, and Ukraine (Aytan *et al.,* 2020; Yuan *et al.,* 2022).

Microplastics originate from fragmented plastic debris, microbeads in products, and synthetic textile fibers. Their small size means they can be easily ingested by marine organisms, leading to physical harm and even toxic effects (Auta *et al.,* 2017). Furthermore, they can carry dangerous contaminants like heavy metals and persistent organic pollutants (POPs), which can bioaccumulate and potentially transfer through the food web, posing risks to both marine life and subsequently human health (Galloway, 2015). The Black Sea is particularly vulnerable to this kind of pollution, due to its limited water exchange with the Mediterranean, dense coastal populations, and major rivers like the Danube, Dniester, and Dnieper, which carry pollutants, including microplastics, from urban, agricultural, and industrial sources (Siegfried *et al.,* 2017). Moreover, the unique geomorphology of the Black Sea as a semi-enclosed basin favors the accumulation of pollutants that tend to get trapped (Kudelsky, 2011) increasing the accumulation of different pollutants as microplastics over time.

Recent studies have found microplastics in the Black Sea's surface waters, sediments, and marine life, but their distribution, concentration, and sources remain poorly understood (Berov and Klayn, 2020). Additional research is necessary to fully characterize important object properties including size, shape, polymer type and associated contaminants to properly determine he ecological risks. For example, microplastics in surface waters globally can reach thousands to hundreds of thousands of particles per cubic meter, indicating the severity of the issue (Maes *et al.,* 2017).

Understanding the full effects of microplastic pollution in the Black Sea is very important for developing effective strategies to combat it. This study aims to provide a comprehensive analysis of microplastic contamination in water samples from the Black Sea, focusing on the distribution, concentration, and characterization of microplastics. By integrating data from various sampling locations and depths, this research will contribute to a better understanding of the sources, pathways, and fate of microplastics in this ecologically and economically significant marine environment.

2. MATERIALS AND METHODS

In March 2024, five water samples were taken from sites along the Romanian coastal waters of the western Black Sea. The sampling locations included Sulina, Sf. Gheorghe, Mamaia, Constanța and Eforie (Fig. 1). This approach ensured a through representation of the area's environmental conditions and allowed for a detailed analysis of the presence and distribution patterns of microplastics.

2.1. Sample preparation

The analytical procedures were conducted in the microplastic laboratory at the GeoEcoMar headquarters in Bucharest, Romania. The water samples were initially filtered through a metal sieve with the same mesh size as the net used during collection to minimize the sample volume. The sample processing involved an organic digestion step, which was performed using a mixed solution of potassium hydroxide (KOH, 10M) and hydrogen peroxide (H_2O_2, 30%). This digestion process typically took 5-7 days, during which the glass containers were continuously agitated using an oscillatory shaker, following the methodology outlined by Ehlers *et al.* (2019) and Scherer *et al.* (2020). To ensure a safe and effective filtering process, the pH of the samples was neutralized using formic acid (HCOOH, 95%) and distilled water. The resulting mixtures from each sample were then filtered through 4.7 mm, 1.2 µm fiberglass membranes using a vacuum pump and a three-post stainless-steel Buchner system.

2.2. Visual and polymeric evaluation

The visual examination of microplastics (MPs) was carried out using a Leica EZ4W stereomicroscope, allowing for quantitative evaluation and detailed analysis of the MPs morphology, color, and size, following the procedure described by Hidalgo-Ruz *et al.* (2012).

For polymeric analysis, we did spectrometric testing using the RAMAN Craig Apollo-M to identify different types of microplastics. This instrument uses a confocal laser beam to collect Raman spectra in the VIS-NIR range for solid samples. It is equipped with a 785 nm laser and a spectrometer system with a maximum output power of 80 nW and a bandwidth of <0.02 nm. The microscope includes three objectives: a 10X VIS-NIR BF Objective (EC-Epi), a 20X VIS-NIR BF/DF Objective (EPI-Neo) and a 50X VIS-BIR BF/DF Objective (Epi-Neo). For instrument control, image processing, spectral acquisition, and data analysis, we used the 64-bit Lambdafire-R Raman Spectrometer Control & Analysis Software. Once the Raman spectra was obtained, we analyzed the data with the KnowItAll Spectral Database Search Software (Wiley), which contains 25.000 searchable Raman spectra.

2.3. Quality assurance

Before sample preparation, the working environment was cleaned with ethanol to prevent contamination. For laboratory procedures, glass and stainless-steel tools were used, and operators wore cotton lab coats during both laboratory work and microscopic studies. During chemical digestion and storage, all sample containers were covered with aluminium foil or Parafilm. Additionally, all glassware and utensils used in the field and laboratory were rinsed with distilled water prior to use.

3. RESULTS AND DISCUSSION

Through our analysis, we identified and quantified a total of 2526 microplastic particles across all examined samples. To better understand the type of MPs, we categorized them into two size groups: smaller than 1 mm and larger than 1 mm. Of these, 1553 particles were less than 1 mm, while 973 were greater than 1 mm. These counts represent all particles that were identified as plastic, distinguished by their unique color, morphology and external characteristics.

Analysis of surface water samples showed an average microplastic concentration of 3.07 particles per cubic meter. In the area near Sulina (SU08), an average concentration of 3.41 particles per cubic meter was recorded, while the Sf. Gheorghe (SFG08) region showed a slightly higher concentration, reaching 4.06 particles per cubic meter. The water sample from Eforie (EFO04) had a concentration similar to that found Sulina, around 3.42 MPs/m^3. Lower concentrations were observed in the sample from Mamaia (MA06) reaching 2.64 MPs/m^3 and in the sample from Constanta area (MOD04), reaching 1.82 MPs/m^3 (Table 2).

Fig. 1. Sampling sites in the Western Black Sea coastal water.

Table 1. Sampling details of the water samples.

Sample name	Date and hour	Depth (m)	Coordinates start		Coordinates stop		Index Flowmeter		Water Volume Calculated (m^3)
			Long.	Latit.	Long.	Latit.	Start	Stop	
SU08	21.03.2024; 12:40	11.1	29° 46.018′	45° 6.925′	29° 45.749′	45° 6.929′	80896	82152	105.504
SFG08	23.03.24; 09:22	10	28° 38.358′	44° 51.959′	29° 38.028′	44° 52.121′	82153	84630	208.068
MA06	26.03.24; 13:31	10.7	28° 39.117′	44° 13.467′	28° 38.867′	44° 13.367′	84631	86249	135.912
MOD04	26.03.24; 14:08	7	28° 39.850′	44° 11.100′	28° 40.517′	44° 10.817′	86249	89068	236.796
EF004	26.03.24; 15:10	10.7	28° 38.633′	44° 4.783′	28° 38.617′	44° 4.617′	89068	90921	155.652

Table 2. Abundance and morphology of the MPs particles identified in the water samples.

Sample name	Foils	Fiber	Fragments	Spherules	Clumps	Total MPs	Water Volume (m^3)	MPs/m^3
SU08	2	267	88	3	0	360	105.504	**3.41219**
SFG08	0	818	19	0	7	844	208.068	**4.05637**
MA06	0	359	0	0	0	359	135.912	**2.64142**
MOD04	0	422	7	0	1	430	236.796	**1.81591**
EF004	3	473	55	0	2	533	155.652	**3.42431**

Overall, black microplastics were the most common in all samples, with the highest amounts found in MA-06-24, followed by SFG-08. This dominance suggests that the primary sources of microplastics in these areas may be linked to black-colored materials such as tire particles, industrial plastics, or rubbers. Blue microplastics were also found in large numbers in certain samples, including SUL-08-24 and EFO-04-24. This could indicate sources related to marine debris or packaging waste, as blue-colored plastics are often used in marine products, like fishing gear.

Red microplastics were consistently found in every sample, though in smaller quantities. The reduced concentrations imply that they may either be less common in the investigated areas or breakdown more slowly. Only small amounts of white and yellow microplastics were found in some of the samples. These might originate from packaging materials, or synthetic fibers.

The data presented in the figure 2 provides an in-depth look at the morphology of microplastics found in the samples, identifying five key categories. Overall, fibers were the most common type, suggesting that textile-based pollution is a major contributor. Fragments also made up a significant portion of the microplastic content, suggesting that plastic degradation is an ongoing issue. Foils, spherules, and clumps appeared only in select samples. Although they are found in smaller quantities, their presence suggests improper waste disposal, industrial pollution or long-term environmental exposure and aggregation of microplastic particles over time.

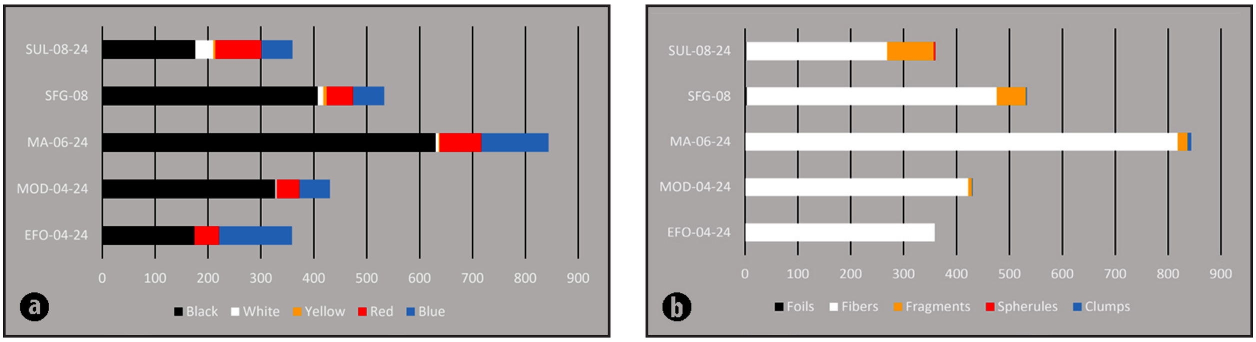

Fig. 2. Quantitative and Qualitative Assessment: (**a**) colors and (**b**) morphology (Down) of the identified MPs particles.

Together, the color and morphology charts (Fig. 2) reveal a clearer understanding of microplastic pollution sources. The dominance of black microplastics in combination with the high occurrence of fragments and fibers, suggests that both industrial sources (*e.g.*, tire particles, synthetic fibers) and degradation of plastics are major contributors.

In terms of size distribution (Fig. 3), the data shows that the number of particles smaller than 1 mm is higher than those bigger than 1 mm. In one of the samples, the number of smaller particles was almost double than the larger ones, indicating that that this area might be experiencing more severe environmental impacts. Areas where the distribution between larger and smaller particles was more balanced, most likely reflects a mix of both fresh plastic waste and older, degraded plastic.

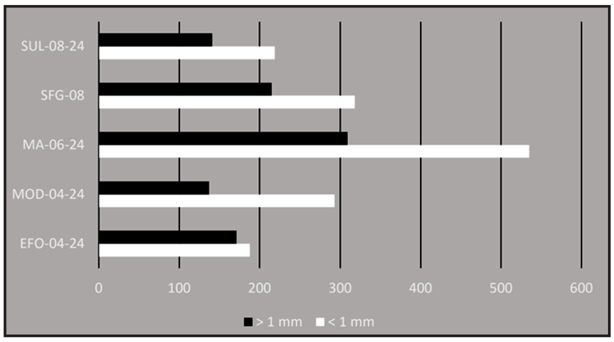

Fig. 3. Contrast between MPs < 1 mm and MPs > 1 mm

The results of our microplastics analysis shows that most of the identified MPs are classified as polyethylene-based polymers (PE, Fig. 4 a, d, e), followed by polypropylene (PP, Fig. 4 b).

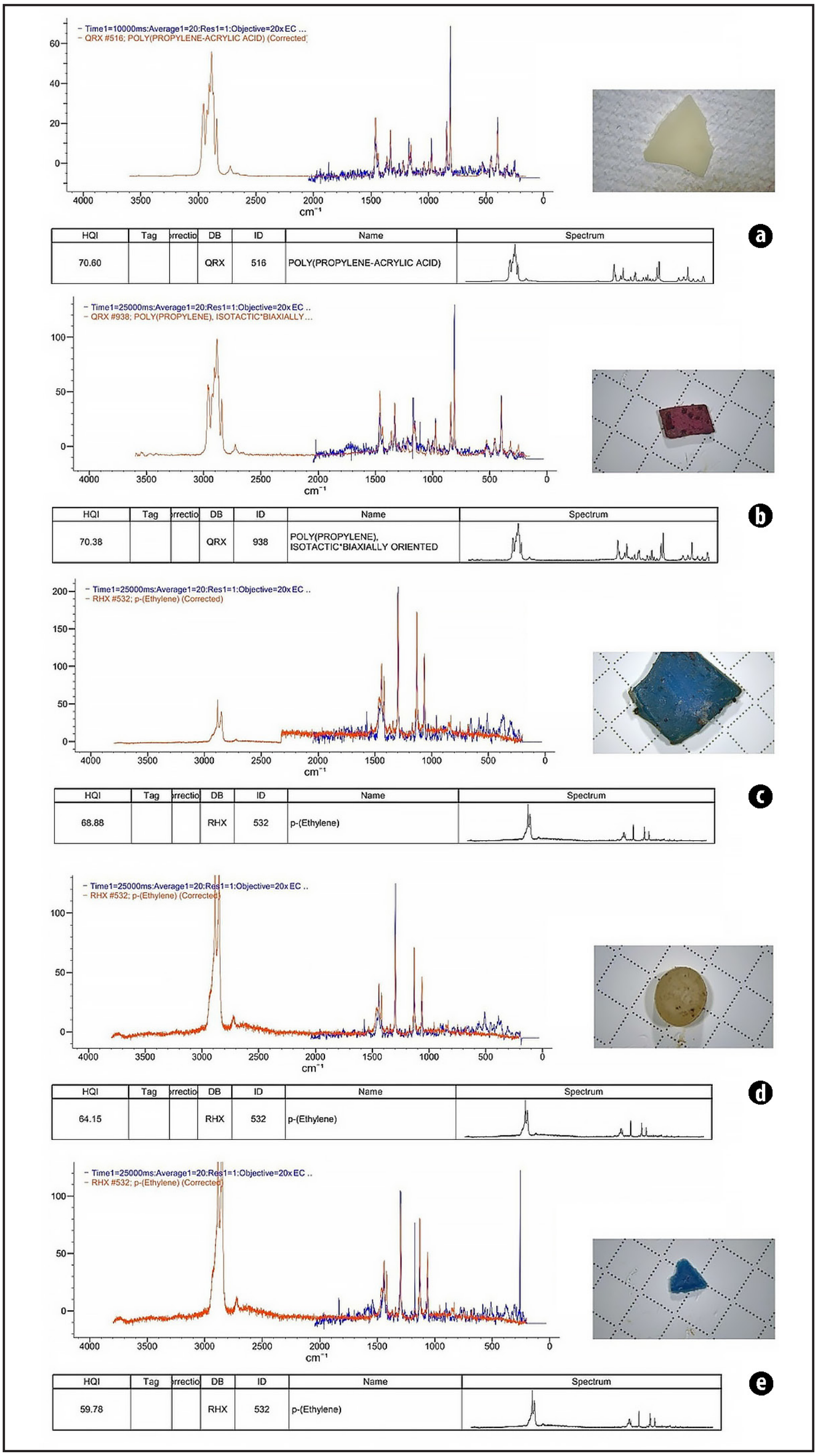

Fig. 4. Examples of Raman microspectrometry results: (**a**, **b**) Polypropylene; (**c**, **d**, **e**) Polyethylene; the x axis represents the wavenumber (cm^{-1}) and the y axis represents the intensity of the scattered light.

The investigated particles identified as PE are observed with diverse visual characteristics, and may originate from different industries. The polypropylene polymers are commonly used in food packaging, plastic containers, adhesives, as well as in car parts and medical supplies.

Polyethylene is widely used in agriculture, exemplified by greenhouse films, irrigation pipes, fishing gear, nets, marine equipment and, also, in food packaging, plastic bottles and household products. All polymeric materials most likely entered the natural environment through everyday plastic waste, industrial pollution, or marine activities.

Polyethylene and polypropylene-based MPs are very susceptible to oxidation, meaning they can break down faster when exposed to oxygen-rich water, which speeds up their decay and fragmentation (Singh & Sharma, 2008).

Compared to the findings of Pojar *et al.* (2021), which reported an average concentration of 7 MPs/ m^3 in similar areas, the current findings indicate a decrease in microplastic levels. Potential factors for this reduction could include more effective waste management, localized cleanup efforts or less plastic waste entering the sea from rivers and coastal areas. This change in microplastic contents, however, might also be explained by seasonal variations, environmental changes, or differences in sampling methods.

A more direct comparison can be made with the results of MPs pollution displayed by Baboş *et al.* (2023), as the present study is focused on the same sampling locations (Fig. 5). In the year 2023, the average concentration of microplastics was at 0.58 MPs/m^3, which is much lower than the 3.07 MPs/m^3 from our current study. This sharp increase could be the results of more plastic waste entering the Black Sea through riverine and coastal sources, potential inefficiencies in pollution control measures or even natural environmental factors that may have redistributed microplastic in water column.

4. CONCLUSIONS

This study highlights the significant presence of microplastic particles in the Romanian coastal waters of the wester Black Sea. Identifying a total of 2526 particles in a volume of 842 m^3 filtered from the surface sea water collected from 5 different sites, it is underlined the pressing issue of the marine plastic pollution in this region. The highest levels were recorded near Sf. Gheorghe and Sulina, suggesting that these areas may be receiving higher inputs of plastic pollution, likely due to their proximity to the Danube River and nearby urban sources. The findings reveal that fibers, often associated with textile pollution, are the most common type of microplastic, followed by fragments, likely resulting from degradation of packaging items.

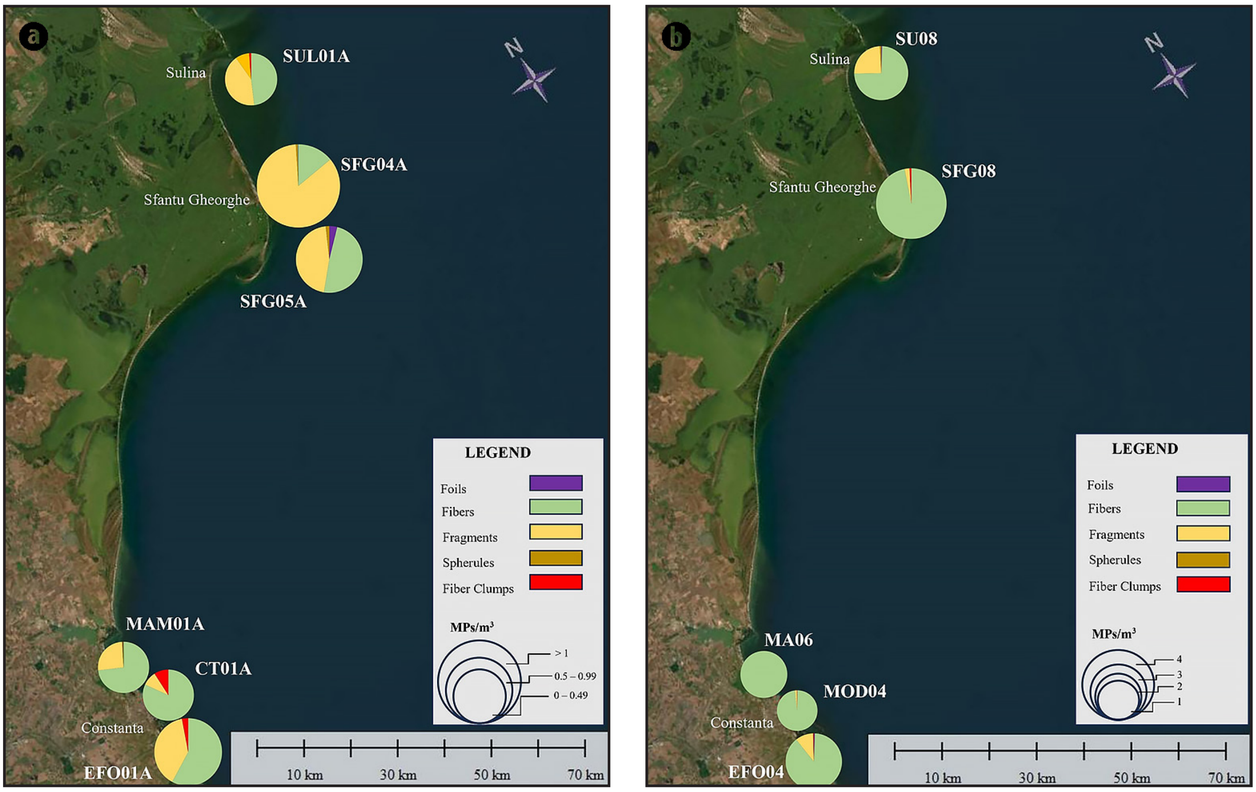

Fig. 5. Distribution of microplastics in the western Black Sea at the sampling locations: (**a**) year 2023 (after Baboş *et al.*, 2024), (**b**) year 2024, present study.

Raman spectrometry analysis showed that polyethylene and polypropylene are the dominant polymer types, suggesting that microplastics in the sampled areas mainly originate from plastic packaging, fishing gears and industrial sources. Those type of polymers are known to degrade over time, leading to a constant increase in microplastic in the surface waters.

While previous studies from 2021 reported higher average microplastic concentrations, there has been a recent reduction, potentially indicating the effectiveness of waste management or cleanup efforts in some areas. However, comparisons with data from Baboş *et al.* (2023) show a sharp rise in microplastic levels in certain locations, suggesting that pollution sources remain inconsistent or that seasonal and environmental factors play a role in redistributing microplastics across the water column.

Despite the ongoing efforts to combat marine pollution in the Black Sea, more research is needed to monitor long-term microplastic trends and review the impact of the current reduction strategies. These findings add to growing evidence that microplastic pollution in the Black Sea is a serious and ongoing environmental issue. The study highlights the need for coordinated efforts at both local and regional levels to address pollution sources, improve waste management practices and strengthen the monitoring of microplastic levels.

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