

DEPOSITION OF MICROPLASTICS IN THE SEA OF AZOV: A CRITICAL DATA ANALYSIS IN THE CONTEXT OF THE MARGINAL FILTER CONCEPT

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Received: April 21st 2026 / Accepted: July 24th 2026 / Published: October 1st 2026

<https://doi.org/10.24057/2071-9388-2026-4363>

ABSTRACT. This study investigated the accumulation of microplastics (MP) in the bottom sediments of the Sea of Azov and developed a detection method using pyrolysis gas chromatography-mass spectrometry (Pyr-GC-MS). Relationships between polymer concentration, sediment granulometric composition, depth of occurrence, hydrochemical parameters, and the distribution of benthic organisms were analyzed. Analysis of 20 samples revealed an average MP concentration of ~62 µg/g, with a maximum of 196 µg/g. Polyvinyl chloride (PVC) was the dominant polymer, reflecting its extensive use in regional industry. Correlation patterns were identified as inflection points on graphs of MP content and salinity versus sediment granulometric composition and depth. These points correspond to sampling stations near the western boundary of the Don River estuary (the Taganrog Bay area near Dolgaya Spit) and in the discharge zone of the Kuban River flow. It was established that the primary accumulation of MP occurs near anthropogenic sources (Taganrog, Berdyansk) and on the periphery of the Don and Kuban deltas in clay silts and sands. The estuarine sections of the rivers act as a natural barrier, facilitating MP deposition through coagulation with suspended organic particles. At the same time, no influence on fundamental ecological patterns was detected, with the relationships remaining within the logarithmic dependencies of benthic biomass on abundance.

The obtained data provide a basis for standardizing MP assessment methods and for further research with a detailed station grid covering various sediment types and benthic habitat conditions.

KEYWORDS: microplastic, the Sea of Azov, sedimentogenesis, benthos, bottom sediments, pyrolysis GC-MS

CITATION: Yurasov Y. I., Antsiferova M. A., Tolstunov M. I., Kleshchenkov A. V., Savikin A. I., Podoprighora E. A. (2026). Deposition Of Microplastics In The Sea Of Azov: A Critical Data Analysis In The Context Of The Marginal Filter Concept. *Geography, Environment, Sustainability*, 3 (19), 152-164

<https://doi.org/10.24057/2071-9388-2026-4363>

ACKNOWLEDGEMENTS: The publication was financially supported by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2024-528 of 24.04.2024 on the implementation of a large-scale research project within the priority areas of scientific and technological development) on the equipment of the CKP SSC-RAS.

Conflict of interests: The authors reported no potential conflict of interests.

INTRODUCTION

Microplastics (MP)—technogenic (anthropogenic) polymer particles smaller than 5 mm (Thompson et al. 2004)—have long been recognized as active participants in sedimentation processes within the Sea of Azov and other water bodies (Lisitzin 1994). The use of plastic products has increased dramatically in recent decades, with service lives ranging from months to decades. Mass irresponsible disposal has led to widespread contamination of aquatic environments by MP. According to a 2024 report by the Organization for Economic Co-operation and Development (OECD 2020)¹, global plastic production reached 435 million tons in 2020 and is projected to increase to 736 million tons by 2040 at current rates. The most common

polymers are polypropylene, followed by high- and low-density polyethylene (Fig. 1).

These particles are classified into primary (intentionally manufactured) and secondary types, the latter formed through degradation of larger plastic items. MP enters water bodies via wastewater, urban runoff, and landfill leachate, with small particles—particularly fibers—readily passing through treatment facilities (Rochman and Hoellein 2020). River discharge constitutes the main transport pathway. As noted by Lisina et al. (2021), rivers are the main source of microplastics input into the oceans, with 65–90% of plastics carried into the ocean with river runoff. Their pilot study on the Volga River revealed significant MP concentrations, particularly downstream of large cities, confirming that Russian rivers are important vectors of

¹OECD.org, (2025). OECD Official Website. [online] Available at: <https://www.oecd.org/> [Accessed 14 Oct. 2025].

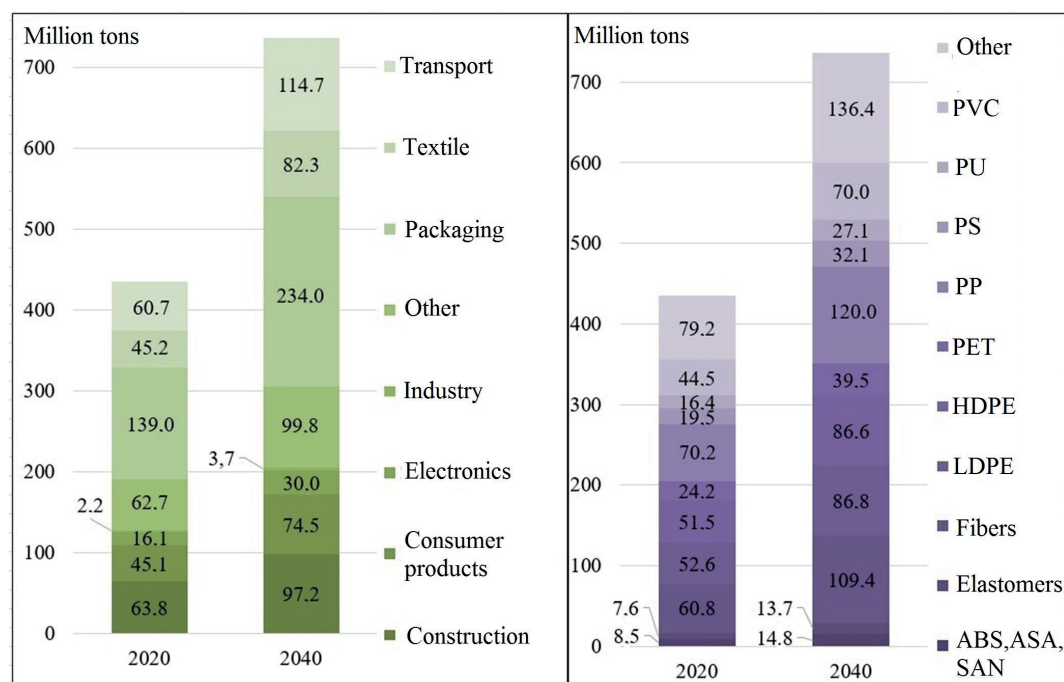


Fig. 1. Plastic Production (Data from the OECD report, 2020)

MP to marine environments. Once introduced, particles undergo dispersion and initial sedimentation; however, their ultimate fate is largely controlled by biological processes. Biofilm formation ('eco-corona'), aggregation with organic matter (incorporation into marine snow), trophic transfer, and bioturbation by benthic organisms (including macrozoobenthos) drive MP redistribution, burial, and resuspension at the sediment–water interface.

The behavior of microplastics in aquatic environments depends on both the diverse characteristics of the particles themselves and prevailing environmental conditions (Antsiferova et al. 2024). Particle sedimentation is influenced by density, shape, the presence of impurities, as well as biofouling and surface degradation. Bottom sediments serve as the ultimate sink for MP (Lassen et al. 2015); however, redistribution within sediments can occur. For instance, Frank et al. (2023a) experimentally demonstrated that oligochaetes promote MP burial in bottom sediments through bioturbation. Global data confirm that MP concentrations in bottom sediments are generally significantly higher than in surface waters or the water column (Lassen et al. 2015). Elevated concentrations have been recorded across diverse regions: the Arctic (42–6595 items/kg), Mariana Trench ridge sediments (270–6200 items/kg), the Mediterranean coastal zone (approximately 900 items/kg), and the Baltic Sea (average 860 items/kg). Distribution patterns reveal accumulation of larger MP particles in coastal sediments and finer particles in deep-water sediments, with fibers tending to predominate in organic-rich areas.

Beyond their physical presence, microplastics are ingested by hydrobionts—from microzooplankton, such as dinoflagellates (Rauen et al. 2024), to fish and other vertebrates (GOST 1980; Rauen et al. 2023)² — accumulate in organisms, and can transfer through trophic interactions (Smith et al. 2018). These particles sorb chemical pollutants (e.g., bisphenol A, heavy metals) and serve as vectors for pathogenic microorganisms (Andrady 2011; Liu et al. 2019). Chemical additives (stabilizers, plasticizers) and residual monomers pose additional toxicity risks (Badea et al. 2023; Lithner et al. 2011). In fish, MP accumulation in gills causes hypoxia, reduced activity, and reproductive impairment (Frank

et al. 2023); ingestion may obstruct the gastrointestinal tract in small vertebrates (Rauen et al. 2023). In humans, MP exposure is linked to inflammation, toxicity, microbiome disruption, and potential penetration into the circulatory system and brain (Wu et al. 2023). Hazard increases with decreasing particle size, making nanoplastics (<100 nm (Xie et al. 2021)) the most biologically dangerous. Risk assessment is complicated by artificially high experimental concentrations and varying toxicological potential among polymers: polyethylene and polystyrene sorb more persistent organic pollutants than PET and PVC, while PVC and polystyrene themselves may release hazardous monomers (Lithner et al. 2011). These four polymers dominate global production, underscoring the scale of the problem.

Plastic pollution negatively affects benthic detritivores, partly due to antibacterial additives in polymers (Rathore et al. 2019). MP accumulation in bottom sediments slows organic matter decomposition and alters geochemical processes. Since organic matter decomposition is a key source of greenhouse gases (CO₂, CH₄), microplastics may potentially affect water–atmosphere gas exchange by modifying detritivore activity and decomposition rates, although this mechanism requires further investigation (Rauen et al. 2023; Sadchikov and Ostroumov 2017). Studying the role of microplastics in sedimentation processes is therefore essential for assessing anthropogenic impacts on biogeochemical cycles in marine ecosystems (Rochman et al. 2013).

In light of the foregoing, the aim of the present study is to quantify the accumulation of microplastics in the bottom sediments of the Sea of Azov, and analyze its relationship with sediment granulometric composition and benthic community structure, as well as to adapt a simplified pyrolysis gas chromatography-mass spectrometry method for the identification and quantification of microplastics.

STUDY SITE

The Sea of Azov is located in Eastern Europe. It is connected to the Black Sea by the Kerch Strait. The Sea of Azov is the shallowest and one of the smallest seas in the world. It is the farthest inland sea from the ocean (Fig. 2).

²GOST 12536-79. (1980). Soils. Methods of Laboratory Determination of Grain-Size (Granulometric) and Microaggregate Distribution. Moscow: Publishing House of Standards, p. 40. (in Russian)

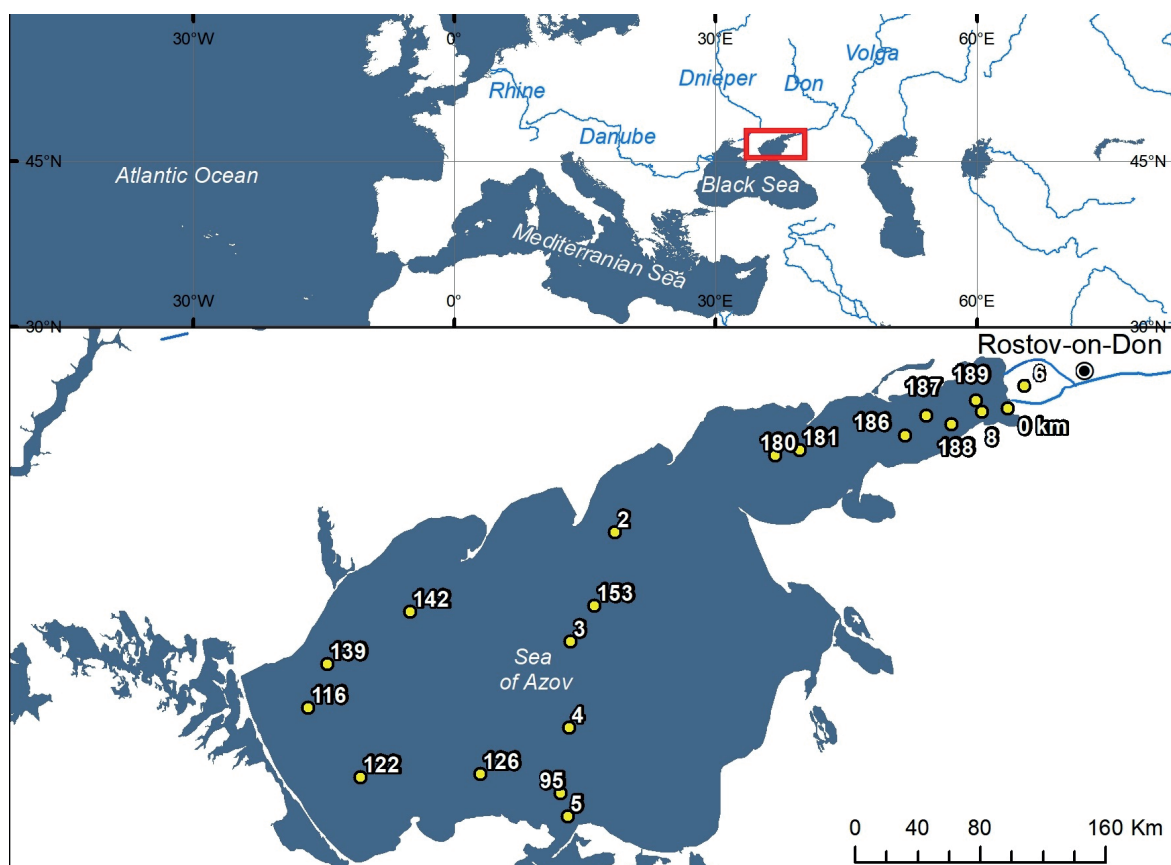


Fig. 2. The Sea of Azov. The dots indicate sampling stations

The Sea of Azov, a semi-enclosed basin characterized by high anthropogenic pressure, is critically vulnerable to plastic pollution (Lassen et al. 2015). The main sources of microplastic input include major cities (Mariupol, Taganrog, Berdyansk), discharges from the Don and Kuban rivers draining urbanized territories, flows from smaller rivers (e.g., Kalmius), areas with high industrial concentration, and recreational zones (Yeysk, Primorsko-Akhtarsk). All these objects are considered potential sources of microplastic pollution in the sea's waters.

The Sea of Azov is a semi-enclosed sea, significantly influenced by the discharge of the Don and Kuban rivers. The current state of the Sea of Azov is characterized by a substantial positive anomaly in water temperature and salinity, a phenomenon not previously documented in the history of research on this water body (Berdnikov et al. 2022).

Water salinity in the Sea of Azov varies considerably, ranging from nearly fresh water with a salinity of 0.8 psu in the Don River delta to 13.4 psu at the outlet of Taganrog Bay into the main sea basin. The highest salinity levels are observed in the Kerch Strait area, where they are substantially influenced by the inflow of Black Sea waters.

This study includes an analysis of the granulometric composition of bottom sediments as a key factor in the accumulation of pollutants and the formation of technogenic silts (Lukyanov and Schwartzman 2013). An established geochemical pattern confirms the predominant accumulation of pollutants in pelitic fractions due to their high sorption capacity. Accordingly, one of the objectives of this work is to identify the relationship between microplastic concentration and the type of bottom sediments in the Sea of Azov, the characteristics of which have been detailed in the works of G.G. Matishov et al. (2016). Clay silts (content of fraction <0.01 mm $>70\%$) predominate, occupying the central part of the sea. Aleurites (0.1 – 0.01 mm) are locally found in mixed forms, and sands (fraction 1.0 – 0.1 mm, $>50\%$ content) are concentrated in the coastal zone down

to depths of 2–6 m. The gravel fraction (10 – 1 mm) consists mainly of shell detritus. A clear spatial pattern of decreasing particle size from the coast towards the central part of the sea is observed (Matishov 2007).

Studies from the early 2000s on anthropogenic sedimentogenesis in the Sea of Azov found that accumulation rates of anthropogenic material (including synthetic fibers and paint particles, now classified as microplastics) were comparable to those of natural sediments, indicating the formation of natural-anthropogenic bottom sediment types (Khrustalev and Ivlieva 1999).

The benthic communities of the Sea of Azov are characterized by relatively low species diversity, associated with the sea's low salinity and shallow depth. The dominant groups are Bivalvia (bivalve mollusks), Polychaeta (polychaete worms), and Crustacea (crustaceans). Benthic fauna forms a key link in the sea's trophic networks, serving as the main food source for many fish species. Consequently, the structure and condition of benthic communities directly determine the productivity of the entire Sea of Azov ecosystem.

MATERIALS AND METHODS

1. Sampling Procedure

This study provides a comprehensive analysis of polymer content in the bottom sediments of the Sea of Azov, including quantitative and qualitative assessment of microplastics (MP), determination of sediment granulometric composition, and evaluation of the impact on benthic organisms. The applied methodology enables detection of MP across the entire size range.

Material was collected during the spring–summer period of 2024 aboard the R/V “Deneb” in the waters of the Sea of Azov. Bottom sediment samples for subsequent analysis of benthic organisms and MP were obtained using

a Van Veen grab sampler with a sampling area of 0.048 m² to a depth of 0.2 m.

The sampling depth of 0.2 m is sufficient to capture particles accumulated since the onset of mass plastic production in the 1950s. This is supported by regional sedimentation rate data: according to Matishov et al. (Fedorov and Trofimov 2008; Matishov et al. 2006; Panov and Spichak 1961), it ranges from 2 to 3.3 mm/year. Calculations indicate that over 74 years, technogenic particles, including MP, could have been deposited to a depth of 0.14–0.24 m, which falls within the depth interval of the collected samples.

Quantitative macrozoobenthos samples were collected at 24 stations covering various biotopes of the Sea of Azov. A modified Van Veen grab sampler (0.048 m²) was employed following standard hydrobiological methods (Manual 1983).

2. Macrozoobenthos processing

Field processing: samples were subjected to cascading sieving. First, the material was passed through a 0.5 cm mesh sieve to extract large organisms, which were immediately preserved in 70% ethanol for subsequent morphometric analysis. The remaining sample was then washed on a 0.5 mm mesh gauze sieve. All obtained material was fixed in a 4% formaldehyde solution and dispensed into plastic containers.

Laboratory processing: sorting and counting of organisms were performed in Petri dishes with a printed grid. Linear dimensions were recorded for each specimen. Large organisms (crustaceans, mollusks) were measured with calipers (accuracy 0.1 mm), while the millimeter grid of the Petri dish was used for small forms (oligochaetes, polychaetes, chironomids). A specimen was considered whole if its anterior part and head were preserved. For bivalve mollusks, shell fragments were counted if soft tissues remained in the hinge part.

Biomass determination: fixed material was weighed after drying on filter paper (1 minute for small samples or until wet spots disappeared for large ones). Mass was measured on analytical balances with an accuracy of 1 mg.

3. Microplastic analysis

MPs were identified using pyrolysis gas chromatography–mass spectrometry (Pyr-GC-MS) with sample preparation according to the NOAA method (Masura et al. 2015), which removes organic and mineral components from the sample. The procedure involved sequential steps: filtration through stainless-steel sieves (0.1 and 0.5 mm mesh) to remove fractions outside the MP size range, liquid oxidation in H₂O₂ with Fe addition, and density separation in ZnCl₂.

To ensure analytical purity and minimize background contamination, strict precautions were observed at all stages. Only metal equipment, stainless steel sieves, and glassware were used; all items were thoroughly cleaned and stored wrapped in aluminum foil to prevent plastic contact. Reagents were pre-filtered, and all work was performed wearing nitrile gloves and cotton lab coats under a fume hood. To monitor potential contamination, Petri dishes with distilled water were exposed in the laboratory throughout the sample processing period, and procedural blanks were analyzed.

4. Chromatographic analysis

Chromatographic analysis was performed using a “Maestro GC” gas chromatograph coupled with a “Maestro MSD” triple quadrupole mass spectrometer (electron ionization source). Identification and quantification of

polymers were performed using the Maestro software package. In line with ASTM D8401-24 (ASTM 2024), we ensured reliable identification by using not single peaks but a combination of characteristic ions and their intensity ratios at specific retention times. For example, for PVC, the diagnostic markers include hydrogen chloride, benzene, naphthalene, and chlorindane. This approach allows the polymer to be reliably distinguished from any other organochlorine compounds that may be present in the sample. Total MP content (µg/g) and dominant polymer types were determined for each sample.

To optimize the method, two chromatographic analyses were conducted per station: the first following density separation, and the second after complete sample preparation. This approach allowed assessment of potential stage omission without loss of accuracy, which is important for future automation and acceleration of analysis.

Unlike visual sorting and counting, commonly used in near-bottom studies (Zhao et al. 2025), Pyr-GC-MS automates the process and eliminates counting errors.

5. Granulometric analysis

Granulometric analysis was performed using two complementary methods: sieve analysis and laser diffraction. Sample preparation followed GOST 12536-79³ “Methods for laboratory determination of granulometric (grain) and microaggregate composition” (GOST 1980). A “Laska TD 220” laser granulometer (measurement range 10–500 µm) was used. Three parallel measurement cycles were conducted for each sample, followed by averaging.

The combined use of sieve and laser diffraction analyses was based on their complementary roles in sediment characterization. Sieve analysis provided a traditional classification of sediment types, establishing the overall lithological context. However, laser diffraction is required due to limitations of conventional sieving: large particles often fail to enter the laser measurement zone because of their high sedimentation rate, and their content in the small analytical sample (0.1 g) may not be statistically representative. Furthermore, laser data are expressed in volume percentages, precluding direct comparison with weight-based methods conventional in granulometry (Bezrukov and Lisitsyn 1960). Therefore, laser diffraction was used to obtain precise particle size distribution within the dominant sediment type (clayey silts), enabling detailed correlation between mean particle diameter and MP accumulation, while sieve analysis provided the broader lithological framework.

Bottom sediment samples underwent mechanical (grinding with a pestle) and physical disaggregation (ultrasonic bath for 5 minutes). The material was then sieved through a cascade of sieves with mesh sizes of 10, 5, 2, 1, 0.5, 0.25, and 0.1 mm. The fraction remaining on the pan (<0.1 mm) was analyzed using a “Laska TD 220” laser granulometer.

Sediments were classified by granulometric composition according to the scheme of Strakhov et al. (1954), later modified by Bezrukov and Lisitsyn (1960) for low-mineralization seas.

6. Hydrographic measurements

Hydrographic parameters (temperature, salinity, and depth) were recorded at each station using a CTD-60M oceanographic sonde and the onboard echo sounder

³GOST 12536-79. (1980). Soils. Methods of Laboratory Determination of Grain-Size (Granulometric) and Microaggregate Distribution. Moscow: Publishing House of Standards, p. 40. (in Russian)

of the R/V “Deneb”. To calculate salinity, we used water conductivity and temperature data acquired with the SST-SDA Sea & Sun Technology software package. The measurement accuracy was ± 0.005 °C for temperature and ± 0.002 mS/cm for conductivity. We validated the probe's readings in the laboratory by comparing them with data from an *SBE-19 V2 Plus* oceanographic probe, which is calibrated and certified annually at a metrological center.

RESULTS

The figures present pyrograms of bottom sediments obtained through pyrolysis at 600 °C for a series of stations. The grouping was performed visually based on similarity. Pyrolysis products are fragments of organic matter formed by microbial activity. Dominant peaks constitute a complex organic matrix (Figs. 3–4) that can mask signals from trace components like microplastics. The main identified pyrolysis products of natural organic matter are nitrogenous bases and carboxylic acids.

The set of substances comprising the pyrolytic matrix turned out to be almost identical for bottom sediments within the study region. As an example (Fig. 3), data from Station 189 are presented, where dihydroxy-diisobutyl ester of malonic acid and 2,2-dimethylpropane were identified in the bottom sediments with a reliability above 60%.

After the stages of wet oxidation and density separation, the number of peaks on the pyrograms significantly

decreases, and primarily peaks corresponding to fragments of polymer materials remain, along with a small amount of undigested organic matter (Fig. 4). For example, in the sample from station 188, a hydrogen chloride peak was clearly detected, which is a marker for the presence of chlorinated plastics, primarily polyvinyl chloride (PVC). A similar peak was also recorded in the “0 km” sample.

Microplastic concentrations at stations 2, 4, 186, and 187 are more than 4 times higher than the background levels recorded at other stations. The pyrogram of the most contaminated sample (Station 187) is shown in Fig. 5. The predominant type of polymer at these points was polyvinyl chloride (PVC). This polymer is widely used in the production of building materials (window profiles, pipes, linoleum), household items (artificial leather, films, shoe plastic compounds), and in electrical engineering (cable insulation).

Table 1 presents the microplastic concentrations at the studied stations, as well as oceanographic parameters (salinity, transparency, temperature) and depth at the sampling points. Particle sizes were measured with an instrument having a measuring range of 0.1–1000 μm . The maximum permissible relative errors for the characteristic diameters are: $\delta(D_{10}) \pm 15\%$, $\delta(D_{50}) \pm 10\%$, and $\delta(D_{90}) \pm 15\%$.

The average microplastic content in the bottom sediments of the Sea of Azov was 61.7 $\mu\text{g/g}$, with a concentration range of 19–196 $\mu\text{g/g}$. The highest levels were recorded in the Kerch Strait area (195 $\mu\text{g/g}$), near the Berdyansk Spit (167 $\mu\text{g/g}$), and in the Don River estuary (up

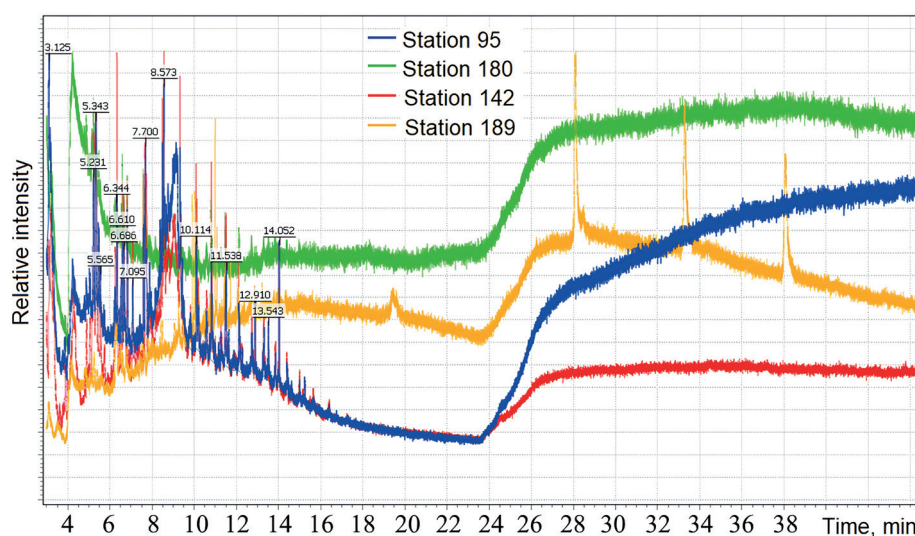


Fig. 3. Pyrogram of bottom sediments from stations 95, 180, 142, 189

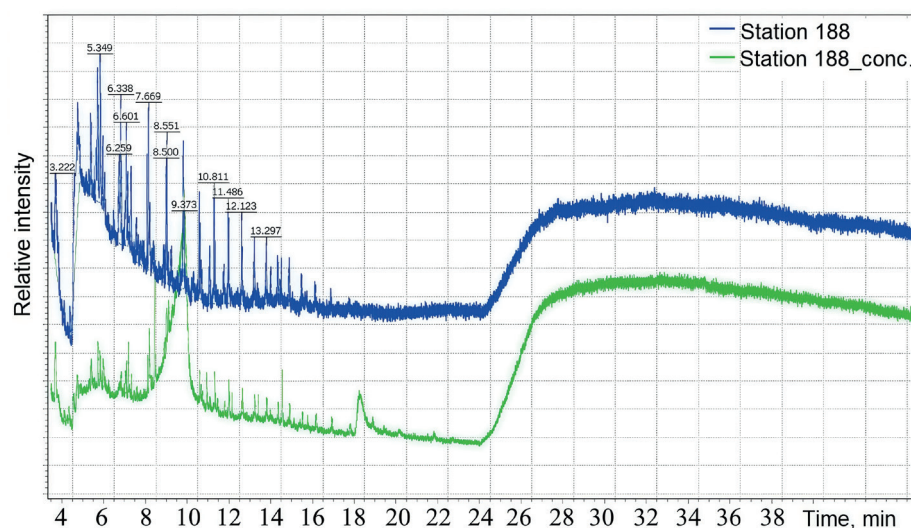


Fig. 4. Comparison of pyrograms from station 188 before and after wet oxidation with subsequent density separation

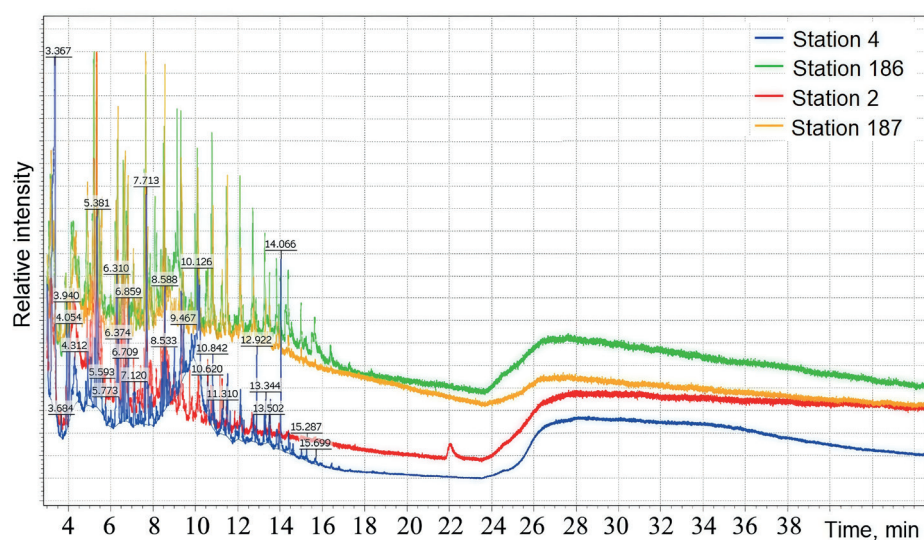


Fig. 5. Pyrogram of bottom sediments from stations 4, 186, 2, 187

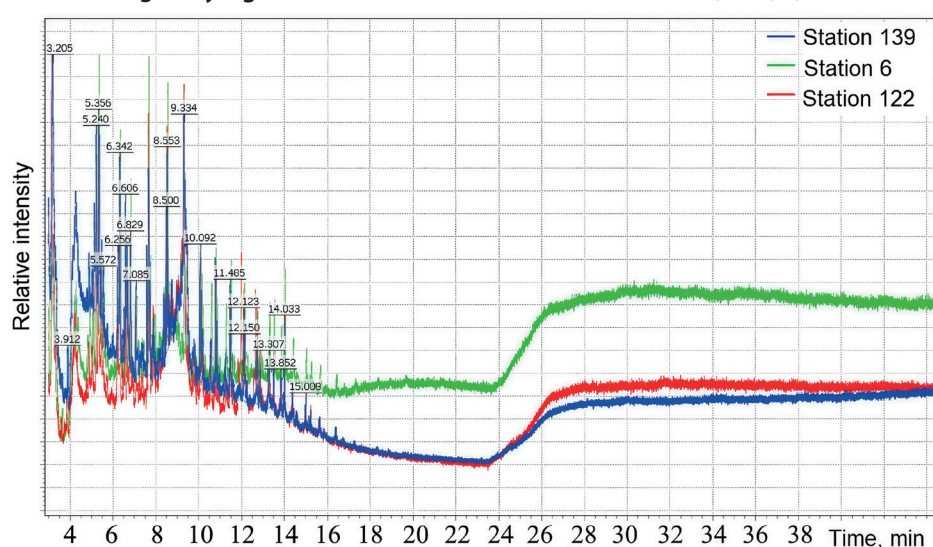


Fig. 6. Pyrogram of bottom sediments from stations 139, 6, 122

to 164 µg/g). Spatial distribution is controlled by discharge from the Don and Kuban rivers, inflow of Black Sea waters through the Kerch Strait, point sources from coastal cities (Taganrog, Berdyansk, Kerch), and intensive shipping. Microplastic concentrations in the Sea of Azov (up to 195 µg/g) significantly exceed those in open ocean bottom layers (~50 µg/g) (Barrett et al. 2020) and sediment cores from other regions.

According to granulometric analysis (Table 2), clay silts (fraction <0.1 mm) predominate in the bottom sediments of the Sea of Azov, with a maximum content of particles sized 0.002–0.05 mm. Fine sand fractions are confined to the estuarine region of the Don River, the zone influenced by the Kerch Strait, and the area of the Arabat Spit (St. 0 km, 122, 180, 187≠189). As shown in Fig. 6, the gravel fraction, represented mainly by shell debris, predominates over silty sediments near the Kerch Strait, as well as the Arabat and Biryuchi Island spits (St. 5, 95, 116, 142).

It should be noted that the stations dominated by shell material and sand showed minimal accumulation of microplastics. Most of the bottom sediments at the sampling points are represented by fine-grained clay silts, and it is with this type of sediment that the maximum concentrations of polymers are associated. An exception is station 2, where the sediments are represented by silts with sandy admixtures and large shell fragments (over 10 cm). The average particle diameter of the silty sediments at these stations, measured automatically using the LASKA instrument, ranges from 3.2 to 4.4 µm. In general, a clear

trend is observed: as the average particle size decreases, the concentration of polymers increases.

This relationship is confirmed by the graph of microplastic concentration distribution versus the average sediment particle size (Fig. 8a). As can be seen from the graph, the highest MP concentrations are associated with the average particle size range of 4 µm, which corresponds to clay silts. When the particle size increases to 5–9 µm (the zone corresponding to fine sand), the microplastic content significantly decreases. The discovered inverse correlation is well approximated by a hyperbolic function (Eq. 1):

$$f(x) = a + \frac{b}{x - c} \quad (1)$$

where coefficients a , b , and c are empirically determined values.

The observed pattern is explained by the dynamics of bottom sediments. Coastal stations with coarse fractions (gravel, shell debris) are subject to hydrodynamic forces that prevent microplastic accumulation. In contrast, the calm conditions of clay silt accumulation promote effective burial of microplastics through sorption and coagulation with fine mineral particles.

A similar hyperbolic relationship is observed for other parameters. The distribution of salinity versus average particle size (Fig. 8c) and versus depth (Fig. 8d) is also well described by a hyperbolic function of the following form (Eq. 2):

Table 1. Microplastic concentrations at studied stations, oceanographic parameters, depth, and assessment of benthic organism abundance at sampling points according to the April 2024 expedition data

Station	MP, µg/g	Depth, m	Salinity, psu	Temperature, °C	Secchi disk transparency, m	Mean diameter, µm	Benthos	
							Total abundance, ind./m²	Biomass, g/m²
8	19.818	4.9	5.1	13,2	0,6	4.678	–	–
6	65.502	2.7	—	—	0,7	4.288	–	–
0 km	30.282	3.3	0.8	15,9	0,7	4.145	–	–
189	31.696	3.7	4.2	14,9	1,2	2.914	–	–
188	33.947	4.8	6.7	13,2	1,3	7.686	–	–
187	163.901	3.2	7.6	16,8	0,7	3.859	–	–
186	139.076	4.5	8.6	16,7	0,7	3.858	–	–
181	38.683	5.2	10.5	15,3	0,9	4.088	–	–
180	31.046	5.4	13.4	15,3	1,1	8.866	–	–
2	166.808	10.6	14	14,8	1,4	4.228	1700	1269.108
153	30.721	11.2	14.3	12,6	0,7	5.085	400	991
3	34.831	11	14.9	12,6	0,7	4.526	650	1214.212
4	195.599	10.2	14.8	13,6	1	4.489	150	380.055
95	32.75	10.1	15	14,1	1,4	5.476	1000	2261.46
5	31.181	9.6	16.9	14	1,7	4.004	3050	1697.343
126	37.917	9.9	14.7	12,6	0,9	6.07	800	2104.288
122	40.583	7.1	14.6	13,5	1,1	3.999	550	875.714
116	31.278	8.2	14.4	13,8	0,9	7.894	1500	3838.321
139	42.59	8.2	14.3	14,2	1	7.986	1325	2375.269
142	37.454	10.4	14.5	13,2	0,9	5.183	1350	4498.308

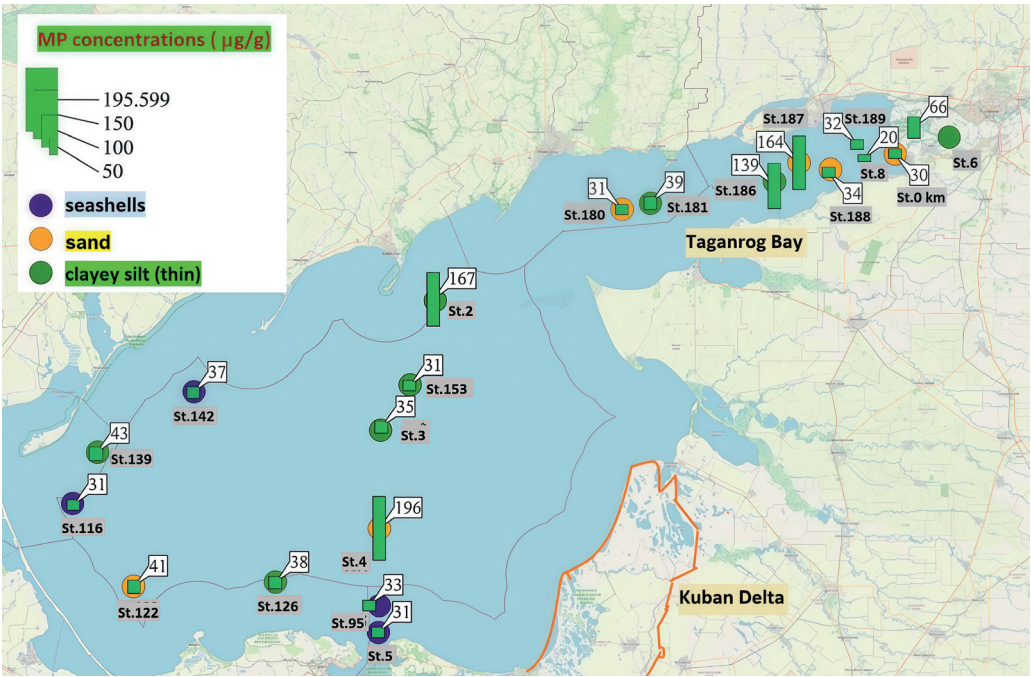


Fig. 7. Map of microplastic distribution in the Sea of Azov and granulometric composition of sediments

Table 2. Granulometric composition of bottom sediments according to laser and sieve analysis data

Station	Sieve analysis				Laser analysis		Mean diameter	Fraction type
	mm	%	mm	%	mm	%	μm	
187	< 0.1	52	0.25–0.1	40	0.005–0.01	72	3.859	Clay silts (fine); Fine sand
186	< 0.1	71	—	—	0.002–0.005	42	3.858	Clay silts (fine)
181	< 0.1	73	—	—	0.002–0.005	42	4.088	Clay silts (fine)
180	< 0.1	65	0.1	34	0.01–0.05	34	8.866	Clay silts (fine)
2	< 0.1	58	10–5	18	0.002–0.005	40	4.228	Clay silts (fine); Fine sand; Gravel (shell debris)
3	< 0.1	94	—	—	0.005–0.01	38	4.526	Clay silts (fine)
4	0.1	42	10–5	26	0.002–0.005	40	4.489	Clay silt; Shell debris
5	10	40	0.1	29	0.002–0.005	36	5.476	Gravel (shell debris)
95	0.1	70	—	—	0.002–0.005	41	4.004	Gravel (shell debris)
116	< 0.1	32	10–5	40	0.002–0.005	30	7.894	Gravel (shell debris); Clay silts (fine)
122	< 0.1	58	0.1	27	0.002–0.005	48	3.999	Clay silts (fine); Fine sand
126	< 0.1	95	—	—	0.005–0.01	67	6.07	Clay silts (fine)
139	< 0.1	74	—	—	0.005–0.01	34	7.986	Clay silts (fine)
142	< 0.1	44	10–5	43	0.002–0.005	38	5.183	Clay silts (fine); Gravel (shell debris)
0 km	0.1	60	0.25	18	0.002–0.005	40	4.145	Fine sand
8	< 0.1	88	—	—	0.005–0.01	34	4.678	Clay silts (fine)
6	< 0.1	92	—	—	0.005–0.01	39	4.288	Clay silts (fine)
188	0.1	51	0.25	31	0.01–0.05	28	7.686	Fine sand
153	< 0.1	91	—	—	0.002–0.005	39	5.085	Clay silts (fine)
189	< 0.1	76	—	—	0.002–0.005	48	2.914	Clay silts (fine)

$$f(x) = \frac{a(c-x) + i}{b(d-x) + k} \quad (2)$$

where coefficients a , b , c , d , i , and k are empirically determined values.

The similarity in the shapes of these dependencies for different parameters indicates a commonality in the processes controlling both the salinity at the sampling point and the distribution of microplastics in the bottom sediments of the Sea of Azov.

The discovered correlation between salinity and granulometric composition (Fig. 8c) can be attributed to the dependence of benthic community structure on the salinity gradient. Coarse-grained sediments (gravel, shell debris) form predominantly under conditions of elevated salinity, which are favorable for the development of marine bivalves (*Bivalvia*), such as *Anadara kagoshimensis* and *Cerastoderma glaucum*. At the same time, the accumulation of fine-grained clay silts dominates in zones with reduced salinity, where the sedimentation of terrigenous material prevails over biogenic sedimentation. The distribution of salinity with depth (Fig. 8d), in turn, reflects the hydrological structure of the water column. The identified dependence is likely related to the weakening of vertical mixing in the bottom layers, where saline waters are diluted by the significant inflow of fresh water from rivers (Don, Mius, etc.). A combined analysis of these correlations suggests the existence of a mechanism in the Sea of Azov analogous

to the “marginal filter” described in the works of scientists from the P.P. Shirshov Institute of Oceanology of the Russian Academy of Sciences (Chubarenko et al. 2025). According to this concept, proposed by A.P. Lisitzin (1994), the mixing zone of river and sea waters acts as a natural barrier, trapping suspended particles, including microplastics. In this area, particles settle to the bottom due to coagulation with fine suspended matter and are also captured and processed by specific representatives of the benthos.

Our conclusions regarding the key role of river discharge in transporting microplastics to the Sea of Azov are consistent with global data. Studies from various regions show similar patterns: maximum plastic accumulation occurs not in river mouths but in the inner parts of river plumes, where the flow loses momentum and mixes with seawater (Zavialov et al. 2020). The inflection points in Fig. 8 (a, c, d) correspond to stations near the Don River estuary (Taganrog Bay) and the Kuban River delta (Fig. 8b).

The distribution of microplastics along the coast of the Sea of Azov is determined by the discharge of major rivers (Don, Kuban, Mius). Despite their anthropogenic origin, microplastics participate in sedimentation, and their confirmed characteristic is rapid degradation under the moderately warm climate conditions of regions II7 and II9. Thus, understanding the mechanisms of such a natural barrier in the Sea of Azov has important practical significance. It will allow ecologists to more accurately predict pollution of the aquatic area and develop targeted

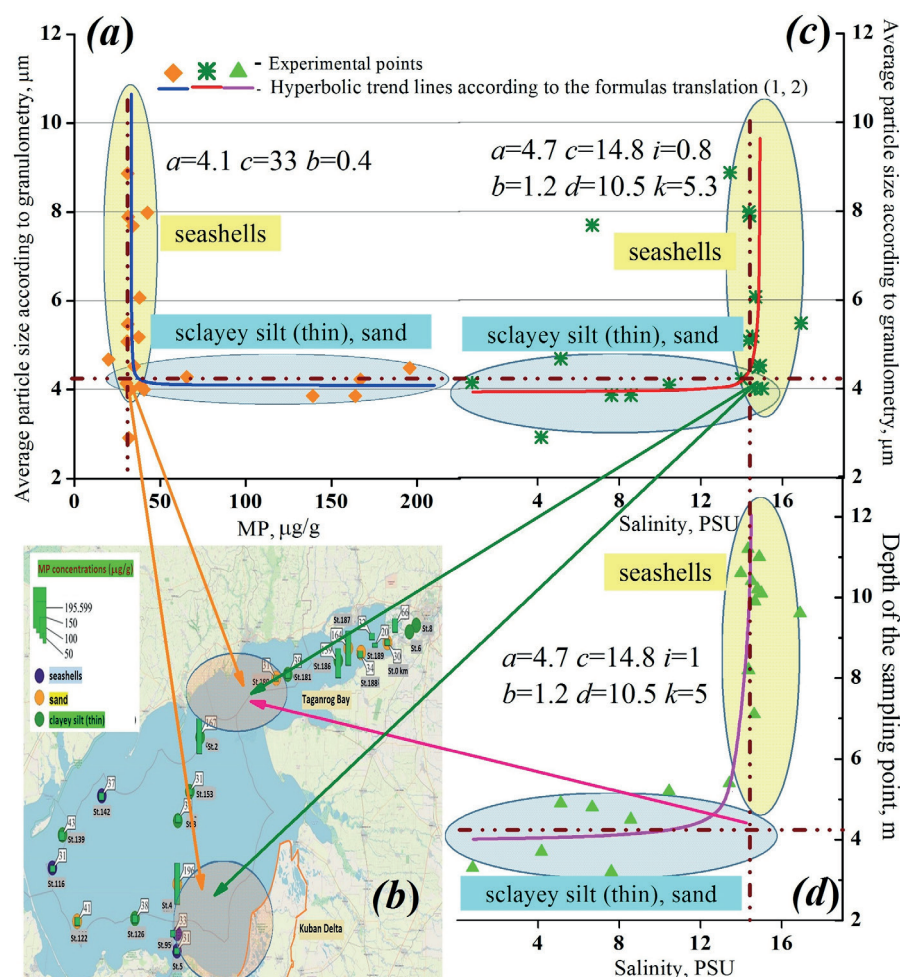


Fig. 8. (a, b, c, d). Microplastic content at the studied sampling stations, showing the environmental oceanographic parameters, sampling point depths, and location within the bottom sediments of the Sea of Azov

programs for the restoration of its ecosystems.

To assess the impact of microplastics on the ecosystems of the Sea of Azov, an analysis of the abundance and biomass of benthic organisms was conducted. The results revealed a clear inverse relationship: an increase in MP concentration correlates with a decrease in benthic biomass (Fig. 9). An exception is observed at Stations 153 and 2 in the Berdyansk Spit area, where the decrease in biomass is likely associated with other factors—specifically, sharp salinity fluctuations and periodic hypoxia.

For a complete assessment of the possible influence of MP on benthic organisms, the relationships between the biomass of benthic organisms (g/m^2) and their abundance ($\text{ind.}/\text{m}^2$) for all studied groups (*Bivalvia*, *Crustacea*, *Polychaeta*, *Gastropoda*) in the Sea of Azov were analyzed. These relationships, as can be seen from Fig. 10, have a logarithmic nature, described by the Eq. 3:

$$f(x) = a \ln(x) - b \quad (3)$$

where coefficients a and b are empirically determined values.

The observed logarithmic abundance-biomass relationship (Fig. 10) reflects a fundamental ecological pattern: high abundance leads to competition that limits individual growth, resulting in communities dominated by small organisms, while low abundance allows individuals to reach larger sizes. The size composition of the groups (Fig. 11) confirms this model: *Bivalvia* (50–130 mm) > *Crustacea* (20–40 mm) > *Polychaeta* (5–20 mm) > *Gastropoda* (1–10 mm). The parameters of the relationship in Fig. 9 reflect these species and size differences. Similar patterns are known for marine benthos (Tung et al. 2023), confirming the model's universality.

All stations with reduced biomass (2, 3, 4, 5, 122, 153) follow the general relationship without anomalies, indicating no direct effect of microplastics on biomass even at concentrations of 167–196 $\mu\text{g}/\text{g}$.

Fig. 11, showing the dependence of benthic organism biomass on taxon size, demonstrates a similar pattern across all studied stations: an increase in biomass with the growth of individual sizes in benthic groups is observed without anomalous outliers. At the same time, at station 2, where an elevated microplastic concentration was recorded (167 $\mu\text{g}/\text{g}$), the overall nature of the relationship is preserved and corresponds to the patterns observed at other stations.

The identified logarithmic relationship for benthic organisms (Fig. 11) is opposite in nature to the principle established by M.S. Gilyarov for soil animals (Gilyarov 1944; Polishchuk 2018). However, the model obtained in this work is consistent with dependencies previously observed by other authors for aquatic ecosystems (Marlow et al. 2024). Similar patterns linking biomass and metabolism have been described, in particular, for marine phytoplankton (Fant and Ghedini 2024), which may indicate the universality of the identified relationships in the aquatic environment.

The conducted analysis of the influence of the content of technogenic polymer microparticles (MP) in bottom sediments on the life cycles of benthic organisms did not reveal significant deviations; the results fall within the existing patterns where the abundance of benthic organisms correlates quite accurately with their biomass without anomalous outliers.

To assess the accumulation of microplastics (MP) at the organism level, an analysis of particle content in the soft tissues of the bivalve mollusk *Anadara kagoshimensis* was

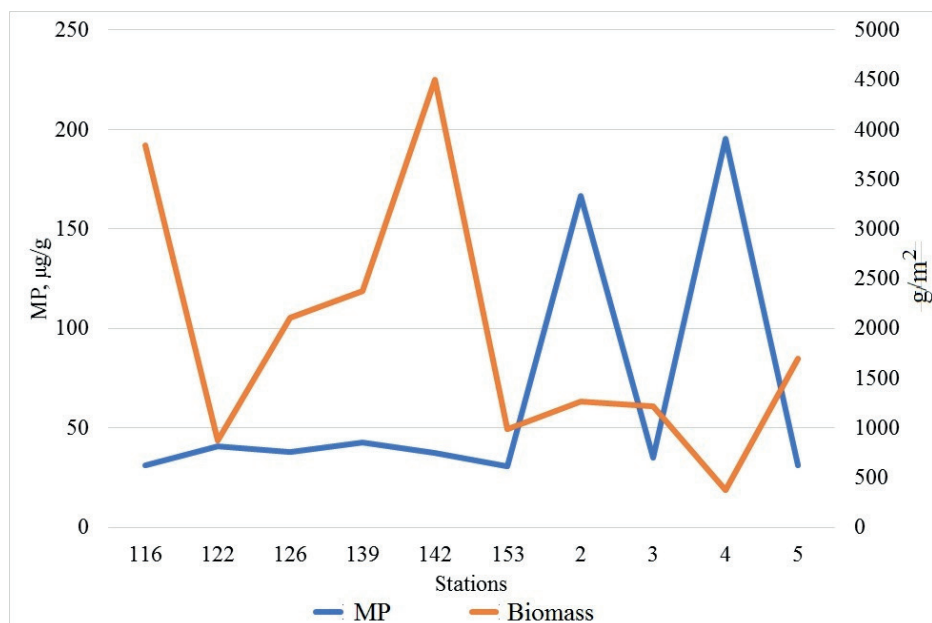


Fig. 9. Relationship between MP concentrations ($\mu\text{g/g}$) and biomass of benthic organisms (g/m^2)

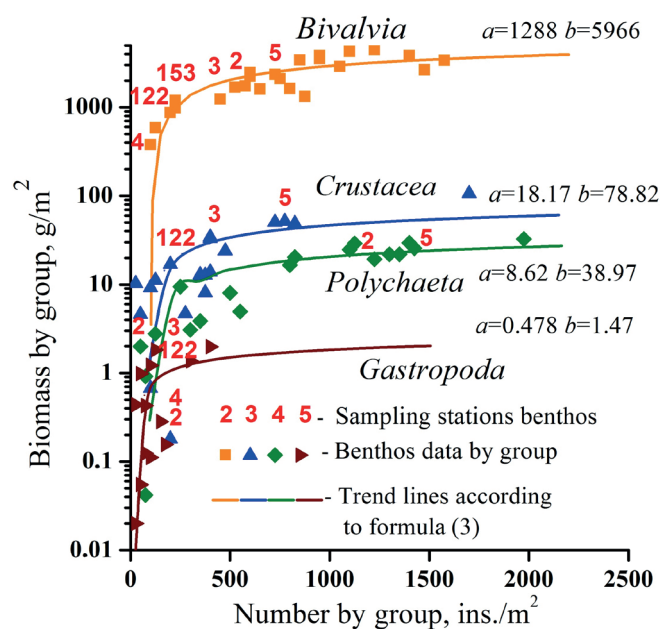


Fig. 10. Distribution of biomass of benthic organisms in the Sea of Azov by groups (g/m^2) – *Bivalvia*, *Crustacea*, *Polychaeta*, *Gastropoda* – depending on their abundance (ind./m^2). 2024 data

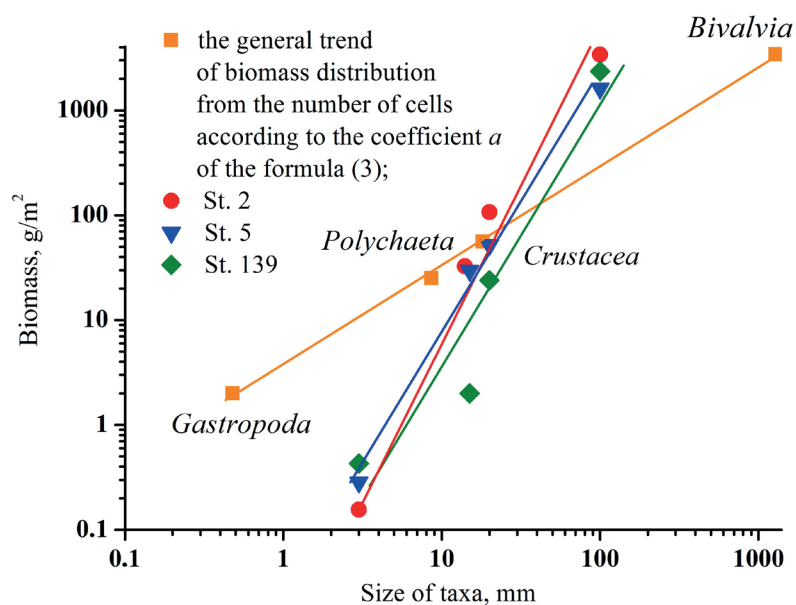


Fig. 11. Dependence of benthic organism biomass on their taxon size

Table 3. The amount of microplastics in *Anadara kagoshimensis*

Station	Instance	Body weight	MP, pieces
122	122.1	2.10	4
122	122.2	1.59	1
122	122.3	1.56	4
2	2.1	0.97	9
2	2.2	0.35	7
2	2.3	0.59	8
4	4.1	6.02	9
4	4.2	6.83	10

conducted. Specimens were collected from stations 122, 2, and 4, with a total of eight individuals examined. This species was selected due to its high abundance in the Sea of Azov and its key role in biofiltration processes.

Microplastic particles identified in the mollusk soft tissues were exclusively fibers of various colors (transparent, pink, black, and blue/light blue). Quantitative analysis revealed that MP content varied among individual specimens, ranging from 1 to 10 particles per organism, depending on the organism's size. The total mass of microplastics in the analyzed samples ranged from 0.01 to 1.4 µg. The highest mean particle count was recorded at station 2 (8 particles/individual), while the lowest was observed at station 122 (3 particles/individual), as detailed in Table 3. According to pyrolysis gas chromatography data, the predominant polymer type was polystyrene. More detailed studies on microplastic uptake by living organisms will be presented in future publications by the author's team.

CONCLUSIONS

Global plastic production is increasing annually, leading to a proportional rise in microplastic (MP) emissions into the environment. This poses a fundamental challenge, as growing technological pressures on water bodies necessitate unified assessment standards and innovative analytical methods. Pyrolysis gas chromatography–mass spectrometry (Pyr-GC-MS) enables identification of both polymers and their additives, overcoming the limitations of visual particle counting, which is hindered by variability in particle size, shape, and density.

This study presents the first application of Pyr-GC-MS to characterize MP in bottom sediments of the Sea

of Azov, integrating hydrochemical parameters and sediment granulometry. Mean MP concentration was ~61 µg/g, reaching 196 µg/g. Polyvinyl chloride (PVC) dominated, reflecting its regional industrial use. A clear inverse relationship was found between MP content and sediment grain size: maximum accumulation occurred in fine-grained clay silts (3.2–4.4 µm), and minimum in coarse sediments (sand, gravel, shell detritus).

Elevated MP concentrations near Taganrog, Berdyansk, and the Don and Kuban estuaries indicate anthropogenic sources. Estuaries act as geochemical barriers ("marginal filters"), promoting MP deposition via aggregation with suspended organic matter and fine particles. Correlations between MP, salinity, and grain size do not imply a causal link between MP and salinity. Instead, they reflect shared hydrological control: freshwater discharge creates salinity gradients and delivers MP, while hydrodynamics govern fine particle settling in low-energy zones. Salinity thus serves as a tracer of river plume dynamics and mixing zones where MP preferentially accumulate.

No significant disruptions to benthic communities were detected based on total abundance and biomass, but this finding requires caution. Lack of community-level effects does not rule out impacts on sensitive taxa or sublethal responses. These data provide a foundation, not a definitive assessment, of MP impacts in the Sea of Azov. Further research with detailed station grids, species composition analysis, ecological indices, taxon-specific sensitivity, and trophic transfer studies is needed. Long-term monitoring is essential to distinguish natural variability from anthropogenic effects and assess cumulative impacts as MP concentrations rise. ■

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