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EXPLORING THE MICROPLASTICS DISTRIBUTION IN THE BOTTOM SEDIMENTS OF THE WESTERN BLACK SEA

(Представлено членом редакційної колегії д-ром геол. наук, ст. наук. співроб. О.Л. Шевченком)

Background. *The spread and accumulation of plastic waste in the environment is now a recognized global problem. The development of an effective strategy for managing plastic waste and minimizing its impact on the marine environment is not possible without conducting field studies in bottom sediments. Determination of their content in the upper layer of precipitation and study of qualitative and quantitative characteristics will allow to outline the patterns of their entry into the water area, distribution and accumulation, risks of impact on marine organisms.*

Methods. *Visual determination of microplastic particles was carried out under the monocular of SIGETA MB-12 LCD optical microscope. An alternative method of identification, the hot needle test, was also used to determine plastic under the microscope. Raman spectroscopy was used to perform structural identification. Laboratory studies were performed using a single-stage MDR-23 spectrometer equipped with a cooled CCD detector and a Micromed microscope.*

Results. *The analysis of each sample and subsequent generalization showed the presence of plastic particles at all points of the sampling area, in different quantities and composition. The results of our studies confirm that microplastic particles in the surface sediments are quite abundant throughout the entire research area, and they are represented by different types everywhere, with fibers dominating in terms of morphological characteristics and polyethylene and polypropylene in terms of chemical types. There is no stable dependence of redistribution of microplastics of different densities on distance from the shore. The only thing that can be confirmed is uneven lateral distribution within the shelf zone, which is quite possibly related to the impact of the anthropogenic plane load on the surface bottom sediments.*

Conclusions. *Studies have shown that microplastic particles in the surface sediments are quite abundant throughout the survey area, and they are represented by different types everywhere, with fibers dominating in terms of morphological characteristics. As for the distribution of microplastics in surface sediments depending on natural conditions, we can document the fact that the amount of polymers, in terms of dry weight of soil matrix samples, increases in the direction of the mainland slope. An important result of the work was the identification of a number of topical issues, shortcomings and uncertainties in laboratory research methods, sample preparation and identifying microplastics, which should be addressed in the future.*

Keywords: *microplastics, bottom sediments, research methods, ecology, spectroscopy, visual examinations.*

Background

The spread and accumulation of plastic waste in the environment is now a recognized global problem (PlasticEurope, 2018; Geyer, Jambeck, & Law, 2017; Hoornweg, & Bhada-Tata, 2012). As with many other types of pollutants, the final link in their accumulation is the water layer, and subsequently the bottom sediments of water areas, including the seas. At the same time, the patterns of distribution of artificial polymers in water areas are mostly natural, and are determined by hydrochemical, hydrological and, in part, hydrobiological conditions. The main factors of anthropogenic impact are the nature and intensity of the sources of pollutants and their chemical composition (in particular, the density indicators and the propensity of polymers to decompose under certain conditions).

For ecosystems of water areas, microplastics (MP) are considered the most dangerous in terms of dimension – the degradation products of plastic waste (Wright, & Kelly, 2017; Kershaw, Turra, & Galgani, 2019; Andredy, 2017; Lambert, & Wagner, 2016). Contamination of surface bottom sediments with microplastics is a potential natural hazard, and their distribution in the geological component of marine environments is the subject of important scientific research (Hidalgo-Ruz et al., 2012; Andrady, 2011; Kershaw, Turra, &

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Galgani, 2019; Guidance on Monitoring..., 2013). The development of an effective strategy for managing plastic waste and minimizing its impact on the marine environment is not possible without conducting field studies in areas of their final accumulation, i.e. bottom sediments. Determination of their content in the upper layer of precipitation and study of qualitative and quantitative characteristics will allow to outline the patterns of their entry into the water area, distribution and accumulation, risks of impact on marine organisms.

Research location, station network and sampling methods

The State Scientific Institution "MorGeoEcoCenter of the National Academy of Sciences of Ukraine" within the framework of the international DOORS project carried out a study of microplastics in the bottom sediments of the water area within the Romanian shelf and part of the mainland slope of the Black Sea (Fig. 1), with the possibility of going to sea and sampling bottom sediments in 2023 due to the international DOORS research project ("Developing Optimal and Open Research Support for the Black Sea". The expedition was carried out on board the research vessel Mare Nigrum of the Romanian National Institute of Marine Geology and Geoecology (GeoEcoMar). Below is a diagram of location of the stations on the shelf and mainland slope of the study area (Fig. 1)

It is known that the Black Sea is the most vulnerable and exposed to various pollution, given its status as an inland semi-enclosed sea body with a strong influence of runoff from rivers with large catchment areas – the Danube, Dnipro, Southern Bug, as well as desalinated water from the Azov Sea through the Kerch Strait. The western part of the Black Sea is mainly influenced by the Danube River runoff, a powerful source of anthropogenic substances, including plastic waste from drained land areas. The study area is hydrologically determined by the influence of these water massifs, and the mineral, organic and anthropogenic suspended solids brought by them partially reach the study area and participate in sedimentation processes. It should be noted that the volume and intensity of MT, according to publications by foreign experts, are also largely regulated by the contribution of rivers, as the main source of microplastics for marine ecosystems, and at the same time the most saturated way of transporting plastic to the seas (Duis, & Coors, 2016; Lebreton et al., 2017; Faure et al., 2015; Schmidt et al., 2018).

The layout of the stations within the specified area allowed testing various elements of the underwater terrain: shelf and continental slope (including the sides of the Mangali submarine-canyon system). Sampling from the vessel was carried out in the water depth range from 25 to 1080 m along a defined network of profiles using a Multi Corer (Mark II) sampler into 4 core tubes (10 cm diameter), 25 % of the samples for further comparison of sampling methods were collected using a Van-Veen Grab (Hydro-Bios KIEL, 35 x 40 cm opening). For the analysis of microplastics, the surface and near-surface layer of bottom sediments having a thickness of 5 cm was selected. Samples were taken into aluminum containers, stored and transported to the laboratory at the temperature of –18°C. A total of 19 samples were collected for laboratory testing.

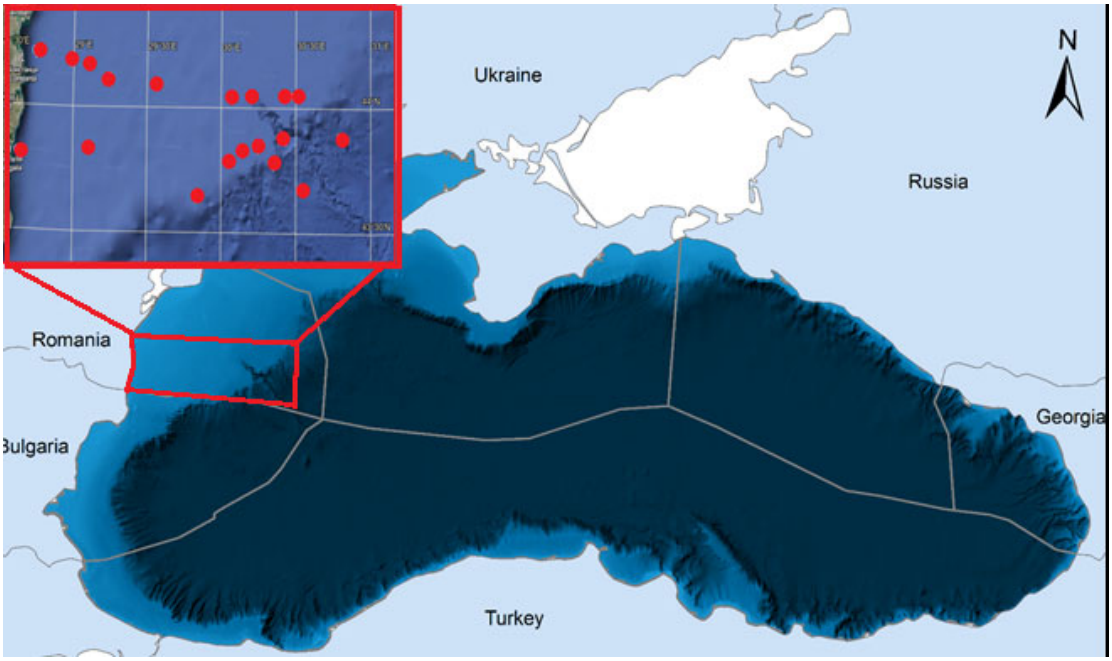

Fig. 1. Map of the study area with bottom surface relief elements and sampling points indicated

Precautions were also taken during the sampling process to avoid background plastic contamination through the air. Since the weight of the samples fluctuated significantly depending on their water content, the analysis results were subsequently recalculated using the dry weight of sediment. The methodology of the analytical studies carried out at the SSI "MorGeoEcoCenter of the National Academy of Sciences of Ukraine" was as close as possible to the relevant guidelines, in particular (Guidance on the Monitoring…, 2023; Kershaw, Turra, & Galgani, 2019; Hanke et al., 2013; Guide to microplastic identification, 2012; Masura et al., 2015), but had certain adjustments related to the nature of mechanical and mineral composition of the samples, the technical capabilities of laboratory equipment and practical skills regarding the effectiveness of certain sequences of separation of MPs from sediment samples.

The sample preparation procedure included: drying without preliminary sifting through sieves, flotation in a zinc chloride solution and selection of the lightest component, repeated precipitation and division in a separation funnel,

aging in hydrogen peroxide, and treatment with isopropyl alcohol. Each of the stages of sample preparation required certain conditions, the time range of sample exposure. At the end of each procedure, samples were washed in distilled water and dried (McDermid, & McMullen, 2004). Given the density of the most used categories of plastic polymers (ranging from 0.8 to 1.4 g/cm^3) and the precipitation matrix (more than 2.5 g/cm^3), our studies used a solution to separate the mineral component and microplastic particles using zinc chloride (at the density of 1.8 g/cm^3). Minimization of the natural organic component of the suspended matter was achieved by settling in a concentrated solution of hydrogen peroxide 35 % (Liebezeit, & Dubaish, 2012; Imhof et al., 2012; Nuelle et al., 2014).

Filtration processes at each stage of sample preparation were carried out, due to certain technical capabilities and technological limitations, through a filter polyamide cloth with a cell diameter of 26 μm. This is in line with the microplastics recommended for measurement provided in Guidance on the Monitoring of Marine Litter in European Seas, 2023. Also, due to the use of a polyamide fiber filter during laboratory work, transparent linear objects that corresponded to the parameters of the filter fibers were not included in the results of microplastics counting. The direct process of determining pollutants was based on two stages:

1) visual characteristics using optical devices (microscope, magnifying glass, etc.),

2) physicochemical characteristics using hardware complexes for probable fragments of MP that need to be confirmed.

Visual determination of microplastic particles was carried out under the monocular of SIGETA MB-12 LCD optical microscope, which is designed to work in wide or mixed light with magnification of 40x–640x with 4x, 10x, 40x lens objectives and interchangeable attachments. Evaluation under the microscope was carried out according to a number of methods presented in the literature (Kershaw, Turra, & Galgani, 2019; Hanke et al., 2013; Blair et al., 2019; Vermeiren et al., 2020; Mariano et al., 2021). The main indicators-identifiers were color, linear size ratio and particle morphology. Color was also one of the main characteristics during the visual identification of plastics. An alternative method of identification, the hot needle test, was also used to determine plastic under the microscope (De Witte et al., 2014).

Raman spectroscopy was used to perform structural identification (in fact, to verify the results of optical studies). Laboratory studies were performed using a single-stage MDR-23 spectrometer equipped with a cooled CCD detector (Andor iDus 420, Great Britain) and a Micromed microscope. Raman spectra were excited by radiation from solid-state lasers with wavelengths of 457 nm, 532 nm, 671 nm, and 785 nm. In order to prevent thermally induced modification of the samples during their examination, the laser power density on the samples was less than 10^3 W/cm^2. Spectral resolution of the spectrometer was determined by the width of the phonon band from the silicon monocrystalline substrate and was 3 cm^{-1} when the spectra were excited by laser radiation with λ=457 nm and 1.5 cm^{-1} when the spectra were excited by radiation with λ=785 nm. The frequency position of the phonon band from Si (521.0 cm^{-1}) was used as a reference to determine the frequency position of the other Raman bands.

Methods

On average, the fixed total number of solid matter fragments of mineral, organic, and anthropogenic origin with dimensions from 1000 to 26 μm in the processed samples exceeded 200 pieces on average, and the selection of potential MP fragments less than 300 μm from the total particle array was difficult. Among other things, this is due to the fact that at density of the separation solution of 1.8 g/cm^3 they float to the surface, in addition to plant/animal particles and artificial polymers, some organic and mineral aggregates, coal fragments, and even loose carbonate formations of varying degrees of decomposition, probably of organic origin (Fig. 2).

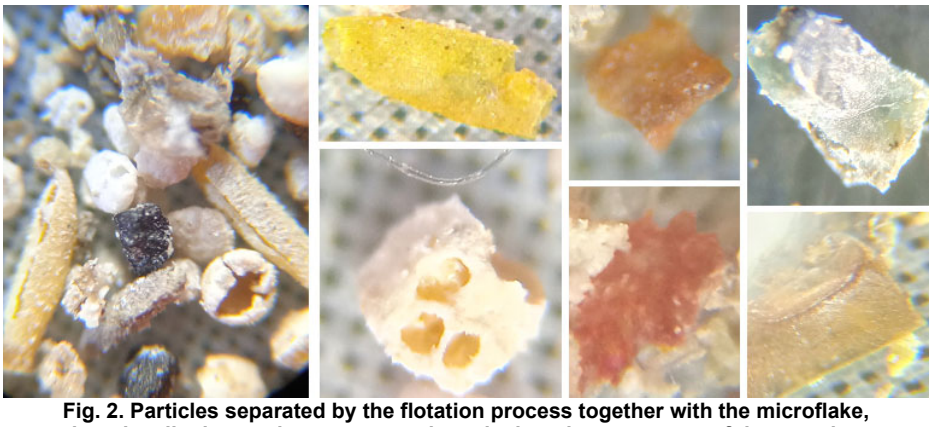

Fig. 2. Particles separated by the flotation process together with the microflake, but visually detected as organogenic and mineral components of the samples

The procedure of visual counting and hardware confirmation was based on a number of methodological guidelines, one of the most up-to-date of which was the Guidance on the Monitoring of Marine Litter in European Seas, 2023. For the study, control samples were selected in groups from different specimens in order to reach the 20 units or 10 % of the total content specified by the methodology. Accordingly, several representative groups were formed, represented by a sample of different morphological and color assemblages, which will be described below, to verify them using Raman spectroscopy. This made it possible to statistically process the data and determine the percentage of error for each type of particles studied by color and morphological category. If the identity of some of its components was not confirmed, the percentage of the latter in the control group was considered the error factor by which the recalculation was performed. In general, the procedure for working with samples can be described as follows (Fig. 3).

The comparative unit was 200 grams of dry sediment, with a mandatory note on the weight ratio of dry and wet samples.

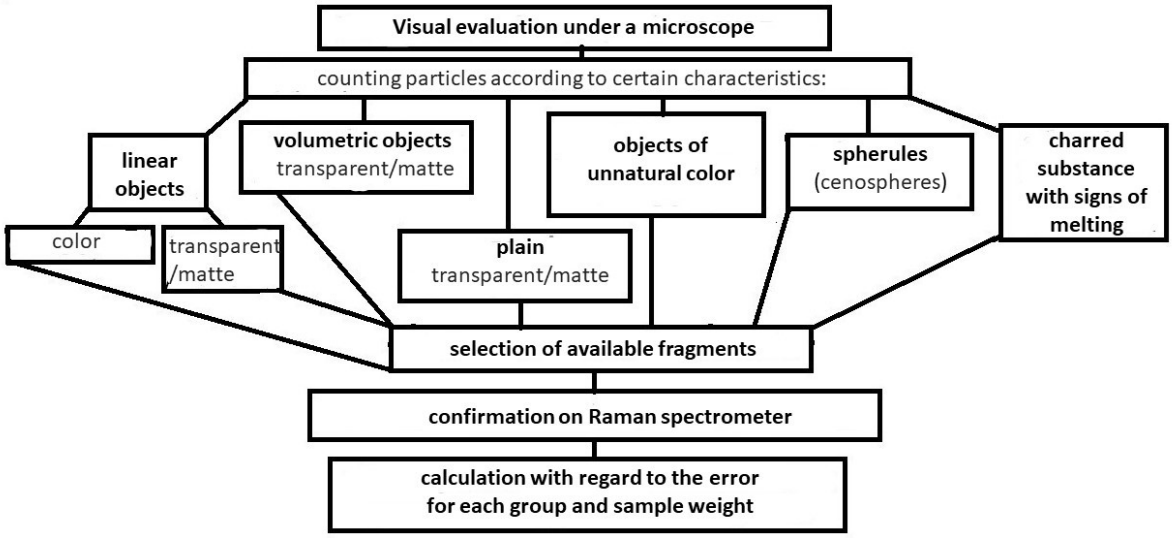

Fig. 3. Schematic view of the types, stages of detection and verification of MP particles in prepared samples

Results

Optical examinations under the microscope showed that all particles visually identified as plastic can be grouped according to morphological features. Visual assessment under the microscope was carried out according to a number of methods presented in the literature (Guide to microplastic identification, 2012; Blair et al., 2019; Vermeiren et al., 2020; Mariano et al., 2021); the main identifying indicators were color, linear size ratio and particle morphology. Data on the main morphological classes of particles recommended for classification by the international methodology were used (Guidance on the Monitoring…, 2023). At the same time, these recommendations were adjusted and expanded in accordance with the regional features of the sampling area and the types and characteristics of particles that were identified and verified on the Raman spectroscope. In particular, the polymer component was divided into the following groups according to the external features:

1. *A group of linear objects* in which the length was significantly greater than the diameter (of fibers). The following criteria were used to determine the elongated MP particles, which are generally presented in all methodological literature: absence of cellular or organic structures in the fiber, uniform thickness, no tapering towards the ends, and three-dimensional bending. The "hot needle" method was also used for verification, for which it was the most achievable category in terms of fragment size. The approximate percentage of the polymer component, which was confirmed by the methods of "hot needle" and spectroscopy, was for colored fragments – 60 %, colorless (transparent, white, matte) – less than 30 %. As a rule, a group of linear objects is present in all the samples studied and is represented by polyester, polypropylene, and polyamide. In most cases, the length reaches 100–2000 μm, in cross-section – 10–20 μm, less often – up to 40–70 μm. In some cases, spectroscopy did not give a positive result due to intense luminescence, and the overall ratio of the sample to the polymer group was confirmed by the hot needle test (Fig. 4).

2. *Colored objects* of an atypical shape for natural particles, visually captured as fragments of artificial entities. The main indicator is a saturated unnatural color (pink, blue, green) and morphological parameters that are non-typical for natural particles. The size, as a rule, is from 20 μm to 300 μm, less often – up to 1.5 mm. They are found infrequently, with an average of one to two fragments per sample (in some samples, monotypic particles of several units are found, which probably indicates the decomposition of one larger object during the period of stay in the sediments or mechanical impact during mixing). As studies have shown, the particle color is of considerable importance, same as during the determination of linear objects. In particular, yellow, brown, pale red, and orange colors can correspond to animal remains (root fragments, chitinous or other particles of exoskeletons, shells, etc.) much more often than particles of other colors. This color category was not included in the MP count, although some particles turned out to be polymer fragments. Approximate percentage of the polymer component is 60 % for the first color group (green, red, blue, pink fragments). MPs, as a rule, represent polypropylene, polystyrene and polyethylene, two cases each – polyurethane and polyethylene terephthalate.

3. *Flat particles* – matte or transparent particles that are turned transparent by the lower illumination of the microscope. Ranked second in their prevalence after fibers. The particles have a significant range of dimensions – from 20 μm to 2–3 mm, on average – 20–400 μm. A fragment of the largest dimension was captured in sample No. 15 – a 2.3 mm long transparent polypropylene film. The film, by the way, was extremely non-resistant to mechanical stress, dividing into a large number of fragments. As a rule, flat particles can be subdivided into two types – the first is shapeless thin and elastic film of varying degrees of transparency with torn edges, the second is transparent or matte scales with a certain structure and type of cracking. The confirmed percentage of the polymer component is 40 %, the highest flaw in the identification process on the Raman spectrometer remains a high degree of luminescence. This group is mainly represented by polyethylene, polypropylene, some individual objects – by polychlorovinyl.

4. *Bulk (volumetric) particles* are represented by fragments that are not visible under the lower illumination of the microscope, or usually have comparable dimensions in three projections. They – are available in transparent and matte surfaces, with a wide range of sizes from 26 microns to 900 microns. This category is also characterized, as for minerals, by different types of gloss – glass, greasy and opaque. They have different structure and degree of surface rusting and fracture, mainly shell-shaped and flat. The percentage of particles verified in the sample for this category also reaches 40 %.

Fig. 4. Representative fragments visually fixed as representatives of different groups of synthetic polymers: by rows – linear objects, colored fragments, flat particles, bulk particles, spherules, substance with traces of high-temperature processes

5. *Spherules, balls* – a category that is commonly found in samples, with dimensions ranging from 20 μm to 120 μm, with an average of 70 μm. Usually, objects of spherical shape are subject to consideration and counting. Others, in particular those that had an oval shape and were represented in larger quantities, were not taken into account. In terms of size, color, and insolubility in hydrogen peroxide, they were similar to fragments of biological origin, in particular, the shells of organisms at different stages of life. The spheres usually had colors ranging from transparent to dark brown, and varying degrees of rusting and shape defects. The percentage of confidence is low – less than 30 %, and a big problem is the separation of spheres from samples for analysis on spectrometer. If the spherules turned out to be cenospheres (hollow), then they were not counted, as were the objects of light brown, yellow, and white color. The approximate percentage of verified particles from those sampled was not more than 30 %.

6. The allocation of such a category of MP as a *substance with traces of exposure to high-temperature processes* is associated with the detection of fragments that are similar in shape and color to charred particles with different shine and breakage, for which diagnostics at different points sometimes gave different Raman spectra, some of which correspond to synthetic polymers (Fig. 5).

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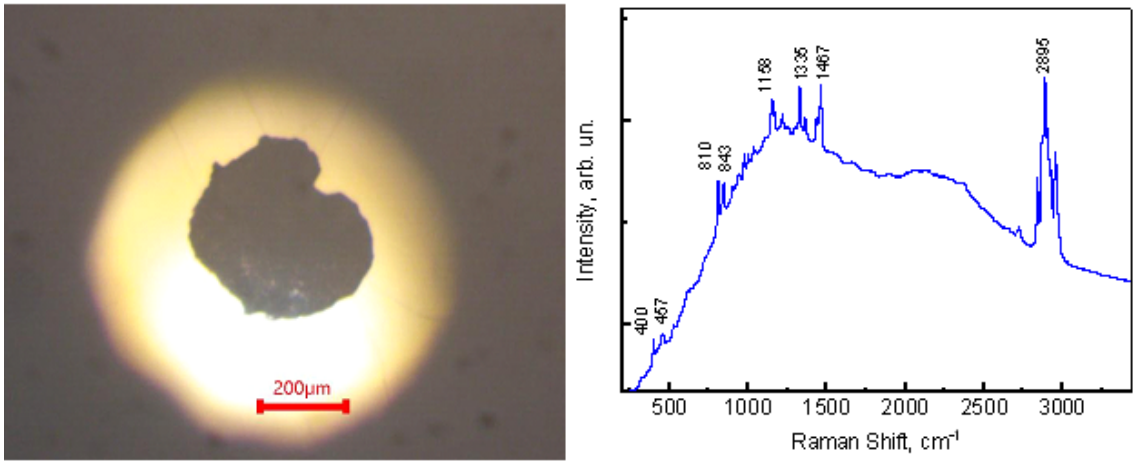

Fig. 5. A particle that looks like a burnt and melted fragment of a substance shows vibrational bands in the Raman spectrum characteristic for polypropylene

These are likely fragments of so-called pyroplastics, derivatives of synthetic polymers that have been subjected to intense temperature exposure (melted or severely softened) and subsequent mechanical destruction. This type of microplastics has attracted the attention of researchers in recent years in their publications (Ellrich et al., 2023). Partially burnt or melted polymers, which could also be subjected to erosion by waves and wind, are represented, according to the literature, by polyethylene and polypropylene.

The analysis of each sample and subsequent generalization showed the presence of plastic particles at all points of the sampling area, in different quantities and composition. The results of our studies confirm that microplastic particles in the surface sediments are quite abundant throughout the entire research area, and they are represented by different types everywhere, with fibers dominating in terms of morphological characteristics and polyethylene and polypropylene in terms of chemical types.

The minimum defined number of MP particles in the sample was 10 units per 200 grams of dry matter, and the maximum was more than 100, respectively. It should be noted that the high levels of artificial polymers for a number of samples were obtained by recalculating the amount of substance taken at different points to a single comparative value (this will be described in the discussion section). The size of the detected fragments was, on average, 100–300 microns, with individual specimens reaching 1.5–3 mm. Fibers dominated the defined categories, with pyroplastics making up the smallest category by number of units. The map and the consolidated diagram (Fig. 6, 7) present the overall data on the presence of different categories of MP in the collected samples according to the collection stations, both in terms of actual distribution and percentage of the defined categories in each sample.

There are currently few publications on the distribution, species composition, and dynamics of microplastics within the shelf and mainland slope of the western Black Sea. Despite the content of these works (Pojar et al., 2021; D'-Hont et al., 2021), in general, there is not enough information to compare and correct the data we obtained. According to the results of our research, there is no stable dependence of redistribution of microplastics of different densities on distance from the shore, similar to the distribution of the material component of sediments. The only thing that can be confirmed, based on the information received, is uneven lateral distribution within the shelf zone, which is quite possibly related to the impact of the anthropogenic plane load on the surface bottom sediments. In particular, we are talking about the location and distribution of possible dumping zones on the shelf, the impact of which caused the concentration of pollutants within certain sufficiently large areas of the shelf. This may be evidenced, in particular, by the large amount of carbon-containing substances in certain test points (stations 1, 3 – probably particles of natural coal, burnt substances, etc.).

One of the peculiarities of the microplastics content in the surface sediments of the survey area is the relative stability of their concentration (quantitative and qualitative indicators) in the sediments of the mainland slope (samples 7, 15, 16, 17, 18). It should also be noted that the low concentrations of MP at point 10 are likely related to technical problems while sampling from the vessel: during lifting of the scoop, the sediment was washed with water due to incomplete closure of the sampler flaps.

As for the planar distribution of different types of polymers, the Raman spectrometer identification procedure involved the creation of mixed control groups from different samples, which makes it impossible to calculate the types of MPs by composition at individual stations. This is due to the small size of the samples and the corresponding difficulty in sampling (particles smaller than a certain size cannot be visually distinguished from other material or sorted because they cannot be controlled due to their small size). At the same time, the analysis of the sorted part of the fragments using methods that facilitate proper plastic identification (Hidalgo-Ruz et al., 2012; Dekiff et al., 2014), is a necessary element of MPs verification and their subsequent counting.

It is worth noting certain problematic issues related to the definition of MPs and their calculation, peculiarities of field and laboratory work that could affect the quality of the results calculation, and the identification and consideration of which should improve the accuracy of the results and their informational value. They are:

1) The number of MP particles per sample unit was recalculated to dry sludge. The ratio of dry sample weight to wet sample weight for samples collected in different areas of the shelf averaged 1:2.5 and ranged from 1:1.6 (sample No. 2) to 1:10 (sample No. 18). The increase in the ratio is observed, as a rule, for samples taken with a multicorer, and in terms of the planar distribution – for samples taken at considerable depths. Perhaps this is due to the peculiarities of sampling by different types of devices (the possibility of sampling "silt" with a multicorer, or with different material composition of sediments and their saturation with water and shell/detritus material).

2) The above-mentioned problem of different sample weights creates another problem - determining the methodology for proportional conversion of the number of MP particles in samples of different volumes to one reference mass. Given the solution of such problems in the literature (D'Hont et al., 2021), it was decided, in case of different sample volumes, to reduce the number of identified particles by a proportional increase or decrease to the reference weight.

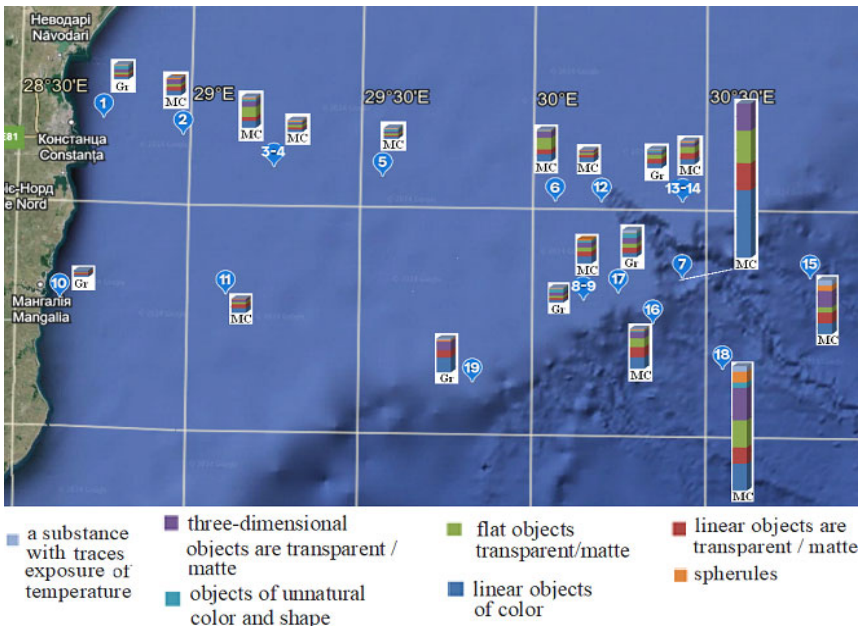

Fig. 6. A map of the study area with sampling points and diagrams of the distribution of different categories of MPs and their number. Captions under the diagrams indicate the types of samplers (multicorer, scoop)

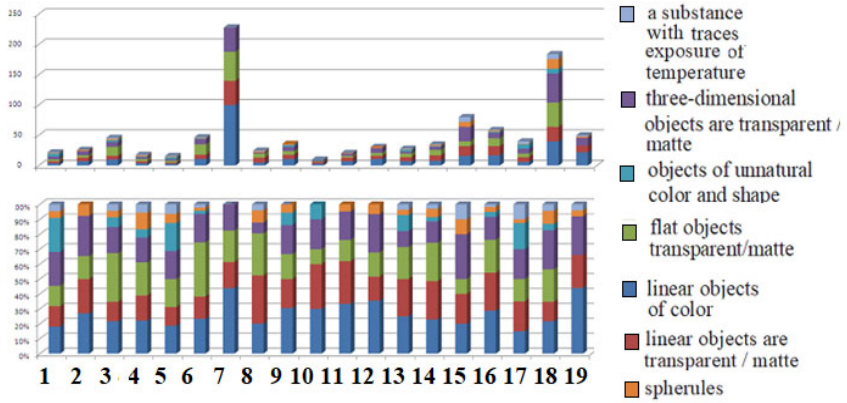

Fig. 7. Consolidated diagram of the distribution of different categories of MPs in station samples:
1) actual distribution, 2) percentage in each sample

For example, halving the amount of particles to 200 g for sample No. 8 (with 400 g removed from it for analysis) seems logical, and the feasibility of a proportional increase in the amount of MP for sample No. 18 by almost 8 times from the existing 0.026 g to 200 g remains questionable. This is especially true for rarely encountered categories of MPs – for example, 1 spherule, the probability of detection of which is insignificant, should be proportionally recalculated eight times.

3) Regarding bringing the density of zinc chloride solution to 1.8 g/cm^3, the following should be noted: with the unconditional benefit of detecting certain types of high-density MPs (polyurethane, polyesters, polyvinyl chloride), a significant amount of mineral substance (loose carbonate objects, a significant amount of carbonaceous substance, organo-mineral aggregates, etc.) may emerge during the flotation process, which introduces certain complications in the procedure for calculating or selecting MPs. Studies have shown that the aggregation of sediment fragments of the siltstone-pelite component, namely the presence of accumulations of organic-mineral particles, can remain even after liquid separation and retention in solutions to remove organic matter (in particular, H_2O_2,). This refers to the potential loss of counting artificial polymer particles remaining in the mineral matrix with a density higher than the flotation solution (Fig. 8).

Perhaps, in this case, attention should be paid to systems for defragmenting the mineral base of samples and qualitatively separating adherent particles. It should be borne in mind that excessive mechanical separation destroys fragile MP particles, and the use of concentrated alkalis and acids to remove organic matter can lead to the dissolution of certain types of polymers.

4) The previous paragraph outlines another important issue that requires consideration and improvement in sample preparation and particle identification processes. As practice

has shown, when determining microplastics in the bottom sediments of offshore areas, particles of several millimeters in size are prone to defragmentation due to their relatively large size, especially during a set of laboratory operations for their isolation. This introduces some uncertainty into the system of counting particles and their dimensions. For example, in one of the samples collected within the mainland slope, a rather large microplastic particle was found in zinc chloride during density separation (station No. 15/Argo-Sirena, PP film measuring 0.7×2.3 mm). In the process of subsequent procedures – washing with distillate, settling in hydrogen peroxide, processing in alcohol, the sample significantly decreased in size, decomposing into a large number of small fragments. At the final stage of quantification, all potential MP fragments (25 units!) that looked similar to film fragments were not included into the count (Fig. 9).

Fig. 8. Fragments of the substance isolated by the flotation process:
1) microplastics (a blue particle), "ingrown" into the mineral-organic aggregate. The particle size is 20-25 microns;
2) a plastic line of an undefined type of black polymer, in an organo-mineral matrix formed, probably, by benthic biocenoses

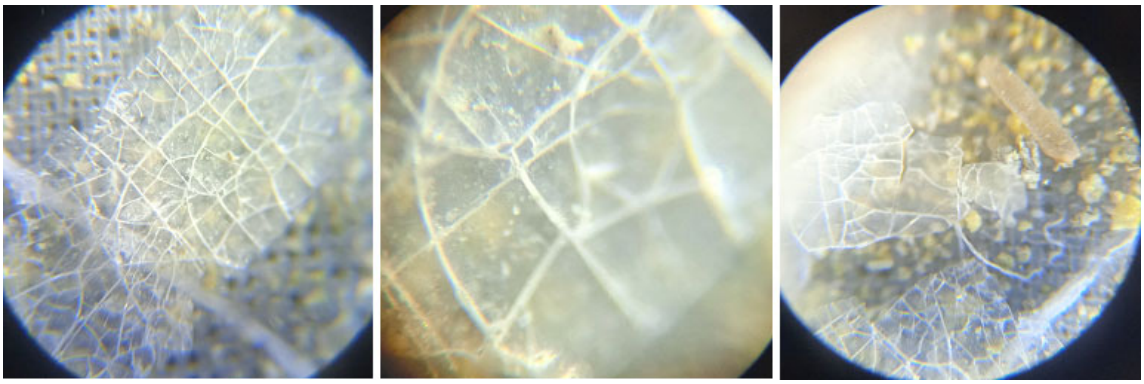

Fig. 9. A microplastic (polypropylene) fragment that resembles a strip in shape (1), its texture in the enlarged photo (2), and sample fragments (3)

In general, in many samples, on the one hand, the absence of MP samples of the upper dimensional limit of 0.3–0.5 cm is noteworthy, and on the other hand, the presence of the same type (single-color) MP fragments in some samples (as can be seen in the station summaries given above). This indicates either the decomposition of relatively large particles of MP in the bottom sediments or their destruction during sample processing. Nevertheless, this is a significant issue that should be given further attention and unambiguous interpretation.

5) The qualitative identification of MP particles in the sediments, as well as determination of the types of selected synthetic polymers, remains a problematic issue. Verification procedures on Raman spectrometer also do not always give unambiguous results. For example, measurements at different points on the surface of a single particle often give different readings due to its component composition, coloring, degree of degradation/rusting, and other factors.

Discussion and conclusions

The results, in general, confirm the data presented in the literature on this topic (D'Hont et al., 2021, Pojar et al., 2021). Studies have shown that microplastic particles in the surface sediments are represented by different types everywhere, with fibers dominating in terms of morphological characteristics. Size of the detected fragments averaged 100-300 microns, with individual specimens reaching 1.5–3 mm. In terms of percentage redistribution among different types of polymers, polyethylene and polypropylene dominated, with polystyrene, polyester, and polyamide accounting for a much smaller share. Single fragments were found of polyvinyl chloride (1 object) and polyurethane (3 objects). Given the density (in g/cm^3) of polyethylene terephthalate (polyester) – 1.24–2.3, polyvinyl chloride – 1.16–1.58, and polyurethane – 1.23 – all these objects were detected due to high density of the zinc chloride solution

As for the distribution of MPs in surface sediments depending on natural conditions (different facies zones, depth distribution, currents, sediment types, and bottom relief), we can document the fact that the amount of polymers, in terms of dry weight of soil matrix samples, increases in the direction of the mainland slope. This raises certain questions about the intensity of dispersed matter

accumulation on sloping bottom areas unstable to accumulation, although the issue of MP concentration in pradeltas has been raised in a number of literature sources (Pellegrini et al., 2023)

It should be noted that since many unidentified particles are overlooked due to their small size, the actual number of MPs in the samples may be 50–70 % higher.

An important result of the work was the identification of a number of topical issues, shortcomings and uncertainties in laboratory research methods, sample preparation and identifying MPs, which should be addressed in the future. The development of non-destructive and at the same time highly effective in terms of the amount of material recovered and identified methods of sample processing and analysis will have a significant impact on the quality of results obtained in the future.

Finally, we would like to note the following: the research currently being conducted by the scientists of MorGeoEcoCenter of the National Academy of Sciences of Ukraine under the DOORS project allows us to gain important practical experience in identifying artificial polymers in geological environment, establish information bases, and define an arsenal of research methods in accordance with the developed European standards. The acquisition of practical experience and further integration into the international system to study the distribution of plastic waste, in particular, microplastics in the Black Sea geo-ecosystems, in the future opens up wide opportunities for Ukrainian geo-ecologists to participate in important international environmental projects, including the implementation of EU's Mission Starfish 2030: Restore our Oceans and Waters.

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ДОСЛІДЖЕННЯ РОЗПОДІЛУ МІКРОПЛАСТИКУ В ДОННИХ ВІДЛАДАХ ЗАХІДНОЇ ЧАСТИНИ ЧОРНОГО МОРЯ

Вступ. *Розповсюдження та накопичення пластикових відходів у навколишньому середовищі нині є визнаною глобальною проблемою. Розробка ефективної стратегії управління пластиковими відходами та мінімізації їх впливу на морське середовище неможлива без проведення польових досліджень у місцях їх накопичення, особливо у донних відкладах. Визначення їх вмісту у верхньому шарі осадів та вивчення якісних і кількісних характеристик дає змогу окреслити закономірності їх надходження в акваторію, поширення та накопичення, ризики впливу на морські організми.*

Методи. *Візуальне визначення мікрочастинок пластику проводили під монокуляром оптичного мікроскопа SIGETA MB-12 LCD. Альтернативний метод ідентифікації, тест гарячою голкою, також використовувався для визначення пластику під мікроскопом. Раманівську спектроскопію було використано для проведення структурної ідентифікації. Лабораторні дослідження проводили на одноканальному спектрометрі MDR-23 з охолоджуваним CCD-детектором і мікроскопом Micromed.*

Результати. *Аналіз кожного зразка та подальше узагальнення показали наявність частинок пластику в усіх точках зони відбору, у різних кількостях та складі. Результати досліджень підтверджують, що мікрочастинки пластику в поверхневих відкладах досить поширені на всій території досліджень і повсюдно вони представлені різними типами, де за морфологічними характеристиками домінують волокна, а за хімічними типами – поліетилен і поліпропілен. Стабільної залежності перерозподілу мікропластику різної щільності від відстані від берега немає. Єдине, що можна підтвердити, це нерівномірність латерального розподілу в межах шельфової зони, що цілком імовірно пов'язане з впливом антропогенного площинного навантаження на поверхневі донні відклади.*

Висновки. *Дослідження показали, що мікрочастинки пластику в поверхневих відкладах досить поширені на всій території обстеження, і всюди вони представлені різними типами, з домінуючими за морфологічними характеристиками волокнами. Що стосується розподілу мікропластику в поверхневих відкладах залежно від природних умов, було з'ясовано, що кількість полімерів, у перерахунку на суху вагу зразків ґрунтової матриці, збільшується в напрямку схилу материка. Важливим результатом роботи стало виявлення ряду актуальних питань, недоліків і невизначеностей у лабораторних методах дослідження, пробопідготовці та ідентифікації мікропластику, які потребують вирішення в майбутньому.*

Ключові слова: *мікропластик, донні відклади, методика досліджень, екологія, спектроскопія, візуальні обстеження.*

Автори заявляють про відсутність конфлікту інтересів. Спонсори не брали участі в розробленні дослідження; у зборі, аналізі чи інтерпретації даних; у написанні рукопису; в рішенні про публікацію результатів.

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