The choice of a method for selecting and determining the quantitative and qualitative content of microplastics in wastewater

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Abstract. A general growth in the polymers production and consumption leads to an increase in the new types of wastes. In conjunction with the lack of secondary recycling power this fact is being a reason for appearance of a new processes that is potentially destructive for the environment. In particular, plastic wastes that is being stored in the wastewater of large cities under a combination of aggressive factors action such as humidity, mechanical and UV-erosion degrades into small-size particles, famously known as microplastics (MP). The study presented is devoted to the methodology development for acquisition, quantitative and qualitative analysis of wastewater derived microplastics. An experimental part deals with real wastewater samples collected at different infrastructurally-important objects of Rostov-on-Don and Aksai cities. For all the sampling locations the presence of urban-generated MP particles is approved. The results show that the research methods used are able to satisfy the output data quality conditions. However, the significant time and cost consumption of the research chain developed limits its wide practical application.

1 Introduction

A feature of modern civilization is the massive use of plastics in technology, industry and everyday life. Environmental pollution by microplastics (MP) (plastics with a diameter of less than 5 mm) is one of the main environmental problems worldwide. In the last decade, microplastics have been widely considered in the foreign scientific literature as pollutants for the environment and biota. There are seven main types of plastics, which differ in chemical composition, raw material component, modifiers used and physico-mechanical properties: PET, HDPE, PVC, LDPE, PP, PS. Plastics consist mainly of polymerized gases, and in order to give them flexibility, elasticity, resistance to environmental influences, and increase impact strength, various modifiers, stabilizers and antioxidants are added to them during production (naphthalene sulfonates, formaldehyde, fatty acid amides, siloxane, phthalic and trimellitic acid esters, dioctyl phthalate, dimethyl phthalate, dibutyl phthalate, dibutylsebacinate), which, during the destruction of plastics, can enter the environment.

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forming a secondary anthropogenic load. In this case, plastic can be considered as a "transporter" of pollutants.

Global research interest in microplastics is caused by its specific behavior in aquatic and terrestrial environments [1, 2]: poor decomposition, which leads to accumulation; the ability to form persistent organic pollutants (POPS) due to their large specific surface area; potential ingestion into living organisms.

Having such a diverse chemical composition, plastics are able to form a negative impact on all geospheric shells of the Earth, while changing their structure and composition, as well as the conditions of existence of living organisms in them. In 2019, the Scientific Policy Council of the European Academies (SAPEA) and the Committee of Scientific Advisers of the European Commission and the Council (SAM) emphasized the relevance and need to study the harm of microplastics in relation to human health and the sustainable functioning of ecosystems. Most research focuses on the identification and characterization of microplastics in freshwater, seawater, and terrestrial environments. It has been established that microplastic pollution can affect both ecosystem food chains and human health [3-14].

Большинство научных обзоров были посвящены микропластикну в пресноводных, океанических и наземных природных средах [15-32].

In general, according to the ways of formation, microplastics can be divided into two groups: primary and secondary. Primary microplastics formed from products of everyday use (for example, detergents, scrubbers and toothpaste), which may include: Acrylates Copolymer (AC), Styrene-Acrylates Copolymer, Acrylates Crosspolymer (ACS), Ethylene-Vinylacetate Copolymer (EVA), Nylon-6, Nylon-12, Polyacrylate, Polyethylene (PE), Polyethylene terephthalat (PET), Polymethyl Methacrylate, Polypropylene (PP), Polyquaternium-7, Polystyrene, Polyurethane (PUR). Fendall and Sewell (2009) identified and characterized microplastics from four commercially available face wash products, and it was found that the size of the most extracted microplastics was less than 0.5 mm and had various irregular shapes. Chan (2015) characterized polyethylene microgranules in exfoliating facial cleansers, such as size, color, and concentration. The results showed that the average size of the microbeads ranged from 60 to 800 microns in diameter. It was found that most of the microbeads are white and opaque.

Cheung and Fok (2017) extracted microgranules from nine different commercially available facial cleansers from mainland China. The predominant particle size of the microbeads was in the range of 24-800 microns. The average number of microbeads detected ranged from 5,219 microbeads/g of product to 50,391 microbeads/g of product. The predominant shape of microbeads from facial cleansers was incorrect. In another study, Kalcikova et al. (2017) characterized microbeads in body and face wash products, and the size of most microbeads was less than 100 microns. More microplastics of a larger size were found in body wash products, while, on the contrary, face wash products mainly contained microplastics of a smaller size. The average concentration of PE in body wash products (4.82 g/100 ml) was significantly higher than in face wash products (0.74 g/100 ml).

Scientists have determined the estimated volume of particle release. Kalchikova et al. (2017) estimated that 1 should be 21 particles/m3. Cheung and Fok (2017) reported that approximately 209.7 trillion microparticles (equivalent to 306.9 tons) formed when using face wash products can enter the aquatic environment of mainland China annually. Secondary microplastics are formed as a result of crushing large plastics into small particles formed as a result of photooxidation, mechanical, chemical or biological influences [33, 34]. Synthetic microfibers as a secondary microplastic formed as a result of the use of synthetic polymers in clothing are considered the most common type of microplastic environmental pollution [35]. In addition, microfibers can accidentally enter the body of a living being and, consequently, enter the food chain and harm human health.
In addition to entering the aquatic environment, microfibers can also enter terrestrial soils by applying silt as fertilizer. During normal household washing of synthetic fibers, thousands of microfibers can be released, and the resulting wastewater either enters the soil or sewage through the sewer. The effect of the number of washings of synthetic fabrics on the number of expandable drags was investigated by Napper and Thompson (2016). The studies were conducted at a washing temperature (30-40 °C), detergent and conditioner on the amount of microfibers released from polyester (PEST), acrylic and cotton PEST during washing. In the case of PEST, the amount of microfiber loss gradually decreased from 2.79 mg at the 1st wash to 1.63 mg at the 5th wash, which was similar to the trend observed for PEST acrylic and cotton. The result may indicate that old clothes emit fewer microfibers than new ones. In addition, the use of conditioner and detergent significantly affected the amount of fibers released. Obviously, when washing in the presence of detergent and conditioner, more fibers would be released. Based on the assumption of a washing load of 6 kg, the authors calculated that the number of microfibers formed during the washing of PEST fabrics, acrylic and cotton PEST fabrics. The washing parameters (temperature, time, water hardness and mechanical action), as well as the effect of industrial washing on the release of microfibers, were also studied. The use of detergent has led to an increase in the release of microfibers. In particular, the release of microfibers increased significantly from 162 ± 52 microfibers/g of fabric to 1273 ± 177 or 3538 ± 664 microfibers/g of fabric when using liquid or powder detergent, respectively. This increase may be due to the content of inorganic substances (e.g. zeolite) in the detergent, which can cause friction with synthetic fabrics during the home washing process. Another reason may be due to the high pH value of the detergent, especially when using a powder detergent, since an alkaline detergent can damage the surface of tissues due to slow surface hydrolysis. A similar observation was reported by Hernandez et al. (2017), in which it was noted that the use of detergent is the most important factor affecting the total mass of microfibers released. According to scientists, after washing at home, 6,000,000 microfibers can be formed, based on the assumption of a 5-kilogram load of fabrics.

Karni Almroth et al. (2018) estimated the number of microfibers released from three common synthetic materials (acrylic, nylon and PEST) under various washing conditions, and it was observed that PEST fleece fabrics emit the largest amount of microfibers during washing. The authors also noted that the number of microfibers crushed during washing depended on the thickness of the yarn and needle. In particular, a higher degree of microfiber release was obtained when washing tightly knitted fabrics for pest control. It was found that aging of clothing is another significant factor affecting the release of microfibers during home washing, and the use of aged clothing led to an increase in the mass of microfibers compared to new clothes.

The little-studied areas include the quantitative and qualitative composition of microplastics accumulating in wastewater. According to modern research, wastewater is considered one of the largest sources of microplastics entering the natural environment. The concept of wastewater has different interpretations in different countries. According to Russian environmental legislation, wastewater is rainwater, meltwater, infiltration, irrigation, drainage water, wastewater from a centralized wastewater disposal system and other waters, the discharge (discharge) of which into water bodies is carried out after their use or which runoff is carried out from the catchment area (GOST R 59053-2020. The national standard of the Russian Federation. Environmental protection. Protection and rational use of waters. Terms and definitions) (approved and put into effect by the Order of Rosstandart dated 30.09.2020 N 705-st). The complexity of wastewater research is related to their heterogeneity both in terms of sources of education and composition. Sewage treatment plants in any country are a...
complex of special structures, both municipal, urban and private, designed to purify wastewater from the pollutants contained in them. Further, the purified water is either used in the future, or discharged into natural reservoirs.

Despite the fact that traditional wastewater treatment methods have a high efficiency (about 99%) of removing microplastics, significant amounts of pollutants from microplastics can still enter the aquatic environment, given that a large amount of wastewater is discharged daily. To solve this problem, Lares et al. (2018) evaluated the efficiency of removing microplastics using an advanced treatment (i.e., a membrane bioreactor), and this treatment resulted in a higher removal efficiency (99.4%) than with the conventional method of producing activated sludge (98.3%). Talviti et al. (2017a) investigated the effectiveness of removing microplastics from wastewater using four different advanced final stage purification technologies, including membrane bioreactor, disc filter, rapid purification sludge is usually formed as a result of primary and secondary wastewater treatment. Mahon et al. (2017) found that about 99% of microplastics remain in sediment after several stages of wastewater treatment, which makes sludge used in agriculture (also known as biosolids) an important source of environmental pollution by microplastics. Many studies have reported an abundance of microplastics in sediment.

Lee and Kim (2018) compared three biological treatments, namely anaerobic-oxygen-free-aerobic and examined the removal rates of microplastics. The authors reported that the concentration of microplastics in the wastewater of the anaerobic oxygen-free-aerobic batch reactor and environmental processes was 0.44 particles/l, 0.14 particles/l and 0.28 particles/l, respectively. The efficiency of isolation of microplastics for all three treatments was in the range of 98-99%. This may indicate that most of the microplastics were removed using a treatment used to remove grease, sand and primary deposition. In addition, higher removal efficiency was obtained from smaller microplastics (106-300 μm). Anaerobic digestion treatment has led to a decrease in the number of microplastics, which may be due to the decomposition of polymers by microorganisms in the anaerobic digestion system.

Scientists' quantitative assessment of MP concentrations in wastewater in different cities of the world gives different values. Thus, according to Gatidou et al. (2019), the concentration of microplastics can be up to 3160 particles/dm³ in untreated wastewater and 125 particles/dm³ in treated wastewater. Wastewater treatment at municipal wastewater treatment plants removes from 72% to 99.4% by weight of MPs. However, they are not biodegradable in typical wastewater treatment processes, and thus more than 90% accumulates in sewage sludge, where their concentration reaches 170.9 × 10³ particles/kg of dry matter (ds) (Gatidou et al., 2019).

Van Wesel et al. (2016) used a mathematical model to estimate the amount of microplastic contamination caused by PCCP. According to three different emission scenarios, including minimum, medium and maximum, the estimated concentration of microplastics in the final wastewater was 0.2 lg/l, 2.7 lg/l and 66 lg/l, respectively.

The conducted studies of the quantitative and qualitative composition of microplastics in wastewater reveal environmental problems of pollution of environmental objects.

2 Materials and techniques

Wastewater was collected by a portable microplastic sampling system (MPN). The degree of contamination of the water body was monitored using the HI98713 turbidity meter, since the indicator of total turbidity of water directly depends on the amount of suspended particles in the water. Microplastic is an integral part of the total suspension. During the sampling, the water temperature was also monitored using a TM10-3 thermometer. The volume of the sampled sample was recorded using the VKM-20 water meter included in the instrument.
The classification of the selected waters as wastewater in the field at the sampling sites was carried out according to organoleptic parameters (odor) according to PNDF 12.16.1-10. Sampling was carried out from a depth of 15 cm, since the largest part of microplastics is usually concentrated in the surface horizon. The minimum volume of the selected sample should be at least 200 liters. Since microplastics are an inert contaminant, pretreatment of the sample at the sampling point is not required. When sampling wastewater from sewer wells, samplers were used, fixed on a rope, the length of which allows sampling without overhanging into the well.

The treatment and sample preparation of wastewater for the production of microplastic particles included four stages: density separation, filtration, sieving, and purification. All of them are aimed at separating microplastic particles from the main sample material – water, and external (organic) contamination. To determine the concentration of microplastics in the wastewater sample, the particles were visually sorted under a microscope and weighed on analytical scales. When examining the dry residue on the filter, with a mesh size of 100 microns, the following characteristics were determined to identify the microplastics: elasticity under pressure, absence of cellular or fibrous structure, bright color, unusual shape. Information about the morphological and morphometric features of the particles, such as size, shape, and color, was recorded. A stereo Micromed MS-1 var microscope was used to determine the quality of microplastics. The electron spectroscopy method was used for the qualitative study of microplastic particles.

3 Results

The reasonable choice of the wastewater sampling site is one of the important stages of the analysis for the quantitative and qualitative determination of microplastics in a large city. For field research in 2023, 21 wastewater sampling points were identified in the territory of Rostov-on-Don and the Rostov region, taking into account the recommendations of "Sampling of land surface waters and treated wastewater" from 2012-02 (P 52.24.353-2012) and the guidance document "Organization and conduct of routine observations of the state and pollution of land surface waters (RD 52.24.309)."

The following indicators were taken into account:

1. The inclusion of the watercourse in the urban planning structure of the city, the administrative division.
2. The length of the drainage watercourse and the catchment area.
3. Anthropogenic load on the drainage watercourse, taking into account the functional areas of the city.
4. Availability of places where wastewater enters the drainage watercourse.
5. Availability of places for centralized wastewater discharge into water bodies.
6. Availability of wastewater collectors. A map of wastewater sampling points is shown in Figure 1. Detailed situational plans for the location of wastewater sampling points are shown in Table 1.
![Wastewater collection map](image)

Table 1: Wastewater sampling points on the territory of the Rostov agglomeration.

<table>
<thead>
<tr>
<th>Sample Point</th>
<th>Geographical Coordinates</th>
<th>Turbidity, FNU</th>
<th>Volume, cubic meters</th>
<th>Water temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1C</td>
<td>4016.39546, 213.39807</td>
<td>39.80125</td>
<td>86481.23400</td>
<td>39.15679</td>
</tr>
<tr>
<td>2C</td>
<td>4016.39587, 205.22680</td>
<td>39.22675</td>
<td>66498.23400</td>
<td>39.15679</td>
</tr>
<tr>
<td>3C</td>
<td>4016.22537, 187.22762</td>
<td>39.22675</td>
<td>22676.23400</td>
<td>39.15679</td>
</tr>
<tr>
<td>4C</td>
<td>4016.22340, 18893.22675</td>
<td>39.22675</td>
<td>18893.23400</td>
<td>39.15679</td>
</tr>
<tr>
<td>5C</td>
<td>4016.22675, 22675.24870</td>
<td>39.22675</td>
<td>22675.23400</td>
<td>39.15679</td>
</tr>
<tr>
<td>6C</td>
<td>4016.22675, 24504.24770</td>
<td>39.22675</td>
<td>24504.23400</td>
<td>39.15679</td>
</tr>
<tr>
<td>7C</td>
<td>4016.22537, 19349.20637</td>
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<td>19349.23400</td>
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</tr>
<tr>
<td>8C</td>
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<td>20637.33835</td>
<td>39.15679</td>
</tr>
<tr>
<td>9C</td>
<td>4016.22537, 30054.30054</td>
<td>39.22675</td>
<td>30054.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>10C</td>
<td>4016.22537, 33835.30054</td>
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<td>33835.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>11C</td>
<td>4016.22537, 30054.30054</td>
<td>39.22675</td>
<td>30054.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>12C</td>
<td>4016.22537, 33835.30054</td>
<td>39.22675</td>
<td>33835.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>13C</td>
<td>4016.22537, 30054.30054</td>
<td>39.22675</td>
<td>30054.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>14C</td>
<td>4016.22537, 33835.30054</td>
<td>39.22675</td>
<td>33835.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>15C</td>
<td>4016.22537, 30054.30054</td>
<td>39.22675</td>
<td>30054.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>16C</td>
<td>4016.22537, 33835.30054</td>
<td>39.22675</td>
<td>33835.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>17C</td>
<td>4016.22537, 30054.30054</td>
<td>39.22675</td>
<td>30054.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>18C</td>
<td>4016.22537, 33835.30054</td>
<td>39.22675</td>
<td>33835.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>19C</td>
<td>4016.22537, 30054.30054</td>
<td>39.22675</td>
<td>30054.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>20C</td>
<td>4016.22537, 33835.30054</td>
<td>39.22675</td>
<td>33835.30054</td>
<td>39.15679</td>
</tr>
<tr>
<td>21C</td>
<td>4016.22537, 30054.30054</td>
<td>39.22675</td>
<td>30054.30054</td>
<td>39.15679</td>
</tr>
</tbody>
</table>
All wastewater sampling points within the urban agglomeration can be divided into several types: 

1. Centralized wastewater releases from treatment facilities (points 1C (Suvorovsky microdistrict), point 2C (Aksai), point 11C (wastewater discharge from treatment facilities of Rostovvodokanal OJSC)). An example of such points is shown in Figure 1.

2. Transit drainage urban highways (rivers, streams and gullies) below the established places of discharge of domestic wastewater and atmospheric waters from the basin (points 3C-8C, 13C, 17C).


4. Atmospheric rainwater runoff (20C).

Table 2 and Figure 2 show the sample results of an experimental evaluation of the qualitative determination of microplastics in wastewater samples using the electron microscopy method.

Fig. 2. MP sample after laboratory treatment, dry residue.
Table 2. The results of an experimental evaluation of electron microscopy for the qualitative determination of microplastics in wastewater samples.

<table>
<thead>
<tr>
<th>Photo of a particle with an electron microscope</th>
<th>The spectrum of the particle</th>
<th>Decoding the spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>The O signal does not merge with the C signal, it can be assumed that a fragment of a synthetic PET fiber or a polymer of the C-H group.</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>A thread ~ 3.2 mm long and ~20 microns thick, in the spectrum, the O signal does not merge with the C signal, it can be assumed that a fragment of a synthetic PET fiber or a polymer of the C-H group.</td>
</tr>
<tr>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>A particle of ~1.3×0.6 mm in size, third-party substances with a silicon base are probably present on the surface, according to the structure and oxygen signal, it can be assumed that it is PET.</td>
</tr>
<tr>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>The filament is ~0.4 mm long and ~30-35 microns thick, the O signal is distinct in the spectrum, does not merge with the C signal, it can be assumed that it is PET, the elements Na, Cl, K are most likely caused by the environment (residues of adsorbed salts).</td>
</tr>
<tr>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>A fibrous film measuring ~0.6×0.4 mm, a distinct oxygen signal most likely indicates belonging to PET.</td>
</tr>
</tbody>
</table>
The thread is ~0.9 mm long and ~10–15 microns thick, the O signal is weak in the spectrum, but does not merge with the C signal, it can be assumed that the fiber is PP, PE or PS.

A set of porous fibers with a total size of ~1.4×0.3 mm, the fibers disintegrate, residues of adsorbed substances are probably present on the surface, the presence of iron may indicate color or is part of the residues, the oxygen line allows the MP to be attributed to PET.

A thread ~2.0 mm long and ~15–20 microns thick, in the spectrum the O signal does not merge with the C signal, it can be assumed that a fragment of a synthetic PET fiber or a polymer of the C-H group (PP, PE, PS).

A fragment of a thread ~3.9 mm long and ~30–35 microns thick, the O signal is weak in the spectrum, possibly merges with the C signal, it can be assumed that this fragment is nylon or PP.

4 Discussion

As a result of the research, it has been shown that despite the sample preparation carried out, various impurities, mainly of a silicon base, are often present on the surface of MP particles. Also, along with silicon, lines of sulfur, aluminum, titanium, iron, etc. appear. The samples often contained fibers or filaments of several thickness groups (10–15 microns, 20–25 microns, 30–35 microns and about 50 microns), which have different structures, and their spectra differ in the presence of oxygen.
When studying MP in real wastewater samples, it is necessary to take into account the influence of natural and chemical processes, as a result of which oxygen may appear in the spectra even in MP samples belonging to C-H group polymers (such as PP, PS, PE, etc.).

The bulk of the studied particles have an irregular shape, differ in morphology by roughness, the presence of a cellular structure, layered and/or fibrous structure. In most cases, contamination remains on the surface of the selected MP particles, which, apparently, are associated with absorption processes occurring as a result of oxidation and degradation of MP particles in natural conditions.

Also, using the method of electron microscopy, it is possible to refute the affiliation of potential particles to MP. Thus, the morphological features (layered surface, narrowing of thickness closer to the edge of the thread), combined with the analysis of the energy dispersion spectrum (sulfur lines were recorded), showed that some threads are not actually polymers, but are fragments, apparently, of the hairline of possibly animals, birds or insects.

The study of real samples is a very time-consuming process that requires processing a huge amount of information, literature data, studying the technical conditions for the manufacture and use of various plastics, etc.

5 Conclusion

Based on the material presented the following conclusions can be done:

1. The research performed indicates the urban-generated MP particles presence in all the 21 wastewater samples collected.
2. The wastewater-derived MP particles chemical and physical structure is strongly affected by external environment factors.
3. A structural changes in MP particles leads to limitations of some qualitative research methods applicability.
4. Among the studied the electron microscopy (EM) is the most reliable and informative approach.
5. The EM process is time and cost consuming that limits its wide practical application.

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