Microplastic in the Coastal Sea Waters of Russian Far East

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Abstract. Their availability, low cost, applicability in virtually any industrial sector and any household have not only resulted in plastics becoming an everywhere used material, but owing to its specific structure resulting in an issue pertaining to environmental pollution. There are 13 monitoring stations within research area to include recreational and industrial areas differing in hydrodynamic behaviour. The research geography bearing in mind the Russia's scale is not vast so far, yet it is being expanded yearly. Research was done at seven Vladivostok beaches, two beaches at the head of the Amur Bay and three beaches of the Posyet Bay. All the samples taken at the western side of the bay at the depths of 2-6m contained microplastic particles. Quality analysis of all the samples collected was carried out using mass-spectrometric method and that of infrared microscopy. It has been found that the chemical constitution of the samples studied is represented mostly by polyethylene, polypropylene, particles of polystyrene and polyvinyl chloride. Coastal samples frequently contain cellulose. A certain amount of methylaniline, formaldehydes, and monocarbozides was detected. All the said gives ground for ascertaining harmful influence of microplastics not only on sea water quality but on the state of marine biota.

1. Introduction
Plastic products have become ingrained into our everyday lives since the middle of the XX century, which is due to their strength, wear resistance, low cost and bio-inertness. Every year, there is an increase in production volumes, two-thirds of which are disposable items and packaging materials. Along with the increase in demand for plastics, the problem associated with the accumulation of waste is being updated. The most common polymers are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC). These substances are all represented in the structure of the litter recorded both in the coastal zone and in the sea waters. Studies have shown that about 60% of the litter is represented by plastic waste, with more than 80% of pollution sources of the coastal-marine zone having a land-based origin (primarily recreational activities). Of marine sources it is fisheries that should be noted, which share of waste in the structure of marine litter is about 20%. Polyolefins (PE and PP) and nylons are most widely represented there, as the materials used in fishing gear manufacture [1, 2, 3]. In addition to the plastic waste itself, the so-called microplastics has become a threat in recent years. This term, just like the term "marine litter" has become firmly established among the scientific community. It has been experimentally found out that plastics is decomposed at a relatively high rate in the marine environment under the influence of natural and climatic factors [4]. Their structure is liable to break down as a result of hydrolysis, photolysis and other processes, thus accelerating the processes of deformation and weathering.
Therefore, within several years, the formation of fragments of various dimensions, including microplastics, is possible, the number of which increases annually in practically all the waters of the World Ocean.

Microplastics enters the marine environment mainly in two ways: directly with waste effluent (particles can be contained in various consumer products: cosmetic scrubs, synthetic abrasives, etc.), or with weathering of the macroplastics. Experiments conducted by Japanese scientists in which the plastic was subjected to natural temperature and hydrodynamic processes [5] showed that, for example, polystyrene is fragmented after a year, and when it decomposes hazardous substances are diagnosed in water (for example, bisphenol A, circulating hydrocarbon and others), affecting the endocrine system and leading to oncological diseases.

In addition to those listed, there are some other components, such as polyvinyl chloride, polymethyl methacrylate, phenolic plastics, amino plastics and polycarbonates. Although all these components belong to the group of polymers, with their break down in the marine environment, different substances influencing the physiological, morphological and even genetic properties of a human body in varying ways are emitted. For example, decomposition of polystyrene results in release of styrene proper and butadiene, both are possessing carcinogenic and mutagenic effects [6, 7]. With degrading of polycarbonates, bisphenol A is released, which is considered one of the most dangerous substances affecting the reproductive capacity of living organisms. Thus, the assessment of the distribution of microplastics in the coastal marine areas and its impact on the environment are important environmental issues, which are studied by specialists in various regions of the world. Russia is no exception.

2. Material and methods

Active studies of microplastics in the marine environment in the South of the Russian Far East have been conducted by the experts of the Far Eastern Federal University and the Maritime State University named after Admiral G.I. Nevelskoy since 2014 [8]. The research done within the previous forty years has shown that the pollution of the World Ocean with plastics has attained such a scale that this material has already become a part of the diet of marine life, and, subsequent to them, a part of the human diet [9, 10]. One of the most obvious problems of plastic contamination is the death of sea animals and birds, which easily take multi-colored pieces of plastics for something edible, plastic particles, fill their gastrointestinal tracts, and as a result of which a bion perishes with hunger.

The concentration of pollutants and the sources of their input to the coastal and marine environment in Russia differ significantly from other regions. And the inhabitants of Russia do not even suspect that the microplastics is an international problem, focusing only on relatively large plastic objects. It should also be noted that Russia lacks special legislation to cover the issues of litter in the coastal zone and in the sea areas in general, in contrast to, for example, countries of southeast Asia, where plastic contamination of the surface, the water column and bottom substrates is regulated at a national level.

The coast of the Far East Russia features a relatively low development. Small population density, the development of the predominantly extractive sector, distinguish the region among the nearest neighbors. However, an unfavorable ecological condition is characteristic of its southern part. The Peter the Great Bay stands out not only as a unique natural and climatic region, where the species of temperate and subtropical latitudes conjoin, but also as a rather polluted water area, especially in its northern part. Numerous sources of pollution, discharging conditionally purified waters into the bay, also input plastic particles.

A similar situation (with varying gravity degree) is typical for all the port water areas. Therefore, in order to work out a strategy for managing surface contamination, the primary task is the development of a methodological base, namely the development of a method for monitoring floating litter. Furthermore, the main task of monitoring is determining the main patterns of occurrence, migration of the litter and its accumulation locations. The regularity of the process will allow to establish sources of
pollution and determine the movements of litter, and therefore, to optimize the system of treatment operations.

Accordingly, 13 monitoring points have been allocated in the Peter the Great Bay (the Sea of Japan / East Sea) to include recreational and industrial areas that differ in hydrodynamic regime, in five of which plastic samples are encountered on a regular basis [11]. The geography of the study considering the scale of Russia is small so far, but its expansion is annually noted. Figure 1 shows the reference points for monitoring microplastics in the northern part of the Peter the Great Bay. In samples taken from the Bosporus of the East Strait and the Golden Horn Bay, microplastic particles of about 2-3 mm in size are regularly found. In the open areas of the Ussuriisky and Amursky Bays the microplastics is practically not represented.

Figure 1. Monitoring sites in Vladivostok coastal zone.

3. Finding and discussion
The analysis of environmental conditions in the areas where the particles are detected allows for a suggestion that the most likely sources of pollutant input are the coastal sources. Figure 2 shows an example of microplastic fragments found in the waters surrounding Vladivostok. Virtually all particles are polyethylene and polypropylene. The maximum size of the identified sample is 11 mm (in the Ulysses Bay).

The analysis of the methodological base used for sampling has shown that there is no single approach to the selection of microplastics in the marine environment. At the same time, there are fundamental similarities, which were taken as a basis for sampling in Russian waters. The most expedient seems to be the use of plankton networks, which net-mesh size allows retaining the smallest particles. In our case, small Apstein nets with a beaker1 were used. Sampling is carried out by trawling from a small craft carried out for 10 minutes at each monitoring station. Thus, taking into account the size of the net, the speed of the vessel and the time of collection, the volume of the pumped water was
about 10 cubic meters. Then, the lifted net was further washed with seawater to collect the microplastics from its walls. The entire pollutant was then slid into a metal beaker, which completes the net. The obtained sample was placed in a marked container to determine the qualitative composition of the collected microplastics.

![Ulysses bay](image)

![Patroclos bay](image)

![Ajax bay](image)

![Channel (Russkiy island)](image)

**Figure 2.** Microplastic fragments in the samples.

A qualitative analysis of the samples was carried out on the basis of the Nanocentre of the Far Eastern Federal University using the methods of infrared microscopy (IR) and spectrophotometry. Using an infrared microscope the Shimadzu AIM-8800 the dimensional composition was fixed. Further, the samples were analyzed at an IRTraser-100 IR spectrophotometer with a Quest FTIR attachment (frustrated total internal reflection) of a horizontal type (Shimadzu, Japan) with a measurement range of 400 to 4000 cm\(^{-1}\) and a resolution of 2 cm\(^{-1}\). The identification was carried out by automatic comparison with the Spectrum Library (STJ-Europe Spectral Database, Germany). The method is based on physical phenomena that arise when the light is reflected at the interface between two media with different optical densities. When the light, passing through a medium with a relatively high refractive index (an FTIR crystal) falls on the interface with a medium with a lower refractive index (sample) at an angle of incidence greater than the critical angle (the maximum angle of total reflection), then the radiation from this boundary surface is reflected almost completely. However, even with complete reflection, the radiation still penetrates into the medium bordering the crystal to a small depth.

The depth of penetration of the light beam into the sample is a function of the wavelength, the refractive indices of the crystal and the test substance, and the angle of incidence. Depending on whether the neighboring medium absorbs or does not absorb the radiation, that is, in this case a sample, the intensity of the reflected light changes. As a result, a reflection spectrum similar to the transmission spectrum is obtained. In this spectrum, the wave numbers at which the absorption
specific for a given substance takes place will be the same as when measured in transmitted light. This approach is a modern non-destructive method of analysis in the infrared region of the spectrum, which makes it possible to obtain exhaustive information from a microscopic sample. In combination with the IR spectrometer, a powerful system is formed indispensable for the study of solid samples.

Among all synthetic materials, polyethylene, a substance obtained by polymerization of ethylene molecules, while observing certain technological processes is considered to be the clear leader. Polyethylene is used not only as a packaging material, but also in the construction industry. This substance is most often found in the structure of microplastics. As for cellulose, which is also very common in the samples obtained, it is characterized by polymorphic properties and is used for the production of artificial fibers, which also provides ample opportunities for its both domestic and industrial application, which increases the likelihood of its input to the marine environment. In samples taken from the northern coast of the Russkiy Island in the way of Pospelov Cape, particles of polyethylene and cellulose are found everywhere. Figure 3 shows the results of laboratory processing of materials.

Thus, it should be stated that most of the detected microplastic particles belong to environmentally hazardous compounds. As it already been mentioned, in samples from Ajax and Ulysses bays, it is the polypropylene, one of the most common polymers, which is most frequently found. This is accounted for by its characteristics, due to a variety of methods of its production and processing. It is obtained directly from gaseous propylene by polymerization. This polymer is most often used for the manufacture of disposable tableware, which accounts for almost 90% of recreational waste.

Considering the structure of the macroplastics found in these areas, it should be noted that the recreational activity is the source of the input of these pollutants to the marine environment (in the...
Ulysses Bay area there is a large yacht mooring, while the area of the Ajax Bay is a leisure and recreation center of the townspeople).

Field survey routes are regularly adjusted in accordance with hydrodynamic factors; however, in the most probable areas of microplastics distribution in the near-surface layer, they remain unchanged. Figure 4 shows a regular sampling route in the coastal waters of Vladivostok. According to the results of this passage of 2016, microplastics is not encountered at all points, which is probably due to the active removal of particles into the open part of the bay. In 2017, the first large-scale expedition was conducted to study microplastics in the open water area of Peter the Great Bay. During a week-long expedition, 220 nautical miles were covered and samples were taken at 10 points, in 4 of these microplastics was not found. In the remaining 6 samples polystyrene, polypropylene and polyethylene prevailed (35-50%). A particularly large number of them was recorded in the waters off the Slavyanka Bay. Also a small amount of cellulose and fiber was recorded.

![Figure 4. Sampling route in the coastal waters of Vladivostok in 2016-2017.](image)

Since 2016, we have been studying the content of microplastics in the coastal grounds. Studies were carried out on seven beaches of Vladivostok, two beaches in the top of the Amur Bay and three beaches of the Bay of Posiet. Sampling from the shoreline was carried out at regular intervals (about 300 meters). In each point a square of 1m x 1m was selected, from each corner of which as well as from the center a scoop of soil weighing about 100 grams was taken. The sample was thoroughly mixed. This way more than 100 soil samples were selected in two steps (autumn, spring). Subsequent laboratory analysis of the first series of samples showed that after sample settling, the fragments of the microplastics were visually detected on an irregular basis. Therefore, an express method was used, which allows extraction from the entire volume of the sample obtained. For this purpose trichloromethane which dissolves all kinds of plastics was used. The whole volume of the sample was
thoroughly mixed with trichloromethane, and then the solution was separated from the soil through a paper filter.

A rotary evaporator was used for segregating concentrated microplastics. The sediment obtained after evaporation was analyzed by means of an IR spectrophotometer. Unfortunately, this method does not allow us to determine the size composition of the microplastics, but its concentration in the study area is very small, which makes it feasible to study only its qualitative composition at this stage. As the results of the analysis showed, the main pollutants of coastal soils are polyethylene and styrene. Paraffins are found in small amounts. Table 1 shows microplastics qualitative analysis of samples series which collected in Vladivostok beaches in 2017.

Table 1. Microplastic qualitative analysis.

| Composition / sample number | 1  | 2  | 3  | 4  | 5  | 6  |
|-----------------------------|----|----|----|----|----|----|
| Polyether and nylon, %      | 40 | 37 | 27 | 42 | 25 | 20 |
| Polypropylene, %            | 20 | 30 | 26 | 10 | 27 | 18 |
| Vinyl, %                    | 12 | 6  | 5  | 20 | 14 | 20 |
| Polystyrene, %              | 15 | 2  | 24 | 15 | 23 | 25 |
| Polyvinylchloride, %        | 4  | 3  | 4  | 7  | 0  | 9  |
| Other, %                    | 9  | 22 | 14 | 6  | 11 | 8  |

The amount of data received is large, so software tools from the family of geoinformation systems are used for their processing, interpretation and subsequent visualization. GIS-technologies also allow automating certain stages of monitoring for planning the observations and revealing the regularities. Features of GIS allow developing maps of pollution dynamics, carrying out a comparative analysis, and the available statistical database becomes an important tool in decision-making on the status of the water area.

Observations made give us the grounds to ascertain that the microplastics is regularly found in the water area of Peter the Great Bay. A qualitative analysis of the obtained samples suggests that this type of pollutant can adversely affect the quality of sea water and the state of marine biota. To assess pollution trends and the impact of microplastics the main components of ecosystems, research in this field will be continued.

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