



Assessment of seasonal variability of input of microplastics from the Northern Dvina River to the Arctic Ocean

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ABSTRACT

Northern Dvina River is one of the largest rivers in the European Arctic flowing into the White Sea through the populated regions with developed industry. Floating plastics include microplastics (0.5–5 mm) and mesoplastics (5–25 mm) were observed on seasonal variations in the Northern Dvina River mouth. The samples were collected every month from September to November 2019 and from May to October 2020 with a Neuston net that was togged 3 nautical miles in the Korbelyy Branch of the River delta. Chemical composition of the plastic particles was determined using a Fourier transmission infrared spectrometer. The majority of the microplastics were identified as polyethylene 52.6%, followed by polypropylene 36.8%. After estimating the export fluxes of microplastics from the Northern Dvina River to the Arctic, there is no significant seasonal variation of the river export of microplastics. The microplastics export rate during the spring flood period in May turned out to be maximum, 58 items/s, while the minimum discharge was in September with a value of 9 items/s. The average weight concentration of microplastics was 18.5 $\mu\text{g}/\text{m}^3$, which is higher than it was found in the Barents Sea – 12.5 $\mu\text{g}/\text{m}^3$ and several times higher than in the Eurasian Arctic on average - 3.7 $\mu\text{g}/\text{m}^3$. These results indicate that the Northern Dvina River is being one of the main sources of microplastic pollution of the White and the Barents Seas.

1. Introduction

The presence of macroplastic and microplastic is confirmed in all environments, including river and marine systems. Plastic pollution is recognized as a threat to ecosystems, habitats and wildlife (Missawi et al., 2020; Paffenhöfer and Köster, 2020; Pannetier et al. 2020). Scientists have made progress in studying the ecological dynamics of microplastics (plastic particles sized 1 μm – 5 mm (GESAMP, 2019)) in the ocean (Burrows et al., 2020; Chubarenko et al., 2016; Lusher et al., 2015), but the qualitative and quantitative composition, the main sources and the ecological role of microplastics supply from the rivers remain poorly understood. Meanwhile, a study of freshwater river

systems is necessary to understand the fate of plastic in the hydrosphere. Rivers (especially urban rivers or rivers flowing through densely populated regions) seem to be the dominant sources of plastic and microplastic pollution (Horton et al., 2017; Rochman and Hoellein, 2020; Skalska et al., 2020). It should be assumed that a significant amount of microplastics can accumulate in the rivers in the form of fibers, pellets, films, and fragments, which will differ in their properties from marine plastic (Klein et al., 2018). Important reason for studying microplastics in Arctic rivers is a higher level of pollution of the Arctic Ocean regions affected by the Atlantic waters compared with the regions affected by the Great Siberian Rivers plumes (Yakushev et al., 2021). Rivers flowing into the Arctic Seas remain a blank spot in the study of microplastic

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pollution. Only recently, some results of studying of rivers Ob' and Tom' were published (Frank et al., 2021b). Majority of the main Arctic rivers (i.e. Yenisey, Ob', Lena, Kolyma, Pechora) flow through low populated regions, at least in their lower reaches. In contrast, the Northern Dvina River is an urban river flowing through the densely populated regions with developed industry, with a city Arkhangelsk situated in its delta, and there are needed studies of its probably exceptional role in the Arctic pollution with marine litter and microplastics. This is the main question we address in this work.

More and more attention is paid to the study of the temporal and spatial pollution of fresh water by microplastics. Research time range from a few hours (Piñon-Colin et al., 2020; Xia et al., 2020) to decades (Kataoka et al., 2019; Nihei et al., 2020). It should be noted that each time period is interesting in its own way. Thanks to the variability of several hours, it is possible to estimate the contribution to pollution from wastewater treatment plants. The variability over several days will show the influence of settlements, and seasonal variability allows conclusions to be drawn about the influence of shipping and human economic activity (Talbot and Chang, 2022). Instant research at several different points is necessary and useful, but it does not provide a complete picture of what is happening. This is due to changes in many parameters that affect the measurements: wind speed and direction (Kukulka et al., 2012), river flow speed, seasonal flood (Treilles et al., 2022) and others. Therefore, we consider it important to study the variability of concentration and removal of microplastics from the point of view of temporal variability on a seasonal scale.

In this study, we tried to answer the formulated above questions with a main goal of evaluating of a role of the Northern Dvina River runoff in the Arctic Ocean plastic pollution. For our work, we used the method of trawling the water surface with a Neuston net. As a result, an assessment of the plastic pollution of the Northern Dvina River in different seasons was carried out and the export of plastic into the White Sea was calculated.

2. Materials and methods

2.1. Study area

Our studies were organized as monitoring sampling in the delta of the Northern Dvina River. This river belongs to the Arctic Ocean basin (Fig. 1) and flows through relatively densely populated areas. The river basin of the Northern Dvina includes the major parts of the Vologda and the Arkhangelsk region, as well as areas in the western part of the Komi Republic and in the northern part of the Kirov region, and minor areas in the north of Yaroslavl and Kostroma region. The cities of Arkhangelsk and Vologda, as well as many smaller towns, many of those of significant historical importance such as Veliky Ustyug, Totma, Solvychevodsk, and Kholmogory, are located in the river basin of the Northern Dvina. Totally about 1 mln people live in the Northern Dvina River Basin (according to website census statistics <https://showdata.gks.ru/repor t/278932/>).

The samples were collected in the ice-free period every month from

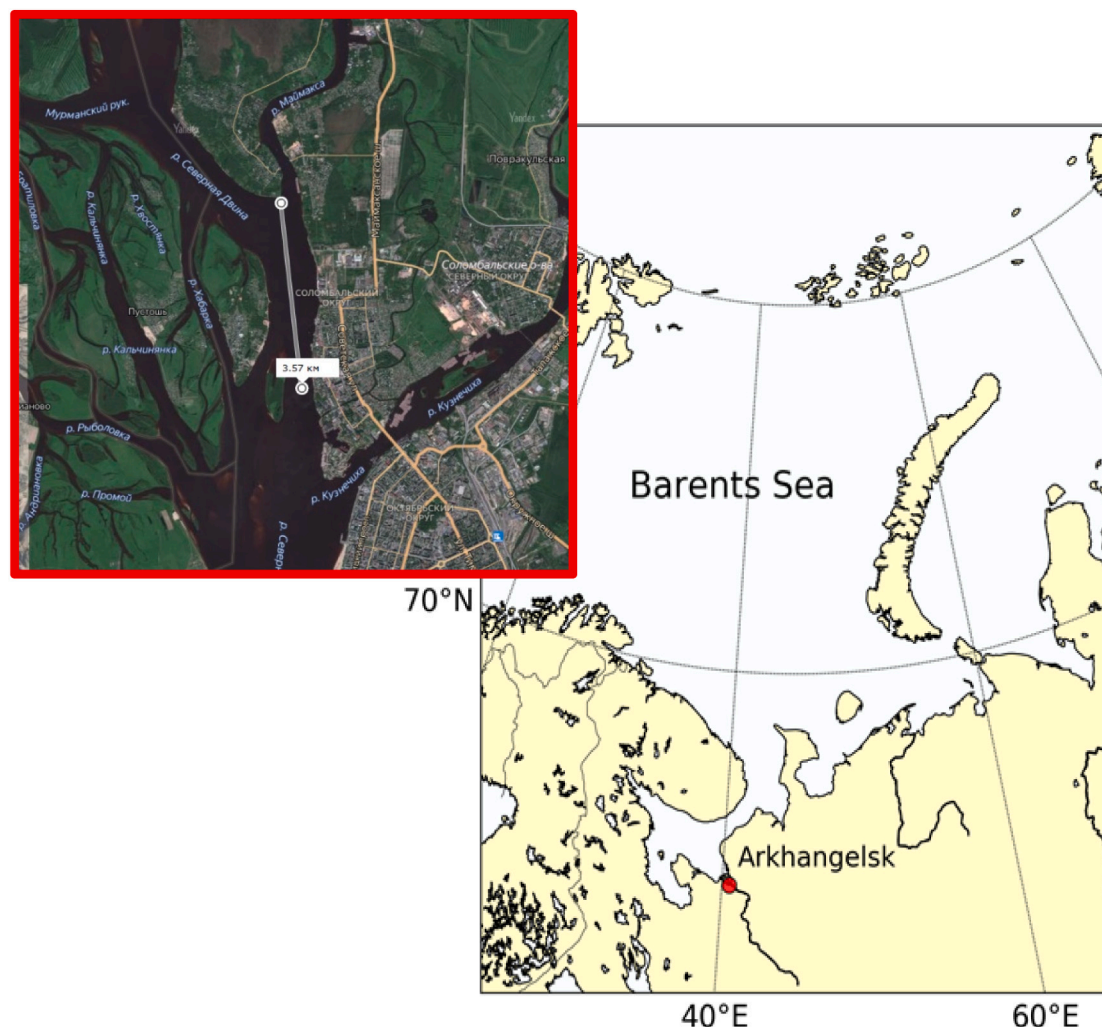


Fig. 1. Position of a transect where Neuston net sampling was organized.

September to November 2019 and from May to October 2020 in the Korobel'nyy Branch of the River delta (Fig. 1). Surface water samples were taken from the 3 nautical mile transect near the city of Arkhangelsk.

2.2. Sampling

The samples were collected with a Neuston net with an opening 30×50 cm. The mesh design assumes water filtration from the surface to a depth of 15 cm. The mesh size is $330 \mu\text{m}$. The net was attached to the side of a rubber boat. Trawling was carried out against the current of the river. After the trawling, the net was washed with water and the collected filtrate was placed in a glass jar with a lid. The volume of filtered water was calculated taking into account the length of the transect, the geometric dimensions of the net and the speed of the boat. The jar lid was marked and then transported to the laboratory. One trawl lasted about 30 min (we were guided by the distance and necessarily covered 3 nautical miles), after each trawl one sample was taken. A total of 9 samples were obtained.

2.3. Sample handling and laboratory analysis

Each sample was processed manually by visual analysis. This technique made it possible to detect plastic particles up to 0.5 mm in size. The sample jar was placed in a fume hood, after which large visible particles of potential plastic were taken out. The samples were rinsed with filtered distilled water (through a $0.45 \mu\text{m}$ filter) to avoid external contamination with microplastic particles and fibers. After that, smaller particles were identified in the solution using density separation and removed with tweezers. The solution was then filtered through a sieve (0.5 mm) followed by control checking for particles on the sieve with magnifying glass.

All the potential plastics particles found in the sample were numbered and photographed on graph paper to measure the original sizes. Each particle was weighed on a balance with an accuracy of the 5th decimal place (Laboratory balance XP 205 DR Analytical range: 0.0001–220 g, accuracy 0.00001 g). Since the study considered only particles visible to the naked eye, each of them was individually weighed on a balance. To obtain the total weight, the weights of all particles were added.

After that, identification of each particle was made by Fourier-transformed infrared spectroscopy (FT-IR). IR spectra were recorded using a Vertex 70 Fourier transmission infrared spectrometer and a GladiATR diamond prism attachment for disturbed total internal reflection. Spectra recording conditions: range $4000\text{--}400 \text{ cm}^{-1}$, resolution 4 cm^{-1} , 128 scans. Atmospheric air was used as instruments background. Each spectrum was analyzed manually.

To control contamination during sample processing, a sample blank was analyzed. When analyzing samples, an open Petri dish with a moistened paper filter (GF/A) was placed next to the sample, which was analyzed after each sample (Tosić et al., 2020). No background contamination was found on the filters. In addition, the polymer composition of all plastic equipment (including sampling devices) was determined and particles with a similar polymer composition were also not detected in the samples.

At the end of the work with the sample, the total number of plastic particles, the total number of particles with sizes up to 5 mm (microplastics) and larger than 5 mm (mesoplastics), their weights, type of plastic and dimensions were recorded.

3. Results

After processing of all collected samples (9), there was totally found 19 microplastic particles (< 5 mm) and 4 mesoplastic particles (5–25 mm). In spite of a number of microplastics particles is much higher, their contribution in the weight of total plastics (i.e. a sum of micro- and

mesoplastic) is small. The total weight of microplastics was 49.8 mg, and the weight of the total plastics was 153.0 mg.

Seasonal variability of the microplastics and mesoplastics abundance and weight concentration are shown in Fig. 2. Generally, no clear trend of seasonal variability can be detected; the concentrations of microplastics oscillates in the limits $0.003\text{--}0.010 \text{ items/m}^3$ or $0.02\text{--}0.04 \text{ mg/m}^3$. Being recalculated into the surface concentrations the microplastics abundance will give $10^3\text{--}10^4 \text{ items/km}^2$. The found here average concentration of microplastics was 0.007 items/m^3 (800 items/km^2) is close to the average concentration of surface microplastics observed in the open Barents Sea, 0.005 items/m^3 (1000 items/km^2) (Yakushev et al., 2021).

Including into analysis mesoplastics particles, when they were detected, increase the abundance concentration at about 60% (Fig. 2, top), but the weight concentration increases in seven times (Fig. 2 bottom).

Particles with different types of morphology (fragments, films, fibers, spheres, foams) were found as a result of our research. The overwhelming majority of particles were fragments (82%). In Fig. 3 you can see the particles found during the sampling.

Chemical composition of the found plastic items is shown in Fig. 4. The majority of the microplastics were identified as polyethylene (PE) 52.6%, followed by polypropylene (PP) 36.8% and Ethylene Ethyl Acrylate Copolymer (EEA) 10.5%. For the sum of total plastic the largest share belonged also to PE (47.83%), followed by PP (34.78%), 8.70% for EAA and 4.345% each for polyurethane (PU) and polystyrene (PS). All found items had positive buoyancy including PU foam and expanded PS.

The measured micro- and mesoplastics concentrations were used for

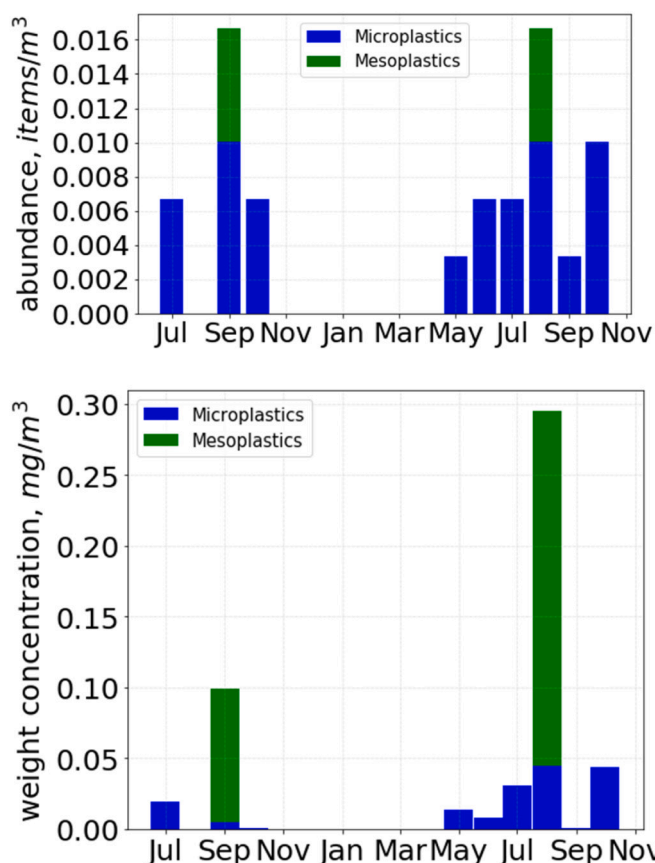


Fig. 2. Observed variability of abundance (top) and weight concentration (bottom) of microplastics (blue) and mesoplastics (green) in the Northern Dvina, collected with a Neuston net in 2019–2020. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

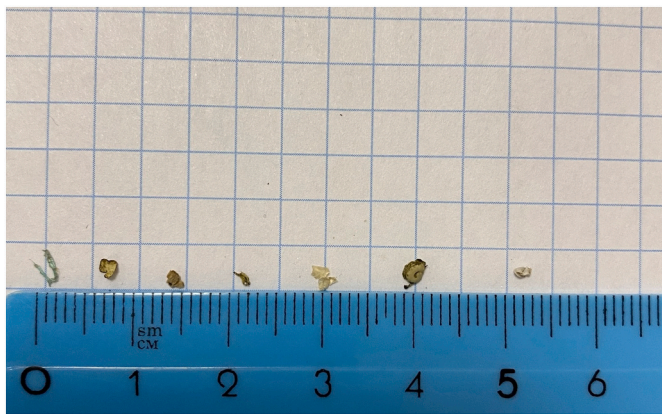


Fig. 3. Potential plastic particles found in the surface water.

estimations of monthly riverine loads. For this we interpolated data shown in Fig. 4 for every month and multiplied to the Northern Dvina climatic discharges (Fig. 5) during the period of the observations.

We calculated the volumetric concentrations, knowing the volume of water filtered through the mesh and the amount/weight of microplastics and total plastic. The climatic discharge was obtained from the literature data. Next, we multiplied the concentrations by the climatic discharge and obtained the removal of plastic particles with the river water.

The calculated seasonal variability of the load of microplastics and mesoplastics with the Northern Dvina River are shown in Fig. 6. A maximum load of 250 mg/s of microplastics and 800 mg/s of total plastics can be detected in May, and during the rest period of the year the load oscillates in the limits 10–60 mg/s for microplastics and 10–170 mg/s for total plastics. Our calculations show that the water discharge should play the main role in the seasonal variability of the plastics load (compare Figs. 5 and 6), while observed changes of concentrations has a minor significance (compare Figs. 2 and 6). In the abundance units, the

microplastics input rate during the spring flood period in May turned out to be maximum, 37.8 items/s and the minimum input rate can be found in September with a value of to 5.3 items/s.

4. Discussion

Considering the discharge of water treatment facilities, rivers can be one of the main sources of plastic pollution in the world's oceans (Kapp and Yeatman, 2018), and the plastics content in the water depends on the human activity in the river basins (Kataoka et al., 2019). As it was noted, the Northern Dvina River is a single Arctic River flowing in its downstream through populated region with developed industry. In the Table 1 we compare our results with the plastic concentrations measured in the other rivers with the same technique, including confirmation of all the particles with Fourier Transmission Infrared Spectrometer. The dominant part of the references has estimates of the particles abundance expressed in items/km². Our estimates about 10³–10⁴ items/km² are 1–2 orders of magnitude lower than in the River Rhine and Chinese rivers (10⁵–10⁶ items/km²), and about 5 times less than measured in the Chesapeake Bay. For abundance estimates expressed in items/m³, our numbers 0.004–0.010 items/m³ are 3 times lower than in the Tamar estuary. The latter can be explained by a lower size limit of the particles.

This comparison allows concluding that the Northern Dvina River is polluted with microplastics but in a lower degree than rivers in other regions.

Similar results were obtained in the study of other rivers. For example, in a study of the seasonal variability of microplastics in the Rhine (Mani and Burkhardt-Holm, 2020), researchers came to the same conclusion that there was no seasonal variability. Another study of Italy's greatest river, the Po (Munari et al., 2021), shows a similar trend, with a maximum in spring. At the same time, there is some difference in autumn concentrations, which are minimal in our study and reach a maximum in the study of the Po River. Such differences can be explained, in particular, by the different hydrological regimes of the

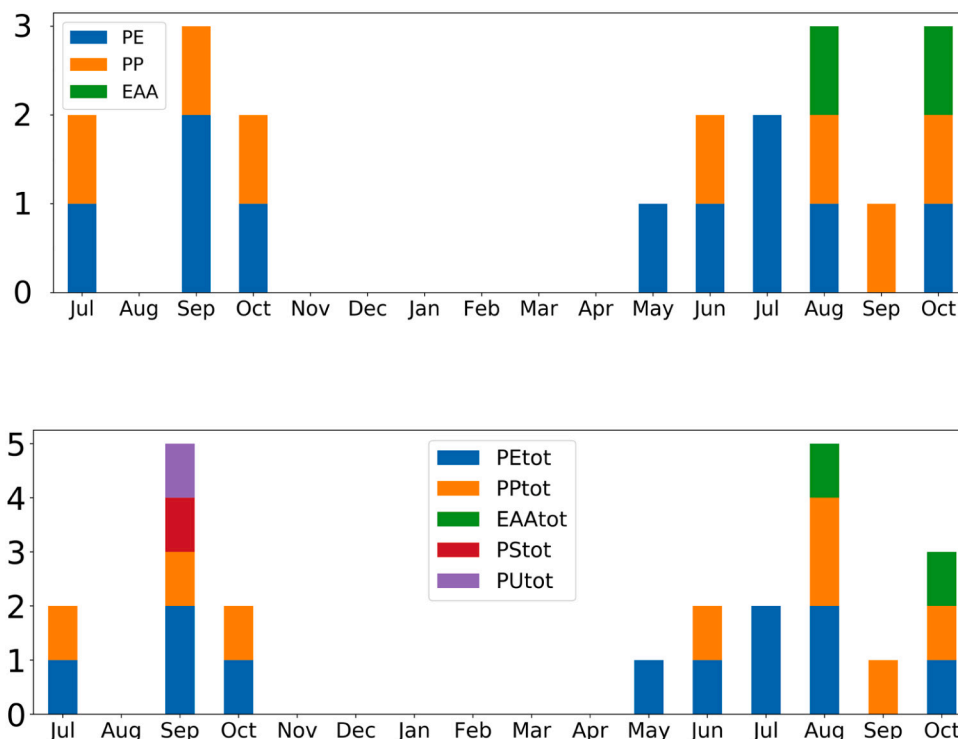


Fig. 4. Seasonal variability of chemical composition of microplastics (top) and a sum of micro- and mesoplastics (bottom) in the Northern Dvina collected with a Neuston net in 2019–2020.

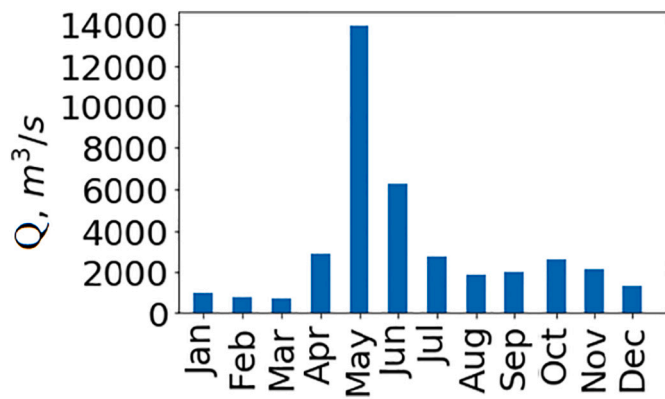


Fig. 5. Climatic monthly water discharges (Q , m^3/s) of the Northern Dvina River (Magritsky et al., 2017).

rivers.

As a comment, we would like to add a recent study of microplastic pollution of the Yenisei River and Nizhnyaya Tunguska River (Frank et al., 2021a). The average MPs content in the surface water of the Yenisei large tributary, the Nizhnyaya Tunguska River, varied from 1.2 to 4.5 items/ m^3 . The contamination estimates are much higher than those obtained in our study. This can be explained by the small particle size limit (about 0,3 mm) and visual analysis of found items only.

The standard classification of the floating plastic particles includes class for microplastics, as particles less than 5 mm, and class for macroplastics or marine litter that are particles greater than 25 mm (GESAMP, 2019). These classifications are connected with the methods of collecting the samples with surface nets from a representative large volumes or by visual identifications for macro litter. In this work, we in

particular paid attention to the mesoplastics particles, ranging from 5 to 25 mm. The microplastics sized 1 μm – 5 mm are most common form of plastics in the marine environment (Barboza et al., 2019), but as we show here in spite of much smaller abundance of the mesoplastics particles they play a dominant role in the weight concentration of the total plastics. These mesoplastics particles are by no means main sources of secondary microplastics, and they, together with the macroplastics should be taken into account in the studies of the plastics transport form the rivers.

We are far from the first to pay attention to the joint study of macro- and microplastics. In the work of Isobe et al. (2014), scientists investigated the propagation selectivity of micro- and mesoplastics. They concluded that larger particles are concentrated near the coast, while smaller particles are more often found further from the coastline. There are research works devoted to the study of micro- and mesoplastics in the sediments. Young and Elliott (2016) describe the characteristics of both micro- and mesoplastic types of particles. Ecotoxicologists are also focusing on the parallel study of both types of plastic particles. The article by Karami et al. (2018) researchers are detecting the presence of micro- and mesoplastic particles in canned sardines, and describe the different behavior of the particles in the body when ingested and their potential harm.

It is especially important to compare the obtained concentrations with the concentrations of particles in the Arctic seas. The average weight concentration of microplastics was 18.5 $\mu g/m^3$, which is more than in the Barents Sea – 12.5 $\mu g/m^3$ and several times more than in the Arctic Ocean on average - 3.7 $\mu g/m^3$ (Yakushev et al., 2021). In our opinion, these data may indicate that the Northern Dvina is one of the sources of plastic pollution in the Arctic seas.

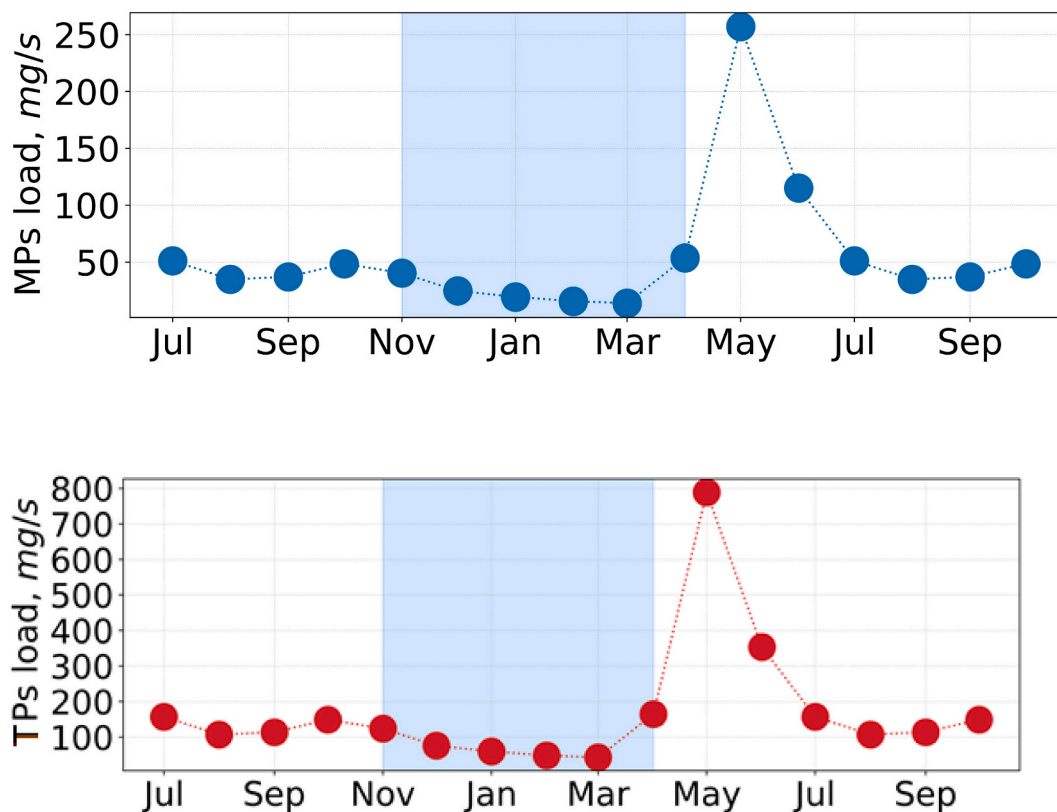


Fig. 6. Seasonal variability of load of microplastics (top) and total plastics (bottom) in mg/s calculated with climatic discharges of the Northern Dvina River. Blue colour corresponds to the period when the river is covered with ice. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Comparison of abundance and weight concentrations of FTIR confirmed MPs in different rivers.

River	Size, mm	MP abundance items/m ³	MP abundance items/km ²	Reference
N.Dvina	0.333–5	0.004–0.010	0.6–1.4 × 10 ⁴	Our data
Dutch rivers and Amsterdam Channels	–	1 × 10 ⁵ (mean) 1.87 × 10 ⁵ (max)		(Leslie et al., 2017)
Rhine river	>0.3		8.93 × 10 ⁵ (mean) 3.96 × 10 ⁶ (max)	(Mani et al., 2015)
Three Gorges Dam	>0.112		6.4 × 10 ⁶ (mean) 13.6 × 10 ⁶ (max)	(Zhang et al., 2015)
Taihu lake	>0.333		6.8 × 10 ⁶ (max)	(Su et al., 2016)
Four estuaries in the Chesapeake Bay	0.3–5.0		5 × 10 ⁴ –2 × 10 ⁶ (range)	(Yonkos et al., 2014)
Pearl river estuary	0.35–5.0	2.376 (mean) 8.221 (max)		(Lam et al., 2020)
Koshi river	0.1–5.0	202 ± 100 (mean)		(Yang et al., 2021)
Songhua river	0.05–5.0	6.67 (min) 160 (max)		(Ma et al., 2022)
Garonne river	0.7–5.0	0.15 (mean)		(Reis et al., 2021)

5. Conclusion

In this work we evaluated the export of the micro- and mesoplastics from the Northern Dvina River flowing through the density populated regions to the Arctic. All major positive buoyancy plastics have been found in our samples (including PU foam). The same chemical composition and different abundance of microplastics in different months can be explained by general volumes of production and use of certain polymers in industry and in daily life. The results also showed no seasonal variations of the microplastics abundance or weight concentrations in the waters of the Northern Dvina. The calculated loads of microplastics and total plastics during the year ranges from 10 to 60 mg/s to 10–170 mg/s respectively with a maximum during the flood period in May when they reached 250 mg/s for microplastics and 800 mg/s for total plastics. The seasonal variations of the plastics load is governed mainly by the water discharge variability. Comparison with other rivers allows us to conclude that the Northern Dvina river is less polluted with microplastics than other rivers (about 1–2 orders of magnitude lower). The data obtained conclude that Northern Dvina river is one of the main sources of microplastic pollution of the White Sea with concentrations corresponding to those in the Arctic.

CRedit authorship contribution statement

Igor Zhdanov: Writing – original draft, Formal analysis, Writing – review & editing. **Alexey Likhov:** Investigation. **Artem Belesov:** Formal analysis. **Aleksandr Kozhevnikov:** Formal analysis, Resources. **Svetlana Pakhomova:** Methodology, Formal analysis, Writing – original draft, Writing – review & editing. **Anfisa Berezina:** Visualization, Data curation. **Natalia Frolova:** Writing – original draft. **Ekaterina Kotova:** Investigation, Project administration. **Andrey Leshchev:** Investigation. **Xinhong Wang:** Writing – review & editing. **Peter Zavalov:** Writing – review & editing, Resources, Project administration. **Evgeniy Yakushev:** Conceptualization, Methodology, Resources, Writing – original draft, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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