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Contribution of microparticles to the transport of pollution by rivers and groundwaters in a large city

S V Yasinskii[1], E V Venitsianov[2], E A Kashutina[1], M V Sidorova[1], A A Ershova[3] and I N Makeeva[3]

[1]Institute of Geography, Russian Academy of Sciences, Moscow
[2]Institute of Water Problems, Russian Academy of Sciences, Moscow
[3]Russian State Hydrometeorological University, St. Petersburg, Russia

eugeny.venitsianov@gmail.ru, kashutina@igras.ru

Abstract. Most components of the composition of natural waters exist in several phases – in the water mass, in suspensions, colloids, on Fe and Mn hydroxides, in detritus. They are often characterized by different toxicity. The smaller the particle of the suspension, the higher is its sorption capacity. Priority pollutants and their content in urban water bodies of Nizhny Novgorod in the summer-autumn low water period of 2020 were identified: organic substances, petroleum products, ammonium, surfactants, iron and manganese. More than half of their total transport is carried out by suspensions. In the estuaries of rivers with particles in the range of 0.22-2 microns, up to 70% of iron is carried by suspensions, up to 45% of manganese and about half of petroleum products and surfactants. Studied water objects (rivers, springs and water tunnels) are also polluted with synthetic microfibers of anthropogenic origin.

1. Introduction

In water quality measurements, gross concentrations of components are usually determined. However, most of the water components, primarily heavy metals, exist in several phases, often characterized by different toxicities. The presented concentrations are usually the sum of several concentrations - in the water mass, in suspensions (mineral, organic), in organic colloids, in organisms of aquatic biota, on Fe and Mn hydroxides. These phases interact and the main mechanism here is sorption, i.e. absorption of molecules (ions) of a substance contained in one of the phases by another phase in contact [1].

Water bodies almost always contain suspensions of different sizes: sandy, clayey, silty particles, detritus, etc. These can be particles of both natural and anthropogenic origin.

A decrease in the size of suspended particles leads to an increase in their specific surface area and an increase in their sorption capacity [2]. Suspended microparticles are therefore carriers of other components, including pollutants [3]. Bacteria and viruses are also well adsorbed by river suspended matter [4].

Microparticles practically do not settle in the flow. So, if particles larger than 0.08 mm are deposited at a water velocity of more than 3–5 cm/s (natural streams and ponds), then the sedimentation rate of particles with a size of 0.03–0.05 mm decreases to 0.25 mm / s and is possible only in stagnant water [5]. Particles of submicron size and less practically do not precipitate in water. The smaller the particle, the longer the path of its migration both in water and in living organisms when they are absorbed. The most harmful for health are particles with a size of up to 10 microns and especially nanoparticles [6], and both these microparticles and pollutants sorbed can be harmful. The growth in the production and use of nanomaterials leads to an increase in their content in the environment, which can have serious consequences for human health and the environment [7].

Xenobiotics are the most dangerous for biota and humans [8]. Their synergistic action is possible [8].

In recent years, interest in the study of microplastics has sharply increased as an inevitable consequence of the growth in the production and consumption of synthetic materials, which themselves can be safe, but when dispersed they turn into a highly effective sorbent for toxicants. Microplastics are found in all water bodies of the planet, even in the most remote ones, including the Arctic and Antarctic [9,10]. Studies in Russia are few and are devoted mostly to marine ecosystems, focusing on the Baltic Sea region [11, 12, 13] and Arctic seas [14]. Recent study also showed microplastic pollution in Lake Baikal [15].

Large cities are the most important sources of water pollution by various toxicants. The range of pollutants from megacities, as a rule, is much wider than from non-urban areas [16]. In urban areas, cars are the source of more than 50% of all particles less than 10 microns in size [17].

Water bodies of Nizhny Novgorod, a city with a population of more than a million people, and the industrial center of the Volga basin were studied as a testing ground for studying the role of suspended sediments and particulate matter in the transport of pollutants (figure 1).

Oka and Volga serve as sources of water supply for the city and receivers of waste and storm water, which presents high demands on the quality of these water bodies. Control of contaminants transported with microparticles is required.

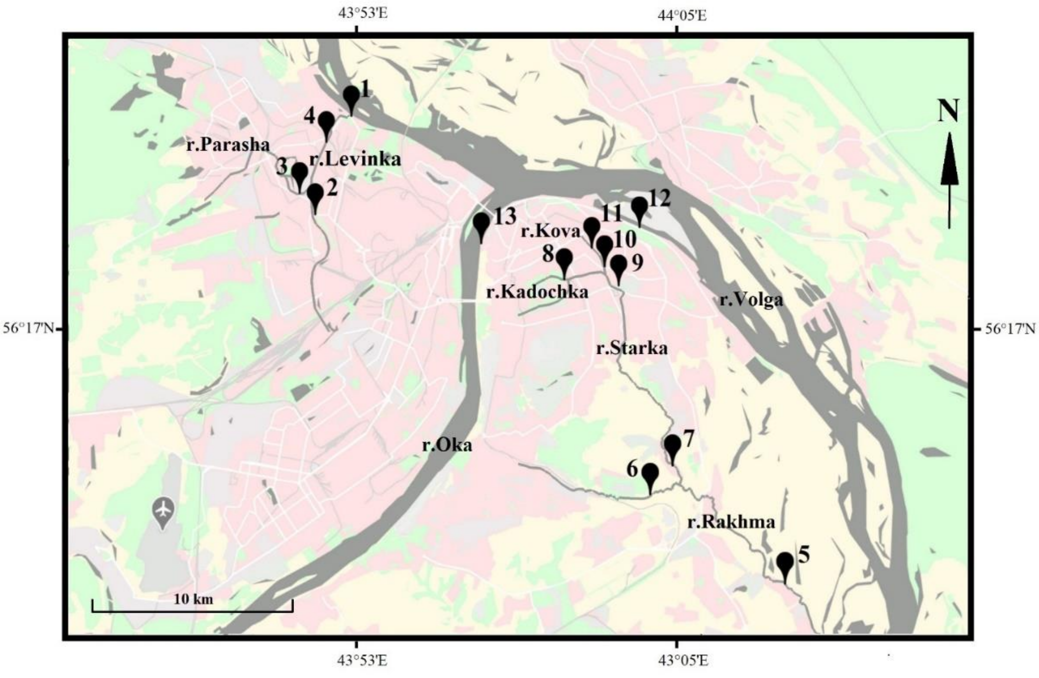


Figure 1. Map of sampling stations around Nizhny Novgorod.

2. Materials and methods

An important stage in the study of micropollutants as carriers of sorbed pollutants is the chemical analysis, which includes three main stages:

- fractionation of suspensions by particle size;
- multistage desorption of sorbed components from the surface of microparticles in order to isolate groups of components (metals, organic compounds);

- chemical analysis of the eluate by modern methods (chromatomass spectrometry, ICP-MS, etc.).

During the summer-autumn dry season in July - September 2020, the staff of the Institute of Geography of the Russian Academy of Sciences took samples of river waters in the basins of the Levinka rivers in the Zarechnaya part of Nizhny Novgorod and Rakhma in its Nagornaya part. In addition, samples of groundwater were taken, including springs and tunnels - artificial underground structures in Nizhny Novgorod designed for groundwater drainage – 13 stations in total (figure 1). To assess the flows of substances, water flow rates were measured in parallel with sampling. The selected water samples were analyzed at the Center for Collective Use of Chemistry Research Institute, N.I. Lobachevsky State University, Nizhny Novgorod. Analysis of water for microplastic content was carried out at the Russian State Hydrometeorological University, St. Petersburg.

Standard methods for the determination of chemicals in water bodies were used. Both the gross indicators of pollution and the phase composition of the pollutants were analyzed.

Determined components:

- the concentration of suspended solids and their dispersed composition;
- BOD5, COD;
- ammonium ions, synthetic surfactants, phenols, petroleum products;
- trace elements: Mn, Fe, Co, Ni, Cu, Zn, Cd, Al, Pb, As, Cr, Na, K, Mg, Ca, Sr, Ba, Si, Ag;
- anions: chlorides, sulfates, nitrates, phosphates, nitrites.

The concentrations of components in water bodies were determined in solutions and in different fractions of suspensions. Water samples were sequentially passed through a blue-ribbon filter with a pore diameter of 2 μm, and then through a cellulose acetate filter with pores of 0.22 μm. The initial collected water samples, successive filtrates, and filter cakes were analyzed.

2.1. Microplastic sampling and analysis

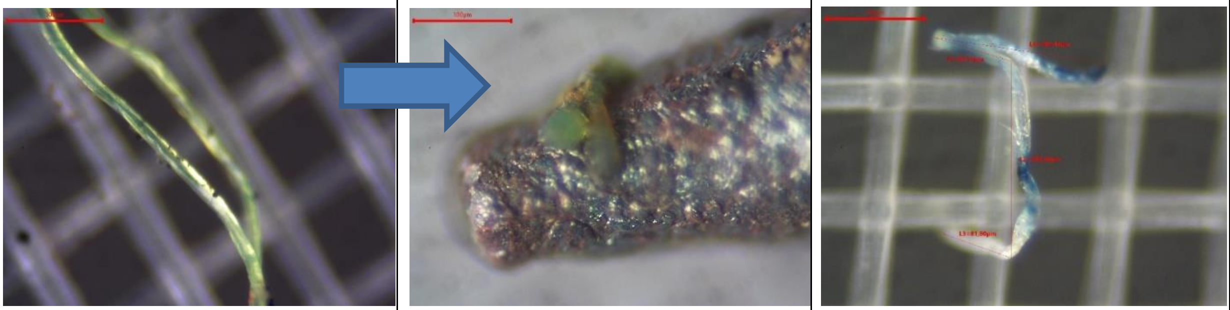
5 samples were taken in river waters, springs and tunnels of the studied region, 10 litres per sample. Most of the samples contained high amount of organics, thus the first stage of laboratory analysis included the organic material digestion using a Fenton oxidation reaction [18]. Water samples were filtered through 132 μm filters and dried at natural conditions. Samples quantitative and qualitative analysis was performed using the visual microscopy (10-40 magnification) using the “hot-needle test” [19]. Confirmed polymer particles were counted and described upon their shape, colour and dimensions. Quality control was performed by eliminating the polymer materials in a lab («clean-lab» conditions) and by using only glass and steel instruments.

3. Results and discussion

In the urban water bodies of Nizhny Novgorod in low-water period of 2020 increased concentrations of organic matter (in terms of COD), oil products, ammonium, synthetic surfactants, iron and manganese were observed. The analytical data are representative, the identified pollutants are "traditional" for the rivers of Nizhny Novgorod [20, 21, 22]. During the summer-autumn low-water period in 2020 at least half of the total transport of priority pollutants in the water of urban rivers is made by suspensions. At the same time, during the passage of streams in the river beds to the river mouths, the proportion of transport by particles of more than 2 μm decreased and the proportion of transport by particles in the range 0.22 - 2 μm increased. In the summer-autumn low-water period of 2020 up to 70% of the iron flux is carried by the suspensions, up to 45% of manganese, and about half of oil products and synthetic surfactants are transferred in river mouths with particles in this range of particle sizes.

Surface and underground waters of Nizhny Novgorod are characterized by significant pollution with synthetic microfibers of anthropogenic origin: most of them are filamentous synthetic fibers of bright colors, ranging in size from 90 to 2000 microns, average concentrations - from 0.5 to 1.3 particles per liter (figure 2). The highest concentration was observed at r. Levinka mouth (st.1), the next polluted water source was a spring near Kova (st. 11) and the less polluted site was in the tunnel (st. 13).

The most likely sources of these fibers in water bodies can be considered domestic waste waters, that might find their way into the springs and tunnels under study. Further analysis of wastewater input into these water objects is planned.



a) b) c)

Figure 2. Microplastic particles (synthetic microfibers) in the samples: synthetic particle before (a) and after (b) thermal (hot-needle) test, c) blue fiber (cell scale - 100 μm).

4. Conclusions

The characteristic intervals of concentrations of priority pollutants in the rivers of Nizhny Novgorod have been determined. Increased concentrations of organic substances (by COD), oil products, ammonium, synthetic surfactants, manganese and iron are observed. For the first time estimates of microparticles contribution to the transfer of substances from the city territory were obtained for small rivers and groundwater in a large city. During the summer-autumn low-water period in 2020 at least half of the total transfer of the above priority pollutants is carried by suspended matter. About a quarter of the flow of these pollutants is associated with the transport of microparticles with a size of 0.22-2 microns (for iron - about a third).

For the first time estimates of microplastic pollution of urban water were obtained for this region showing the presence of synthetic microfibers in all the sampled locations, including springs and river waters. The findings are important for further investigation of pollution discharge problems and selection of water protection measures.

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