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Assessment of Self-Cleaning from Heavy Metal Contamination of the European Territory of Russia Northern River Ecosystem

A A Zimovets[1], A E Ovsepyan[1]

[1]Department of physical geography, ecology and environment protection, Institute of Earth Sciences, Southern Federal University, Zorge, 40, Rostov-on-Don, 344090, Russia

E-mail: mir-zagadka@yandex.ru

Abstract. Self-purification from heavy metals (Cu, Ni, Pb, Zn, Cd and Cr) was assessed in the estuary area of the one of the largest river ecosystems in the European territory of Russia – the Northern Dvina River estuary. The conditional degree of self-purification of river waters and bottom sediments for winter and summer is calculated. It is noted that the highest values of self-purification of river waters are observed in winter for Cu (54%), Pb (25%), Cd (67%), Cr (82%), and in summer – Zn (44%) and Ni (50%). It was found that the processes of migration of Ni, Zn and Pb from bottom sediments to water predominate in winter, while in summer this process is typical for Pb, Cd and Cu. The index of river water pollution in the seasonal dynamics of heavy metal content was established.

1. Introduction

Studying the natural potential of rivers by determining the intensity of their self-purification processes, along with determining the levels of pollutants in the water components, is one of the main criteria for regulating the anthropogenic load on the water ecosystems of rivers used for economic and drinking purposes [1]. One of the most toxic and widespread pollutants of present day is heavy metals, which are capable of active migration, transformation and bioaccumulation [2, 3]. The presence of heavy metals in the environment leads to a number of adverse impacts. Until the impacts are dealt with, health and mortality problems break out, as well as the disturbance of food chains [4, 5]. The problem of heavy metal contamination of reservoirs and watercourses is particularly acute in the Northern regions of our country [6].

The Northern Dvina River estuary is located in the Arkhangelsk region within the North of the European part of Russia (EPR). This region is characterized by increased vulnerability associated with the prevailing specific climatic conditions that determine the flow characteristics. So in the summer, in high temperatures, there is an activation of chemical and biochemical processes, while in the cold part of the year, they slow down. Under these conditions, water ecosystems require more time to self-clean and restore to their original state after the cessation or significant weakening of anthropogenic impact [7]. Thus, all this determines the relevance of the research, the results of which can be used in practical activities for making management decisions in the field of restoration of water ecosystems.

The purpose of the study is to assess the self-cleaning ability of the river ecosystem from heavy metals to determine the current ecological state of the Northern Dvina River estuary.

2. Materials and methods

The Northern Dvina River, with a length of 750 km and a basin area of 357 000 km^2, is one of the largest rivers in the North of the European territory of Russia. Of particular interest is the Northern Dvina River estuary area, which is a complex hydrochemical object that is affected, on the one hand, by the salty waters of the White Sea due to wind-surges processes, and on the other – by the anthropogenic impact of a large transport and industrial hub formed by the cities of Arkhangelsk, Novodvinsk and Severodvinsk [8]. Here, the main pollutants of the aquatic ecosystem include enterprises of the forestry, engineering, fuel and energy complex, as well as discharges and emissions from public utilities and transport [9, 10].

The geography of research covers a vast area of the lower reaches of the river from the confluence of the Pinega River to the delta maritime edge and the south-eastern part of the Dvina Bay of the White Sea. The research was conducted at 16 sampling stations (figure 1).

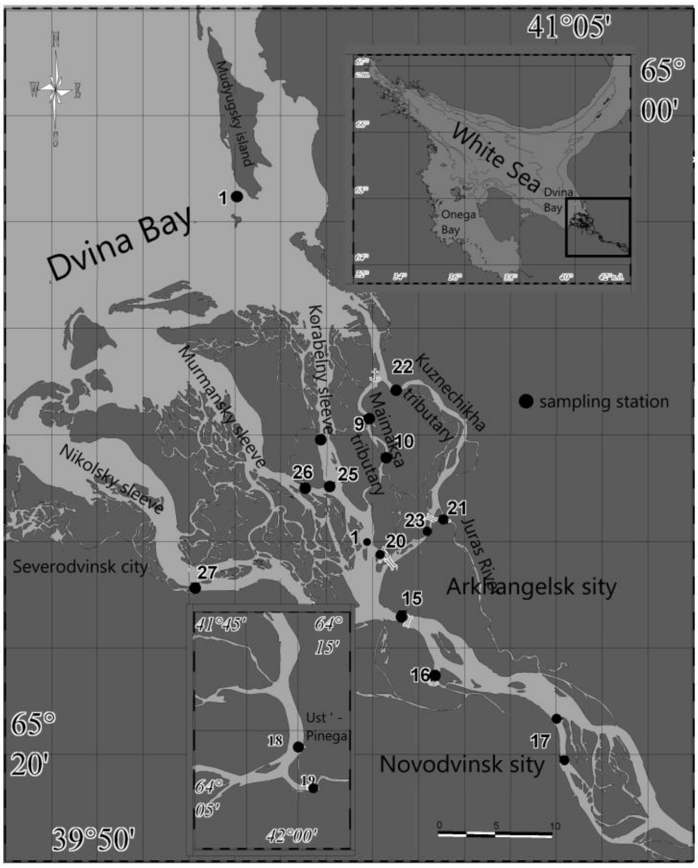

Figure 1. The sampling stations on the Northern Dvina River estuary.

The materials for this work were selected samples of river water and bottom sediments to determine the content of heavy metals of the priority group – Pb, Cd, Cu, Ni, Zn and Cr. The research was conducted in the summer and winter periods of 2016-2017 years. This report is part of a long-term geochemical research conducted by research scientist of the Department of physical geography, ecology and nature protection of the Institute of Earth Sciences of the Southern Federal University under the Professor Yu.A. Fedorov in the Northern part of the European territory of Russia [11-14]. During the study period, the total number of river water and bottom sediment samples studied was more than 100.

The total and dissolved forms of heavy metals in the river water were determined by the atomic absorption method with electrothermal atomization of samples according to the method guidance document of the Hydrochemical Institute № 52.24.377-95 "Mass concentration of metals in waters". The total metal content in bottom sediments was analyzed using the x-ray fluorescence method on the SPECTROSCAN MAX-GV.

The total degree of self-purification of the river ecosystem from heavy metals was calculated using the formula: CC = $100\frac{(Ci-Cf)}{Ci}$, CC – degree of self-cleaning, %; C_i и C_f – metal content in the initial and final range of the site [15].

To compare the degree of self-purification of river water and bottom sediments, is used the relative purification index: ОКС = $\frac{CCbs}{CCwater}$, CC_{bs} – degree of self-cleaning of bottom sediments, CC_{water} – degree of self-cleaning of river water [16].

Water pollution index was used to assess water quality in the Northern Dvina River estuary: WPI=$\frac{1}{n}\sum_{i-1}^{n}\frac{Ci}{MPC}$, n – the number used of indicators, C_i – the actual content of the pollutants, *MPC* – maximum permissible concentration (Cu – 1,0 μkgl^{-1}; Ni – 10; Zn – 10; Pb – в 6,0; Cd – 0,5 и Cr – 20 μkgl^{-1}) [17].

Statistical data processing was carried out by the programs "Microsoft Excel".

3. Results and discusses

Studies have shown that the maximum degree of self-purification of water in winter is observed for Cu (54%), Pb (25.0), Cd (67), Cr (82%), and for bottom sediments – Zn (42%) and Ni (56%) (figure 2).

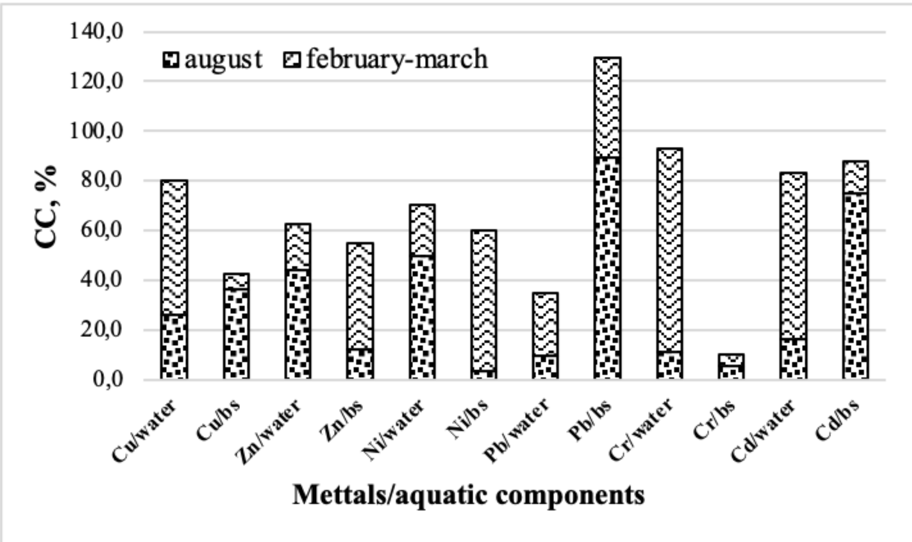

Figure 2. The degree of self-purification of river waters and bottom sediments of the Northern Dvina estuary in the seasonal dynamics of heavy metal content.

It should be noted that during the research period (february-march), the Northern Dvina River estuary was covered with ice, which excludes the entry heavy metals into the river ecosystem with atmospheric precipitation and runoff [18]. It is possible pollutants come from anthropogenic sources to the aquatic ecosystem through an atmospheric channel. This fact is supported by the results of previous studies [19], when extremely high concentrations of the total dissolved form of lead (118.9 μgl^{-1}) and cadmium (0.41 μgl^{-1}) were determined in the thawed snow in the area of operation of thermal power plants against of trace and low concentrations of these metals found at other stations.

It is the sequence of decreasing the self-purification of the river water from heavy metals in winter – Cr > Cd > Cu > Pb > Ni > Zn and bottom sediments – Ni > Zn > Pb > Cd > Cu > Cr. It can be seen that these two ranked sequences are mutually inverted relative to each other.

In summer the maximum self-purification of water is observed for Zn (44%) and Ni (50%), and bottom sediments – Cu (37%), Pb (90%) and Cd (75%). In the degree of self-purification level of river water from heavy metals in the summer period can be represented as Ni > Zn > Cu > Cd > Cr > Pb and bottom sediments – Pb > Cd > Cu > Zn > Cr > Ni. As in the previous case, there are two similar sequences in the opposite orientation.

It should be noted that high rates of self-purification of river waters are typical for Cu both in the cold season and in the warm season, despite the fact that the concentration of this metal in the river water of the estuary of the Northern Dvina exceeds MPC throughout the river by 4-20 times. Also, MPC exceedances are noted for Cr (2-3 times) – in the channels and branches of the Northern Dvina Delta and Zn (6-17 times) – in large enterprises of the woodworking industry [19, 21]. But for Cr, a high degree of river water purification was detected in winter, while for Zn, this indicator was higher in summer. Thus, despite the fact that the ecosystem of the Northern Dvina River estuary region functions in conditions of high concentrations of a number of metals, this section of the river is characterized by a high self-cleaning capacity in different seasons of the year.

Interpreting the values of the relative self-cleaning coefficient for metals (figure 3), it was found that the degree of self-cleaning of bottom sediments is higher than the degree of self-cleaning of water in summer than in winter.

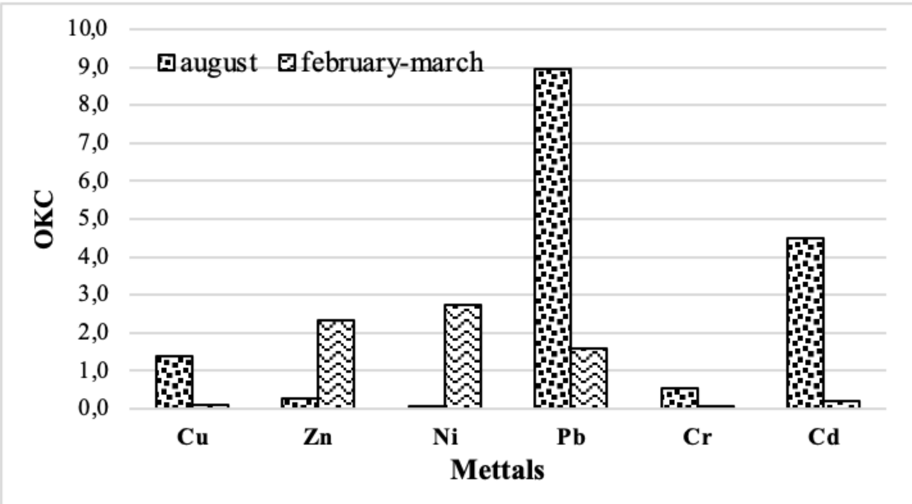

Figure 3. The relative index of the degree of self-purification of the Northern Dvina River estuary from heavy metals.

The processes of migration of Ni, Zn and Pb from bottom sediments to water predominate in winter, while in summer this process is typical for Pb, Cd, and Cu. According to the ranked series of decreasing intensity of migration of heavy metals from bottom sediments to river water in the warm season (Pb > Cd > Cu > Cr > Zn >Ni) and cold season (Ni > Zn > Pb > Cd > Cu > Cr), the most mobile metal is Pb, and Cr can be attributed to inert elements. The behavior of other metals is most likely determined by seasonal differences in the sources of metals entering the water, changes in physical and chemical parameters, and other processes [20].

To assess the quality of river water in the Northern Dvina River estuary, the water pollution index was calculated, according to which it was established that in winter there is a class 3 water quality, polluted water (water pollution index = 2.7), and in summer – a class 4 water quality, dirty water (water pollution index = 4.3). The low level of water pollution index indicates that the winter period is the most favorable for the processes of self-purification of river water from heavy metals, since during this period additional sources of heavy metals entering through the atmospheric channel and surface runoff.

4. Conclusion

It is established that a high degree of self-purification of water is observed in winter for most of the studied heavy metals. Thus, in winter, the maximum self-purification of water is observed for Cu (54%), Pb (25%), Cd (67%), Cr (82%), and for bottom sediments – Zn (42%) and Ni (56%); in summer, a high degree of self-purification of river water is observed for Zn (44%) and Ni (50%), and bottom sediments-Cu (37%), Pb (90%) and Cd (75%). These processes are confirmed by high values of the relative self-purification coefficient for a number of metals that actively migrate from bottom sediments to river waters. The most mobile metal is Pb, while the inert elements include Cr.

It was found that high rates of self-purification of river waters are typical for Cu both in the cold season and in the warm season, despite the fact that the concentration of this metal in the river water of the estuary of the Northern Dvina exceeds the maximum permissible concentrations throughout the river throughout the year.

It is determined that for the ranked series of the degree of self-purification of river waters and bottom sediments from heavy metals, the values are inverted relative to each other, which indicates that the processes of self-purification of the aquatic ecosystem are controlled by various factors depending on the season, the source of metal intake, the prevailing physical and geographical conditions and et al.

In winter, the aquatic ecosystem of the Northern Dvina River estuary is characterized as polluted in terms of water quality, while in summer it is dirty. The low index of water pollution indicates that the winter period is the most favorable for the self-purification of river water from heavy metals, since during this period additional sources of heavy metals entering through the atmospheric channel and with a flat flush are excluded.

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