Features of the Natural and Anthropogenic Fluxes of Heavy Metals Formation and Assessment of Cleansing Ability of Northern European Territory of Russia Mouth Rivers

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Abstract. The Northern Dvina River estuary is characterized by specific natural conditions (long cold winters, short cool summers, podzolic type of soil formation, high waterlogging (up to 20%) and high forest cover (about 80%) of the territory), the influence of tidal and wind waves of the White Sea, providing deep penetration into the delta river of salt water, as well as significant anthropogenic influence on the part of the enterprises of pulp and paper industry and forestry, thermal power engineering, etc., located in the cities of Arkhangelsk, Novodvinsk and Severodvinsk. All this has a significant impact on the formation of concentrations and fluxes of heavy metals in the study area. The following balance sheet components are actively involved in heavy metal transport: precipitation (solid and liquid), soils and vegetation; river water (water, suspended matter and bottom sediments); hydrobionts; groundwater; and industrial discharges and emissions. Natural and anthropogenic flows of heavy metals were calculated, and the cleaning capacity of the Northern Dvina River estuary was estimated. On the basis of the obtained data, a conceptual balance model was developed, which describes the processes of transfer of heavy metals between the studied components.

1. Introduction
Northern regions characterized by specific natural conditions affecting the speed and characteristics of geochemical and biochemical processes, are most vulnerable to any kind of anthropogenic impact, which makes them attractive to scientists engaged in environmental and geochemical studies. The Northern Dvina River is one of the largest rivers of the North of the European part of Russia (EPR), 744 km long, flowing into the Dvina Bay of the White Sea. The estuary area has a length of 135 km, covering a vast area from the confluence of the river Pinega to the sea edge of the Delta. The Delta of the river is a triangle, where three main sleeves are distinguished – Nikolsky, Murmansk and Korabel’ny, and two large branches – Kuznechiha and Maimaksa. On the river within the city of Arkhangelsk there are significant tidal currents that extend 90 km up to the Pinega River estuary [3]. In the mouth of the Northern Dvina River there are three major industrial transport hubs – Arkhangelsk, Novodvinsk and Severodvinsk [1]. Emissions and discharges of the pulp and paper industry, electric power industry, shipbuilding and ship repair facilities, as well as vehicle emissions and sewage of municipal services, significantly affect the quality of all components of the environment – air, river water, bottom sediments, soil and biota [5, 11-16]. All this has a significant
impact on the processes of accumulation, dispersion and transformation of forms of migration and finding of heavy metals in various components of the environment, as well as on their boundaries [9]. The aim of the research is to study the features of the formation of concentrations and migration processes of heavy metals (on example of mercury and copper), as well as the modeling of their flows in various environmental components of the Northern Dvina River estuary.

2. Materials and methods
Complex ecological and geochemical studies were carried out in the Northern Dvina River Estuary (from 2004 to 2016). In the Northern Dvina River estuary at 18 observation stations, including 9 – in the river, 8 – in its Delta and 1 – on the estuary (figure 1). A total of 177 samples of precipitation (rain and snow), river water, sediments and soils were selected, 852 definitions were made [4]. The particular interest for the purposes of modeling fluxes of heavy metals represented by mercury and copper. Mercury is the most toxic heavy metal [6-8], the main source of which in the ecosystem of the Northern Dvina River has long been the pulp and paper industry [4, 10]. Copper is a biophilic element coming to the studied areas from both natural and anthropogenic sources.

Figure 1. The observation stations on the territory of the Northern Dvina River estuary.

In samples of atmospheric precipitation and river waters, the gross and total dissolved forms of copper were determined by atomic absorption method with electrothermal atomization of samples on AA-spectrometer "QUANTUM-Z. ETA" by the method of RD GHI 52.24.377-95 "Mass concentration of metals in water" and mercury by atomic absorption in cold vapor according to certified methods [18]. The gross copper content in bottom sediments and soils was determined by x-
ray fluorescence method on the device x-ray "SPECTROSCAN MAX-GV", mercury – by atomic absorption in cold vapor.

The variation of cooper and mercury content varies forms migration presents at the table 1.

**Table 1.** The concentrations distribution of various forms mercury and copper migration in the Northern Dvina River Estuary.

| forms of mercury migration | total mercury content [11] | total copper content [12] | content of dissolved mercury [11] | content of dissolved copper [12] |
|----------------------------|---------------------------|---------------------------|----------------------------------|-------------------------------|
| Atmospheric precipitations, μg·l⁻¹ | 0.005-0.2 | 3.3-27.0 | - | 2.4-14.0 |
| Water (low water phase), μg·l⁻¹ | 0.02 | 14.9 | - | 8.3 |
| Bottom sediment (layer 0-5 cm), μg·g⁻¹ d.w. | 0.012 | 20.8 | 0.025 | 10.5 |
| Soils (layer 0-5 cm), μg·g⁻¹ d.w. | 0.02-4.0 | 11.0-66.0 | 0.11 | 35.1 |

*bold* marked average values

On the basis of the data on the content of heavy metals in various components of the environment, an assessment of mercury and copper fluxes in the river systems of the Northern Dvina River with atmospheric precipitation and plane washout, the calculation of the removal of metals with river waters in the Dvina Bay of the White Sea (table 2) was carried out using the method given in [2, 11, 17, 19].

**Table 2.** Mercury and copper flows in to the components of Northern Dvina River Estuary.

| Components | mercury | copper |
|------------|---------|--------|
| Atmospheric runoff volumes, tons per year [4, 11] | 0.0046 | 1.68 |
| The volume of runoff from soils, tons per year [Fedorov, Zimovec, 2011, Ovsepyan, Fedorov, 2011 [4, 11] | 0.28 | 88.9 |
| The volume of heavy metals removal from river flow in the sea, tons per year [4, 11] | 0.39 | 171.5 |
| Sewage, tons per year [20] | - | 0.026 |

On the basis of the obtained data was compiled conceptual balance model that describes the transport processes of heavy metals between the principal components of the landscape. It can be graphically represented (figure 2).
Figure 2. The graphical model of heavy metals flows in the ecosystem.

In the form of a formula, the balance of heavy metals can be represented as follows:

\[
V(HM) = A_a(HM) + A_{soil}(HM) + A_{sewage}(HM) + A_{gw}(HM) - R_{rf}(HM) \pm BM
\] (1)

somewhere: \(A(HM)\) – the volume of heavy metals accumulation in the estuarine region of the river (includes the content of metals in water, suspended matter, sediments and hydrobios); \(A_{a}(HM)\) – removal of heavy metals with atmospheric precipitation; \(R_{soil}(HM)\) – the volume of removal of heavy metals from the soil; \(R_{sewage}(HM)\) – the transport of heavy metals with wastewater; \(R_{gw}(HM)\) – the transport of heavy metals with groundwater; \(R(HM)\) – the volume of heavy metals removal from river flow in the sea; \(BM\) – balance mismatch due to the inaccuracy of the definition of the components of the balance sheet.

Thus, these environmental components are actively involved in the transport of heavy metals: 1 – atmospheric precipitation (solid и liquid), 2 – soils and plants; 3 – river water (water, suspended matter, bottom sediments и hydrobios); 4 – ground water и 5 – sewage. Of course, there may be more components of the balance, but we have taken, in our opinion, the main ones.

Calculate the balance for the Northern Dvina River estuary, using the data from tables 2.

Since there are no data on the content of copper in groundwater in the literature sources, we assume this value as \(X\):

\[
V(Cu) = 1.68+88.9+0.042-171.5 \pm BM = \pm BM-80.87 \text{ tons per year (2)}
\]

For mercury in the study area, there are no official data on emissions from wastewater (since the main suppliers of this pollutant – the Arkhangelsk and Solombalsky pulp and paper mills – have excluded mercury compounds from the production cycle) and the content in groundwater, we will not take this indicator into account in the calculations. Thus, the balance equation has the following form:

\[
V(Hg) = 0.0046 + 0.28 - 0.39 = \pm BM - 0.11 \text{ tons per year (3)}
\]

3. Conclusion

When considering the model of metal flows for the main components of the balance, it is revealed that a sufficiently large amount of mercury and copper is carried with the river flow into the White Sea and this is due to the self-cleaning ability of the rivers, where a significant amount of pollutants is removed.
on mechanical and geochemical barriers. It is also worth noting that a significant role in the accumulation of metals is played by unaccounted factors – the introduction of groundwater, unauthorized discharges of industrial enterprises and transport to the river, as well as the production of hydrobionts.

In our opinion, the obtained results can be applied in the assessment of self-cleaning capacity of water bodies in the North of the European territory of Russia and the prediction of areas with high environmental risk, where the most toxic forms of heavy metals prevail.

4. References
[1] Brekhovskikh V F, Volkova Z V, Kolesnichenko N N 2003 Surface water quality problems in the Northern Dvina basin (Moscow: Nauka) p 233
[2] Dauwalter V, Kashulin N A, Sandimirov S S, Radin N E 2009 Bulletin of the MSU 3 507:515
[3] Zotin M I and Mikhailov V N 1965 Hydrology of the mouth area of the Northern Dvina River (Leningrad: Gidrometeoizdat) p 376
[4] Fedorov Yu A and Zimovec A.A. 2011 Proc. 11th Int. Multidisciplinary Sci. GeoConf. & EXPO (Albena, Bulgaria) vol 3 p 171
[5] Fedorov Yu A, Ovsepyan A E, Zimovets A A, Savitskiy V A, Lisitsyn A P, Shevchenko V P, Novigatsky A N, Dotsenko I V 2018 Handbook of Environmental Chemistry (Berlin, Heidelberg, Springer) 1:34
[6] Fitzgerald W F and R P Mason 1996 The global mercury cycle: oceanic and anthropogenic aspects. in: Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances. EdW. Baeyens, R. Ebinghaus and O. Vasiliev (Dordrecht, Kluwer Academic Publishers) p 85
[7] Mercury in the Arctic 2011 Arctic Monitoring and Assessment Programme (AMAP) (Oslo, Norway) 193 p
[8] Minamata Convention on Mercury 2017 URL: http://mercuryconvention.org/Portals/11/documents/Booklets/Minamata_convention_Russian.pdf
[9] Mur Dzh V and Ramamurti S 1987 Heavy Metals in Natural Waters (Moscow: Mir) p 285
[10] Ovanesiants A M, Krasil'nikova T A, Ivanov A B 2008 Meteorologija i gidrologija 6 p 98
[11] Ovsepyan A E and Fedorov Yu A 2011 Mercury in the mouth area of the Northern Dvina River (Rostov-on-Don –Moscow: ZAO Rostizdat) p 198
[12] Ovsepyan A E, Fedorov Yu A, Zimovets A A, Savitskiy V A 2016 Proc. 16th International Multidisciplinary Scientific GeoConference, SGEM (Albena, Bulgaria) vol I pp 243
[13] Ovsepyan A E, Fedorov Yu A, Zimovets A A, Savitskiy V 2016 World of Scientific Discoveries (Krasnoyarsk: Science and Innovation Center Publishing House) 5 p 117
[14] Ovsepyan A E, Zimovets A A 2017 Proc. 17th International Multidisciplinary Scientific GeoConference SGEM (Vienna, Austria) vol 17 p 135
[15] Ovsepyan A E, Zimovets A A, Fedorov Yu A 2015 Proc. 5th International Conference on Science and Technology (London) pp 208
[16] Ovsepyan A E, Zimovets A A, Fedorov Yu A 2017 Proc. 17th International Multidisciplinary Scientific GeoConference, SGEM (Vienna, Austria) vol 17 pp 713
[17] Pacyna J M, Cousins I T, Halsall C, Raultio A, Pawlak J, Pacyna E G, Sundseth K, Wilson S, Munthe J 2015 Environmental science and Policy 50 pp 200
[18] RD 52.24.479-95. 1995 The method of measurements of mass concentration of mercury in waters by atomic absorption cold vapor (M: Rosgidromet) p. 25
[19] Shavrak E I 2012 Water: Chemistry and Ecology 4 p 3
[20] The State and environmental protection of the Arkhangelsk region in 2016 2017 ed A N Kravtsova (Arkhangelsk: the Ministry of natural resources and forestry of Arkhangelsk region) p 453
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