Factors Determining Migration and Transformation of Mercury in the Mouths of Northern Rivers

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Abstract. Mercury is one of the priority pollutants of our time, but also a unique element that can form organic and inorganic compounds of various degrees of toxicity. The toxicity of mercury is influenced by the form of metal finding, environmental factors, ways of metal and its compounds entering the organisms of living beings, and concentrations. In this paper, we consider the factors that determine the migration and transformation of mercury in complex hydrochemical areas of rivers-estuaries. The research is based on the results of observations carried out since 2004 at the mouths of the Northern Dvina, Pechora and Kyanda Rivers. The hydrological and hydrochemical conditions of waters and bottom sediments have been analyzed. Various forms of the occurrence and migration of mercury in the waters and bottom sediments of the objects under consideration have been studied. Conclusions about the priority factors that determine the behavior of mercury for each water body and, in general, for the estuarine areas of this natural zone have been drawn.

1. Introduction
It is known that mercury is an element found in all components of the environment, where it is usually found in trace concentrations. Getting into streams and reservoirs by various routes, mercury, due to its high migratory ability, goes through various stages of transformation. Mercury pollution of the environment remains an urgent problem in the modern world. The number of studies devoted to mercury pollution is growing every year, and the geography and coverage of the studied natural objects is expanding [1, 2]. One of the most important steps towards overcoming it was the adoption of the convention on the reduction and phase out of the use of mercury in various fields of human activity [3]. However, there is one more aspect that must be taken into account - natural objects with already accumulated mercury pollution, which under certain conditions can become suppliers of mercury compounds to the environment. In our work, special attention is paid to water bodies located in the North of the European territory of Russia (ETR), one of which, the Northern Dvina, for many years experienced the influence of effluents from pulp and paper mills, the production cycle of which included mercury. Special attention is required to consider the conditions and processes of accumulation/dispersion of mercury in the estuarine areas of rivers, which are the arena for the interaction of many physical, chemical, biological factors. For 15 years, researchers from the Southern Federal University, the authors of this study, have been studying the processes of migration, transformation of mercury, its dynamics, as well as levels of concentration in the components of the natural environment of water bodies in the North of the ETR.
2. Goals and objectives
The aim of the work is to determine the priority factors that determine the processes of migration and transformation of mercury in the estuarine areas of northern rivers.

The tasks were solved as follows: on the basis of the available research, to analyze the influence of such factors as temperature, water salinity, oxygen content, content of organic acids in water, hydrodynamic activity on the processes of migration and transformation of mercury; determine the factors influencing the processes of mercury sorption in bottom sediments; to identify the priority factors that determine the self-cleaning ability of the considered ecosystems from mercury.

So, as a result of field studies carried out on the rivers Northern Dvina, Pechora, Kyanda, which can be read in more detail in the following works [4-10], it became possible to analyze the level of relationship between the mercury content in water and the main physical - its chemical characteristics.

3. The results of research and analysis
Below are the dependencies obtained for various factors.

3.1. Hg in Water
As a result of regression analysis, the following equations were obtained that describe the relationship between the content of the dissolved form of mercury and temperature:

Dependence of the content of total dissolved mercury on temperature in the bottom water layer

\[ y = 0.0155x - 0.2128 \quad (R^2 = 0.4242 \quad r = 0.65; \quad p \leq 0.05) \] (1)

Dependence of the content of total dissolved mercury on temperature in the surface layer of water

\[ y = 0.0566x - 1.002 \quad (R^2 = 0.4211 \quad r = 0.65; \quad p \leq 0.05) \] (2)

Note that these dependences are relevant for the warm season (according to experimental data, when the temperature fluctuates within the range of 12.4 °C and higher). Under such conditions, temperature can contribute to the biogenic and abiotic transformation of organic matter in bottom sediments and, as a consequence, the activation of processes that promote the transition of mercury from them into the water column. As the temperature rises, the mercury methylation processes may intensify. Thus, E.Bacci [11] showed that the methylation rate can increase by 2 - 5 times with an increase in temperature from 3 to 13 °C. It is important to take this into account when assessing the flow of mercury and the degree of pollution of water bodies. It is also important to consider that most surface waters are oversaturated with Hg⁰ compared to the atmosphere, especially in summer [12, 13]. Due to its high volatility, elemental mercury quickly leaves the aquatic environment at normal temperatures. Volatilization of Hg⁰ from the water surface plays an important role in the global mercury cycle [14]. This is indirectly confirmed by the presence of a weak relationship between the concentration of gross mercury and water temperature. This indicates the effect of relatively high temperatures for northern waters on the increase in the concentration of mercury migrating in dissolved form. However, with a further increase in water temperatures (more than 25 °C), the mercury content will decrease due to the volatilization of Hg⁰, dimethylmercury forms through the water layers into the water layers of the air.

The next factor that we ranked as a priority is salinity.

Significant negative correlation coefficients were found between the content of the total dissolved form of mercury and salinity. Moreover, in the bottom layer of water, where the salinity is higher, the relationship is closer (r = -0.72).

For the bottom horizon, the equation describing the relationship between mercury and salinity is as follows:

\[ y = -0.004x + 0.0767 \quad (R^2 = 0.5082 \quad r = -0.72, \quad p \leq 0.05) \] (3)

Dependence of mercury content on salinity in the surface layer of water

\[ y = -0.0119x + 0.0766 \quad (R^2 = 0.3444 \quad r = -0.59) \] (4)

Note that salinity can have a twofold effect at high tide. The increase in salinity causes water stratification in the branches and channels. In this regard, the water column, depending on the content of chlorine ions and pH values (the latter, due to a relatively narrow range, play a lesser role), may
differ greatly in the content and forms of mercury occurrence at the same stations. So, as a result of mixing fresh and salty waters and an increase in the content of chlorine ions to a concentration of 0.527–0.726 mg/l, the toxicity of waters will increase. At the same time, under the influence of chloride ions, there will be an increase in the leaching of mercury from bottom sediments, but at the same time its toxicity, due to its tendency to bind into $\text{HgCl}_2^-$ complexes, should decrease with a further increase in chlorine content. The process of mercury methylation with an increase in salinity, in turn, will be suppressed. The same phenomena occur in the zone of mixing of river waters with the waters of the White Sea in the Dvina Bay. This is illustrated by observations under low and high water conditions in the Maimaksa channel [4, 15].

For water conditions with salinity up to 1000 mg/l, the following model of the content of chlorine ions from water salinity was obtained:

$$y = 0.0791x - 9.0547 \quad (R^2 = 0.4793, r = 0.7) \quad (5)$$

With a mineralization above 1000 mg/l, the following dependence applies:

$$y = 0.5692x - 262.02 \quad (R^2 = 0.9979, r = 0.99) \quad (6)$$

In order to generalize the model for calculating the concentration of chloride ions and the subsequent determination of the forms of occurrence of mercury based on long-term data on the value of mineralization and the content of chlorides provided by SUGMS, the following formula was derived:

$$y = 518.11x - 99.566 \quad (r = 0.999) \quad (7),$$

where ‘$y$’ is the chlorine ion content, mg/l; ‘$x$’ - salinity, ‰. This formula is valid for a salinity range of 0.2–15.0 ‰. It should be noted that this pattern "works" when mercury concentrations in water are higher than the background, i.e. for mercury-contaminated river waters. If relatively clean river waters are mixed with sea waters, Hg concentrations in the water of this zone will increase (due to higher background concentrations of mercury in sea waters compared to river waters). In particular, this effect was observed at the mouth of the Kyanda River [7, 16].

There is a weak negative correlation between the concentration of the gross and dissolved forms of mercury and the oxygen content.

Dependence of the content of total dissolved mercury on the oxygen content in the surface layer of water

$$y = -0.0374x + 0.3119 \quad (R^2 = 0.1681, r = -0.41) \quad (8)$$

Dependence of the mercury content on the oxygen concentration in the bottom water layer

$$y = -0.0532x + 0.4159 \quad (R^2 = 0.5887, r = -0.77) \quad (9)$$

In the near-bottom layer of water, this relationship becomes closer, while in the surface layer, the relationship between the concentration of oxygen and mercury is manifested either very weakly or absent altogether. The negative relationship between the oxygen and mercury content is probably associated with the existence of a more reducing environment in the bottom layer, which, under low tide conditions, due primarily to the increased concentration of bacteria here - sulfate reducers and methanogens, stimulates the formation and emission of methylmercury from bottom sediments into the water. Thus, the oxygen content has an insignificant effect directly on the mercury content; this factor must be taken into account when calculating the forms of mercury occurrence in bottom sediments.

A close relationship was revealed between the content of fulvic acids (FA) in water and dissolved mercury ($r = 0.71$).

$$y = 131.25x + 16.894 \quad (10)$$

where “$x$” is the mercury content, μg/l, “$y$” is the fulvic acid content in water, mg/l.

This, as well as the directly proportional relationship between the ratio of permanganate to dichromate oxidizability and the content of the dissolved form of mercury migration ($r = 0.61$) [17, 18], indicates that the latter migrates in the form of organic complexes. The data obtained are consistent with the early studies of various authors, in particular, it was investigated [19] that at a water color of 45° and pH = 7.0, the fulvate complex of mercury (up to 99.3%) is dominant. In all likelihood, such a distribution is typical for the waters of the Northern Dvina River. With the mixing
of river waters with the waters of the Dvina Bay and an increase in salinity, fulvate complexes are destroyed, the forms of occurrence of mercury are determined by the processes described above.

Speaking about such an undoubtedly important factor as the hydrometric characteristics of the river, we note that in this case this factor does not play a decisive role, that is, it is not a priority. This is due to the presence of sources of direct input of mercury into the river. Of the hydrological conditions, it is important that there are mechanical barriers in the river bed, which affect the change in the flow rate - thus, here we can speak of the gradient of the river flow rate as an influencing factor - with a sufficiently sharp decrease in the speed on the mechanical barriers, complex formation with suspended solids occurs and deposition of mercury into bottom sediments - as evidenced by our studies at this natural site [4, 20].

3.2. Hg in bottom sediments

For bottom sediments, the factors influencing the processes of migration and transformation of mercury are somewhat different.

Important factors for increasing the accumulation of mercury in bottom sediments will be: the presence of mechanical and hydrochemical barriers, granulometric composition of bottom sediments, Eh, sulfur concentration in bottom sediments, chloride concentration, qualitative composition of microbiocenosis, organic matter content.

The study of such a factor as the tidal phenomena present here showed that the mercury content in the bottom water horizons varied slightly during ebb and flow [4]. This allows us to speak about the small effect of tidal activity on the desorption of mercury from sediments in this natural object. A similar phenomenon is also noted in studies by Heyes et al. [21] for the estuary of the Hudson River, where it is said that the ebb and flow phenomena did not cause erosion of sediments and mercury desorption. Similar conclusions were also obtained by the authors [22] for other elements in the estuary region of the Northern Dvina River.

When mercury enters the bottom sediments, it migrates into the depths, desorbs into the bottom layers of water and is removed with suspension during active roiling during storm events (tracked during expeditionary research). Dissolved forms of mercury (methylated, tetrameric chloride) enter the water from bottom sediments. In the barrier zone, the salinity in the bottom water level changes twice a day by an average of 2 ‰. At low tide and in those parts of the river at high tide, where saline waters from the Dvina Bay do not penetrate, and where the sulfate content remains low, methanogenesis prevails over sulfate reduction in bottom sediments and the bottom layer of water. According to [23], under such conditions, the work of bacteria - methanogens, is activated, and, as a consequence, the formation of methane and methylation of mercury are enhanced.

At sampling stations, where there is practically no effect of surges, water salinity is constant and low, as well as, accordingly, the content of sulfate ions. Therefore, the most probable factors and processes that can bring the system out of balance here will be: anthropogenic (thermal, mercury and organic pollution) and natural (avalanche sedimentation, seasonal changes in temperature, oxygen content, and Eh and pH values).

Bottom sediments of the Northern Dvina River are characterized by predominantly neutral reaction, reducing conditions (6.58-7.71; -176… + 73). Among them, there are precipitations formed under conditions of increased anthropogenic impact [24].

When passing from the bottom water layer to the bottom sediment horizon, a sharp change in pH and Eh values is clearly visible. Bottom sediments are characterized by neutral, to slightly acidic environmental conditions, and predominantly low, down to -200 mV, ORP values.

The studied regularities of the behavior of mercury in the water of this object made it possible to identify the main influencing factors that regulate the course of the migration and transformation of mercury: water temperature; salinity/mineralization; oxygen content; content of fulvic acids; hydrodynamic activity; in bottom sediments: concentration of organic matter; content of sulfur, chlorides; the nature of bottom sediments (granulometric, elemental composition, microbiocenosis); Eh.
4. Justification of the self-cleaning ability index

For a quantitative description and subsequent scoring of these factors, the following criteria were proposed: the sum of annual temperatures exceeding 12 °C, the river flow rate, the sorption capacity of substances, the annual sum of days with a prevalence of S <1.24 E, the average annual value of Eh, the sum of days with the FA/HA ratio <1, the percentage of the sand fraction in bottom sediments.

To assess the ability of aquatic ecosystems to self-clean, it is proposed to use the index (I), calculated by summing the point values of the selected criteria (a 5-point scale is adopted), taking into account their weight coefficients reflecting the role of each factor in the processes of migration and transformation of mercury.

\[ I = \tau T + \upsilon V + \sigma S + \epsilon E + \delta D + \phi F + \gamma \]  

Where T is the annual sum of temperatures exceeding 12°C; V - river flow speed; S - average annual salinity; E - average annual value of Eh; D - percentage of sand fraction in bottom sediments; F is the average annual value of the FA/HA ratio.

The values of the weighting factors were obtained on the basis of a statistical analysis of the data of long-term observations of the processes of migration and transformation of mercury.

The next important task is the choice of the dependent variable. In the conditions of this particular object, it is complicated by the presence here of sources of direct mercury entering into the water in the course of uncontrolled processes. Thus, in order to generalize the model, it is advisable to stipulate the conditions for the functioning of this model - namely: this model is applicable to the existing mercury pollution. Over time and under the influence of environmental factors, the ratio between the concentration of mercury in the bottom water horizon and the background concentration of mercury in the bottom horizons will decrease, approaching 1.

According to the research results, a close relationship was revealed between the concentrations of gross mercury in the bottom water horizon and the upper horizon of bottom sediments, described by the regression equation:

\[ y = 0.2448x + 0.0834 \quad (R^2 = 0.5344, \ r = 0.73) \]  

This dependence is relevant practically throughout the entire simulated area, with the exception of the estuarine seashore, where sea water masses begin to prevail in the immediate contact zone of sea and river waters.

5. Conclusion

Having analyzed all the available data, we believe that the processes of self-cleaning of the ecosystem with respect to mercury pollution can be judged by the ratio of the concentrations of the gross form of mercury in the bottom water horizon to the content of metal compounds in the upper horizons of bottom sediments. In areas with unfavorable conditions relative to mercury pollution, this ratio will be higher than 1, in areas with more favorable conditions, it will decrease, which will indicate the fixation of mercury in bottom sediments, and its removal (possibly temporary), thus, from the biogeochemical cycle. Note that this value will lose its relevance when the mercury concentration drops to the background level or below the background level, since at low mercury values even a ratio equal to or greater than 1 can be considered safe, and the self-cleaning process is complete.

Applying the methodology described in the work [25], with the author's modifications, the values of the selected criteria for assessing self-cleaning ability were graded on a 5-point scale. For the sorption capacity of bottom sediments, a qualitative scale was used, in which the maximum number of points (5) was assigned to silty sediments, the minimum - to sand and gravel.

For the river speed, the maximum number of points was assigned to the highest speeds, the minimum - to those approaching 0 m/s.

For the rest of the criteria, the point gradation was made according to the following formula:

\[ X = 1 + 4 \frac{(x-x_{\text{min}})}{(x_{\text{max}}-x_{\text{min}})} \]  

where X is the value of the criterion at different sections of the watercourse, xmin, xmax are their limiting values.

Multiple regression analysis of the results of field observations made it possible to obtain an equation that simulates the dependence of the rate of mercury transition into bottom sediments
(transformations), expressed as the ratio of the concentration of the gross form of mercury in the bottom water horizon to the content of this form in the upper horizon of bottom sediments on the main environmental factors. Note that, based on the results of the analysis, a decision was made on the possibility of neglecting such quantities as the current velocity and the average annual value of Eh.

\[ \ln k = 0.85T - 0.55S - 0.2D + 0.43F - 17.27, \]

The multiple correlation coefficient of the resulting equation is 0.967, which gives us reason to trust the statistical significance of the regression coefficients included in the equation. We will take these coefficients as the desired weight coefficients reflecting the role of the main influencing factors on the purification of watercourses from mercury, and the dependent variable, expressed in points of a five-point scale, corresponds to the self-cleaning ability index \( I \).

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