

Mercury in the Water of Small Rivers of the Onega Bay Basin of the White Sea

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Abstract—The results of expeditionary studies of the behavior of mercury in the water of small rivers in the basin of Onega Bay of the White Sea are presented. The priority forms of mercury migration are determined, and the forms of its occurrence along the main stem of the Kyanda River are estimated. The interrelations between the contents of various forms of mercury on the one hand and the salinity, pH, and Eh of waters on the other hand are analyzed. The influence of the hydrological phases on the transformation of inorganic forms of mercury is revealed. The differences in the levels of contents of dissolved mercury and its relation to salinity in the estuarine areas of marginal filters of the subarctic rivers under natural and anthropogenic conditions are established.

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Mercury pollution has a global character, which is expressed in the presence of increased concentrations in the different subarctic regions that are located both near large industrial and residential centers and at a significant distance from them [1–5]. The small rivers in the Onega Bay basin that are not subjected to direct anthropogenic impact are a valuable source of information on the background concentrations of mercury and the behavior of the element in the water in various segments of the marginal filter.

The studies of the Kyanda River mouth area (Fig. 1) were performed by the personnel of the Northwestern Department of Shirshov Institute of Oceanology, Russian Academy of Sciences, and the Institute of Earth Sciences, Southern Federal University [6]. The contents of different forms of mercury migration were estimated under a modified procedure that was used earlier in different water bodies in the northern European part of Russia [2, 3]. More than 300 values of physicochemical indices were calculated (oxygen content, salinity, temperature, pH, and Eh), including 80 values of concentrations of different forms of mercury migration and its total content at ten stations in Onega Bay and in the Kyanda, Malozhma, and Chiksha rivers. Based on the values of the physicochemical

parameters and the mercury content, the regression equations and correlation coefficients (R) were calculated.

The temperature of the river waters varied within +18.2...+21.6°C during the expedition. It was the highest in the lowest tide and the lowest in the highest tide [6]. The water salinity along the Kyanda River–Onega Bay profile varied within 2.39–24.39 PSU (on average, 11.5 PSU) [6] and increased towards the river mouth regardless of the tidal stage. The pH values varied along the profile within 6.78–8.65 (on average, 7.72) with a common tendency toward their decrease towards the sea edge. The Eh values along the river–bay section varied within +102...+185 mV (average value of +143 mV). The oxygen content along the Kyanda River profile ranged from 7.11 to 8.97 mg/L (on average, 7.96 mg/L), demonstrating a tendency towards its decrease (except for the low water stage) along the river profile towards the river–bay mixing zone. The lowest contents of dissolved oxygen at all water sampling stations were recorded at the highest tide, from 7.11 to 7.63 mg/L (on average, 7.32 mg/L), and the highest ones, from 7.89 to 8.97 mg/L (on average, 8.57 mg/L) in the low water.

The content of different forms of mercury migration and of its total concentrations was characterized by the significant spatial and temporal variability (Fig. 2). The total content of mercury in the water changed within 0.007–0.016 µg/L (on average, 0.013 µg/L). The maximum concentration was observed at high tide at 1–2 km upstream, and the minimum concen-

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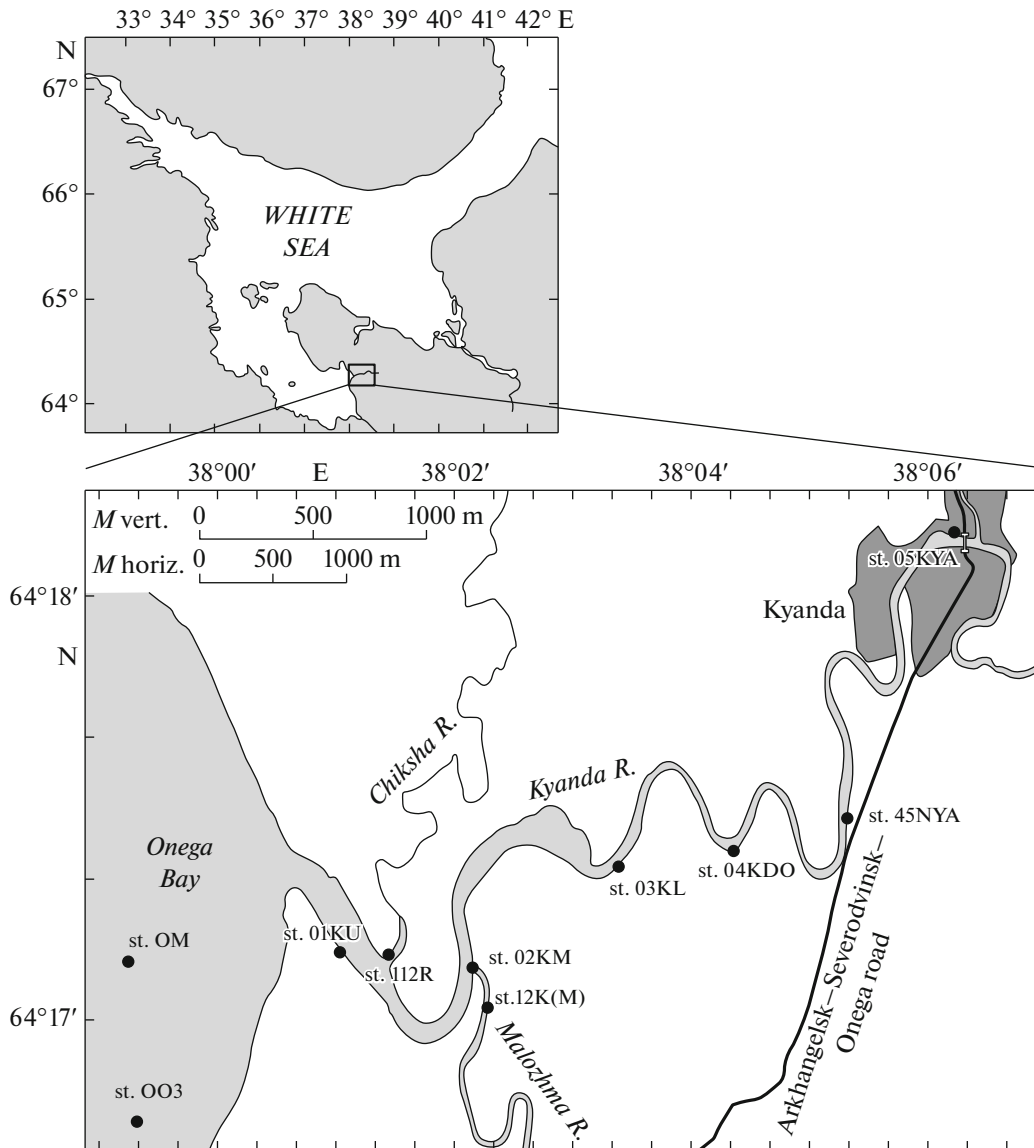


Fig. 1. Location of the study area and the sampling stations in the Kyanda River in August 2014.

tration was in the bay itself towards the east from its mouth (st. OO3). Relatively low concentrations of total mercury were found in the water of the upper reaches of the river, st. 05KYA. The content of the total dissolved form of mercury varied from 0.003 to 0.009 $\mu\text{g/L}$ (on average, 0.007 $\mu\text{g/L}$). The maximum values were recorded at high tide on a 2.5-km segment from the river mouth upstream along the Kyanda River. The minimum values were found at low tide at OO3 station, the relatively low concentrations of the total dissolved form are typical of st. 05KYA and the Malozhma River mouth (st. 12K(M)). The mercury content in particulate matter varied from 0.003 to 0.007 $\mu\text{g/L}$ and was lower on average (0.005 $\mu\text{g/L}$) than the concentrations of the total dissolved form of mercury.

The distribution of the concentrations of all forms of mercury migration along the river profile demonstrates a tendency towards its decrease from the mouth to the upper reaches (Fig. 2). The largest concentrations of different forms of mercury migration were discovered during the high tide phase at the stations located near the places where the Kyanda River flows into Onega Bay. All the samples contain a dissolved form of mercury migration in amounts that do not exceed the maximum allowable concentrations of fishery freshwater bodies.

An inverse linear relationship (R from -0.52 to -0.40 ; $p < 0.05$) was revealed between the contents of all forms of element migration and the total mercury on the one hand and the values of the temperature, pH, Eh, on the other hand. A close direct relationship

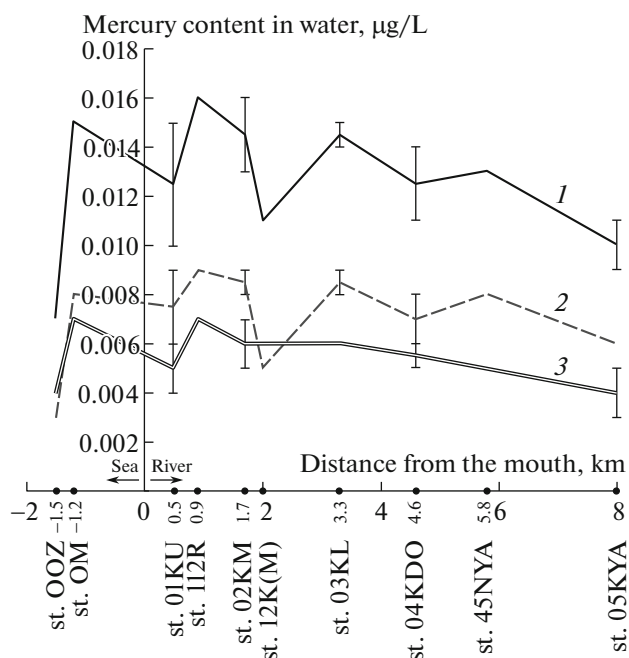


Fig. 2. Limits of variations and average concentrations of different forms of mercury migration in the water along the Onega Bay–Kyanda River profile. (1) Total mercury content, (2) content of the dissolved form of mercury migration, (3) content of the particulate form of mercury migration.

(R from 0.56 to 0.64; $p < 0.01$) was established between the salinity and all forms of mercury migration and the total content of mercury in the water, in which case it was the highest when the migration form was dissolved. This indicates that the salinity factor exerts a dominant influence on the distribution of all forms of mercury migration in the water along the Kyanda River–Onega Bay profile, while the temperature and pH play a smaller role. We note that, for the marginal filter of the Northern Dvina River, the salinity and the dissolved mercury content showed an inverse dependence [2, 3].

For the Kyanda River and its tributaries, the dominance of the dissolved form of mercury over the metal content in the particulate matter was established (56% of mercury migrates in the dissolved form on the average). Both maximum (67%) and minimum (43%) relative contents of mercury in the dissolved form were found during the low tide. The dominant inorganic forms of mercury in the Kyanda River water were determined by the model calculations and the diagram of the dependence of water pH on the inverse logarithm of the chloride concentration [7]. It was found that, at low tide, the dominant inorganic forms of

mercury in the river water are mercury hydroxide ($\text{Hg}(\text{OH})_2$) in the salinity interval of 2.52–2.73 PSU and dimercury chloride (HgCl_2) at a change in the salinity from 4.85 to 10.76 PSU. Water-dissolved mercury dominates in the form of tetra-mercury chloride ($[\text{HgCl}_4]^{2-}$) at salinity of 25.66 PSU in the sea waters of Onega Bay. As the salinity changes within the interval of 11.91–24.39 PSU, the inorganic toxic form of mercury HgCl_2 , which is dominant at low tide, is replaced with a $[\text{HgCl}_4]^{2-}$ form with low toxicity at high tide.

Thus, inorganic mercury may change its migration forms having different toxicity at the same stations and in the different hydrological phases. According to the regularity established, as a rule, the content of a dissolved form of mercury migration depends inversely on the salinity in the estuarine segments of the marginal filters of the subarctic rivers that are under severe anthropogenic pressure and depend directly on salinity in the reference areas (the Kyanda River).

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