Sources assessment of heavy metals inflow in the Pestovo water storage reservoir

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Abstract One of the most important water quality indicators is the heavy metals content. Heavy metals (HMs) are one of the top pollutants in the list because even very small concentrations of them are highly toxic. The peculiarity of HMs as pollutants is also that there is practically no bio-degradation for them – they only move from one natural reservoir to another, interacting with living organisms and leaving traces of this interaction. Moving from one link of the trophic chain of ecosystems to another, they gradually concentrate in the master links of food chains, as well as in bottom deposits (BD). In particular, HMs can take a long time to gain a foothold in the root stalks of perennial aquatic plants. Excess of their content over the background values in the conditions of the Moscow region is a purely anthropogenic factor. Sources of environmental input can be any activity types: industry, agriculture, motor transport. However, the analysis of the heavy metals input in territories differently located about heat power engineering and oil refining facilities, allows us to assert that the main source is emissions through high pipes of enterprises of ash residues, while there are multiple exceedances of MAC in soils and surface waters, close to the pollution source. As you move away from the pollution sources, the content of HMs in snow, water, soil, and bottom deposits decreases significantly and tends to change over the years, which is associated with changes in the air-mass transport within the region.

1. Introduction

One of the most important indicators of the quality of natural waters, determining the possibility of their use, is the content of heavy metals (HMs), respectively, of their income and migration in the aquatic environment and in the catchment of water reservoirs devoted to the many works addressing this problem in various regions of the world [1], under conditions of relatively low pollution, for example, Upper Volga, Upper Volga water storage reservoirs [2–4]. At the same time, there are territories with high anthropogenic load and developed industry, where the receipt of HMs in the environment, including in water reservoirs, can pose a serious problem [5]. For example, the city of Dzerzhinskij, whose territory is directly adjacent to Moscow, is adjacent to CHPP 26 and the Moscow oil refinery, so that the pollution levels in the soils and water reservoirs on this territory significantly exceed the sanitary standards [6, 7]. An example of such territories shows that even the presence of a multi-stage gas cleaning system at enterprises that discharge combustion products through high pipes does not guarantee the complete absence of dust discharges containing heavy metal compounds. This problem is increased interest, due to the construction beginning of waste-to-energy facilities in the...
Moscow region, which also emit combustion products into the atmosphere, which in turn can have an additional negative impact on water storage reservoirs that serve as a water supply source. All HMs sources in the Moscow Region are anthropogenic, for the water storage reservoirs of the Canal named after Moscow, such can be HMs coming from the waters of the Volga source, land runoff coming from the reservoir basin as a result of various types of economic activity at the catch basin, including agriculture, industrial production, and municipal drainage generated in residential areas can also serve as a source, located on the catch basin of headwaters flowing into water storage reservoirs [3]. Another pollution source could be the emissions associated with the operation of motor vehicles. In the case of the discharge of ash residues through high pipes, the HMs dispersion area can reach 50 km. Fallen HMs in the catch basin, brought by the transfer of air masses, can migrate with land runoff to the water surface reservoir. This raises the question of placing such facilities, the construction of which is planned in the region, in the catch basin of a drinking water source. In the course of a comprehensive environmental investigation of water conservation zones, the waters of the Uchinsky and Pestovsky water storage reservoirs in 2018–2019, we conducted snow surveys, took samples of water, ice, soil, bottom deposits, determined their chemical composition, in particular the content of some HMs. A comparison of the data obtained with the already known data obtained during the water bodies survey will allow us to assess the trends of their changes in the future location of industrial facilities in the surrounding areas.

The purpose of the study is to assess the volume of HMs intake with air mass transfer and identify ways of their migration in the water reservoir, soils of the water conservation zone of the water storage reservoir.

2. Materials and methods
Snow surveys and sampling of ice, water, and bottom deposits in the central part of the reservoir's water area were conducted in the early spring period of 2018–2019 using generally accepted methods. Snow survey was carried out on the profile sites with the snow cores selection by the VS-43 weight snow gauge. Layer by layer snow selection was carried out with special wooden shovels from cores (length 35 cm, width 15 cm, height 20 cm). Ice sampling was performed using a borer. Soil and vegetation samples were taken during the summer period at sample areas located in the water conservation zone of water storage reservoirs. Geobotanical descriptions and descriptions of soil profile cut were carried out and were taken soil samples along the horizons. To determine the HMs content in selected samples, snow, ice, water, and soil, methods were used for determining mass-spectral with inductively coupled plasma (MS), atomic emission with inductively coupled plasma (AE) using iCAPQc mass spectrometers and Optima4300DV atomic emission spectrometers.

3. Results and discussion
The obtained data on the average content of certain HMs: iron, lead, and zinc cadmium, which differ in toxicity to environmental components and behavior when ingested in various environments, in selected samples of snow, ice, and bottom deposits, samples of which were selected in the water area and water conservation zone of water storage reservoirs in 2018–2019, are shown in table 1.2. The results of determining the same HMs in average soil samples taken at sample areas laid in the water conservation zone of the Pestovo water storage reservoir in a mixed forest 100–200 m from the water's edge, as well as moss samples were taken at the same areas, are shown in table 3.

Comparative analysis of the data in tables 1 and 2 shows changes in HMs concentrations in snow, ice, water, and bottom deposits at the sampling point — the middle part of the reservoir's water area in different years. Since sampling in 2019 was performed in late spring. There is a slight increase in the content of iron and zinc in the ice surface layer formed as a result of snow melting in winter. An increased concentration of elements such as Fe, Pb, and Zn in snow and the ice surface layer in both years indicates their precipitation with snow, that is, the supply is provided by the air masses transfer. The maximum content of these elements is observed in bottom deposits, that is, intrabasin processes contribute to active self-purification, HMs accumulation in bottom deposits. A fairly rapid decrease in
the concentrations of these elements in water is demonstrated and can be observed as a high bottom accumulation coefficient (BAC). Cadmium, on the contrary, gets into the water reservoir minimally accumulates in bottom deposits, its concentration in water and bottom deposits differ little some deviations can be explained by the influence of local pollution sources. Since the detected cadmium concentrations in snow and the ice surface layer in both years of observations are significantly less than its content in the bottom water and bottom deposits, the most likely source is the supply of water from the Volga source, as well as from the flow of headwaters whose catch basin is subject to large scale residential development (table 2).

Table 1. Average values of heavy metals content in snow, water, and bottom deposits of the central part of the Pestovo water storage reservoir in 2018.

| No. | Place of sampling       | Fe  | Pb  | Zn  | Cd  |
|-----|-------------------------|-----|-----|-----|-----|
| 1   | Snow surface            | 346 | 7.4 | 23.1| 0.1 |
| 3   | Surface ice             | 66  | 8.2 | 35.6| 0.02|
| 2   | Ice 20 cm               | 71  | 3.5 | 13.8| 0.05|
| 4   | Water 1.5 m             | 109 | 0.8 | 8.7 | 0.7 |
| 5   | Water 15 m              | 80  | 1.02| 11.2| 0.6 |
| 3   | Bottom deposits 15m     | 1289| 24.3| 237 | 0.54|

Table 2. Average values of heavy metals content in snow, water, and bottom deposits of the central part of the Pestovo water storage reservoir in 2019.

| No. | Place of sampling       | Fe  | Pb  | Zn  | Cd  |
|-----|-------------------------|-----|-----|-----|-----|
| 1   | Snow surface            | 116 | 4.2 | 14.6| 0.06|
| 3   | Surface ice             | 272 | 3.5 | 55.6| 0.08|
| 2   | Ice 20 cm               | 66  | 2.2 | 20  | 0.05|
| 4   | Water 1.5 m             | 78.5| 6.5 | 9.11| 0.34|
| 5   | Water 15 m              | 91.9| 1.1 | 7.8 | 1.47|
| 3   | Bottom deposits 15m     | 1135| 30.8| 254 | 0.78|

Table 3 also shows a different distribution of HMs in mosses, the soil of the water conservation zone of the water storage reservoir, iron accumulates significantly in the moss and soil profile, concentrations 8–10 times higher than its content in snow. Lead accumulates in the soil profile and mosses to a lesser extent than iron, its content is only 2.2–3 times higher than the content in snow. The zinc distribution in soils and mosses is generally the same for the lead. The cadmium content in mosses and soils is 2–3 times higher than in snow, while its concentration falls in deep soils, meaning that it can be assumed to bind the humus. The concentration difference of the considered HMs over the years revealed during snow surveys, which reaches 1.5–2 times, can be explained by changes in the atmosphere dynamics, in the prevailing wind, the amount of precipitation in the years under consideration, while cadmium in quantities multiples of its intake with precipitation may come from unidentified sources (table 2). All the HMs concentrations detected in this study in the water area of the water storage reservoir were significantly lower than the MAC.
Table 3. Average values of heavy metals content in soil and vegetation in the coastal area of the Pestovo water storage reservoir in 2019.

| No. | Place of sampling               | Content of elements, µg/kg | Fe  | Pb  | Zn  | Cd  |
|-----|---------------------------------|----------------------------|-----|-----|-----|-----|
| 1   | Peat dust                        |                            | 432 | 2.8 | 29  | 0.18|
| 2   | The average mnumer               |                            | 2290| 15  | 59  | 0.28|
| 3   | Mixed forest, soil horizon A0    |                            | 3686| 12.7| 51  | 0.28|
| 4   | Mixed forest, soil horizon B1, 25 cm |                      | 3215| 15  | 40  | 0.11|

Comparison of the data obtained in the study with the known results of similar studies performed for other areas of the Moscow region located significantly closer to potential sources of HMs emissions shows that the approach of the study area to potential sources of dust discharges into the atmosphere shows a significant increase in the concentration of HMs in soils and surface water bodies. There are increased concentrations of HMs in soils, at the level of 1-3 MAC, in water reservoirs up to 30 MAC for Pb, Zn, Cd, and have been repeatedly recorded in studies of the ecological state of Dzerzhinskij city, located in the influence zone of CHPP 26 and the Moscow oil refinery [6, 7].

A significant increase in HM concentration in all soils in the area and almost a tenfold increase in the water concentrations of several hydrologically not connected water reservoirs in the area, indicates an active release HMs with an ash industrial emissions on the soil surface and their migration with surface runoff, resulting in HM concentrate in water and bottom deposits.

The pollution pattern observed in this way corresponds to the known HM distribution when released through high pipes. It can be assumed that despite modern gas cleaning systems, some of the dust discharges of enterprises constantly enter the atmosphere and are dispersed over the surrounding area. Another source of dust can be ash dumps. This conclusion is very interesting in connection with the construction program in the Moscow region of waste incineration plants that use energy from garbage incineration to generate heat and electrical energy. At the moment, there are two enterprises of the SUE "Ecotechprom" in Moscow: the TPP using an alternative fuel type in Altufiev (MEP N 2) and MEP N 4, which is part of the complex for the neutralization and processing of solid municipal and biological waste in Rudnevo [5, 8].

Solid municipal waste (SMW), in contrast to fossil hydrocarbons, presumably serving as an HM source in the territory of Dzerzhinsk, contain plastic waste, which as fillers, dyes, widely used compounds of metals such as Zn, Ti, Pb, Cd, Fe, in quantities that are significantly large, sometimes reaching tens of percent by weight, which, despite the declared five-stage gas cleaning system increases the pollution risk, so when designing the location of such objects, it is necessary to observe the maximum distances from water use objects [9]. To verify these conclusions, additional studies of HM distribution in water reservoirs at different distances from emission sources are required.

4. Conclusion

As a result of the conducted research, it was found that the water area of the Pestovo water storage reservoir is characterized by a predominant supply of heavy metals such as iron, lead, and zinc, mainly with the air masses transfer within the region. Cadmium is detected in the water of the water storage reservoir in a concentration significantly higher than its content in snow, that is, its main source is the supply of water from headwaters or the Volga source. The amount and composition of HM determined in snow and water of water storage reservoir vary over the years as a result of changes in the atmosphere dynamics, but in all cases, the detected concentrations do not exceed the sanitary standards for these elements. A comparison of the pollution levels identified within the water-collecting area of the water storage reservoir with the territories most closely spaced the fuel and energy sector, for example, the Dzerzhinsky city, in which there are large TPP in the immediate vicinity.
vicinity is the Moscow oil refinery, with emissions to the atmosphere, shows a well-known pattern in the pollution distribution if released through tall pipes near the pollution source of the HM content in soil greatly exceeds MAC, the observed accumulation in water and bottom deposits of water reservoirs. Since the distance from the water area of water storage reservoirs to fuel power production objects is currently quite large, the existing pollution level is insignificant. The behavior of HM falling in the catch basin area is different, so zinc and lead accumulate in the soil of water conservation zones, bottom deposits, and cadmium is almost not accumulated and enters the water intake. Taking into account the results obtained, the only way to limit the flow of HM into the water of the water storage reservoir is to place fuel power production objects, such as waste incineration plants, at the maximum distance from the water source.

References
[1] Herut B and Kress N 1997 Particulate metals contamination in the Kishon River estuary Israel. Mar. Pollut. Bull. 34(9) 706–711
[2] Kolomiytsev N V and Korzhenevskiy B I 2017 Theoret. and Appl. Ecol. 2 24–8
[3] Tolkachev G U, Kolomiytsev N V and Korzhenevskiy B I 2017 Ameliorat. and water manag. 6 35–9
[4] Suslov S V, Gruzdev V S, Gruzdeva L P and Khrustaleva M A 2017 Ameliorat. and water manag. 6 12–6
[5] Trifonova T A, Podolets A A, Selivanov O G and Martsev A A 2018 Theoret. and Appl. Ecol. 2 94–101
[6] Shapovalov D A, Baloyan B M, Uxobotina E V and Chromov V M 2009 Ameliorat. and water manag. 6 2–23
[7] Riabova E G 2019 Theoret. and Appl. Ecol. 1 36–40
[8] Alioshina T A and Chernishev S N 2012 Bull. MSUCE 9 185–90
[9] Kolomiytsev N V, Korzhenevskiy B I and Tolkachev G U 2019 Use and resources conservat. in Russ. 2(158) 82–7