Mercury behaviour features in soils and bottom sediments of technogenic landscapes water bodies in the Rostov region

Anna Mikhailenko[1*], *Yuri* Fedorov[1], *and Daria* Kostenko[2]

[1]Institute of Earth Sciences, Southern Federal University, Rostov-on-Don, Russia
[2]Academy of Biology and Biotechnology, Southern Federal University, Rostov-on-Don, Russia

Abstract. Mercury is one of the priority pollutants entering the Rostov region`s water bodies from numerous natural and anthropogenic sources. Analysis of heavy metal extraction in the world indicates a reduction in its use in production. Based on expedition and laboratory studies, the mercury concentrations levels in soils and bottom sediments were determined. The bottom sediments of the region belong to the low and medium range of impact, areas of high pollution are formed within residential areas and in coal-mining areas. Hg concentrations do not exceed MPC in soils.

1 Introduction

The aquatic and terrestrial ecosystems pollution study by heavy metals is one of the current directions of modern geochemical research. Mercury is one of the most environmentally significant pollutants. The Rostov region water bodies are experiencing a powerful anthropogenic impact, a significant contribution to which is made by the coal deposits of the Donetsk basin, the coals and host rocks of which contain mercury in elevated concentrations [1-3]. It has been established that mercury emissions are currently observed along deep faults and their feathering cracks, as well as in areas of hydrocarbon exploration and production.

The mercury mining production dynamics in the world has been analysed (Figure 1). According to data [4-7], mercury consumption in many countries has significantly decreased. In the USA, that component has not been produced as the main mineral raw material since 1992, the metal is no longer used as part of dyes and in the production of batteries. Despite this, the highest production figures were recorded in 2017, whereas the values did not exceed 1400 tons in 2008.

Atmospheric local, regional and global transport of mercury contributes to the balance. Thus, it was determined that up to 28% of mercury from its total intake in the study area is transferred with atmospheric precipitation [8]. Also, a significant contribution is made by agricultural lands on which the mercury-containing fungicide granozan was used for some time, the use of which is currently prohibited. However, some of it may remain within periodically flooded zones [9].

* Corresponding author: mikhailenkoanna@gmail.com

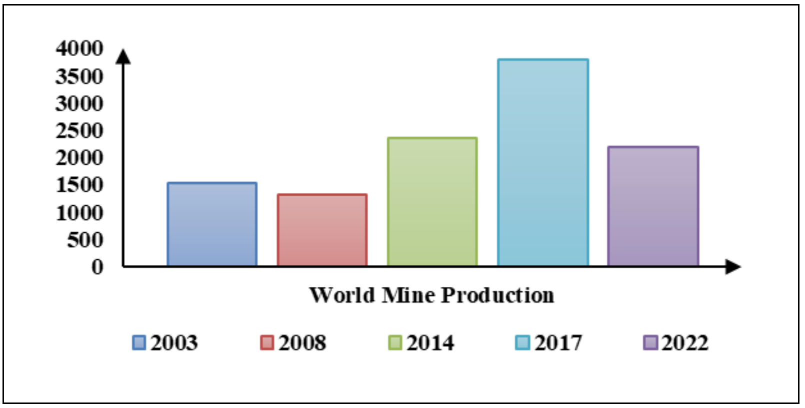

Fig. 1. Mercury production in 2003-2022 (tons) [4-7].

According to the data [10-13], the mercury content was 0.095 µg/g, with the maximum values reaching 0.14 µg/g d.m., and the minimum – 0.02 µg/g in the bottom sediments of the lower reaches of the Don River in the period 2013-2022 years. The average metal content was 0.021 µg/g (min – 0.007, max – 0.22 µg/g) in the region agricultural soils. It was shown in [14] that mercury concentrations vary from 0.024 to 0.126 µg/g d.m., and on average amounted to 0.063 µg/g d.m.in the bottom sediment layer (0-2 cm) of the Lower Don small and medium-sized rivers. In [15], the mercury content was analysed in the soils and bottom sediments of the Don river delta, it was determined that the concentrations ranged from 0.033 to 0.337 µg/g (on average 0.097 µg/g) and from 0.026 to 0.133 µg/g (on average 0.096 µg/g), respectively. The authors [16] note that the Hg content in soils did not exceed the MPC (2.1 µg/g) and was in the range of 0.035-0.065 µg/g (on average 0.053 µg/g).

2 Materials and methods

This work is based on data obtained within the framework of complex expedition work [17-18]. At the studied monitoring stations (Figure 2) sampling of soils and sediments was carried out according to the methods of GOST 17.1.5.01-80, GOST 17.4.4.02-84, GOST 31861-2012. The scientific group analysed samples of technogenic origin bottom sediments, within residential areas, as well as conditionally background sites located at a distance from major sources of pollution. The redox potential and pH parameters were determined using a voltmeter. Soils are represented by urbanozems and chernozems. The mercury content in the samples was measured by the authors according to the method of HDPE F 16.1:2:2.2.80-2013 (M 03-09-2013) on the analyser RA-915M in the interdepartmental laboratory of the Southern Federal University.

Using the Microsoft Excel program, a mathematical and statistical calculation of the data was performed and the Pearson correlation coefficients (r) between the physicochemical parameters and mercury concentrations in bottom sediments were calculated.

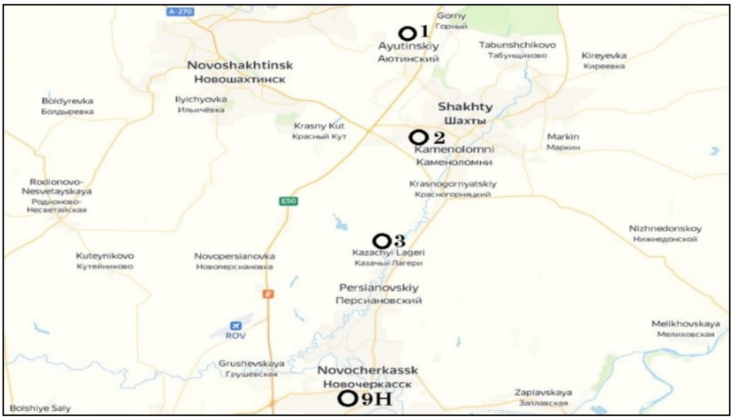

Fig. 2. Location map of sampling stations [17-18].

3 Results and Discussion

The data obtained for the three horizons 0-2, 2-5 and 5-10 cm are summarized in Table 1. It is determined that the maximum concentrations are characteristic of the upper layer of bottom sediments. The concentrations in the soils did not exceed the maximum permissible concentrations. At the same time, a very high correlation (0.97) was established between the metal content in soils and the upper layer of bottom sediments.

Table 1. Mercury concentrations in sediments and soils.

Horizon, cm	Concentration, µg/g d.m.		
	max	min	average
0-2 cm	0.986	0.043	0.373
2-5 cm	0.654	0.037	0.356
5-10 cm	0.372	0.033	0.233
Soils	0.580	0.04	0.21

Physicochemical parameters, such as the hydrogen index (pH) and redox potential (Eh), play an important role in the heavy metal's behavior, including mercury, at the "water-bottom sediment" boundary. In this regard, the analysis of their values in the selected columns of bottom sediments was carried out (Table 2). It was determined that the pH varied from 6.84 to 7.67, and the Eh data ranged from -224.2 to +367.9 mV, which determines the origin of both oxidative and reducing processes in lithosediments. It should also be noted an increase in the values of the parameters under consideration along the horizons – 0-2 cm < 2-5 cm < 5-10 cm.

Table 2. Eh and pH values in bottom sediments.

Station number	pH			Eh, mV		
	max	min	average	max	min	average
St.1	7.24	6.92	7.1	+367.9	-151.4	+175.1
St.2	7.48	7.33	7.4	+217.3	+210.8	+214.05
St.3	7.67	6.84	7.3	-129.0	-151.5	-137.8
St.9N	7.67	7.5	7.6	-136.4	-224.2	-173.1

At the station 1, located at the foot of the Ayutinskaya mine, a bottom sediments column with a capacity of 10 cm was a dense black silt, viscous, with a slight putrid smell.

The data of the hydrogen index indicate a neutral environment (on average 7.1). RedOx in bottom sediments is characterized by a high oxidative (on average +175.1 mV), as well as a reducing environment (Eh<0) in the upper horizon. The maximum mercury concentration of 0.99 μg/g d.m. is marked in the 0-2 cm horizon, which is a liquefied sludge. Rocky inclusions are noted in the 2-5 cm sediment layer, and an admixture of loam in the 5-10 cm layer. There is a gradual decrease in the metal content with depth, the minimum values – 0.372 μg/g d.m. are marked at 5-10 cm depth. The Hg average concentration in the soils at this site was 0.58 μg/g d.m.

At the station 2, located in the Yuzhnaya mine, the bottom sediments are composed of oily, black, granular silt, with a pungent smell of hydrogen sulfide. At a depth of 5-10 cm, there are traces of vegetation. The column capacity was 30 cm. The hydrogen index and RedOx value, as at the station 1, indicate the neutrality of the medium (7.4) and the oxidizing conditions (on average +214.05 mV). Mercury concentrations varied from 0.192 μg/g d.m. to 0.631 μg/g d.m. averaged 0.357 μg/g d.m. The maximum content is typical for 2-5 cm layer and practically coincides with the value recorded in this horizon at the station 1. The Hg average concentration in the soil was 0.11 μg/g d.m.

At the station 3, located on the Ayuta river, near the confluence with the Grushevka river, a sediments column with a capacity of 20 cm with a pronounced smell of hydrogen sulfide and a large amount of organic matter throughout the depth was selected. The pH values ranged from 6.84 to 7.67, which indicates a change in conditions from neutral to slightly alkaline. Ions in a chemical reaction have a high reduction capacity in terms of RedOx (on average -137.8 mV). Mercury concentrations here are significantly lower than at the previous two stations and vary from 0.033 to 0.043 μg/g d.m., averaging 0.038 μg/g d.m. The content in the soil was 0.04 μg/g d.m. The low concentrations relative to other stations are due to the considerable distance from the direct pollution sources.

At the station 9N on the Tuzlov river, a bottom sediments column with a capacity of 12 cm was selected, in which crushed stone and household waste were found. The sediments are not uniform in depth – the horizon is 0-2 cm sandy-silty, dark gray, 2-5 cm - a clay layer of dark gray, 5-10 cm – dense, clay, black, 10-12 cm - a layer of black, the structure is dense and clay, man–made inclusions have been detected. The pH and Eh values are comparable to the values typical for the station 3 (on average 7.6; -173.1 mV). Mercury concentrations ranged from 0.102 to 0.191 μg/g d.m., averaged 0.145 μg/g d.m. The average content in the soil was 0.11 μg/g d.m.

The evaluation of the close relationship between the physicochemical parameters and the mercury content in the bottom sediments was estimated by averaged values (Figure 3). A moderate direct positive relationship is characteristic of the resulting Hg – Eh pair (r = 0.46), whereas for the Hg – pH pair the situation is reversed (r = - 0.43). This indicates the specific nature of the environment and the direction of the processes occurring in them under the influence of natural and anthropogenic factors. In the work [14] devoted to that area of research, no correlation dependencies were established.

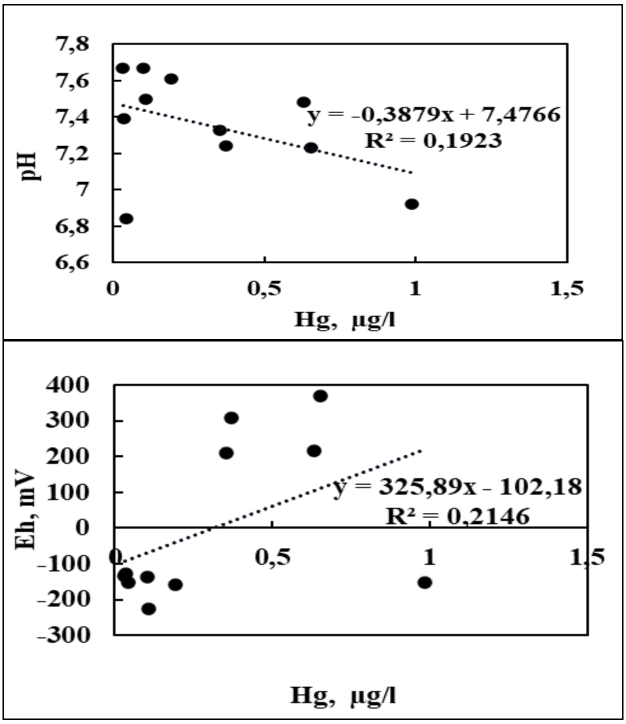

Fig. 3. Mercury concentration dependences in bottom sediments with physico-chemical parameters.

4 Conclusion

Based on the performed study, it can be concluded that the mercury content of the deposits under consideration belongs to the low and medium range of exposure, and their pollution level is due to the distance from the pollution`s source. Thus, the maximum values are typical for the upper layers of bottom sediments located in the immediate vicinity of the pollution source. The Hg concentration in soils did not exceed the MPC level, while the synchronous metal distribution in the media under consideration was established. The mercury accumulation and migration intensity in bottom sediments is in direct and inverse dependence with physicochemical parameters. The studied objects are characterized by a moderate positive correlation for the Hg – Eh pair (r = 0.46), and the reverse for the Hg – pH pair (r = - 0.43), which is slightly higher than the previously established correlation dependencies in this research area.

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References

1. L. Kizilstein, Ecogeochemistry of impurity elements in coals (2002)
2. V. Rylov, Yu. Fedorov, M. Gamov. Izvestiya, Vuzov. Severo-Kavkazskii Region, Natural Sci., **2**, **168**, 107-111 (2012)

3. V. Rylov, Yu. Fedorov, M. Gamov, SGEM, Bulgaria (2016)
4. U.S. Geological Survey, Mineral Commodity Summaries (2007)
5. U.S. Geological Survey, Mineral Commodity Summaries (2014)
6. U.S. Geological Survey, Mineral Commodity Summaries (2017)
7. U.S. Geological Survey, Mineral Commodity Summaries (2023)
8. Yu. Fedorov, A. Mikhailenko, L. Dmitrik, I. Dotsenko, D. Solodko, V. Chepurnaya, Limnology and Freshwater Biology, **1**, 838-839 (2020)
9. Yu. Fedorov, O. Berezin, M. Velichko, L. Predeina, Yu. Andreev, N. Khansivarova, Ecosystem studies of the Azov Sea and the coast, 150-166 (2002)
10. Ecological Bulletin of the Don "On the state of the environment and natural resources of the Rostov region in 2017" (2018)
11. Ecological Bulletin of the Don "On the state of the environment and natural resources of the Rostov region in 2019" (2020)
12. Ecological Bulletin of the Don "On the state of the environment and natural resources of the Rostov region in 2021" (2022)
13. Ecological Bulletin of the Don "On the state of the environment and natural resources of the Rostov region in 2022" (2023)
14. Yu. Fedorov, A. Mikhailenko, D. Garkusha, I. Dotsenko, L. Dmitrik, *Environmental problems*, Conf. Proceed. of the IX Int. Scient. and Pract.Conf., 650-655 (2020)
15. A. Mikhailenko, Engineering Bulletin of the Don**, 3**, **37**, 170 (2015)
16. S. Mandzhieva, T. Minkina, O. Nazarenko, N. Gromakova, E. Antonenko, L. Mashtykova, V. Chaplygin. Environmental, industrial and energy security – 2017, 840-843 (2017)
17. A. Mikhaylenko, D. Kostenko, Conf. Proceed. of the Water resources in the context of global challenges, **1**, 215-219 (2023)
18. Yu. Fedorov,V. Chepurnaya, D. Garkusha, I. Dotsenko, A. Mikhailenko, Yu. Popov, I. Gavrilova, Geology, Geography and global energy, **2**, **86**, 89-105 (2022)