Heavy metal distribution in the soils and benthal deposits of the seym basin

Elena Protsenko*, *Olga* Gridasova, *Mihail* Kumani, and *JuliJa* Rubanik

Kursk State University, Kursk, Russia

Abstract. Benthal deposits form under climatic, chemical, physical, biological, mechanical, and hydrological influences in water bodies and their surfaces. An analysis of the benthal deposits is integral for assessing the pollution rate in a water body as it indicates the extent of an anthropogenic impact on it. However, the existing methods of benthal deposit analysis are highly underdeveloped. This research aims to estimate the heavy metal pollution in benthal deposits of the Zheleznogorsk region headwaters, Kursk Region. In order to achieve the set goal, the authors formulated the following objectives: (1) to assess the benthal deposit pollution rate via the regional St. Petersburg assessment method (1996); (2) to assess the benthal deposit pollution rate via pollutant threshold limit values for soils; (3) to identify the top priority pollutants of the benthal deposits in the researched headwaters; and (4) to identify factors of heavy metal flow in benthal deposits. The research results revealed the inadequacy of soil sanitary norms applied to benthal deposits. At the same time, the regional St.Petersburg method has broader possibilities of application in the assessment of benthal deposits. However, it requires adjustment to the environmental conditions of the Central Black Earth zone due to composition differences between soils and benthal deposits. The following metals exceeded the ambient content level in the benthal deposits of Zheleznogorsk region headwaters, Kursk Region: chrome, nickel, iron, and zinc. High iron content in rivers has been registered both in the proximity of the Mikhailovsky mining and processing plant [MMPP] and quarry and in headwaters located near the living areas of Zheleznogorsk far higher than the MMPP. All the water collection basins reviewed in this study demonstrated an even distribution of pollutants with no major divergence from the norm around the MMPP-related objects. However, the pollutant concentration exceeded the limit near all the living areas.

1 Introduction

The chemical composition of benthic deposits is traditionally associated with their compounds and mineral constitution. Consequently, the concentration of macro- and microelements in the deposits reflects the mentioned properties.

The content of absorbed sediment microelements depends directly on the dispersion of a fine fraction and its share in the total sediment mass [11; 12]. The organic matter in the

* Corresponding author: protselena@yandex.ru

sediment also positively affects its microelement content. However, nowadays, apart from natural impacts, all components of the environment experience anthropogenic influence. Physical factors affecting the environment include such aspects as the particle-size distribution of sediments or the water catchment area. They contribute to an increase in the metal content of benthal deposits. Chemical factors affect the change in metallic content in benthal deposits and the form of metals and play an important role in the sediment differentiation and prognosis of the biological availability of microelements. This group of factors includes adsorption, diffusion, and inclusion into the crystal structure of minerals [13,14].

A pollution extent of a waterbody cannot be conducted without an analysis of benthal deposits. However, even the research of a single object can demonstrate mixed results due to varying properties of benthal deposits. The output proportion of an element in the sample depends on its moisture content, density, and particle-size distribution.

The microelement content of benthal deposits can be found via the following methods [6]: (1) no adjustment; (2) adjustment; (3) adjustment to the organic matter content; and (4) natural concentration ratio, preindustrial content ratio, etc.

The metallic compounds are determined based on the specificity of pollution sources. At present, the monitoring priority is given to mercury, copper, zinc, cadmium, plumbum, and chrome. To assess freshwater benthal deposits, biological and chemical methods are applied. The biological approach aligns benthal deposit characteristics with pollutant-induced pressure. However, it often fails to point out the reasons for the resulting biological effects. On the other hand, the chemical methods compare to it favorably as they can be applied more easily and can serve as a foundation for modeling methods. However, the interpretation of the heavy metals [HM] content in benthal deposits remains a topic of open discussion due to a lack of united assessment methods and norms.

Benthal deposits provide data necessary for tracking the dynamics of natural water catchment processes and enable the diachronic analysis of the anthropogenic pressure due to varying formation pace. Therefore, they serve as an indicator that illustrates the human-made influence of water bodies [5].

The primary pollutants entering water collection basins become the source of secondary pollution once their content in benthal deposits reaches critical limits. This factor brings about the necessity to regulate the pollutant content in benthal deposits. Today, existing standards for soils are often used for this purpose. However, despite benthal deposits having similar compositions, they differ from soils in both the formation and the fields of application. Therefore, such methods cannot provide a correct estimation.

2 Materials and methods

There are no regulations for the benthal deposit assessment in the Russian Federation. Sanctuary and toxicological aspects, as well as the lack of a united pollution monitoring system for benthal deposits, led to the absence of federal legislation regulating threshold limit values [TLV] and other relevant indicators for benthal deposits. This situation significantly complicates the assessment of their pollution rate [8].

In the current situation, the authors highlight the fact that there are existing organizational requirements for pollutants content monitoring in benthal deposits. The described regulations form a part of the monitoring system for open waters executed by special federal and local authorities. Their responsibilities include, among other matters, the control of the pollutant content in benthal deposits. The most common pollutants with the ability to accumulate are listed in the Guidance on the governmental waterbody monitoring regarding its organization and control over the pollutant content in benthal deposits of water bodies [9; 10]. The monitoring system aimed to control the state of benthal deposits is based on an analysis of their chemical contamination and toxicity. This data later serves as the basis for the organizational requirements regulating the monitoring procedures for benthal deposits and the pollutant content in them. In order to achieve this objective, a sample selection is performed in the survey points. The latter include areas near effluent disposal points of industrial or agricultural facilities, in areas with a record of unsatisfactory water quality, in areas of mixed use (monitoring observations, leach to the sea observations, observations in transboundary waters, etc.). However, the common standards for the area remain lacking. The same stagnation can be seen in the development of regional regulations [7].

The federal subjects are expected to develop individual regulations for benthal deposit monitoring. However, in practice, a full-fledged standard was introduced only in St. Petersburg in 1996. Despite being described as a temporary solution operating until an analogous federal regulation is implemented, the document in question is still in force [2]. In the current situation, of great interest is the application of this document to benthal deposit assessment in other regions, including those far removed from St. Petersburg.

This study aims to assess the heavy metal pollution in benthal deposits of the Zheleznogorsk region headwaters, Kursk Region. In order to achieve the set goal, the authors formulated the following objectives: (1) to assess the benthal deposit pollution rate via the regional St. Petersburg assessment method (1996); (2) to assess the benthal deposit pollution rate via pollutant threshold limit values for soils [3; 4]; (3) to identify the top priority pollutants of the benthal deposits in the Zheleznogorsk region headwaters; and (4) to identify factors of heavy metal flow in benthal deposits of the Seym headwaters on the territory of the Zheleznogorsk region, Kursk Region.

The area under research is situated southeast of Zheleznogorsk in the northeastern part of the Zheleznogorsk region, Kursk Region. The authors collected five samples of benthal deposits in five rivers suffering the greatest exposure to the influence of the mining and processing complex (BeliyNemed, Pesochnaya, Chern, Ryasnik, and Rechitsa). The benthal deposits underwent a laboratory analysis in terms of the total heavy metal content in the ecomonitoring facility of the Kursk State University. The authors utilized the voltammetric analysis method (with mercury and arsenic) and the atomic absorption method through a QUANTA ZETA spectrometer unit.

The sampling was conducted following the river tide with an uneven step length due to specific landscape features of riversides. Respective coordinates were assigned to each sample. This allowed the authors to transfer them to a map and calculate the distance from the river head. Furthermore, they examined each sampling point in terms of the anthropogenic influence in their proximity.

3 Results

Zheleznogorsk was founded in 1957 as a part of the industrial development of the Mikhailovskoye iron ore deposit. The city population is approximately 100,000 people, while its area equals 133.37 km^2. Zheleznogorsk is the second largest city of the Kursk Region. Industrial production constitutes the basis of its economy. The city hosts large and medium enterprises in pulp and paper, food, and mechanical industries, including 18 market leaders. The majority of employment positions in the city are provided by the Mikhailovsky mining and processing plant.

Such a high number of industrial facilities within a limited territory, especially iron ore mining, leads to the development of the Zheleznogorsk ecological pressure area.

The iron ore has been mined in the Mikhailovskoye deposit since 1960. The surface mining technique utilized in the deposit leads to a range of environmental issues, including the deterioration of a natural landscape, soil disturbance, groundwater shortage, changes in hydrological and hydrochemical properties of water bodies, air pollution, chemical flow, extinct biota, lower health and life quality of the population.

As mentioned in the previous section, in this study, the authors compare the heavy metal content in the benthal deposits of the Zheleznogorsk headwaters calculated according to the Hygienic standards for soils [3; 4] and Standards and criteria for assessing the contamination of bottom sediments in water bodies of Saint Petersburg [2]. The latter regulation is also based on the regional standards for soils and their threshold limit values [TLV], tentative permissible concentration [TPC], sanitary regulations on the arsenic and heavy metals contents, and State Union Standards [GOST]. The St. Petersburg regional standard identifies four classes of benthal deposit pollution and four hazardous effects, respectively: class 0 - pure deposits (target objective), class I - mildly polluted deposits (threshold value), class II - permissibly polluted deposits (a supervision level), class III - highly polluted deposits (an intervention level), and class IV - hazardous deposits.

A comparison of the St. Petersburg regional standard for benthal deposits and common TLV/TPC regulations for soils reveals that for soils, a threshold content of every substance except mercury is significantly more strict. For mercury, the soil TLV is 2.1 mg/kg, while benthal deposits are deemed highly polluted when the mercury content reaches 1.6 mg/kg.

None of the discussed regulations is fully suited for the area studied in this paper. Benthal deposits differ from soils and therefore demonstrate different pollution rates with the same pollutant concentration. The assessment of benthal deposit pollution according to the St.Petersburg method is presented in Fig. 1. The colored conventional symbols on the map represent the main pollutant metals that exceeded the threshold content value. As seen in the picture, these include chrome, nickel, iron, and zinc. The purest benthal deposits were found in the Pesochnaya river. There, the authors only detected a nickel excessive concentration in two locations, which is most probably coincidental.

The benthal deposit pollution assessment based on the standards for soils is presented in Fig. 2. The picture indicates a higher frequency of TLV violations for heavy metals that stems from the soil regulations having a more strict nature. In the picture, the conventional symbols for TLV violations are colored green. In both cases, the authors have detected heavy metal pollution, although the degrees vary depending on the analysis method. However, they consider the results obtained through the St.Petersburg method to be of more interest as it enables the assessment of different pollution levels in benthal deposits according to their use. Fig. 1 shows that all four pollution levels can be found in the headwaters of the Zheleznogorsk region. Benthal deposits do not serve the same purpose as soils and are not involved in agricultural plant cultivation.

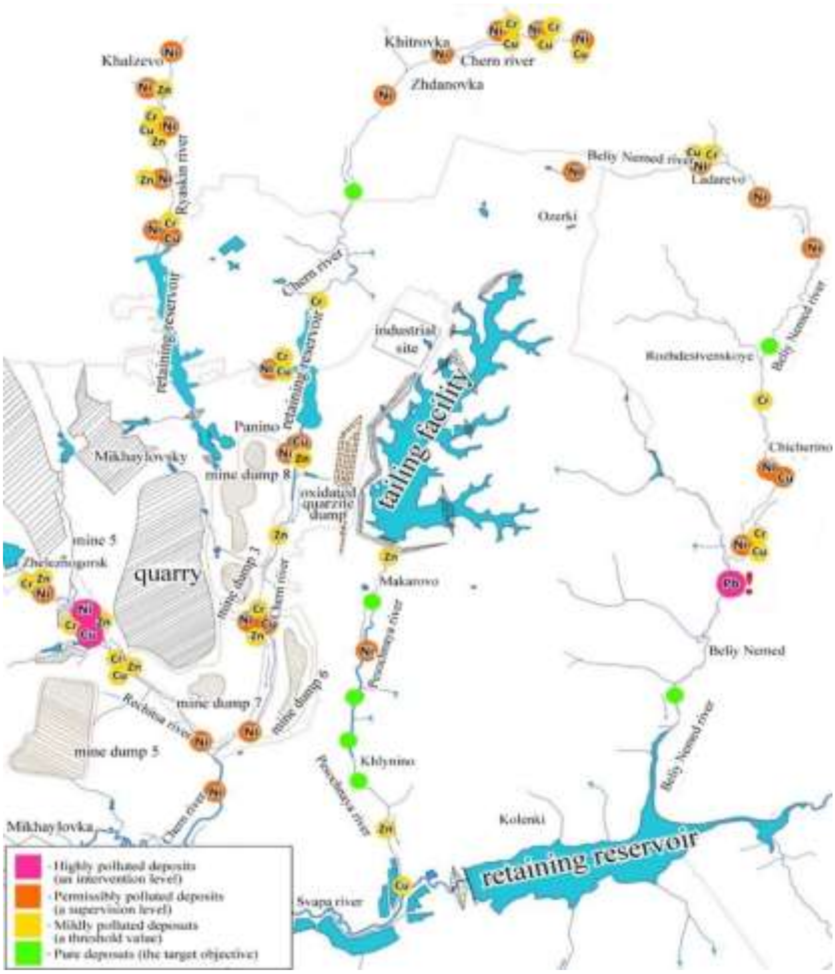

Fig. 1. A map demonstrating the distribution of heavy metal contents in the benthal deposits of the Zheleznogorsk region headwaters, Kursk Region, according to the St.Petersburg standards [2]. *Source*: Compiled by the authors.

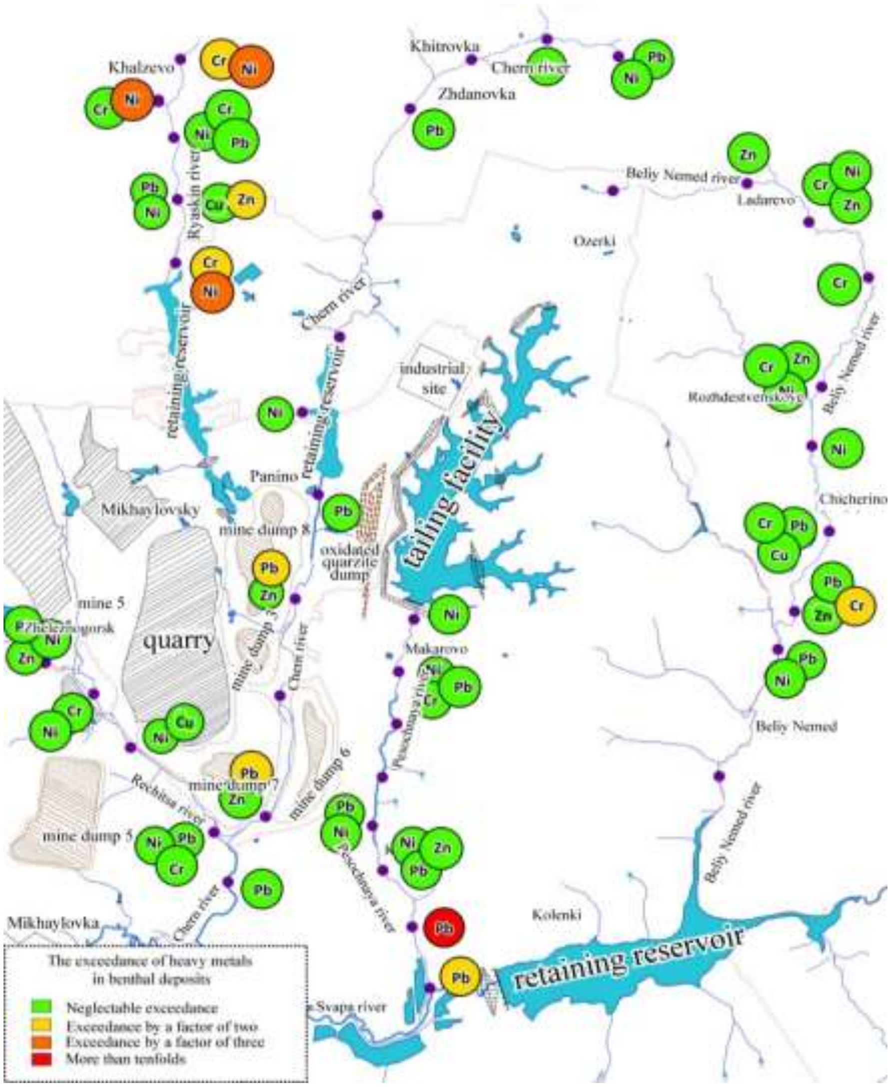

Fig. 2. A map demonstrating the distribution of heavy metal contents in the benthal deposits of the Zheleznogorsk region headwaters, Kursk Region, according to the hygienic standards for soils [3; 4]. *Source*: Compiled by the authors.

4 Discussion

The Mikhailovsky mining and processing plant [MMPP] is the major source of environmental pressure in the Zheleznogorsk region. However, the authors consider other sources of anthropogenic influence in the proximity of the water collection basin under review. Among these are living areas, industrial facility sites, agricultural lands, motorways, and railways. Given that heavy metals come to water collection basins from upper layers of the erosional pattern, every urban territory in the proximity can serve as a pollution source. The authors register elevated iron content in the Chern and Rechitsa rivers not only near the MMPP excavation quarry but in the river heads and near living areas of Zheleznogorsk as well as towns Halsevo and Hitrovka. Pollution is rather consistent in all the water collection sites under examination. No pollutant contents extremely exceeding the standards were registered near the MMPP objects. However, the authors found significant violations of the standards in every living area. In the previous studies [1,10], the authors analyzed dust discharge from the MMPP as a possible pollution source. However, the obtained data indicated that the content of pollutants and heavy metals in iron ore and all its byproducts was much lower than the TLV for soils. A profound analysis of heavy metals distribution in the soil ascertained this conclusion. The authors did not find statistically relevant cases of heavy metal pollution within the sanitary zone of the plant for the period of 45 years. Water surface pollution was localized to minor river stretches near spills of drainage waters and effluents. This study presents the data on benthal deposit pollution with the six heavy metals. Its interpretation requires new methodological approaches to determine the source of the detected pollutants.

In the examined case, the pollutants in benthal deposits of the headwaters can stem from minor industrial facilities, motor transport, community utility systems, and human waste. In minor living areas along the rivers, illegal waste dumping occurs. Moreover, according to the data by environmental protection organizations, lands in proximity suffered from sewage discharge that was aggravated by rain and melting sewage from the nearest living areas. A flawed storm-water sewer and a lack of any kind of a purifying system in it can be the reason for the benthal deposit pollution.

5 Conclusion

The environmental state of benthal deposits directly depends on the pollution of water catchments and soils along rivers. Substantial anthropogenic pressure in the researched region stems from a high concentration of industrial facilities in it, active agricultural land development, and an inadequate community service system.

The main metals that exceeded the content standards in the headwaters of the Zheleznogorsk region, Kursk Region, were the following: chrome, nickel, iron, and zinc. The St.Petersburg assessment method resulted in the most objective and noteworthy data of the pollution distribution in the benthal deposits. The mentioned assessment system allowed the authors to attribute the pollution rates of analyzed deposits to their use. However, an original assessment method should be compiled for the Central Black Earth zone.

The location of pollutants in the benthal deposits of the Zheleznogorsk region, Kursk Region, indicates that the local living area sewage is the source of pollution.

To alleviate the environmental pressure of water catchments, the authors pose the need for research of the heavy metal content in the soils of the region. Additionally, they propose measures to prevent effluent outflow from agricultural lands to waterbodies. The authors point out the necessity to rework the system of rain and melting sewage in the living areas as the mixed storm drainage sewer is unacceptable under such a level of anthropogenic pressure.

References

1. A. A. Borzenkov, I. A. Goneev, M. V. Kumani et al., Regional Environmental Issues **1**, 40–44 (2010)
2. Chief State Sanitary Doctor for Saint-Petersburg (1996) Standards and criteria for assessing the contamination of bottom sediments in water bodies of Saint-Petersburg (Saint-Petersburg, 1996)
3. Chief State Sanitary Doctor of the Russian Federation (2006) Hygienic standards GN 2.1.7.2041-06. Maximum permissible concentrations (MPC) of chemicals in soil (Moscow, 2006)

4. Chief State Sanitary Doctor of the Russian Federation (2009) Hygienic standards GN 2.1.7.2511-09. Approximate permissible concentrations (APC) of chemicals in soil (Moscow, 2009)
5. V. A. Dauvalter, *Geoecology of Bottom Sediments of Lakes* (Memek State Technical University, Murmansk, 2012)
6. U. Forstner, G. T. W. Wittmann, *Metal Pollution in the Aquatic Environment* (Springer-Verlag, Berlin, 1979)
7. D. V. Ivanov, Regional standards for the quality of bottom sediments of water bodies (2009), https://www.elibrary.ru/item.asp?id=41268022
8. N. I. Kurakina, N. S. Shlygina, LETI Transactions on Electrical Engineering & Computer Science **4**, 207–210 (2017)
9. Ministry of Natural Resources and Environment of Russian Federation, Order of the "On Approval of the Guidelines for the Implementation of State Monitoring of Water Bodies in Terms of Organizing and Conducting Observations of the Content of Pollutants in the Bottom Sediments of Water Bodies" (Moscow, 2014)
10. E. P. Protsenko, I. V. Glebova, N. P. Nevedrov, Eurasian Soil Science **51(1)**, 112–119 (2018)
11. Decree of the "On Approval of the Regulations on the Implementation of State Monitoring of Water Bodies" (Moscow, 2007)
12. N. M. Strakhov, Geohimiya **6**, 28–39 (1956)
13. N. M. Strakhov, *On the Theory of the Geochemical Process in Humid Zones. GeokhimiyaOsadochnykhPorodiRud* (Nedra, Moscow, 1968)
14. E. V. Venitsianov, R. N. Rubinstein, *Dynamics of Sorption From Liquid Media* (Nauka, Moscow, 1983)