Ecological assessment of bottom sediments for conditions of an agro-industrial region with high anthropogenic load

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Abstract. Areas of active farming undergo significant soil erosion at catchments and pollution of surface waters and bottom sediments. When these issues in mining regions are coupled with the effects of drainage water and dust emissions from open-pit mining, it becomes critical to evaluate and monitor contamination of water bodies and bottom sediments. The aim of this work was to compare the ecological and geochemical characteristics of sediments in water bodies within the Kursk Magnetic Anomaly (KMA), which has open-pit mining, with rivers and ponds affected by agro-industrial effluents, excluding the impact of drainage water. The concentrations of several heavy metals (Pb, Zn, Cu) and organic matter content in bottom sediments were greater in the Belgorod Oblast than the iron ore district. When using indicators of regional background for KMA water bodies, the man-made impact on sediment pollution was determined, which is reflected in excess concentrations of Mn, Zn, Cu (from 1.5 to 2.8 times). Research of surface and groundwater transformations, their interactions, and the peculiarities of pollutant migration provide the foundation for developing a monitoring system for water bodies affected by mining operations to support management decision-making.

1 Introduction

Research on erosion and accumulation processes in cultivated land with position-dynamic microzones on slopes is based on the understanding that a series of soils along the slope gradient is accompanied by changes in infiltration, washout conjugation, re-sedimentation, and solid matter deposition [1]. Recently, the ecological aspect has been increasingly considered when using the concept of catena, leading to the formation of the idea of cascade landscape-geochemical systems, which is driven by the need to include indicators of diagnostics of geochemical transformations in both migration flows and depositing environments [2,3]. Modern approaches to studying erosion and accumulation processes in agricultural catchments include assessments of erosion losses of soil particles that can absorb pollutants (agrochemicals) [4], as well as the study of pollutant migration pathways from arable slopes into rivers and further into ponds and reservoirs [5,6]. Ecological tensions in

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agricultural catchments and their associated surface waters have stimulated the development of topics that include the assessment and monitoring of heavy metals (HM) and other pollutant contamination in both water masses in rivers and reservoirs and in the bottom sediments [7–9]. These issues are particularly prevalent in mining areas, where the chemical composition of surface water is determined not only by liquid runoff from agricultural catchments and wastewater from municipal services of settlements, but also by mine drainage water [10–12].

The aim of this work was to conduct an ecological and geochemical assessment of bottom sediments from water bodies (river, pond) in the river basin, which is located in the iron ore mining area, and to perform a comparative analysis with the spectrum of pollutants for sediments from a larger region outside the iron ore mining areas.

2 Materials and methods

The resource specificity of the Belgorod Oblast is characterized by the presence of 15 iron ore deposits with a total reserve of over 50 billion tonnes (37% of Russia's reserves) and an annual ore production of 60 million tonnes. Based on this, the chosen study area is the Stary Oskol – Gubkin KMA mining district. The area of the region (within administrative boundaries) is 3220 km^2. The territory is characterized as a typical forest-steppe, with an average annual temperature of 7 °C and annual precipitation of 590 mm. The close proximity of the crystalline basement (60 m from the surface) determines the maximum elevation of the Belgorod Oblast terrain (altutude up to 276 m a.s.l.). The agricultural development of land is high, with 78% of it being agricultural land and 63% being arable land. Mining, particularly open-pit mining using blasting, causes significant environmental damage due to the release of dust, heavy metals (HM), and combustion products into the atmosphere. The Stary Oskol - Gubkin district leads in terms of pollutant emissions into the air from industrial enterprises, accounting for an estimated 74% of all emissions in the Belgorod Oblast.

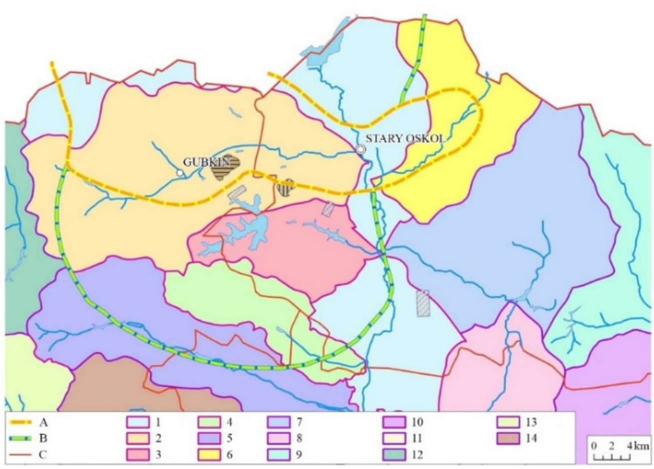
The results were obtained during the implementation of the "Development of Water and Forestry in the Belgorod Oblast" program, which planned for the clearing of channels and water areas for priority water bodies from 2022 to 2025. To this end, local communities formed a pool of 740 sites, including rivers, ponds, and reservoirs. This paper presents the findings of the study of the ecological and geochemical condition of bottom sediments in the western and central parts of the Belgorod Oblast in 2022–2023 (n=65), as well as a specialized study in the east (KMA region) for 9 sites in 2023. Bottom sediments were sampled to a depth of 0.5 m, with each sample taken in triplicate. The ranked list of metals and metalloids for river sediments in the region (Pb, Zn, Co, V, Ni, Cu, Cr, As, Mn, Fe) considered ecotoxicological hazard assessments in The Netherlands [13], with some additions according to national standards and regional geochemical specificities. Standard methodology (Register number FR.1.31.2012.13573) was utilized to determine the concentrations of metals and metalloids in bottom sediments. The atomic absorption method (SKU: RUSS275341) was utilized for measuring the mass fractions of toxic metals in soil samples. Additionally, the content of organic matter (OM) was determined in accordance with GOST 26213-2021.

The primary goal of dredging and cleaning river channels and water areas within the regional program "Our Rivers" was to create recreational areas near settlements and maintain water quality according to fishery standards, while river water contamination by various heavy metals poses a human health risk [14]. A unified methodology for the ecological assessment of sediments in natural and artificial water bodies has not been developed in Russia, leading to differences in approaches to sediment assessment [15]. The calculation of pollutant concentration factors necessitates the selection of background values. Given the changes in solid effluent in the aquatic environment, it is reasonable to use concentrations of pollutants in sediments sampled upstream of the river channel relative to the study area as background concentrations. However, other indicators are often used as background values: the abundance ratio of rocks, sediments or soils, as well as geochemical background and Maximum Permissible Concentrations (MPCs) of soils [15]. With this in mind, our study made comparisons according to three criteria: regional geochemical background (RGB) (based on bottom sediments data at nine sites in the headwaters of the region's rivers (RGB-2)); a conditional background based on sediment data in Bayou Lake at the beginning of the Oskol River tributary after the river receives six tributaries 85 km downstream (RGB-1); and soil MPCs.

3 Results and discussion

Each of the municipal territories (Stary Oskol and Gubkin urban districts) encompasses the basins of five rivers, with four rivers common to these districts. Among these, the Oskol River (with a total length of 472 km, 227 km of which is within the Belgorod Oblast, accounting for 57% of the basin area) serves as the region's primary water artery. The contribution of drainage water from two mining and processing plants and the Stary Oskol water canal to the pollution of the Oskol River can be assessed at two sites: at the headwater, where the water is classified as "clean", and at the border with Ukraine, where, even after self-purification of the river waters, they are classified as "moderately polluted" due to the level of pollution (in fractions of Maximum Permissible Concentrations (MPCs)) by oil products (3.3) and total iron (1.5)).

Within basins, the dependence of geosystems on the direction of runoff and hydrological and geochemical processes is reflected, providing a comprehensive view of the formation of the water regime, as well as sediment and dissolved matter migration [16]. The results of the GIS analysis of the hydrogeological impacts of open-pit mining of iron ores, presented on the Figure 1, show that the area of basins affected by mining operations (due to drainage and waterlogging of the catchment area) is 75,480 ha in Gubkin urban district and 46,476 ha in Stary Oskol urban district.



Boundaries: drainage (A); flooding (B); administrative districts (C). River basins: Oskol (1); Oskolets (2); Chufichka (3); Dubenka (4); Orlik (5); Ublja (6); Kotel (7); Kotla (8); Borovaja Potudan' (9); Grjaznaja Potudan' (10); Okunevskiy Jar (11); Seiym (12); Korocha (13); Ol'shanka (14).

Fig. 1. Distribution of river basins on the territory of the Starooskol-Gubkinsky agro-industrial region and the boundaries of drainage and flooding zones under the influence of open-pit mining of iron ore.

Open-pit mining underscores the need for a comprehensive understanding of the catchment, as groundwater basins have a complex relationship with the topography of river catchments. The creation of man-made landscapes (quarries, dumps) has led to the formation of new types of water bodies (hydraulic dumps, mud dumps, etc.). The disturbance zone of groundwater in the vicinity of the two quarries ranges from 6 to 29 thousand km^2, varying across different horizons. The Oskolets and Chufichka rivers (No. 2 and 3 on the Figure 1) exist due to the discharge of waste and industrial water from the iron ore and related industries. Pollutants accumulate in the bottom sediments, which in years of low water become sources of secondary pollution, impacting benthic plants and organisms. During the ecological assessment of bottom sediments, it is important to consider that the development of deposits, creation of man-made reservoirs, and the pumping and discharge of drainage water into the river network have increased the average annual runoff (by 10–30%) and minimum summer runoff (by 60–80%), enhancing the rivers' self-purification ability [17].

The Belgorod Oblast stands out from other regions due to its highest rates of soil water erosion losses [18]. In the total area of the Belgorod Oblast (27.1 thousand km^2), eroded soils make up 59%. Throughout the region's agricultural history, soil losses are estimated to equate to an average annual erosion rate of 6 t ha^{-1}, a rate that is an order of magnitude higher than soil renewal rates [19]. The large volumes of solid runoff exceeded the self-purification capacity of river water, leading to the siltation of river channels. This was the primary reason for a 35% reduction in the length of the region's river network compared to its state 350 years ago [20].

Solid runoff, formed by erosion in the catchment, undergoes transformations before it reaches water bodies. The analysis of particle size distribution and OM content in dealluvial sediments reveals that erosion selectively chooses silt fractions and particles with lower density due to their OM enrichment. Simultaneously, it's important to note that due to the transformation of organic-mineral matter, which is determined by the specific life in a particular water body, bottom sediments differ from dealluvial and floodplain sediments. Bottom sediments in rivers and freshwater bodies form under the influence of biogeochemical, microbiological, and physical-mechanical processes from the remains of plant and animal organisms living there, the transformation of solid runoff from the catchment area, and the aerial input of mineral and organic impurities.

The results of the soil loss assessment using the adapted USLE model [21] showed that in the KMA region, the density of areas with increased erosion hazard (16–25 units per km^2) is highest in the Belgorod Oblast, and the area of arable land with high erosion hazard (> 20 t ha^{-1} for fallow land conditions) exceeds 10,000 ha [22]. Erosive solid runoff from agricultural landscapes in river catchments includes not only agrochemicals and biocides but also dust emissions from mining operations. Previously, using a basin-wide approach to soil conservation land use [16, 23], it was determined that due to the impact of mining operations, the implementation of ecologically oriented farming was necessary for seven agricultural enterprises across a total area of more than 5000 ha [24].

The land and water bodies near the mining and processing plants are exposed to HM contained in colloidal dust particles. The source of HM accumulation is gas-dust clouds from explosions conducted at quarries, as well as dust blown from quarries and rock dumps (at varying distances from 1100 to 4200 kg/ha per year). Overburden dumps serve as sources of iron inputs to the surrounding lands. Our studies of mining and processing plant dumps revealed that the upper horizons of embryonic soils contained an average of 1.40±0.39% Fe, while parent rocks contained between 3.3 to 4.0% Fe.

In iron ore districts, the release of drainage water from open pits leads to the contamination of surface water, primarily by manganese, iron, and copper ions [17]. The HM content in surface water samples in the mining zone (man-made water bodies, ponds, the Oskolets River) indicates a significant excess of standard indicators for Pb and Cd (on average 12 and 17 times, respectively), as well as for iron (on average 1.8 times). The man-made load on surface waters is reflected in the changes in the geochemistry of bottom sediments, particularly in the concentration of key HMs (Table 1). When comparing average values for eight water bodies in the Oskol River basin and its tributaries, the highest exceedances of RGB-1 (in Bayou Lake) were observed for Mn (2.84 times), Zn (1.66 times), and Cu (1.45 times). Four river stations showed exceedances above the RGB for OM content, while no exceedances for Pb were recorded.

Table 1. Content of heavy metals in the bottom sediments of water bodies of the KMA in comparison with the RGF and arable soils in the Belgorod Oblast.

Gate number	Coordinates	Water body	Pb	Zn	Cu	Mn	OM
			ppm				%
1	51°11'44" N 37°26'51" E	pond	4.5	32.8*	8.8	341**	1.8
2	51°17'00" N 37°35'20" E	river	7.4	53.7**	15.3*	428**	5.8*
3	51°18'30" N 37°50'28" E	river	6.8	42.1*	17.5*	235**	7.6**
4	51°17'34" N 37°49'39" E	river	7.7	54.6**	15.2*	435**	5.5*
5	51°17'22" N 37°43'54" E	river	7.4	20.0	10.8*	143*	2.6
6	50°54'41" N 37°46'23" E	river	9.2	51.0**	14.5*	410**	4.7*
7	50°54'05" N 37°46'08" E	river	10.5	61.1**	15.9*	361**	2.0
8	50°51'52" N 37°46'11" E	river	10.7	55.7**	14.7*	527**	1.7
Average	–	–	8.0±0.7	46.4±4.9	14.1±1.0	360±43	4.0±0.8
RGB-1	50°45'23" N 37°51'35" E	Bayou lake (Oskol R.)	12.9±0.2	28±0.1	9.7±0.2	126.93±0.3	4.1
RGB-2	–	River sources	18.7±1.0	44.0±4.0	20.8±2.3	174.6±36.9	5.9±1.6
–	–	Arable soils	13-16	37-43	14-16	400-800	5.0-5.3

Note: One or two asterisks indicate excesses of heavy metal content over RGF-1 and RGF-2. respectively. Rivers: No. 2. 4. 5 (Oskolets River); No. 3. 6-8 (Oskol River).

The samples collected for the ecological assessment of sediments in rivers and ponds in the west and center of the Belgorod Oblast (n=65) indicated that among HM in sediments, the highest MPC exceedances were observed for Mn, Cu, and Pb. Sediments in eight sites, typically urban rivers, were characterized by unacceptable levels of pollution due to HM, which according to the number of RGB exceedances form a ranked descending series: Zn > Mn > Fe > (Pb, Cu, Ni) > Cr > As. A comparison of average HM concentrations in bottom sediments of eight water bodies of KMA and in arable soils of the Belgorod Oblast shows that, with the exception of zinc, the values of other HMs are comparable, meaning they do not pose an ecological hazard if bottom sediments are used as ameliorants. The mean OM content of sediments was 4.39±0.45%, which was less than that of the arable soil horizon (Table 1). However, due to the content of Mn, Cu, and Zn being comparable to that of arable soils, the use of bottom sediments in the reclamation of poor soils (sandy, eroded, etc.) would be justified. Manganese plays numerous beneficial roles, and its deficiency in soil can lead to reduced OM synthesis and chlorophyll content, resulting in chlorosis disease in plants [25].

In bottom sediments, the manganese content is significantly lower than that in the arable horizon of agricultural soils, even in regions with strong man-made pressure, and is four to five times lower than the MPC established for soils. Copper is one of the biologically important and essential trace elements, and a deficiency in copper often coincides with a deficiency in zinc. However, at high concentrations, copper can become a dangerous phytotoxicant. Our studies revealed that the copper content in bottom sediments from various areas ranged from 14 to 22 mg kg^{-1}, significantly lower than the MPC value of 40 mg kg^{-1} established for soils.

For a comparative analysis of the formation of the ecological and geochemical state in the iron ore district, let's examine the data on concentrations of metals and metalloids in the bottom sediments of rivers and water bodies in the Belgorod Oblast outside the iron ore districts (Table 2). When comparing concentrations of metals and metalloids in bottom sediments, consider the differences in sample sizes for rivers, reservoirs, and headwaters, as well as the influence of ponds and reservoirs on the overall data set for the region (Table 2). Higher concentrations of five out of the eleven elements are found in the bottom sediments of the region's water bodies compared to the headwaters of rivers. Metal concentration ratios in the bottom sediments of rivers and reservoirs most significantly exceed RGB values (2.7–1.3 times) for Mn, Zn, Cu, and to a lesser extent (10% of exceedances) for Ni and Fe. The sediments in the headwaters of rivers more frequently have higher concentrations of OM and Co.

Table 2. Average concentrations of metals and metalloids in bottom sediments of rivers and reservoirs of the Belgorod region outside iron ore areas and for river sources (RGB).

Parameter	Average (n=41)	RGB (n=6)	MPC (soil), ppm	Frequency of MPC exceedances, %
Pb (ppm)	17.83±1.25	18.57±1.28	32	37
Zn (ppm)	57.84±8.21	38.61±4.31	150	10
Co (ppm)	10.27±0.84	14.60±1.01	30	0
V (ppm)	56.52±3.70	58.75±1.54	150	0
Ni (ppm)	24.04±2.18	22.11±3.08	45	13
Cu (ppm)	22.18±1.90	17.05±2.66	40	11
Cr (ppm)	53.34±4.21	70.64±5.22	80	14
As (ppm)	5.15±0.44	6.32±0.44	20	3
Mn (ppm)	291.03±82.32	109.7±53.58	1500	10
Fe (%)	2.11±0.27	1.92±0.16	2.24*	–
OB (%)	4.87±0.53	7.17±1.31	–	–

* RGB, % (average for regional soils)

If we transition from the regional average values to individual sediment samples and compare them with the MPC for soils (Table 2), a ranked descending series of priority pollutants for the region can be established for the most contaminated sediments: Fe > Pb > Cr > Cr > Ni > Cu > Zn > Mn. These pollutants reflect sources of domestic and industrial water use outside the iron ore districts. Simultaneously, it is crucial to note that bottom sediments, as a depositing medium, promote the self-purification of the aquatic environment by binding HM, especially biogenic manganese and partially iron ions, as well as other pollutants; however, on the other hand, the sediments themselves become a source of secondary pollution for the water body.

4 Conclusion

The bottom sediments, formed in agricultural and industrial areas of intensive land use and mineral resource development, have ecological and geochemical characteristics. A particularly significant environmental impact was observed in the iron ore district of the Oskol River basin, where sediments in rivers and ponds were characterized by exceeding RGB concentrations of Mn, Zn, and Cu (from 1.5 to 2.8 times). Utilizing data on pollutant concentrations in 9% of the most polluted bottom sediments, which reflect the influence of surface runoff from agricultural landscapes at catchments, domestic runoff, and process effluents from production facilities outside iron ore districts, a number of priority pollutants for the region were identified: Pb, Cr, Zn (1st hazard class), Ni, Cu (2nd hazard class), as well as Mn and Fe. A comparison of iron and trace element concentrations in sediments of rivers and water bodies of the Belgorod Oblast outside the iron ore mining areas, such as Co, Mn, Cu, and Zn, with RGB values (in river headwaters) showed an excess of the last three elements, but the content of all five elements is not higher than the MPC values established for soils. Of the ten metals and metalloids determined, five (Pb, V, Ni, Cr, As) had concentrations in bottom sediments that did not exceed those in sediments characterizing conditions at the headwaters of rivers. Due to the imbalance of macro- and microelement ratios on large areas of arable land, the prospect of using ecologically safe bottom sediments as a basis for various fertilizers (organic and mineral, composts, including vermicomposts) and using them as ameliorants on low-productive lands near the hydrographic network is of interest. The results of the ecological and geochemical assessment and identification of those sediments that have an unacceptable level of pollution according to HM content of the 1st and 2nd class of hazard, allow for a differentiated approach to the use of extracted sediments in the process of water reservoirs renovation and dredging.

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