Chemical and ecological quality of water and bottom sediments in small rivers of Belgorod oblast

T V Oliva, E Yu Kolesnichenko, A E Solovyova, L V Oliva

Belgorod State Agricultural University named after V. Gorin, 1, Vavilova st., Mayskiy village, Belgorod region, 308503, Russia

E-mail: Oliva_TV@bsaa.edu.ru

Abstract. Belgorod Oblast has limited water resources. The paper explores the chemical and ecological characteristics of water and bottom sediments in the Oskol River tributaries. In samples of water taken from small rivers, Maximum Allowable Concentrations (MAC) for pollutants was excessive, including suspended matter, ammonium ion, nitrite ions, nitrate ions, phosphates ions, BOD₃, and mineral elements. A hydrochemical water pollution index (WPIₜ) ranges from 1.0 to 1.9, which characterizes water bodies in the categories from clean to moderately polluted watercourses. A comparatively high WPIₜ index is recorded in summer for the Kotel River – 1.4, for the Belenkaya River – 2.3, which is attributed to a high concentration of ammonium ions, nitrites and phosphates found to be present in the water. This indicates recent pollution and a changing trophic status of the reservoir. The amount of metals in river water exceeds the MAC norms: for iron – 1.7 - 6 MAC; for copper – 1.6 - 8 MAC; for manganese – 0.8 - 22 MAC; for zinc – 1.9 - 9.9 MAC. Concentrations of micronutrients are subject to significant seasonal fluctuations. No excess of lead is found to be present in surface waters. In the samples of bottom sediments taken from the Oskol River tributaries, no excess of MAC values is found, except for lead (1.1 - 2.9 MAC), manganese (1.6 - 2.2 MAC), copper (1.2 - 1.6 MAC) and phosphate ions (1.3 - 2.3 MAC). It is obvious that the sources of pollution for small rivers are runoff's from agricultural land, livestock farms and household wastewater of nearby settlements.

1. Introduction
Belgorod Oblast has limited water resources and the lowest level of water supply to the population: 1,600 thousand m³/year per person compared to the national average of 31,700 thousand m³/year per person. The regional water resources are mainly represented by small rivers. They are characterized as typically plain with a calm current, smooth longitudinal profile and low inclines. Small rivers and their tributaries, being part of the urban ecosystem, are known to be subject to constant anthropogenic impact [1–4]. Since Belgorod Oblast is a region with intensively developing agricultural production, a catchment area of small rivers is subject to constant pollution [5]. The scientific literature indicates that a modified structure of agricultural land generally increases an overall wastewater level on arable land [6] and brings about a release of significant concentrations of pollutants into surface waters [7–10]. This leads to a decrease in river flows with progressive siltation and overgrowth.

Bottom sediments can be considered as a temporary information indicator of water pollution. The process of accumulation of pollutants in the water and in bottom sediments does not decrease, while insoluble toxicants due to suspended particulate sedimentation increase the overall water pollution and affect living organisms and the environment [11–13]. For a long time, bottom sediments, on the one
hand, accumulate pollutants, but, on the other hand, serve as sources of secondary water pollution. The scientific literature emphasizes that organic matter, lead, cadmium and manganese and other microelements dispersed are concentrated in the bottom sediments of various water bodies [14–17].

Preservation of small rivers implies solving one of the most crucial aspects of environmental protection and sustainable development of territories for safe water use and high-quality water supply. In this regard, it is important to assess the status of small rivers, their ecosystems and components to get an idea of the way river basins function following man-induced impacts.

The paper aims to explore the chemical and ecological quality of water and bottom sediments in small rivers – the Oskol River tributaries. The quality of surface water was monitored in summer and autumn by obtaining separate data on the blending ratio in the water and bottom sediments in small rivers in Belgorod Oblast.

2. Materials and methods

The Oskol River has its source in Kursk Oblast and drains 220 km through the eastern part of Belgorod Oblast. The river has a complex drainage system and receives water from many tributaries on its way. Right-bank tributaries are the Orlik (43 km), Khahan (35 km), Kholok (38 km) Rivers. The left-bank tributaries are the Ublya (50 km), Kotel (41 km), Belenkaya (28 km) Rivers. Downstream the river becomes wider and more powerful and flows into the Seversky Donets River. The catchment area of the Oskol River basin is dominated by arable land and natural forage land with settlements, commercial pig and dairy farms and a number of industrial enterprises, which implies a significant man-made burden on the basin.

Comprehensive environmental studies were carried out in July and September 2017. There were 6 points to sample water and bottom sediment for hydrochemical tests: B1 – up Kotovo village, the Ublya River at 51.3125°N latitude and 37.9933°E longitude; B2 – down Ternovoye village, the Kotel River at 51.1939°N latitude and 37.9090°E longitude; B3 – down Starokhmelevoe village, the Orlik River at 51.0466°N latitude and 37.7477°E longitude; B4 – down Russian Khahan village, the Khahan River at 50.9522°N latitude and 37.7382°E longitude; B5 – up Novy Oskol, the Bolenkaya River at 50.7551°N latitude and 37.9029°E longitude; B6 – down Kiselevka village, the Kholok River at 50.8330°N latitude and 37.7031°E longitude.

The Oskol River is a fishery reservoir. The ecological state of river water was characterized through the maximum allowable concentrations of pollutants in the ambient water in the fishery body (MACₚₐₑ). Concentrations of substances in the ambient water should not have a harmful effect on fish species, likewise other biota.

The surface water was sampled for physical and chemical tests in accordance with GOST 31861-2012. Bottom sediments were taken from the surface layer using disposable sample containers. The quality of surface water was assessed based on the hydrochemical water pollution index (WPIₜ) and the total chemical water pollution indicator (CPI₁₀). Water and bottom sediment samples were tested through the following methods: M-MVI-80, PND F 16.1: 2.3: 3.44, PND F 16.1: 2: 2.2: 3.51, GOST 26423-85, GOST 26424-85, PND F 16.2.2: 2.3: 3.30-02, PND F 16.1: 2: 2.2: 3.67-10, GOST 26424-85, M-MVI-80-2001, GOST 26213-91, PND F 16.1: 2: 2.2: 3.52-08.

3. Results and Discussion

Table 1 shows the average results of physical and chemical water tests from the Oskol River tributaries. The pH water value is of prominent importance for the chemical and biological processes to occur in natural water, which influence the evolution and life of aquatic plant and animal species, the resistance of various patterns of migration and the aggressive action of water on metals. The natural water of the Oskol River tributaries comes under slightly alkaline water. The oxygen regime has a profound effect on the life in the reservoir. Determination of oxygen in surface water indirectly characterizes surface water quality assurance and wastewater treatment regulations.
Table 1. Indices of the physical and chemical ratio in surface water in the target area

| Indices                        | MAC<sub>p</sub> | Oskol River tributaries (July, September) |
|-------------------------------|----------------|------------------------------------------|
|                               |                | Ublya River | Kotel River | Belenkaya River | Orlik River | Khalan River | Kholok River |
| Hydrogen, units pH            | 6.5-8.5        | 7.90        | 7.74        | 7.89            | 7.93        | 8.09         | 7.73         |
| Suspended solids, mg/dm<sup>3</sup> | 10.0          | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |
| Dissolved oxygen, mg/dm<sup>3</sup> | summer        | 9.0         | 12.0        | 24.0            | 21.0        | 11.0         | 17.0         |
| BOD<sub>5</sub>, mg O<sub>2</sub>/dm<sup>3</sup> | 2.0           | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |
| Ammonium ion, mg/dm<sup>3</sup> | 0.5           | 9.0         | 12.0        | 24.0            | 21.0        | 11.0         | 17.0         |
| Nitrate ion, mg/dm<sup>3</sup> | 40.0          | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |
| Nitrite ion, mg/dm<sup>3</sup> | 0.08          | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |
| Phosphate ion, mg/dm<sup>3</sup> | 0.6           | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |
| Phenols, mg/dm<sup>3</sup>    | 0.001         | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |
| Total iron, mg/dm<sup>3</sup> | 0.1           | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |
| Copper, mg/dm<sup>3</sup>     | 0.001         | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |
| Manganese, mg/dm<sup>3</sup>  | 0.01          | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |
| Zinc, mg/dm<sup>3</sup>       | 0.01          | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |
| Lead, mg/dm<sup>3</sup>       | 0.006         | 7.84        | 7.69        | 7.34            | 7.96        | 7.92         | 7.49         |

The minimum O<sub>2</sub> content that ensures the normal evolution of fish species is about 5 mg/dm<sup>3</sup>. Lowering it to 2 mg/dm<sup>3</sup> can cause fish kill (mortality). The oxygen oversaturation of water resulting from photosynthesis is also unfavorable for aquatic organisms. The Kotel, Belenkaya and Orlik River tributaries are deficient in oxygen, which is commonly observed in water bodies with high concentrations of organic pollutants. There was a higher content of suspended solids, assertedly of anthropogenic origin, in the rivers. There are 2 pig farms and 10 dairy farms in the catchment area of these sites. The higher the amount of suspended solids, the worse the hydrochemical regime and biological life in the reservoir, and the heavier the formation of bottom sediments. In terms of oxygen content, the Kotel River can be attributed to class V, dirty, Belenkaya and Orlik – to class IV, polluted, and Ublya, Khalan and Kholok – to class III, moderately polluted.

Biochemical oxygen demand (BOD) characterizes the degree of water pollution with organic compounds. The BOD<sub>5</sub> value from 2.0 to 2.9 mg O<sub>2</sub>/dm<sup>3</sup> characterizes the natural water of the Ublya, Orlik, Khalan, and Kholok Rivers as moderately polluted, and the Belenkaya River – polluted.

The presence of ammonium ions in river water is mainly associated with the biochemical degradation of protein substances, deamination of amino acids and decomposition of urea. It is
believed that they get into the water with livestock wastewater. The presence of ammonium at a concentration of about 1 mg/dm$^3$ reduces the ability of fish hemoglobin to bind oxygen. It was found that in the natural water of the Belenkaya River, the content of ammonium ions is 2.46 MAC and 1.42 MAC in summer and autumn, respectively, which poses a danger to aquatic organisms.

The amount of nitrate ions in the target water does not exceed the MAC value. With a lack of oxygen in the water, phytoplankton and denitrifying bacteria use the oxygen of nitrates for the oxidation of organic substances. The minimum amount of nitrates was found in the water of the Belenkaya and Kotel Rivers. The above-limit subthreshold concentration of nitrate ions of 10 mg/dm$^3$, which affects the sanitary regime of the reservoir, was not observed in any of the target natural reservoirs. Nitrites represent an intermediate stage of bacterial oxidation of ammonium to nitrates and reduction of nitrates with a lack of oxygen to nitrogen and ammonia. There were high concentrations of nitrites in the surface water of the Oskol River tributaries, which indicates their pollution and the intensive decomposition of organic substances in the water.

Phosphorus is the most important biogenic element, the content of which hampers the productivity rate of a water body. Excessive concentration of phosphates in water may reflect the presence of fertilizer impurities, components of domestic wastewater and decomposing biomass. In the water of the Belenkaya and Orlik Rivers, the content of phosphate ions was 1.3 - 4.1 MAC; in the water of other Oskol River tributaries, it does not exceed MAC.

Phenolic pollution of natural water of the Oskol River tributaries was not observed, except for a one-time increased content in the water of the Kotel River in autumn. It should be noted that the Staroskol paint and varnish plant and a manufacturing plant for paint and varnish materials operate within the Kotel River basin, the wastewater of which is likely to contain this pollutant.

The content of a number of metals in river water in some seasons exceeds the MAC norms: for iron – 1.7 - 6 MAC; for copper – 1.6 - 8 MAC; for manganese – 0.8 - 22 MAC; for zinc –1.9 - 9.9 MAC. The concentrations of biogenic microelements are subject to significant seasonal fluctuations. An excess of lead in surface water was not found to be present.

The resultant water pollution index showed that at all sampling points the average WPI$_6$ index had values ranging from 1.0 to 1.9 with a maximum value to be recorded at the Belenkaya River point – the most polluted of all sampling points. According to this integrated indicator, water samples can be classified as clean or moderately polluted watercourses. A relatively high WPI$_6$ index was recorded in the summer for the Kotel River – 1.4, for the Belenkaya River – 2.3, which was due to the increased content of ammonium ions, nitrites and phosphates in the water and indicated recent pollution, as well as a changing trophic status of the reservoir.

Having calculated the total chemical water pollution indicator (CPI$_{10}$), all sampling points were found to have the CPI$_{10}$ index significantly lower than 35, which currently corresponds to a relatively satisfactory state of the water body.

Table 2 shows the average physicochemical indicators of the quality of bottom sediments in the Oskol River tributaries. Due to the lack of approved environmental standards for the characterization of bottom sediments, the MAC for soils was used (GN 2.1.7.2041-06).

The findings show that the samples of bottom sediments in the Oskol River tributaries did not contain excessive MAC values, except for lead (1.1 - 2.9 MAC), manganese (1.6 - 2.2 MAC), copper (1.2 - 1.6 MAC) and phosphate-ions (1.3 - 2.3 MAC). Lead falls into the 1$^{st}$ class hazardous compounds and has a harmful effect on aquatic organisms. The main sources of metal pollution of the water are transport and mineral fertilizers that can contain up to 3% heavy metals. According to literature data, phytoplankton is known to actively adsorb biogenic mineral elements. The bottom sediments contain a high amount of manganese and copper. High concentrations of nitrogen and phosphorus can be attributed both by the natural features of Belgorod Oblast and by polluted wastewater influxes. Comparative analysis of indicators in surface water and bottom sediments in the reservoir may indicate that water pollution of the Oskol River tributaries has occurred for a long time and constantly. The accumulation of biogenic copper, manganese and zinc in bottom sediments indicates that they get into the water from phytoplankton, the level of copper in bottom sediments is
800 times higher than that in river water, zinc – 380 times, manganese – 2400 times higher. A low content of phenols was found in the bottom sediments of the rivers. Under natural conditions, phenols are formed caused by the aquatic metabolic pathway during the biochemical decomposition and transformation of organic substances that occur both in the water column and in bottom sediments.

**Table 2.** Hydrochemical indices of priority pollutants in bottom sediments in the Oskol River tributaries

| Indices                  | MAC | Oskol River tributaries |
|--------------------------|-----|-------------------------|
|                          |     | Ubya River | Kotel River | Belenkaya River | Khlan River | Kholok River |
| Hydrogen, units pH       | 7.60| 7.50 | 7.76 | 7.60 | 7.90 | 7.56 |
| Organic matter, %        | -   | 0.99 | 3.15 | 5.31 | 24.34 | 1.62 | 10.89 |
| Phosphate ion, mg/kg     | 200 | 60.50 | 24.40 | 129.08 | 247.10 | 131.97 | 455.96 |
| Ammonium nitrogen, mg/kg | -   | 20.0 | 31.51 | 7.71 | 20.0 | 37.42 | 5.55 |
| Nitrate nitrogen, mg/kg  | 130 | <0.23 | <0.23 | <0.23 | <0.23 | <0.23 | <0.23 |
| Nitrite nitrogen, mg/kg  | -   | 0.037 | 0.040 | 0.110 | 0.460 | 0.097 | 0.133 |
| Carbonates, mg/kg        | -   | <100 | <100 | <100 | <100 | <100 |
| Copper, mg/kg            | 3.0 | 3.50 | 4.90 | 3.69 | 1.76 | 3.59 | 2.46 |
| Manganese, mg/kg         | 140 | 40.50 | 66.20 | 108.89 | 41.19 | 303.80 | 215.66 |
| Zinc, mg/kg              | 23.0 | 3.80 | 1.82 | 0.43 | 0.50 | 6.02 | 3.03 |
| Lead, mg/kg              | 6.0 | 17.50 | 6.80 | 12.63 | 0.35 | 5.56 | 14.11 |
| Phenols, mg/kg           | -   | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |

4. Conclusion

Comprehensive studies carried out in the water area of the Oskol River tributaries showed that the surface water here is similar in ionic blend and parameters. The surface water pollution is confirmed by the values of WPIs and CPIs. According to these parameters, surface water at all sampling sites are characterized as moderately polluted. The ecological situation still remains quite challenging, with growing concentrations of pollutants to indicate recent and old pollution of the water in the tributaries. The dirtiest tributary draining into the Oskol River is the Belenkaya River that represents an ecosystem jeopardizing the ambient flora and fauna. Long-term pollution of small rivers is, obviously, caused by runoff from agricultural land, livestock farms and household wastewater of settlements. Comprehensive extended monitoring is required to provide a more complete objective characterization of the quality of surface water and specific man-made environmental impacts.

References

[1] Tkachev B P, Bulatov V I 2002 Small rivers: State of the act and ecological problems. Analytical review (State Public Scientific and Technical Library of the Siberian Branch of the Russian Academy of Sciences. Series Ecology) iss 64, 114 p
[2] Sukhanova M P 2016 Advances in modern natural science 4 188–196. Retrieved from: http://natural-sciences.ru/ru/article/view?id=35886
[3] Lapteva E M, Loskutova O A, Khlopov Yu V 2019 Water resources 46(5) 523–532
[4] Yasinsky S V, Venitsianova E V, Vishnevskaya I A 2019 Water resources 46(2) 232–244
[5] Oliva T V, Manokhina L A, Kolesnichenko E Yu, Solovieva A E, Andreeva N V 2020 Advances in modern natural science 12 145–150. DOI 10.17513/use.37551.
[6] Barabannov A T, Dolgov S V, Koronkevich N I 2018 Water resources 45(4) 332–340
[7] Boronina L V, Sadchikov P N, Tajeva S Z, Moskvicheva E V 2016 Water resources 43(4) 419–425
[8] Pavlov V E, Sorokovikova L M, Tomberg I V, Khvostov I V 2014 Water resources 41(5) 541–543
[9] Kokryatskaya N M, Zabelina S A, Savvichev A S, Moreva O Yu, Vorobieva T Ya 2012 *Water resources* **39**(1) 78–91
[10] Gotovtsev A V, Danilov-Danilyan V I, Nikanorov A M 2012 *Water resources* **39**(5) 510-520
[11] Blinova E G, Chesnokova M G 2019 *International Journal of Applied and Basic Research* **10**(1) 75–80. Retrieved from: https://applied-research.ru/ru/article/view?id=12870
[12] Zelenkovskiy P S, Podlipskiy I I, Dubrova S V, Hohryakov V R, Lebedev S V, Izosimova O S, Chubarova I M 2020 *IOP Conf. Series: Earth and Environmental Science* **579** 012044. doi:10.1088/1755-1315/579/1/012044
[13] Larina N S, Shelpakova N A, Larin S I, Dunaeva A P 2008 *Advances in modern natural science* **7** 56–58. Retrieved from: http://natural-sciences.ru/ru/article/view?id=10273
[14] Dudareva I A, Alimova G S, Tokareva A Yu 2017 *Advances in modern natural science* **8** 70–74. Retrieved from: http://natural-sciences.ru/ru/article/view?id=36523
[15] Tukhtaeva Kh T, Islamova N N 2020 *East European Science Journal. Geographic sciences* **2**(57) 14–17
[16] Martynova M V 2008 *Water resources* **35**(3) 358–363
[17] Martynova M V 2014 *Water resources* **41**(2) 180-190