Analysis of Sources of Anthropogenic Pollution of the Transboundary River, the Serevsky Donets, Based on the Dynamics of the Anion Composition (Nitrites, Nitrates, Sulfates, Chlorides, Phosphates) in 2007-2016

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Abstract. The goal of this work is to analyze the long-term dynamics of the content of nitrites, nitrates, sulfates, chlorides and phosphates in the transboundary river Seversky Donets. Material and methods. Regular sampling at three points over 10 years (from 2007 to 2016) was used for this research. Monthly average ions concentration in MPC fractions was analysed. Results. Regularities in the dynamics of the anionic composition, caused by both natural and anthropogenic factors, are revealed. It was discovered that the main sources of phosphates and nitrites are located in the Belgorod region, while sulfate and chloride pollution happens mainly on the territory of Ukraine as a result of the discharge of mine waters by coal industry enterprises. The nitrates concentration has similar quantitative values and dynamics at all considered sampling points, which is determined by the natural mechanisms of nitrogen transformation in warm and cold periods. Also, the comparison of specific combinatorial indices of water pollution (SCIWP) at the considered sampling points for the considered period is carried out. Conclusion. In order to improve the ecological situation, it is recommended to conduct regular sampling and observation, including at a larger number of sampling points, as well as data exchange with the Ukrainian environmental services.

1. Introduction
The problems associated with environmental pollution attract more and more attention every year. The reservoirs of the South of Russia are situated in special climatic and geographical conditions and are subject to significant anthropogenic impact due to the high concentration of the population, the impact of industry and agriculture. The development of agriculture and industry and the growth of the urban population lead to an increase in the pollution of water bodies with organic and mineral substances [1].

The Seversky Donets River is one of the largest rivers in eastern Ukraine and the largest tributary stream of the Don. The total length of the river is 1,053 km, the basin area is 98,900 km². Water consumption - 159m³/s.

There are more than 3000 rivers in the Seversky Donets basin, 425 of them are more than 10 km long and 11 rivers are more than 100 km long. More than a thousand of them flow directly into the

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Seversky Donets. The Seversky Donets feeding is predominantly snow - 65% of the runoff, 33% is fontinal, therefore the water consumption is not consistent throughout the year. [2].

Seversky Donets is actively used in the economy. More than 2 km³ of river water is used annually, half of which is returned as polluted discharges. Thus, 20% of the flow of the Seversky Donets is irretrievably consumed, and another 20% is heavily polluted [3].

The main pollution sources of the river basin of the Seversky Donets are:
- the most negative impact is exerted by the discharged untreated mine waters, which is a consequence of the developed coal mining in the region. A large amount of pollutants, such as chlorides, sulphates, high-density metals, etc, gets into water bodies from mine waters. [4, 5]
- river pollution by fields' runoffs that contain mineral fertilizers, which include nitrates and phosphates. This entails waters eutrophication, and, as a result, the rapid growth of phytoplankton (intensive development of blue-green algae), decrease in the transparency of waters, the death of multicellular algae;
- water pollution by oil and oil products (OP);
- water pollution by human waste - discharge of untreated or insufficiently treated wastewater, etc;

The goal of this work is to consider and evaluate the pollution of the Seversky Donets River with anions: nitrites, nitrates, sulfates, chlorides and phosphates. Also, based on research data for 2007-2016, changes in the concentration of pollutants in the source of the Seversky Donets and as the river flows through the territories of Belgorod (Russia), Kharkov and Lugansk (Ukraine), Rostov (Russia) regions are analysed.

The research carried out in 2007-2016 by the department for the study of water quality and analytical activities of the Federal State Institution "Donvodinformt Center" and the department for quality control of the Federal State Institution "Management of the Belgorod Reservoir Operation" in accordance with the regulatory documents served as the basis for this work[6, 7]. We took the concentrations of anions in the inlet section of the Belgorod reservoir, 997 km from the mouth (source area) as background values and considered the values of the concentrations of anions in two other sections:

1. The Seversky Donets River, at the border of Belgorod and Kharkov (Ukraine) regions, with Novaya Tavolzhanka village, 950 km from the mouth;
2. The Seversky Donets River, at the border of Lugansk (Ukraine) and Rostov regions, Donetsk city, 221 km from the mouth.

2. Discussion

The main pollutants that enter the Seversky Donets River are salts, oil products, phenols, high-density metals, and biogenic substances. The cleanest area of the Seversky Donets river is from its head to Belgorod.

In our country for a comprehensive analysis of pollution of water bodies we use the specific combinatorial index of water pollution (SCIWP) and take into account the "List of fishing standards: maximum permissible concentrations (MPC) of harmful substances in the waters of water bodies of fishing importance" [8, 9]. The specific combinatorial index of water pollution (SCIWP) fluctuates along the flow of the Seversky Donets River mainly from IIIa (polluted) to IIIb (very polluted), except for 2007 (Novaya Tavolzhanka village), 2013, 2015, (Donetsk city) - IVa (dirty).

In order to evaluate the pollution of the Seversky Donets River, we carried out an analysis of the main anions (nitrites, nitrates, sulfates, chlorides and phosphates) and identified possible reasons for their high content in 2007-2016 in the indicated sections of the river.

3. Comparison of nitrite concentrations in the section of the rivers of the Seversky Donets

Nitrites are an intermediate step in the chain of bacterial processes of ammonium oxidation to nitrates (under aerobic conditions) and, on the contrary, of the reduction of nitrates to nitrogen and ammonia (when there is a lack of oxygen). The increased content of nitrites shows an intensification of the processes of decomposition of organic substances under conditions of slower oxidation of NO₂ to
NO$_3$$. This is used as an important sanitary indicator in the current research. In most water bodies, seasonal fluctuations of nitrites are characterized by a decrease in winter and an increase in spring during the decomposition of organic materials [10]. Such a regularity of changes in the content of nitrites is observed in the inlet section of the Belgorod reservoir (head) and at the border of the Belgorod and Kharkov (Ukraine) regions (Novaya Tavolzhanka village); the maximum average values of nitrites are observed from May to July (1.2 MPC - 1.7 MPC and 2.2 MPC - 2.6 MPC, respectively). Then there is a decrease in concentrations and minimum values are observed from November to February (0.6 MPC - 1.1 MPC and 1.1 MPC - 1.4 MPC, respectively).

The opposite situation is observed in the section at the border of Lugansk (Ukraine) and Rostov regions (city of Donetsk). In this case, the negative anthropogenic impact on the section of the river between Belgorod and Rostov regions leads to an increase in nitrite concentrations in winter periods. At the same time, in the summer months, the nitrite ions concentration decreases by the 2-3 times compared to the section at the border of the Belgorod region and Ukraine. The maximum average values of nitrites are observed from November to February (1.6 MPC - 2.3 MPC (max in December 2011, 2012 - 3.0-3.4 MPC)). A decrease in the content of nitrite in the water is observed in the summer period - from 0.9 MPC to 1.3 MPC.

![Figure 1. Average monthly values of nitrite content (in MPC) in the Seversky Donets River for 2007-2016.](image)

In the inlet section of the Belgorod Reservoir, mainly during the researched period, the nitrites concentration rarely exceeds 1.0 MPC, however, in the spring months (from March to May), one-time exceedances of up to 2.0 MPC is observed. In the section of the river near the village of Tavolzhanka, the nitrites concentration varied from 1.0 MPC to 2.5 MPC (until 2010). In 2010-2016, the content of nitrites in the water of the Seversky Donets increased significantly and mostly ranged from 2.0 to 4.0 MPC with a decrease from February to May to 1.0 - 1.5 MPC. In July 2016, the maximum nitrites concentration was observed (4.88 MPC). In the section of the river near the city of Donetsk, changes in nitrites from 1.0 to 2.0 MPC on average are observed during the year. However, in 2011, 2012 and 2015, the concentration increased significantly and varied from 2.0 to 3.5 MPC. It should be noted that a sharp increase in concentration at this sampling point was observed in March 2008 and reached 2.63 MPC.

4. Comparison of nitrate concentrations in the sections of the Seversky Donets River
Nitrates are in a dissolved form in the surface waters. The nitrates concentration in surface waters is subject to noticeable seasonal fluctuations: the minimum during the growing season, it increases in autumn and reaches its peak in winter, when the consumption of nitrogen is minimal, but the decomposition of organic materials and the transition of nitrogen from organic to mineral forms. The range of seasonal fluctuations can serve as one of the indicators of the eutrophication of a water body.
In the Seversky Donets, the exceedances of the MPC for nitrates are not observed and fluctuate in the range from 0 to 0.4 MPC. The maximum values of nitrate concentrations in the inlet section of the Belgorod reservoir are observed in the winter months in 2008, 2012 and 2016 and reach 0.25 MPC. In the section of the river near the village of Tavolzhanka, there is also a tendency to an increase in nitrate concentrations in the winter months, but it increased to 0.67 MPC only in April 2014. In the section of the river near the city of Donetsk, the situation changes quite differently: low concentrations (0.03 - 0.07 MPC) can be observed in the summer months, however, an increase in the content of nitrates (0.2 - 0.3 MPC and higher) begins already starting from September-October and continues up to April-May.

In general, the nitrates concentrations in all three sections are comparable and increase slightly down the stream.

5. Comparison of sulfate concentrations at the Seversky Donets sections
Sulfates are one of the most important anions and are present in almost all surface waters, which are actively participating in the complex sulfur cycle. In the absence of oxygen, effected by sulfate-reducing bacteria, they are deoxidized to hydrogen sulfide and sulfides, which, when oxygen emerges in natural water, are again oxidized to sulfates [11]. The increased content of sulfates deteriorates the organoleptic properties of water and physiologically affects the human body.

As can be seen from the figures, near the head and in the section of the river near the village of Tavolzhanka, sulfate concentrations range from 0.5 to 1.2 MPC. In the section of the river near the city of Donetsk, the content of sulfates in the water increases to 3.0 - 4.0 MPC and has bulk emissions of 6.7 MPC in November 2015 and 7.51 MPC in May 2016.

Comparison of average monthly concentrations for the considered period in both sections on the territory of the Belgorod region in warm months, the sulfates concentrations slightly decreases, but, in general, throughout the year does not exceed the MPC for sulfates. In the section of the river near the city of Donetsk, the amount of sulfates increases by 3-4 times because of the influence of mine waters (the coal mining industry is well developed in the territory of Donbass) [12].

![Figure 2. Average monthly values of nitrate content (in MPC) in the Seversky Donets River in 2007-2016.](image-url)
6. Comparison of chloride concentrations at the Seversky Donets sections
Chlorides are an integral part of most natural waters. The content of chlorides of natural origin in water bodies can have a wide range of fluctuations, depending on the nature of the river's feeding and the area of its flow. In general, for rivers and other fresh water bodies, the amount of chlorides is quite low. At the same time, there is a range of anthropogenic factors that affect the content of chloride ions: industrial discharges, washing out of rocks, the coal mining industry, washing off the mixture from roads to reduce icing during winter periods.

The low chlorides concentration throughout the year in the inlet section of the Belgorod reservoir and in the section of the river near the village of Tavolzhanka (0.6-0.8 MPC and 0.11-0.3 MPC, respectively) indicates that there is a natural source of this type of ions in the water at this sampling point. After the Seversky Donets river passes through the territory of Ukraine, the amount of chlorides increases to 0.6-1.0 MPC in the section of the river near the city of Donetsk (Russia). (Fig.4). The increase in the amount of chlorides is connected with the influence of mine waters, as it also happens in the case of the increase in the content of sulfates.

7. Comparison of the phosphate ions concentration in the sections of the Seversky Donets
Phosphorus belongs to biogenic elements and it is an indicator of biological processes occurring in a water body. Phosphorus compounds can be found in all living organisms. In the absence of
phosphorus compounds in water, the growth and development of aquatic vegetation slows down, but their exceedances lead to strengthening of the processes of eutrophication of water bodies and a deterioration in water quality.

Analyzing the changes in the phosphates concentration during the researched period, it can be noted that the average annual values of the content of phosphates in the Seversky Donets River increase from the head to the mouth. In the inlet section of the Belgorod reservoir (head), the phosphates concentration is in the range of 0.4 - 0.8 (MPC) (maximum values - 2016, minimum - 2014). At the border of Belgorod and Kharkov (Ukraine) regions, Novaya Tavolzhanka village, the phosphate content is in the range of 1.13 - 1.70 (MPC) (maximum values - 2013, minimum - 2007). At the border of Lugansk (Ukraine) and Rostov regions, Donetsk, the phosphates concentration is in the range of 0.8 - 2.2 (MPC) (maximum values - 2009, minimum - 2011). Considering the seasonal changes in the amount of phosphates during the researched period, there can be drawn a conclusion about the periodicity: in the inlet section of the Belgorod reservoir (head) and at the border of the Belgorod and Kharkov (Ukraine) regions, Novaya Tavolzhanka village, the maximum average values of phosphates are observed from July to September (0.7 MPC - 0.9 MPC and 1.6 MPC - 1.8 MPC, respectively). Then the concentration decreases and the minimum values are observed in from December to February (0.3 MPC-0.4 MPC and 1.0 MPC - 1.2 MPC, respectively). At the border of Lugansk (Ukraine) and Rostov regions, city of Donetsk, the maximum average phosphate values are observed from June to September (1.6 MPC - 1.9 MPC (max in June 2009 - 4.0 MPC)), the minimum values are observed from March to April (0.9 MPC - 1.3 MPC).

The phosphates concentration in water is subject to seasonal fluctuations, because it depends on the intensity of the processes of photosynthesis and biochemical decomposition of organic materials. The change in the phosphate content is connected with its consumption by aquatic organisms, as well as the transition to bed deposits during the formation of insoluble phosphates.

8. Conclusion
Taking into account the factors that affect the anionic composition of the Seversky Donets River, the following patterns and factors were identified:

1. The most anions content in the water of the Seversky Donets increases after the river passes through the territory of Ukraine. The increased nitrites concentration in the section of the village of Tavolzhanka is caused by anthropogenic impact on the territory of the Belgorod region.

2. The nitrates content near the head of the river corresponds to natural mechanisms and annual dynamics. Further, the impact of human activity is observed, however, the tendency to the accumulation of nitrites in the winter period is traced on the figure with average monthly concentrations.
3. The sulfates and chlorides concentrations increase dramatically after the river passes through the territory of Ukraine. In this case the most likely reason is the discharge of mine water. Other human activities, acid rain, exchange with soil and rocks also affect the dynamics of sulfates in the Seversky Donets River.

4. Phosphate pollution is connected with household wastewater and the washout of phosphorus-containing fertilizers from agricultural land uses, which is confirmed by an increase in the phosphate ions concentration in the summer period.

5. It is necessary to conduct observation at a greater number of sampling points, the interaction of both states, including the exchange of data on the components under study should be conducted in order to get a more detailed analysis of the state of the Seversky Donets River and the influence of anthropogenic factors of Russia and Ukraine on it.

To sum up, we note that the negative impact on the Seversky Donets River throughout the entire area is being considered. As the main impact is made by people, it is necessary to consider and regiment all key types of human activities in order to improve the ecological situation of this water body.

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