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THE GEOCHEMICAL ESTIMATION OF THE GEOECOLOGICAL STATE LEFT IN FLOWS OF PODOLSK PART OF THE DNISTER RIVER

Об'єктом дослідження є вода, донні відклади та ґрунт з берегів лівих приток Подільської частини річки Дністер (Україна). Одним з найбільш проблемних місць даного дослідження є відсутність аналогічних комплексних спостережень за вмістом у воді, донних відкладах та ґрунті з берегів лівих приток Подільської частини Дністра досліджуваної ділянки. Це ускладнює з'ясування геохімічних особливостей донних відкладів та ґрунтів.

Проби ґрунтів з берегів водотоків для еколого-геохімічних досліджень було відібрано згідно з ГОСТ 17.4.4.02-84 та досліджено із застосуванням кількісного спектрального аналізу валового вмісту елементів. Це дозволило порівняти між собою вміст елементів у ґрунтах та донних відкладах.

З'ясовано, що за механічним складом серед донних осадів річок переважають псаміти, а незначний вміст глинисто-алевритової складової у донних осадах не сприяє нагромадженню у них забруднюючих речовин.

Вміст більшості елементів у воді річок не перевищує гранично допустимі концентрації (ГДК). Лише у районі м. Могилів-Подільський в р. Дерло вміст калію та заліза в 13,28 і 7,4 раз перевищує ГДК відповідно. Загалом вміст досліджуваних елементів у воді переважно не тільки не перевищує, а й значно менше ГДК, як санітарних вимог, так і ГДК стандарту Всесвітньої організації охорони здоров'я.

Дослідження вмісту Cr та Pb у донних відкладах річок Жван, Лядова, Немія, Дерло та Дністер, та ґрунтах їх берегів дозволило з'ясувати, що вміст свинцю і хрому в досліджуваних зразках переважно не перевищує медіанне значення для досліджуваних водотоків.

Загалом геоекологічний стан лівих приток Подільської частини річки Дністер задовільний. Забруднення хімічними елементами має точковий характер. Рекомендується створити спільну міжнародну програму здійснення геоекологічного моніторингу не тільки р. Дністер, а й його лівих і правих приток у межах Подільської частини.

Ключові слова: *геоекологічний стан річки Дністер, транскордонний водотік, гідрохімічний режим, донні відклади.*

1. Introduction

About the state of natural environment the best of all testifies the geoecological state of currents. The inflows of Dnister test the considerable technogenic loading. They accumulate not only the supplies of water but also all contaminations that come from the area of water intake.

In addition, transformation of natural environment of Ukraine was brightly represented on one of especially vulnerable objects of nature – the ground cover. All negative changes that take place with the landed resources touch soils first of all [1]. Rain fallouts carry contaminents from soil to the currents, afterwards they are accumulated in the ground sedimentations.

The ground sedimentations are a basic information generator for the estimation of the state of the water systems. They represent geochemical specialization of reservoirs, give an opportunity to estimate the process of migration, piling up of natural and technogenic components, are the «buffer» of contaminents [2].

Heavy metals (Fe, Cu, Zn, Ni, Pb, Cd, Mn, Cr, etc.) – one of the main groups of chemical pollution of water. However, unlike organic substances that are to some extent subjected to destruction, heavy metals are only redistributed between individual parts of aquatic ecosystems (water, bottom sediments, biota).

Ecologically – hydrochemical researches are the important instrument of monitoring of ecological estimation of the state of natural waters, especially at the modern terms of the intensive use by nature.

Therefore actual is research of the geoecological state of both Podolsk part Dnister and her left inflows for the sake of decision of tasks of rational and ecologically reasonable water consumption, ecological monitoring.

2. The object of research and its technological audit

The research object is water, ground sedimentations and soil from the banks of the left inflows of Podolsk part of the river Dnister (Ukraine). *The article of research* is the geoecological state of the left inflows of Podolsk part of Dnister.

The Dnister is a transboundary river between Ukraine and the Republic of Moldova. This is the second longest river in Ukraine and the ninth in Europe. From the sources to the city Old Sambir Dnister flows among the Carpathian Mountains, further – in the plains of Ukraine and Moldova. From the village of Kozlov (Mogilev-Podolsky district of the Vinnytsia region, Ukraine) to the village of Nimeryuki (Soroca region, Moldova) along the Dnister passes the state border between Ukraine and Moldova [3].

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Further, the river flows through the territory of Moldova. From the village of Pourkar (Stefan-Vodsk district, Moldova), a border between the two states passes through the village of Palanka on the Dniester. Below the village of Palanka Dnister flows through the territory of Ukraine.

The Dnister River Basin is located in the south-western part of Ukraine and in the eastern part of Moldova. The water catchment area of the Dnister basin is 72900 km^2, of which 53490 km^2 or 73 % are located within Ukraine [3]. The length of the river is 1362 km. The Dnister basin is located in seven regions in the southwest of Ukraine (Lviv, Ivano-Frankivsk, Ternopil, Khmelnytsky, Vinnitsa, Chernivtsi and Odesa regions) [3]. A small part of it in the upper part of the pool is in Poland. The pool is in the form of a very elongated, centered oval, about 700 km in length, with an average width of 120 km. Heights in the mountainous part of the basin reach 1000–1800 m [3].

The main issue in assessing the quality of surface waters is the determination of structural and functional indicators of the biological component of aquatic ecosystems as the main factor in ensuring the stability of the conditions for the recreation of water resources. It is based on the ecosystem approach, which provides an analysis of all components of aquatic ecosystems: the aquatic environment, bottom sediments and hydrobionts. Equally important for assessing the geoecological state of water bodies is compliance with the regime of use of coastal protective strips. The characteristics of soils give an opportunity to put together a generalized picture of the geoecological state of the watercourse and the areas of the catchment.

3. The aim and objectives of research

The aim of research is to find out the geoecological state of the left tributaries of the Podilsky part of the Dnister River. In order to achieve this goal, the following tasks must be performed:

1. To clarify the geochemical characteristics of water from the watercourses under investigation, based on the results of laboratory studies, statistical processing and interpretation of the results of analyzes.

2. To clarify geochemical features of bottom sediments and soils from shores on the basis of results of laboratory research, statistical processing and interpretation of the results of analyzes.

3. To perform a comparative analysis of the geochemical characteristics of bottom sediments, soils and water from the left tributaries of the Podilsky part of the Dnister city with the maximum allowable concentrations.

4. Research of existing solutions of the problem

Investigations of the hydrochemical regime and quality of surface waters of the Dnister basin in Ukraine were carried out in 2011 [4]. The results of the public ecological expedition «Dniester» are important, participants of which from 1988 to 1997 carried out hydrological, hydrochemical and geochemical observations of the Dnister and its tributaries [5]. It is worth noting the importance of the results of the study of bottom sediments of the Upper-Middle part of the Dnister River for the analysis of its ecological and geochemical state [6], which was carried out both within the ecological expedition and at its completion. It is important to constantly monitor the state of surface waters of the Dnister River basins by the Dniester-Prut basin water resources department, which is carried out by the laboratories of the State Agency of Ukraine for Water Supply throughout the research area. The state of surface water quality in the Dnister basin was investigated in 54 sections. Of these: 19 squares are located mainly in the river bed, and 35 – in 26 tributaries. However, in the explored area, the outskirts are located only in the city of Mogilev, Podolsky, the Dnister River. Hydrochemical laboratories and hydro geological-reclamation party, in accordance with their authority, carry out the study of surface waters, groundwater, groundwaters, sewage (reverse) waters and soils, but they deviate from their attention bottom sediments [7].

Among the main areas of study of the geoecological state of the Dnister and its tributaries discovered in the resources of the world scientific periodicals, there may be dedicated works [8–10]. These studies are devoted to the ecological state of water of the right tributaries of the Dnister River in the lower part of the territory of Moldova, but they do not consider the state of bottom sediments and soils from the shores.

Conversely, works [11, 12] are devoted to the monitoring of the content of heavy metals in bottom sediments, and they do not at all take into account the content of heavy metals in water and coastal strips of reservoirs.

The hydrological regime of the Dnister River was considered in [13], which is also important to consider when conducting a comprehensive study of a watercourse.

The legal aspects of the prospective interaction between Ukraine and Moldova in the management of the Dnister transboundary watercourse and the monitoring of its ecological status and the state of its inflow were noted in [14, 15]. Since then, cross-border cooperation has improved, countries have developed a common monitoring system for the Dnister and its tributaries, in accordance with the requirements of the Water Directive [16]. Among the investigated indicators are hydrological (water level), meteorological (precipitation amount) and physicochemical indicators of the qualitative state of water.

Thus, the results of the analysis of publications make it possible to conclude that the geoecological state of the Podolsk part of the Dnister River and its tributaries has not been studied extensively, and such a comprehensive comprehensive study of these watercourses is being carried out for the first time. In this case, the results of the study are of international importance.

5. Methods of researches

Selection of water samples, bottom sediments of the left tributaries of the Dnister and soils on the banks of these tributaries in such settlements of the Vinnytsia region (Fig. 1):

– Zhvan River – village Bernashivka of Mohyliv-Podilskyi district and village Zhvan Murovanakurilovets district;

– Karaets River – village Khonykivtsi, Mohyliv-Podilskyi district and in the village. Rivne Muronakurilovets district;

– Lyadova River – village Yarishiv, Mohyliv-Podilskyi district;

– Serebryya River – village Serebrya, Mohyliv-Podilskyi district;
– Nemiya River – village Nemiya, Mohyliv-Podilskyi district;
– Derlo River – the city of Mohyliv-Podilsky, Mohyliv-Podilskyi district;
– Kotlubayivka River – village Bronny, Mohyliv-Podilskyi district;
– Murafa River – village Sloboda Bushan, Yampilsky District;
– Bushanka River – village Bush, Yampil district;
– Murafa River – village Bush, Yampil district;
– Murafa River – village Doroshivka, Yampil district;
– Murafa River – village Myronivka, Yampil district;
– Dnister river – village Oksanivka, Yampil district;
– Murafa River – village Bila, Yampil district;
– Murafa River – village Ulyanovka, Yampilsky;
– the river Rusava – the city of Yampil, Yampil district.

Within the specified settlements, 23 samples of bottom sediments from the alluvium were selected. Precipitation samples were taken during the summer-autumn period in 2013–2014 and in 2017 at a distance of 1.0 m to 5.0 m from the coast and dried by air.

The bottom sediments were studied in a complex manner by the following methods:
– granulometric analysis (sieve method);
– mineralogical studies of heavy and light fraction under the binocular;
– spectral analysis of the total content of the elements (Mn, Co, Nb, Cu, Ti, V, Pb, Cr, Pb, Ag, Bi, Sn, Ga, Sc, Y, Yb, Ba, Zi, Ni, Fe, Sr, Al ; Zr, La, Mo, W, Sb, Zn, Cd, Ge, Be, Ce, Za, Th, As, P).

Geochemical features of bottom sediments were studied on the basis of a complex methodology according to the following scheme [2]:
– sampling;
– preparation of samples for laboratory research;
– mechanical analysis of precipitation with respect to the separation of ten dimensional fractions (>10; 10–7; 7–5; 5–3; 3–2; 2–1; 1–0.5; 0.5–0.25; 0.25–0.1; <0.1 mm).

6. Research results

Data from the studies on the granulometric composition of samples (Table 1) made it possible to find out that the bottom sediments of the left tributaries of the Podilsky part of the Dnister are represented by all granulometric classes of precipitation, among which the most prevailing sand sediments are psamites, which make up about 50 %. The predominance of the sparse component and the insignificant contents of clay-alu-vritus in the bottom sediments of the left tributaries of the Podilsky part of the Dnister does not contribute to the accumulation of pollutants from them.

The alluvium of the Dnister River and its tributary is a product of erosion and redeposition of the Vendian, Silurian, Devonian, Cretaceous, Neogene and Quaternary sediments. Therefore, the mineral composition of the bottom sediments corresponds to that of the catchment rocks. Of ore minerals in the alluvium of the rivers Zhvan, Liadov, Nemiya, Derlo, galenite, sphalerite, chalcopyrite is installed. The gold, which was revealed by the geologists-production workers, the author is not established.

For the waters of Zhvan, Karayets, Liadov, Serebrya, Nemiya, Derlo and Kotlubaivka, a determination was made for nineteen indices: Na, K, Mg, Ca, Fe, HCO_3^-, Cl^-, SO_4^{2-}, Mn, Ni, Ti, V, Cr, Mo, Zr, Nb, Cu, Ba, Pb [2].

The determination was made in dry water residues using spectral analysis methods. For the degree of distribution, the elements in the waters of the left tributaries of the Dnister are divided into four groups:

1) identified in 100 % Na, K, Mg, Ca, Fe, HCO_3^-, Cl^-, SO_4^{2-}, Mn, Cr, Cu;
2) identified in y 50–100 % the samples – Pb, Ni, Ti, V;
3) identified in 0–50 % the samples – Mo, Zr, Ba;
4) not identified in the samples – Nb.

The content of most elements in the water of rivers does not exceed the maximum permissible concentration (MPC). Only in the area of the city of Mogilev-Podolsky in the Dralu River, the potassium content is 66.4 mg/dm^3, and the iron is 2.21 mg/dm^3, which is 13.28 and 7.4 times higher than the MPC, respectively.

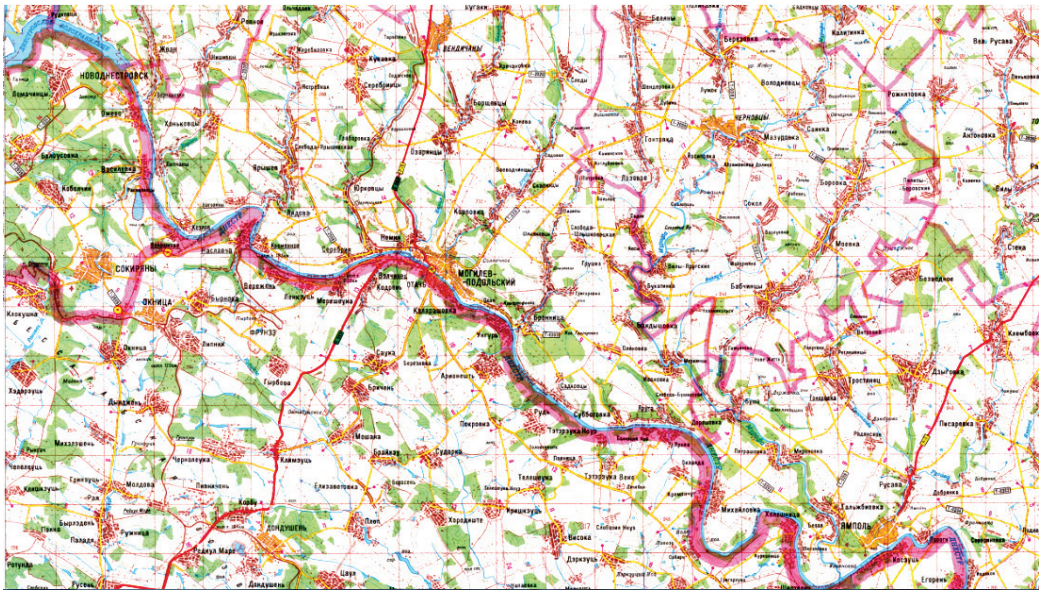

Fig. 1. Site of research area of the left tributaries of the Podilsky part of the Dnister River (Ukraine)

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Table 1

Distribution of granulometric fractions of bottom deposits of left tributaries of the Podilsky part of the Dniester, mass. %

Precipitation	Psephite			Psammite			Aleurite
Granulometric fractions	5–3	3–2	2–1	1–0.5	0.5–0.25	0.25–0.1	<0.1
Averaged weight of 23 samples	6.00 %	9.47 %	8.64 %	20.95 %	12.71 %	15.72 %	6.52 %

Something exceeds the MPC (400 mg/dm^3) content (414.8 mg/dm^3) of HCO_3^- anions. More than twice the maximum permissible concentration limits for the content of titanium 0.2223 mg/dm^3 and zirconium 0.0295 mg/dm^3 in the Dnister within the village Oksanovka Yampilsky district.

Among the elements common to bottom sediments, water and soils from the banks of the watercourses are Mn, Ni, Ti, V, Cr, Mo, Zr, Nb, Cu, Ba, Pb.

Consider the contents of Cr and Pb in the rivers Zhvan, Liadova, Nemiya, Derlo and the city of Dniester. In Fig. 2 shows the distribution of lead in the water of the Dnister and its left tributaries. The content of Pb in the water of the investigated watercourses is not only not exceeding, but much less than the MAC, both sanitary and toxic requirements, and the MAC of the WHO standard (World Health Organization) [17].

The same can be said about chromium. In Fig. 3 shows the distribution of chromium content in the water of the Dnister and its left tributaries.

Consider the contents of Cr and Pb in the bottom sediments of the rivers Zhvan, Lyadov, Nemiya, Derlo and Dnister and the soils of their shores. The results of the studies are shown in Fig. 4. As you can see in Fig. 4, the content of Pb in the samples under study does not predominantly exceed the median value for the investigated watercourses. Except for the contents of the increased content of lead in the bottom sediments of the city of Nemij, which is 3.6 times the median value for the study area. There is also a slight increase in the lead content (1.36 times the median value) in the soil of the banks of the Dralo River. In general, the pollution level of Pb is negligible.

The distribution of chromium content in bottom sediments and in soils selected on the banks of the Dnister and its left tributaries is shown in Fig. 5.

As can be seen in Fig. 5, the content of Cr in the samples of bottom sediments under study is preferably not more than the median value for the investigated watercourses. However, the value of the chromium content in the soil selected on the banks of the city of Lyadov exceeds the median value by half, and for the city of Nemiya by 1.2 times. Such data can be explained by the interregional connection located near the motorway. In general, the level of contamination with chromium is negligible.

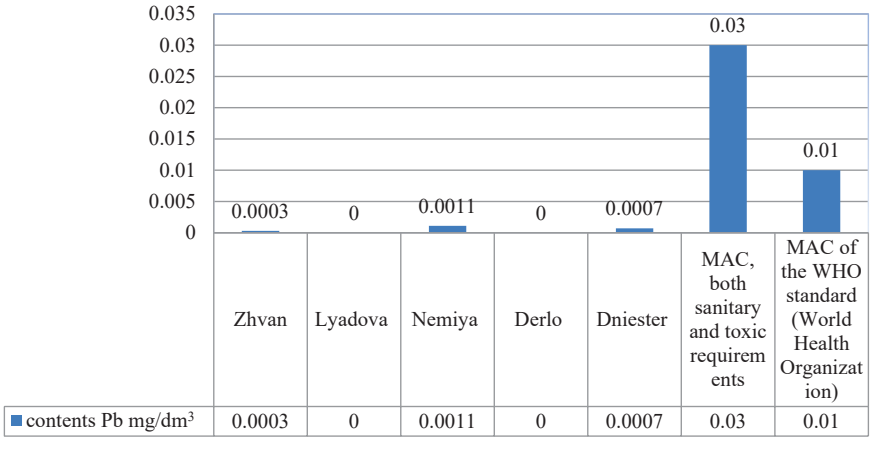


Fig. 2. Contents of lead in the waters of the Dnister and its left tributaries

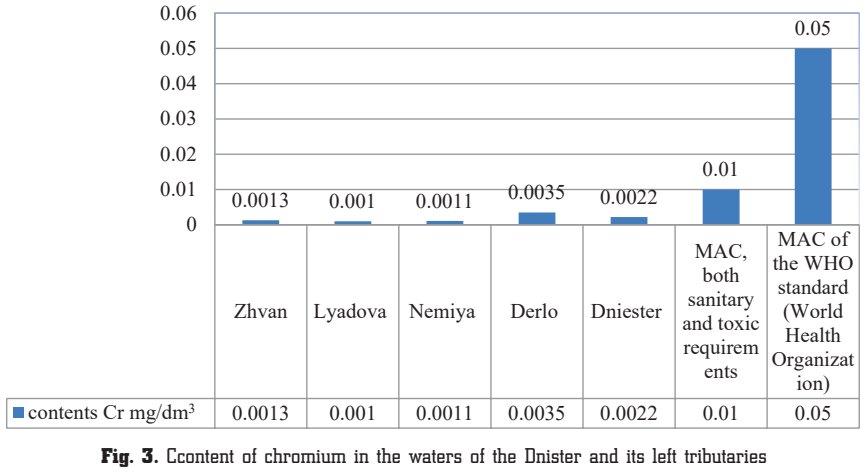
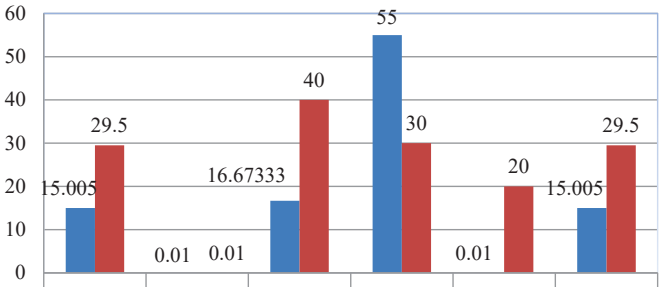
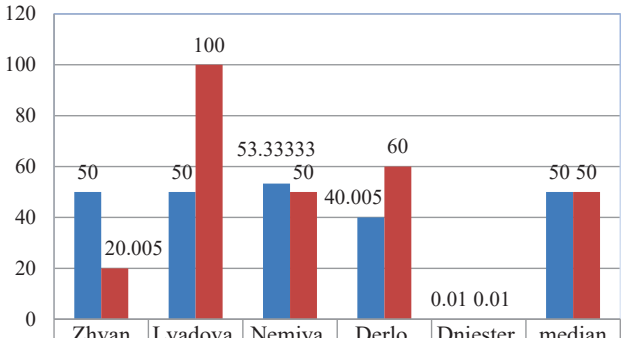


Fig. 3. Ccontent of chromium in the waters of the Dnister and its left tributaries



	Zhvan	Lyadova	Nemiya	Derlo	Dniester	median
content Pb mg/kg in bottom sediments	15.005	0.01	16.67333	55	0.01	15.005
content Pb mg/kg in the soil from the banks	29.5	0.01	40	30	20	29.5

Fig. 4. Content of lead in the bottom sediments and in soils from the banks of the Dnister and its left tributaries



	Zhvan	Lyadova	Nemiya	Derlo	Dniester	median
content Cr mg/kg in bottom sediments	50	50	53.33333	40.005	0.01	50
content Cr mg/kg in the soil from the banks	20.005	100	50	60	0.01	50

Fig. 5. Contents of chromium in bottom sediments and in soils from the banks of the Dnister and its left tributaries

7. SWOT analysis of research results

Strengths. A study was made of the geoecological state of bottom sediments, water and soils on both sides of the banks of the left tributaries of the Dnister of the Podolsky zone. A comprehensive study of soils, sediments and water from the watercourse gives a holistic picture of the state of water bodies as an indicator of the ecological situation in the region. The carried out researches have allowed to draw a conclusion, that as a whole the geo-ecological state of objects of research is good. It should be noted that only constant monitoring and monitoring of the geo-ecological situation of watercourses will enable to record and control the level of anthropogenic load on the environment, to forecast and prevent emergencies related to the pollution of watercourses.

Weaknesses. The weaknesses of the studies carried out are the lack of such studies in the past and the impossibility of comparing the results with the previous research results. However, this is the situation in the country with most of the objects of environmental monitoring, including soils, which are constantly exposed through human economic activity.

Opportunities. Prospects for further research related to the analysis of the application of chemical fertilizers, pesticides to soils in agricultural holdings that are located on both sides of the banks of the studied watercourses and to study their effect on the ecosystem. The Dniester-Prut basin management of water resources should expand the network of stations to study not only the quality of the surface waters of the Dnister River basin, but also to study bottom sediments and the coastal soil of the tributaries of the Dnister River.

Threats. Problems exist in the state of exploration of the geoecological state and the right tributaries of the Dnister (the territory of the Republic of Moldova) and the state of the exchange of information on the geoecological state of the territory between countries.

The Dnister river basin is experiencing significant technological impact as a result of the work of hazardous enterprises in the extractive, chemical, petrochemical, food and agricultural industries. The construction of a large cascade of riverbed reservoirs in the middle reaches of the Dnister significantly affected the natural hydrological state of the river. Therefore, the implementation of geo-ecological monitoring not only of the city of Dniester, but also of its left and right tributaries within the Podolsky part should be carried out not by public organizations or individual scientists, but at the state level. It is advisable to create a common international program of such studies.

8. Conclusions

1. It was found out that the psammiti predominate among the bottom sediments of rivers, and the insignificant

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content of the clayey-aleuric component in the bottom sediments does not contribute to the accumulation of pollutants.

2. It is shown that the content of most elements in the water of rivers does not exceed the maximum allowable concentration. Only in the area of Mogiliv-Podolsky in Derlo, the content of potassium and iron is 13.28 and 7.4 times higher than the MPC, respectively. Something exceeds the MPC content of HCO_3^- anions. More than twice the maximum permissible concentration limits for the content of titanium and zirconium in the Dnister within the limits of sec. Oksanivka Yampilsky district. In general, the content of the elements under investigation in the water predominantly not only does not exceed, but much less than the MPC, both the sanitary-toxicological requirements and the MPC standard of the World Health Organization.

3. Investigation of the contents of Cr and Pb in the bottom sediments of the rivers Zhvan, Lyadova, Nemiya, Derlo and Dnister and the soils of their shores made it possible to find out that the contents of lead and chromium in the samples under study do not predominantly exceed the median.

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