ASSESSMENT OF CHEMICAL COMPOSITIONS OF WATER AND ECOLOGICAL SITUATION IN DNIESTER RIVER

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Abstract: *In the present work are revealed the results of the multi-annual researches on the dynamics of the hydrochemical indexes (salinity, main ions, nutritive elements, trace elements, suspended matter etc.) in the Dniester river. The results of the field and experimental researches show that the content and the dynamics of the majority of the indexes are acceptable and rather favorable for the development of the hydrobionts. Only in less than 2% of the cases the concentration of some metals, can negatively influence upon the production – destruction processes and the development of the hydrobionts in the Dniester river.*

The accomplished researches showed that according to the content of the dissolved oxygen the Dniester river water is acceptable and rather favorable for the development of the hydrobionts. The content of the dissolved oxygen was varying between the limits 6.8-10.6 mg/l, that correspond to the water saturation equal to 68-114%. The concentration of the main ions as well as the degree of water salinity increase continuously downstream the river. The comparison between the data from 2005-2009 and the existent materials from 1993-1996 indicate an insignificant growth of the chlorates and sulfates concentrations, but the total salinity value generally corresponds to the one from 1996.

One of the most important indexes of the water quality is the content of the nutritive and trace elements. We have to mention that the level of nutritive element concentration at present is similar, the concentrations of the nitrates, nitrites, cooper, and zinc, are slightly lower, in comparison with 1993-1996. The building of hydropower stations in Ukraine (HPS-1, HPS-2 and HAPS) and constructions on the Dniester river have negative impact on the river ecosystems:

- *impairment of river hydrological regime.*
- *the river is covering with water plants.*
- *impairment of natural dynamics and processes of migration of chemical elements in the system «water-suspended matter- sediments».*
- *the processes of secondary pollution of water were intensified.*
- *the riverine species of hydrobionts are replaced with lacustric species.*

Keywords: *salinity, main ions, nutritive elements, trace elements, suspended matter, Dniester river, Moldova*

1. INTRODUCTION

The research was conducted in accordance with the national strategy for sustainable use of transboundary aquatic ecosystems, nature conservation and maintaining of biodiversity, as well as the recommendations of international conventions on sustainable use of transboundary water resources. At present the human impact on aquatic ecosystems of Republic of Moldova contributes to radical changes on biodiversity and quantitative structure of hydrobionts communities, water quality, conditions of existence and functioning of hydrobiocenosis. Dniester - the main artery of Moldova Aquatic is a border river, which springs in Ukraine and flows through highly populated areas of Ukraine and Moldova.

Construction of the dam on the river part located on the territory of Ukraine, at the border with Moldova (Novodnestrovsc) with the primary purpose of electricity generation, was finalized during 1985. With the exploitation of the dam, the bottom of the river, which mostly belongs to the territory of Moldova has undergone important changes, which caused major environmental problems due to the change in temperature, water chemical composition, hydrological and hydrobiological regimes and other river characteristics.

In the Naslavcea-Unguri-Soroca river sector water temperature did not exceed 16° C even when air temperature exceeds 35° C, the thermal changes being more evident during spring-summer. The ichthyologic investigations revealed an essential drop in the number and biomass of ichthyofauna and a decrease by 18 times in the fish productivity. Reproduction of fish decreased 30 times, some species are subjected to mass extinction, in some species, resorption of sexual products was recorded in up to 80% of the samples. More intensely the natural areas relatively rich in resources are exploited, primarily the meadow of Medial Dniester. The operation of Novodnestrovsc hydropower node caused changes in hydrobiocenosis which led to a decline or complete disappearance of many organisms. Unfortunately, the negative influence of Dnestrovsk hydropower station is increasing.

2. MATERIALS AND METHODS

The water and suspension samples were collected from Dniester river of Moldovan territory and Dubasari lake (upper, medial and lower sectors). Field sampling and chemical laboratory analysis was performed according to the Hydrochemical and Hydrobiological methods [1, 2]. Biological material was studied by modern hydrobiological methods for collecting and identification of diversity and productivity of phytoplankton [3].

3. RESULTS AND DISCUSSION

Dniester is one of the largest rivers of Europe. It flows from the north-western part of the Eastern Carpathians, the mountain slope Rozlici, its length being equal to 1352 km, the basin area - 72,100 km^2, including the Moldovan territory of 657 km and 19,000 km^2, respectively. The average annual flow reaches up to 10 km^3.

In 1981 on the river sector from sector Ojevo village, Sochireanskii district, Chernautsi region to village Ustie, Borşcevsk district, Ternopol region, Novodnestrovsc a dam lake was built. Its length was 214 km, width - from 200 to 3750 m and depth - from 3 to 56 m. In order to buffer the negative effect of the operation of hydropower station Dnestrovsk I a dam was built on Naslavcea lake. Here, three turbines for electricity generation were installed. The buffer lake (built in Moldova) does not fulfill anymore its original functions drafted in the initial project (leveling of the fluctuations of water levels in the Dniester river on the territory of Moldova and reducing the negative effects of cold water which is discharged from the bottom layers of Dnerstovsk I lake with an average temperature of 12 degrees both during summer and winter).

The thermal regime of the river before the construction of Dnestrovsk hydropower plant is determined by the air temperature and the influence of groundwater. Currently, more and more in the recent years, the influence of this factor started with the complex operation of Dnestrovck GEC-1 and GES-2 - to Naslavcea (Fig. 1).

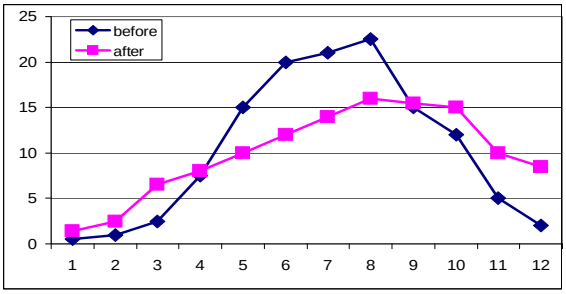
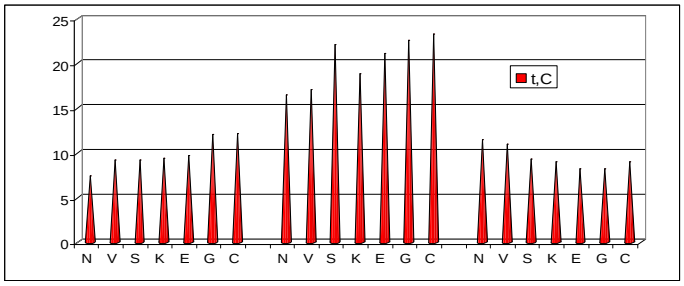


Fig. 1. Thermal regime of the river Dniester before and after the construction of Dnestrovsk hydropower plant

In the Dniester river, on the sector Dnestrovsk-Naslavcea the construction of pump storage hydroelectric plant was planned (in Russian CHEAP ГАЕС).

During the Soviet times after an environmental expertise, the project was stopped because of potential adverse natural conditions and the possible negative effects of this catastrophic CHEAP on Dniester and the Black Sea region. Unfortunately, Ukraine has resumed the construction process of this CHEAP. River sector between Naslavcea and Dnestrovsk has changed in the last two years and no ecological expertise was carried out in the area. The river here is, de facto, leveled on the left side and widened in the area of construction, and the right bank is cut. The hydrological parameters of the river have undergone radical changes since in this area another accumulation lake was built, directly on the river and the river banks are so-called "enhanced" with granite stones. Thus, only on the Moldovan territory, directly above Naslavcea, the area was kept its natural appearance, being covered with vegetation. It is very alarming the fact that the area, where this object was built, has a high erosion risk: Ukrainian scientists have already recorded high pressure of the slope in the area of underground pipes and accumulation lake and also intensification of erosion processes and sliding processes of karst terrain. Investigations show that, according to the dissolved oxygen content, Dubasari lake and Dniester river at Naslavcea-Kamenka sector have been satisfactory for the development of hydrobionts. Dissolved oxygen content was within 7.2-13.1 mg / l, which corresponds to water saturation 65.1-122.7%, being lowest in Naslavcea during summer-autumn (7.59-7.98 mg / l and 65.1-71.7%, accordingly). Since most samples were collected in the first half of the day, between 11-13, when the processes of photosynthesis were already high, we can assume that during the night between 3-5 hours, before the sunrise the dissolved oxygen content in Naslavcea may be unfavorable to metabolism of hydrobionts.

It should be mentioned that during the spring the water level was quite high, which meant that the volume of water discharged from the hydroelectric system was large and the content of organic suspensions was higher than that of mineral suspensions (medial sector of the river), thus, a reversed ratio (in the usual situation the mineral content of the suspension in the river is greater than that of organic). The situation started to improve after the floods of 2008, when on several transects of the river and lake Dubasari sand islands appeared, characteristic for such types of ecosystems, this being the consequence of removal of silt of anthropogenic origin and its replacement with sand by the flows of high water level. During summer and fall (when the water samples were collected) the water level was lower than the multiannual average, while the mineral content of suspensions was higher than that of organic suspensions. The content of suspended matter this year was more favorable for self-purification processes, than during the floods in 2008. Even though, the situation has improved somehow, as regarding the content of suspension, the water temperature values were unfavorable for the development of hydrobionts and functioning of aquatic ecosystems (Fig. 2).



Naslavcea – N
Volcineţ – V
Soroca – S
Camenca – K
Erjovo – E
Goieni – G
Cocieri – C

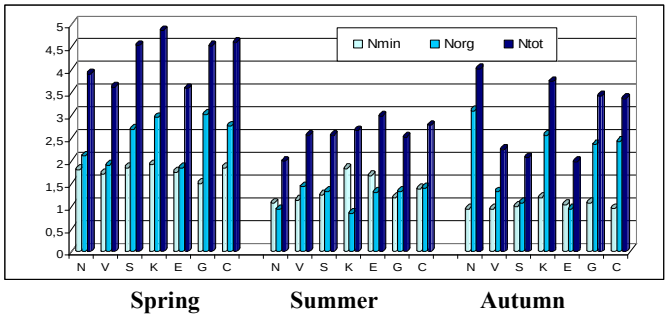
Fig. 2. The dynamics of water temperature in Medial Dniester and lake Dubasari during spring, summer and autumn 2009

From Fig.2 it is visible that during July, when air temperature was above 34 degrees, the Dniester river of Otaci-Naslavcea sector was below 16 degrees, in Soroca and Kamenka it reached 18 degrees and only in Goieni and Cocieri it was above 20 degrees. In autumn, specifically in November, when air temperature was already low, the water temperature in the Medial Dniester, on the opposite, was higher than in Dubasari. During winter the river from Dnestrovck (Ukraine) to Naslavcea did not froze even at air temperatures bellow 30 degrees.

The content of hydrocarbon and carbonate ions in Dniester river varied between 161 and 237g / l which is characteristic for ecosystems with an average mineralization of the Black Sea basin. The highest concentrations were encountered during spring, when water level in the river was high, while in the summer, when river water level was low, the concentrations of carbonates were also low, which contradicts the established patterns for rivers in this geographical area and demonstrates the disparity between the Dniester River hydrological and hydrochemical parameters. Before the construction of hydropower plant Dnestrovsk between water flow or volume and ion content there was a major linear negative correlation. The maximal water hardness values were recorded on the sector Valcineţ-Naslavcea and Otaci, most probable due to the fact that in Ukraine a source of mineralized water or wastewater discharge exist, or on the bottom of the lake Dnestrovsk there are remnants of brine from spillage Steblik that occurred in 80-ies. This difference is greater when the water level is higher. The calcium content in Dniester river varied between 57 and 79 mg / l and magnesium - between 9.7 and 16.7 mg / l, with maximum values during spring, when floods occur.

Since during 2007 there was a drought period, in the dynamics of principal ions a growth of magnesium ion content during summer was observed (Naslavcea-Soroca). Usually the ratio of concentration of calcium and magnesium ions in the river is 2 to 1, but during summer 2007 this ratio at Naslavcea station reached 3.5 to 4.3 (in mg-ecv / l). In 2009 this ratio was even higher - 10 to 1 in the Naslavcea-Valcineţ and 4 to 1 - to Kamenka and 3 to 1 - in the Inferior Dniester. Such influence was seen throughout the territory of Moldova. This phenomenon can be explained by pollution that occur in the upper river, or by entering the environmental sector of the remnant of brine from Steblik, which were stored in Lake Dnestrovck during 80-ies years. The chloride content did not exceed 30 mg / l, with values between 19.4 and 30 mg / l and a maximum value at Naslavcea station. Sulfate ion content range is of 47-70 mg / l having the same dynamics as the chloride content. During 2009 the presence of hydrogen sulfide in Dniester river was recorded for the first time. Ionic composition and mineralization of water bank are determined by major ions content in water flow that comes from the lakes Dnestrovsk and Naslavcea and depends on the operating regimes of these reservoirs. Downstream of the dam Naslavcea the mineralization in the Medial Dniester and in the lake Dubasari varied between 311 and 450 mg / l, being highest in the spring (449 mg / l) and lowest in the summer (311 mg / l). According to the contents of main ions and classification of Alekin, the water refers to the hydrogeno-carbonate class, calcium group, type II. It should be noted that often, specifically during sudden water level

increases, there is an evident increase in water mineralization, primarily due to the high content of sulfates, chlorides, magnesium ions, sodium and potassium. For example, in May 2009, the concentrations of the principal ions in the Naslavcea-Soroca water sector were much higher than those in July, when water level was much lower. Thus, a negative correlation between water flow and mineralization values, a pattern characteristic for rivers, does not exist anymore in the Dniester river. Ammonium ion content varies between 0.002 and 0.016 mg/l and may cause some negative effects on ecosystem functioning that were investigated. Nitrite nitrogen content (0.002-0.024 mg / l) and nitrate (0.98-1.8 mg / l) in Dniester river and Dubasari lake did not fluctuate very much. Nitrate nitrogen dominates quantitatively and content of mineral nitrogen content was favorable for the production-destruction processes and the development of aquatic plants. During 2009 the share of organic nitrogen in the total nitrogen, dissolved in the water of Dniester and lake Dubasari varied within large limits. If during spring the organic nitrogen content throughout the river and lake Dubasari was much higher than that of mineral nitrogen and lake Dubasari, than in the summer, at Kamenka-Erjovo sector, mineral nitrogen content was higher than that of the organic nitrogen content (Fig. 3.).



Naslavcea – N
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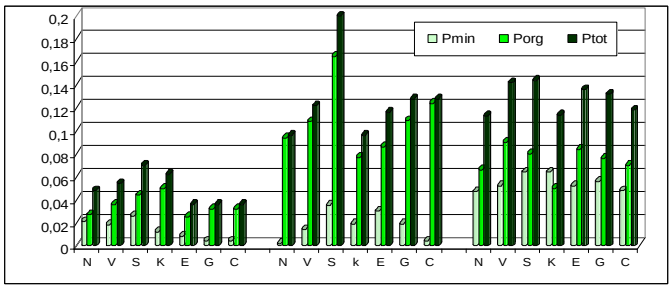
Fig. 3. The dynamics of mineral nitrogen content (N min), organic (N org) and total (N tot) in Dniester river and lake Dubasari during spring, summer 2009 mg / l.

Phosphorus is the most important indicator of trophic status in the natural water basins. The limits of mineral phosphorus in investigated water varied from 0.004 to 0.064 mg / l and that of organic phosphorus – 0.025-0.165 mg / l and of total – 0.036-0.200 mg / l, the latter being maximal at Soroca station (Fig.4). Organic phosphorus concentrations during summer reached the values up to 10 times higher than those of mineral phosphorus, thus the role of organic compounds was crucial in the dynamics of total phosphorus in investigated ecosystems, that showed an unfavorable situation for the functioning of these ecosystems. The values of permanganate oxidability in investigated ecosystems varied between 3.5 and 6.4 MgO / l, being slightly higher at Naslavcea and Soroca and in the spring in the medial sector of the lake Dubasari. In the studied ecosystems the processes of primary production of phytoplankton and destruction of organic matter showed a secondary pollution of aquatic ecosystems.



Naslavcea – N
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Fig. 4. Dynamics of mineral phosphorus (P min), organic (P org) and total (P tot) in Dniester river and lake Dubasari during spring, summer, autumn 2009 mg / l.

The change in the hydrological regime caused the abundant development of aquatic higher plants and lower productivity of the main groups of hydrobionts: the zooplankton - about 4.6 to 7.3 times and zoobenthos - 2-3 times. According to the ichtyological data of the Institute of Zoology, up to 50-60% of the females of valuable fish species have lost their reproductive capacity under modified living conditions.

It has already been established that in the river, throughout the whole territory of Moldova, many reophile species (typical for rivers) are replaced with the characteristic limnophilous species which are characteristic for standing water or lakes *(algarum Cricotopus, Cricotopus sylvestris, Chaetogammarus warpachowskyi, Limnomysis benedeni, Physella integrate Lymnaea peregra, Eudiaptomus gracilis and E.graciloides*) and economically valuable fish species have become rare or disappeared and the lacustric species with short development cycle are replacing them instead. As a result of the operation of existing hydro- units the migration processes of chemical elements have changed in the system "water-suspensions-silt" primarily the metals, whose concentrations became higher in the water than those in suspension [4,5].

Disruption of hydrological regime, with sudden diurnal fluctuations of the water level (up to 1.5 feet for 10-20 minutes, often in the Naslavcea-Otaci sector the water level drops up to the total bottom baring). The change in the thermal regime (spring and autumn the water temperature is 5-7 degrees higher and lower in the summer by not exceeding 14-16 degrees in the Naslavcea-Unguri) already caused a sudden decrease in the self-purification processes and increase in the pollution level of the Dniester River and Dubasari lake.

Acknowledgements: We would like to extend our appreciation to CRDF/MRDA (project MBI-3002, MOBI-3051-CS-03) and SCSTD, Moldova (project 07.407.26 INDA).

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Manuscript received: 30.04.2010
Accepted paper: 05.06.2010
Published online: 22.06.2010