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Original Research

Evaluation of Hydrosphere State of the Dniester River Catchment

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Abstract

This contribution presents the current state of the environment in the largest river basin of West Ukraine, the Dniester, on the background of the total river system of Ukraine. According to the results of the hydro- and lithochemical investigations performed during the period of 1995-2001, the Dniester River system is in a satisfactory state according to total macrocomponents composition, nitric compounds and heavy metals content. But ground waters of the region are regionally polluted by nitrate-ions, thanks to the wide use of mineral fertilizers, wastewaters of animal farms and municipal sewage. Surface waters of the Dniester River, its tributaries and the Dniester Reservoir are strongly regionally polluted by phenols and oil-products, that may be connected with man-made as well as natural factors.

Keywords: the Dniester river basin; heavy metals; oil-products; phenols; surface waters.

Introduction

Anthropogenic changes in river catchments and coastal zones have great significance for the economic situation of regions, the setting of human life and environmental protection. These changes, including deterioration of river water, are currently a subject of increasing concern and call for careful analysis [1,2]. River water quality depends on geological and morphological conditions, vegetation and human activities accompanied by point and non-point or diffuse sources of water pollution in the catchment basin [3]. Therefore, it is difficult to set an absolute standard for river pollution. The impact of point contamination sources (domestic and industrial mainly) can be localized and well-established, whereas the influence of diffuse pollution caused by runoff from agricultural areas and urban centers, inputs of tile drainage water, atmospheric deposition and groundwater as well as the role of geochemical conditions are less obvious and controlled [4,5].

A control of river water quality is of great importance in Ukraine, taking into account a variety of natural conditions, the highly developed industry and agriculture, the recent social-economical changes and the fresh water deficiency in the southern regions. This paper presents the current state of the environment in the largest river basin of West Ukraine, the Dniester on the background of the total river system of Ukraine.

Ukrainian River Basins

Ukraine is situated in the catchment areas of the Azov-Black and the Baltic Seas. The first one covers nearly 96% of the territory and includes entirely or patrially catchments of the main rivers Dnieper, Dniester, Pivdennyj Bug, Danube, Don (Siverskyj Donets) and some smaller

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Table 1. Characteristics of main river basins in Ukraine [6-8].

Main river	Length (Ukrainian part), km	Catchment area (Ukrainian part)/ percents from area of Ukraine, ths km²/%	Average deviation, m/km	Flow rate, m³/s	Modul of run-off, l/s km²	Population in basin, mln. person/ percents of Ukraine population	Water reservoirs		Density of river system, km/ km²
							Area of water mirror, km²	Water volume, km³	
Dnieper	2201 (986)	504 (295)/ 49	0.11	1660	3.3	22.3/43	8752.9	47.44	0.26
Dniester	1352	72 (52.8)/9	0.56	330	5	4.147/8	462	3.52	1.5-0.2
Don (Siverskyj Donets)	1050 (540)	99/9	0.18	160	1.6	6.793/13	209.2	0.946	0.4-0.2
Pivdennyj Bug	806	64/11	0.40	96	1.5	4.145/8	740.3	1.5	0.35

rivers flowing directly to the Azov Sea (Mius, Kalmius). The Baltic Sea catchment is presented by the right tributaries of the Vistula river (Zakhidnyj Bug, Syan). There are over 71,000 rivers in Ukraine, but only 6% of them are longer than 10 km. Characteristics of the main river basins are shown in Table 1.

Potential natural resources of surface water is evaluated as 87.1 km³ annually by an average of many years of data (without Danube flow of 122.7 km³) and as 52.6 km³ in very low-water years. In the total water balance of Ukraine nearly 16% (48 km³ annually) of atmospheric precipitation is spent in river runoff, but they are the main recharge source of the rivers. The plain rivers have snow recharge and the mountain rivers (Carpathian and Crimean) – rain recharge. Ground run-off is of 10-20% of recharge sources both for plain and mountain rivers. The average many years runoff module changes mainly from 1 to 4 $dm^3/s \cdot km^2$, the extreme values are fixed in the Ukrainian Carpathians (up to 35 $dm^3/s \cdot km^2$) and in the southeastern steppe part (lower than 0.1 $dm^3/s \cdot km^2$). There are sharp seasonable changes in the run-off. So, 50-80% of water flow by rivers in the spring. Increase of total dissolved solids (TDS) of the river waters from 0.150 mg/dm^3 in the northwest (Prypyat river basin) to more than 2.5 mg/dm^3 (the southeastern steppe) accompanied by change of macrocomponent composition from hydrocarbonate-calcium to sulphate-calcium with elevated concentrations of sodium- and chloride-ions [8]. Ukraine belongs to the regions with deficient water resources. In the low-water years there is 49,200 m^3/km^2 and 570 m^3/person [6-8]. Water intake and use volumes from the main river basins and Azov sea of Ukraine are shown in Figs. 1 and 2.

Dniester River Basin

Total Characteristic

The Dniester is the second-longest river in Ukraine and the main water artery of Moldova (Fig. 3). It rises in the northeastern slope of the Ukrainian Carpathians at an altitude of 760 m, and flows in the general southeastern direction draining the territory of West Ukraine, Moldova and falls to the Dniester estuary of the Black Sea not far from Odesa (Ukraine). By geological condition the Dniester basin is located in the limits of the south-west part of the East European platform (the left part of the basin mainly), the sub-Carpathian depression and the Folded Carpathians (the right flows basins). The upper right part of the basin situated on the Carpathian slide and their spurs is mountainous for nearly 50 km and the other one – plain.

Traditionally, the Dniester River is divided into three parts: the upper (from the source to the mouth of the river Zolota Lypa), the middle or Podilska (to city Dubosary, Moldova) and the lower one. The upper

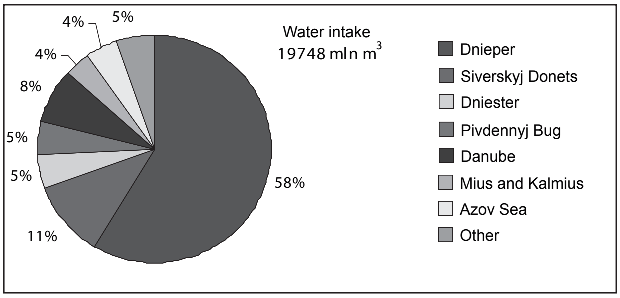

Fig.1. Water intake from the main Ukrainian river basins and Azov sea, 1999 [7].

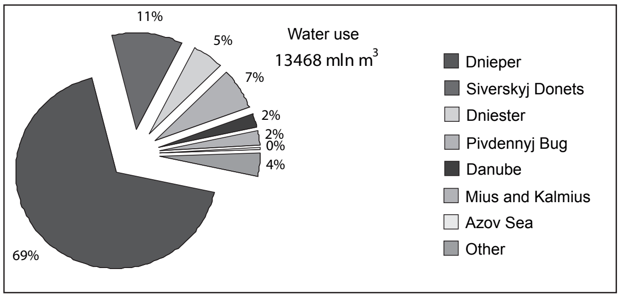

Fig.2. Water use in the main Ukrainian river basins and Azov sea, 1999 [7].

part of the catchment occupies nearly 30% of the total catchment area, but the main part (70%) of river runoff is formed here. The Middle Dniester flows through the deep (near 100 m) and narrow ravine with many meanderings. The Lower Dniester goes through the Sub-Black Sea depression, forming numerous branches. There are carst regions in the Dniester catchment influencing the runoff regime.

River runoff has strong seasonal changes with the spring maximum caused by snow melting and the summer one conditioned by strong rains and downpours in the upper and the middle part of the basin. The summer inundations may be catastrophic (the last one was 1997). Autumn and winter yields are the lowest and most constant. Level variations are the most significant (up to 10 m) in the middle part of the basin [8,9].

Anthropogenic Loading

The Dnister River basin occupies 9% of the Ukrainian territory. Among 4,147,000 persons (8% of total Ukrainian population) within the Ukrainian part of the catchment there are 1,743,000 persons of urban population (5% of the Ukrainian urban population) and 2,545,000 persons of the rural population (15%). Values of water intake and use in the Dniester basin are shown in Figures 1 and 2. Water consumption is distributed between industrial (35%), municipal (35%) and agricultural (with irrigation) (24%) applications [5,6].

The Dniester flows through areas with significant population density (105 people per km^2 generally and 130 people per km^2 in the Moldavian part), high development of industry and agriculture. Specifically such cities as L'viv, Ivano-Frankiv'sk, Chernivtsi, Odessa. Kyshyniv, Dubosary and the significant group of the smaller, are provided by water of the Dniester, its tributaries and ground waters of their valleys. Municipal and industrial sewage of the cities Chernivtsi, Novyj Rozdil, Mykolajiv, Zhudachiv, Zalishchyky, Mogyliv-Podol'skyi, Tyraspol', Bendery, Soroky, Kamjanka, Rybnytsya, and Dubosary get after cleaning or without cleaning to the river [9].

In the Ukrainian part of the Dniester catchment the water accumulation reservoir "Novodnistrovskye" was built in 1985. It is characterized by a length near 208 km, water mirror area – 14,200 ha, total volume of accumulated water - 2 km^3, average width of 730 m (maximum 4 km), average depth – 21 m (maximum 52 m). This reservoir has a complex appointment: hydroenergetics, water supply, irrigation, fishery, and regulation of water regime.

Mining (petroleum and gas, sulphur, potassium salts) and chemical industrial enterprises are widely developed in the Dniester basin. These include the Boryslav oil-industrial region with more than 1000 wildcat and producing wells, the main oil pipeline "Druzhba", Drohobych and Nadvirna oil-refining plants, Stebnyk potassium plant, Kalush chemical plant, Zhydachiv cellulose-paper plant, Producing unit "Sulphur" and the mineral fertilizer plant Nowyj Rozdil. Taking into account such a large anthropogenic loading, is always an extreme situation. The most powerful accident was the destruction of dams of the enriching factory of the Stebnyk potassium plant (1983), when 4.5 mln m^3 of high-mineralized brines got to the Dniester River. The results of this accident were developed from the Tysmennytsya River mouth to the Dniester estuary. The total loss was estimated at 72 mln USD. But the "dosed forced" dropping of wastewaters to the rivers are compared with the accident dropping by results. So, Stebnyk potassium plant has given 3.3 mln m^3 of high-mineralized brines to the Dniester River basin during the last 16 years [10].

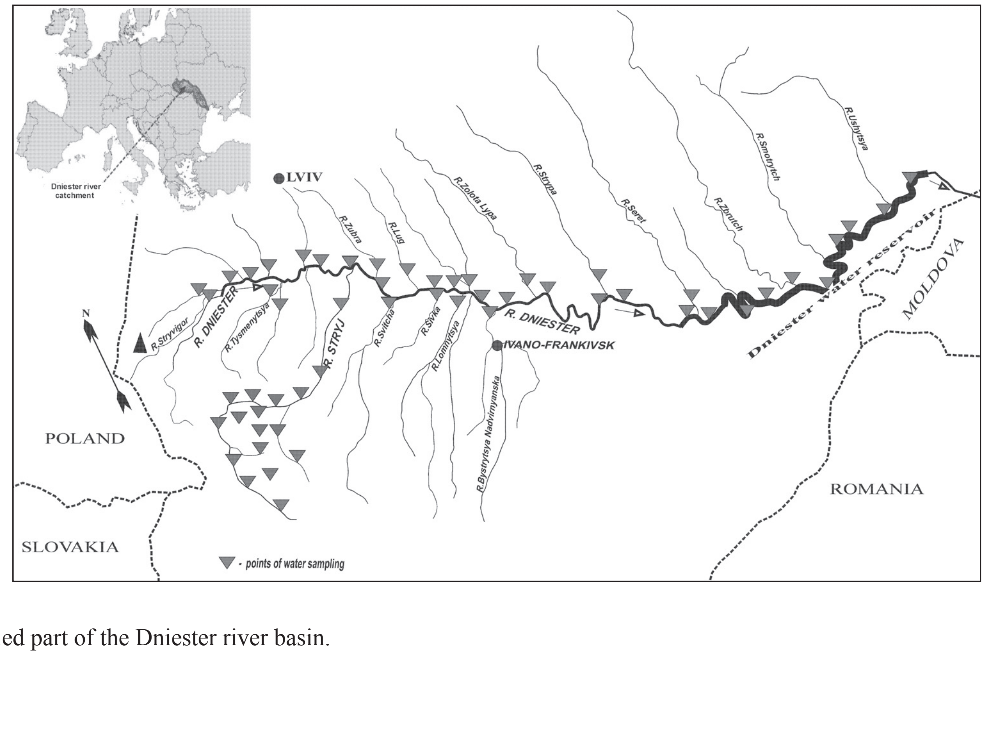

Fig.3. The studied part of the Dniester river basin.

So, mining industry, oil-refining, chemical, woodworking and food industry, municipal wasterwaters and agricultural objects are the main factors of anthropogenic loading on the surface waters of the Dniester basin. In 1999 the volume of sewage water dicharge in the Dniester river was 520 mln m^3 with 82,830 tons of pollutants [7]. The dynamics of pollutant discharge in the Dniester during 1993-1999 is shown in Fig. 4.

According to the data of the Ministry of Ecology and Natural Resouces of Ukraine from 1995 to 1999 in rivers of the Dniester basin a gradual increase in the water level was observed, but the average annual values of TDS during this period did not change. The average annual contents of the major pollutants in the Dniester river water were the following (comparing with the corresponding maximum allowed concentrations (MAC) for drinking water): oil products - 1-3 MAC, phenols - 1-9 MAC, nitrogen compounds - 1-6 MAC, Zn -1-15 MAC, Mn - 15-24 MAC, Cr (VI) - 5-13 MAC. Dniester tributary waters contain N (NH_4) - 1-3 MAC, N (NO_2) - 1-6 MAC, oil products - 1-3 MAC, phenols - 1-9 MAC, Zn - 1-3, Cr (VI) - 6-17 MAC [7]. The state of hydrobiocenosis was studied in the Dniester River and some of its tributaries (rivers Tysmennystya, Stryj, Seret, Bystrystya Solotvynska) according to index of saprobeness by Pantle and Buck and to index of diversity by Shannon. By the average of Pattle and Buck index of saprobness indicators in the most cases surface waters of the Dniester basin were estimated as moderately polluted. In most of the water bodies the average values of Shennon diversity index point to the stability of plankton cenosis. Integral indicators of the state of ecosystems show that the studied rivers are mainly in the state of anthropogenic ecological stress with elements of regress [7].

Data Sources and Study Methods

The state of environment of the Dniester river basin was studied in 1995-2001 by hydrochemical and lithochemical testing, including the expedition works conducted in the summer periods in the limits of the area from the mouth of the Stryvigor river to the Moldavian-Ukrainian State border during the ecological expedition "Dniester," organised by the non-goverment organization "Lion Society" (L'viv, Ukraine). Objects of water and soil sampling and analysis are shown in Table 2.

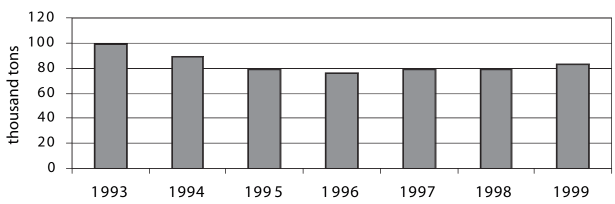

Fig.4. Dynamics of pollutant discharge in the Dniester River in 1999 [7].

Surface waters and alluvial deposits (bottom sediments, bank mud and flood-land soils) were sampled in the river-bed parts of the Dniester before and after potential sources of pollution, before and after falling in the tributaries and in the mouths of the tributaries and in the Dniester water reservoir. In the Dniester reservoir water samples for analyzing contents of heavy metals were taken at the surface and at a depth of 20 m. Ground waters were tested in draw-wells and springs.

Concentrations of major ions (Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-} and Cl^-), pH, water-dissolved oxygen, iron and nitric compounds in waters were analyzed directly after having samples by volume and visual-colorimetrical method. Other analyses were conducted in the spectral laboratory of the Institute of Geology and Geochemistry of Combustible Minerals, L'viv, Ukraine. Mobile speciations of heavy metals in alluvial sediments were studied using 1 N HCl - and 0.2 N HNO_3 extraction. Contents of heavy metals, oil-products and phenols in water were determined by atomic-adsorption and atomic-emission methods, weighting method and spectrophotometric methods respectively.

Results and Discussion

Total Chemical Composition and Nitric Compounds

The majority of the rivers, including the Dniester, and the Dniester reservoir are in the satisfactory conditions by the hydrogen index (pH), the TDS (mineralization), macrocomponent composition, contents of iron-, ammonium-, nitrite-, and nitrate-ions. Rivers Bystrytsya and Muksha have elevated contents of ammonium-ions that may be conditioned by sewage of the cities Ivano-Frankivs'k and Kamjanets'-Podilskyi, respectively polluting these tributaries. Rivers Tysmenytsa and Syvka, waters of which are sulfate-chloride sodium and chloride sodium compositions with TDS 0.6 and 2.2 g/dm^3, stand out sharply against others. It is apparent that technogenic factors play a major part in forming their total chemical composition. The effects of enterprises of cities Stebnyk and Kalush is evident. But the influence of those rivers on the Dniester is local and variable, depending on periodic dumps of sewage.

The tested ground waters contain nitrate-ions in concentrations from 3.4 to 408.8 mg/dm^3 and nitrite-ions - from 0.01 to 0.5 mg/dm^3. Contents of nitrates higher than MAC were fixed in 57% and of nitrites - in 40% of the water samples. By this the elevated amounts of nitrites in ground waters were concentrated in the upper part of the catchment, but there was no regularity in nitrate concentration distribution downstream in the Dniester River. So the ground waters of upper aquifers in the Dniester valley are regionally polluted by nitrate-ions in large measure and locally polluted by nitrite-ions. Wide use of mineral fertilizers, wastewaters of animal farms and municipal sewage are the main factors of nitrate accumulation in the subsurface waters of the region.

Table 2. Objects of Water and Soil Sampling in the Dniester Basin.

Objects	Amount of samples	Analyzed characteristics
Surface water	59	pH, Major ions, NH_4^+, NO_2^-, NO_3^-, Fe_{tot}, K, O_{2dis}, heavy metals (Ni, Co, Mo, Cu, Fe, V, Mn, Ba, Be, Ti, Sr, Cd, Pb, Sn, Zn, Al, Cr, Ag, La, Zr, Y, As), phenols and oil-products
Ground water	67	NH_4^+, NO_2^-, NO_3^-
Alluvial deposits (bottom sediments, bank mud and flood-land soils)	49	Heavy metals (total concentrations and migration forms) (Zr, Co, Mn, Pb, Cr, Ni, V, Mo, Y, La, Sc, Ti, Cu, Ag, Ba, Sr, Sn, Zn, Be, Ga, As, Cd).

Heavy Metals

Concentrations of the most part of analyzed heavy metals in the Dniester river, its tributaries and the Dniester reservoir are significantly lower than their MAC for drinking water and are close to their average contents in unpolluted river waters. The elevated contents of barium, strontium and aluminium have been estimated in some samples of the Dniester River waters and its tributaries. The rivers Bystrytsa-Nadvirnyanska and Dniester before Stryy mouth are most polluted by metals. It is obviously connected with industrial sewage (enterprises of cities Novy Rozdil and Ivano-Frankivsk), but this fouling is local owing to an insignificant ability of metals for migration. In the limits of the Dniester water reservoir the bottom layer of water is enriched by Zn, Mo, Cu and Ni in comparision with the surface layer. So low concentrations of heavy metals in waters of the studied section of the Dnister river basin are caused by an absence of powerful regional sources of pollution, low migration ability of metals and high possibility of self-cleaning of the Dniester water system.

Alluvail sediments of the Dniester valley are characterized by the elevated contents of Co, Ag, Sc, Mo in comparision with their average clark concentrations in soils. Amounts of the other elements are in the limits of clark values. The part of migration form of metals in their total content increases in the row "flood land soil – bank mud – bottom sediment" for every point of testing.

Phenols and Oil-Products

Contents of phenols and oil-products are higher than MAC for drinking waters in all tested rivers in 9-54 and 2-15 times. In the Dniester water in the area from the river Stryvigor to the Dniester water reservoir the defined contents of phenols are from 0.014 (1.5 km upper than the mouth of Syvka) up to 0.081 mg/dm^3 (200 m lower than the mouth of the Strypa river). In most cases the concentrations of phenols are 30-40 μg/dm^3, considerably higher than the limited norm (1 μg/dm^3). Two sections of the Dniester (Stryvigor – Tysmenytsya and Bystrytsya Nadvirnyanska – Strypa) are characterized by the elevated contents of these compounds. In the Dniester tributaries phenols have been found in amounts from 9 (the Svicha river) to 47 μg/dm^3. Such rivers as the Stryvigor, the Tysmenytsya, the Lug, the Bystrytsya Nadvirnyanska, Syvka are the most polluted with concentrations of phenols 35–47 μg/dm^3 [11].

Concentrations of phenols in the Dniester water reservoir are 11-51 μg/dm^3 with the average value 26 μg/dm^3. High concentrations of phenols (18 μg/dm^3 for volatile fractions and up to 2 mg/dm^3 for non-volatiale fractions) have been established in the Dniester water on the territory of Moldova Republic by G.G.Gorbaten'kij *et.al.* [12]. So the regional distributuion of phenol pollution is observed in the Dniester basin, as well as in the other Ukrainian river basins (Fig. 5).

The similar state is observed with oil-products distribution in the Dniester river basin. Concentrations of oil-products in the Dniester river water are in 1.6-14 times higher than MAC for drinking water (0.3 mg/dm^3), in the Dniester reservoir – in 4.5 times. The highest concentrations of these compounds have been found in waters of the rivers Lug, Zbruch, and Syvka. High contents of oil-products and phenols in waters of the Dniester water reservoir with absence there sources of such pollution testify to their ability to long migration and to the danger of the corresponding pollution for the coastal zone of the Black Sea. There is now doubt, that such high contents of phenols and oil-products are the results of the Carpathian mining complex activity. Its influence on the surface water is regional by the fouling of phenols and oil-products. At the same time, these compounds are produced naturally when organic matter of soils is decomposed biochemically and during the formation of

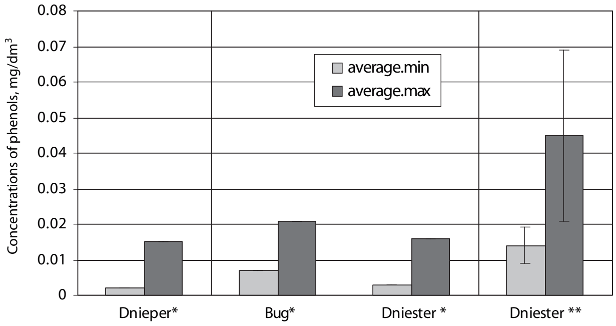

Fig.5. Phenol pollution in Ukrainian rivers.
Notes: * - data of National Report of Ministry of Ecology of the Ukraine for 1999 [7]; ** - results of our study for 1995-1999.

crude oil and oil shales [13,14,15]. Therefore, in our opinion specific geological conditions of the Upper Dniester basin concluding wide distribution of oil, gas and oil shale formations provide the high natural background of phenols and oil-products in the surface water of the region.

Correlation Between Hydrochemical and Hydrobiological Study Results

Hydrobiological investigations of the Upper and the Middle Dniester basin (including the Dniester reservoir) were conducted in the process of the ecological expedition “Dniester” during 1988-1996. The water quality was estimated by the state of hydrobiocenosis using index of saprobeness by Pantle and Buck and to index of diversity by Shannon [13]. According to these investigations the surface waters of the Dnister basin are from “rather pure” to “moderately polluted” with a predominance of local pollution. The concrete results of the hydrobiological study correspond to the hydrochemical data. So, water thickness of the river Svicha, one of the purest rivers of the region by visual observation and total chemical composition, is classified as organically polluted by the state of hydrobiocenosis, although its water is entirely pure by bentos state. It may be conditioned by the influence of elevated contents of oil-products and phenols being concentrated in the upper layers of the water. The similar hydrobiological consequences of the pollution were observed in other rivers of the basin [11,13].

Conclusions and Outlook

The water system of the Dniester river, one of the big European rivers, is in the satisfactory state by total macrocomponents composition, nitric compounds and heavy metals content. The pollution by these characteristics are observed only in the limits of the local areas, mainly close to the pollution objects. Ground waters of the region are regionally polluted by nitrate-ions, thanks to the wide use of mineral fertilizers, wastewaters of animal farms and municipal sewage. Surface waters of the Dniester River, its tributaries and the Dniester reservoir are strongly polluted regionally by phenols and oil-products that may be connected with both natural and anthropogenic factors. The main sources of phenols and oil-products in the Dniester basin are the upper part of the catchment, where on the high natural backround of phenols in surface waters there are many objects of petroleum mining and oil-refinery industry contributing to the anthropogenic phenol pollution. Hydrochemical data of phenol distribution in surface waters of the region correspond to the results of the hydrobiological investigations.Thanks to the high migration ability of phenols and oil-products their elevated concentrations are defined in the Middle Dniester basin including the Dniester reservoir, although there are no significant pollutant-objects.

Partner Water Initiative EU-CECCA (European Union – Countries of Eastern Europe, Caucasus, Central Asia) launched at the World Summit on Sustainable Development in Johannesburg, South Africa, in 2002, gives the main attention to general adoption of river basin-scale policy, planning and management, particularly for transboundary catchments. Within the EU the corresponding projects, such as Eurocat, are realized now [2,14]. It is necessary to use the European adopted approachs to study the Dniester River as a transboundary river whose environmental state is reflected in the conditions of the significant coastal zone of the Black Sea.

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