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11. Quality of running water from Dniester river hydrographic basin (in limits of the Republic of Moldova)

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ABSTRACT. The paper presents the results of studies focused on the quality parameters of Dniester river and its tributaries. Self-purification capacity of the running waters in the studied area has average values of 0.30 - 0.35. Water of the Raut river (main tributary of Dniester river) has a self-purification capacity of 0.25 upstream of Orhei city and only of 0.16 downstream of Orhei city, which confirms the massive impact of wastewater discharged into the river. The investigated surface waters, taking into account the consentrations of organic substances (CCO-Cr and CBO_5) are classified as being of class I (very good) - III (moderately polluted) quality. Water of the Raut river is classified as class II (good) - IV (polluted). Taking into account the Fe and Zn content, the rivers are classified as being of Class I (very good) - II (good) of quality. Content of Cu, Cd and Pb in water ranks it in class II (good) - III (moderately polluted) of quality, except water of the Raut river were their content classified water as class II (good) - >V of quality (very polluted/degraded). Content of heavy metals in underwater sediments are at admissible limits. Only the content of Pb in sediments of the Raut river both upstream and downstream of the Orhei town exceeds 2 times its limit in underwater sediment.

Key words: Self-purification capacity, organic substances concentration (CCO-Cr and CBO_5), heavy metals, underwater sediment

INTRODUCTION

In the process of society socio-economic development, quality and quantity of water are requirements of first priority. Waters with good quality, but insufficient as quantity can not meet the needs of an evolved society. Quality requirements imposed by laws vary from country to country and from one type of use to another – consequently, the notion of contaminated water has a relative character. Water quality does not remain constant over time, but may vary due to many factors, either produced by man (anthropogenic factors) or having natural origin.

In the Republic of Moldova, surface water is the major source for human needs, including drinking water supply.

In Europe more increasingly becomes the problem of the ecological state of natural waters: approx. 20 % of surface water is of high risk to pollution, 60% of European cities exploit irrational groundwater resources and 50 % of wetlands are in danger.

Water pollution is a complex phenomenon that results in a change of the composition of water, damage of aquatic flora and fauna, making it unsuitable for economic or recreational use and harmful for human health.

Thus under intense anthropogenic influence on the water, pollution is an actual problem, with consequences more or less severe on the population.

Therefore, studies aimed at determining quality of the water are increasingly of important role. Water quality can be defined as a set of conventional physical, chemical, bacteriological and biological terms, marked in values, allowing inclusion of a water sample in a particular category, it thus acquiring ownership to serve particular scope.

MATERIALS AND METHODS

Research-methods and calculation, as well analytical methods are corresponding to European legislation, using the methodology recommended by the European Environment Agency.

A diverse range of physical-chemical measurements were performed using classical chemical methods and the physical ones.

The samples were collected in compliance with the necessary requirements, being performed field observations and laboratory measurements.

RESULTS AND DISCUSSION

In order to assess the anthropogenic impact on water quality in the Dniester river there have been taken samples from Dniester river and its tributaries - Ikel, Raut and its tributaries (Ciulucul Mic, Ciulucul Mediu, Ciulucul Mare, Cainar, Cubolta, Camenca) in accordance with regulatory requirements ([***4***]; [***5***]).

In water samples were determined quality indicators, in accordance with national and international standards on harvesting methods and determination of quality parameters for surface water classification (NORCAS-02).

The content of some organic substances and heavy metals in natural waters is comparatively small, so in case of the there were used the freeze concentration, a very affordable and effective method used to concentrate organic compounds ([***1***]; [***11***]; [***13***]). The main advantage consists in the volatile storage of the samples, compounds unstable at high temperatures (their decomposition does not occur) and exclusion of organic solvents ([***6***]; [***10***]) which interferes determinations.

Accuracy of analytical work has been verified using the internal standards ([***3***]; [***9***]; [***12***]) (see version/method A in **Table 1**).

Standards used: ISO, ISO and national.

Table 1

The variants of internal-standard method

Method A	Method B	Method C
In the second sample is added to a precise quantity of substance, are compared with the original sample, were it was introduced search for substance	It is added the substance with atoms in molecules that differ in part after isotope composition ("isotopic dilution")	It is added a precise amount of substance, which has analogous particularities but not identical chemical

Determination of self-purification capacity of natural waters

All natural (hydrodynamic, chemical, biochemical) processes occurring in polluted natural waters or slightly polluted ones lead to improvement of water quality, resulting in pure (clean), natural water particularities and properties – a phenomenon known as self-purification. It is conditioned by hydrodynamic factors (speed of water, the intensity of aeration, evaporation etc.), chemical factors (oxidation, reduction, hydrolysis, complexation etc.), biochemical factors (biochemical oxidation, metabolism, biological accumulation), the solar radiation, the biological activity (flora and fauna). The intensity of factors varies with the change of temperature (stagnating at low temperatures), the degree of dilution of sewage discharged into natural aquatic environment. For its determination it was using the formula proposed by A. Snelis and N. Mancek ([***2***]; [***7***]; [***8***]).

Estimating the chemical composition of natural waters

The results of actual water composition from the Dniester river are shown in **Table 2**.

Table 2

Quality indicators of the Dniester river water

Indicators and units of measurement	Sections			
	Otaci	Soroca	Varancau	Vadul lui Voda
Mineralization, mg/dm^3	250	246	370	416
Dissolved Oxygen, mg/dm^3	7.4	8.3	9.2	7.6
Particles in suspension, mg/dm^3	24.3	27.5	34.2	56.3
Chloride, mg/dm^3	40	42	52	56
Sulfate, mg/dm^3	66	72	84	93
Ammonium, mg/dm^3	0.12	0.14	0.15	0.4
Nitrite, mg/dm^3	0.02	0.02	0.03	0.03
Nitrate, mg/dm^3	7.2	4.2	6.0	8.8
Phosphate, mg/dm^3	0.5	0.2	0.3	0.6
CBO5, mg O2/dm^3	3.6	3.8	4.2	7.5
CCO-Mn, mg O2/dm^3	5.3	4.2	7.5	12.4

A critical situation was observed in the town Otaci section, downstream from the border with Ukraine and the Dubasari region. Here, as consequence of downstream discharge of water from the bottom of Novodnestrovsk reservoir (Ukraine) with a low temperature, was radically disturbed the thermal regime of water during the spring, summer and winter (relatively warm). As a result of thermal stratification of water in the Novodnestrovsk reservoir is discharged downstream from the area under the thermocline.

In rivers water there were evaluated the existence of organic matter forms and was established the ratio (%) of indicators characterizing the level of pollution (CCO-Mn/CCO-Cr, CBO5/CCO-Cr, CBO5/CCO-Mn). It was calculated the degree of present in river water organic matter transformation by correlating indices CCO-Mn / CCO-Cr (easily biodegradable organic matter), BOD5 / COD-Cr (Organic matter hardly degradable), BOD5 / COD-Mn (Organic matter biologically degradable) (**Table 3** and **Table 4**)

Content of anionic surfactants in water of the studied river remains high (0.04 - 0.52 mg/dm^3), indicating once again domestic pollution of surface waters, their content correlating with the number of villages in the basin (**Table 5**).

Self-purification capacity of Dniester river water is middle (at Otaci town) and decreases to low downstream Soroca town (**Fig. 1**) and water self-purification capacity of river Raut water ranges from very small (0.1 - downstream Balti town) to low (0.25 - upstream Orhei town) (**Fig. 3**). Self-purification of water from Raut river tributaries is very low (river Cubolta and Cainari) to lower 0.23 (river Camenca) (**Fig. 1** and **Fig. 2**). Between 0.2 and 0.4 the self-purification has a medium speed, and at less than 0.2 it is slow.

Table 3

The values of BOD_5, COD-Mn and COD-Cr in water characteristic for Dniester river

Sections	CBO_5	CCO-Mn	CCO-Cr
	mg/dm^3 O		
Dniester river, Otaci town	7.9	9.3	22.5
Dniester river, Cosauţi village	7.96	10.3	26.1
Dniester river, Soroca town (downstream)	8.27	10.1	44.3
Dniester river, Varancau village, Soroca	6.02	8.9	28.4

Table 4

Quota (%) of easy and heavy degradable chemical substances, biological degradable

Sections	Organic matter (easily biodegradable), %	Organic matter (hardly degradable), %	Organic matter (biologically degradable),%
Dniester river, Otaci town	41.3	58.7	35
Dniester river, Cosauţi village	39.4	60.6	30
Dniester river, Soroca town (downstream)	22.8	77.2	19
Dniester river, Varancau village, Soroca	31.3	68.7	21

Table 5

Anionic surfactants and copper content in water of Dniester river

Sections	Anionic surfactants (mg/dm^3)	Cu (mg/dm^3)
Dniester river, Otaci town	0.53	0.0019
Dniester river, Cosauţi village	0.26	0.0008
Dniester river, Soroca town (downstream)	0.46	0.0034
Dniester river, Varancau village, Soroca	0.22	0.0015

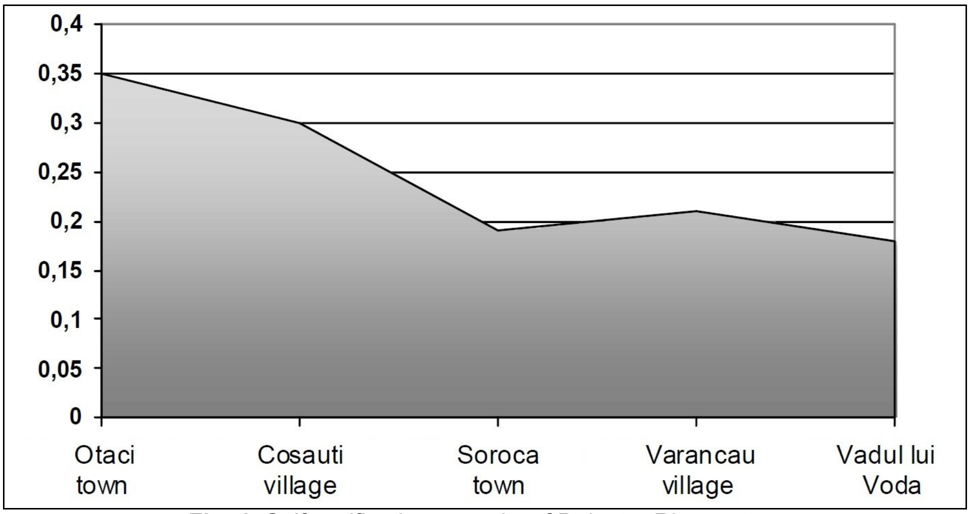

Fig. 1. Self-purification capacity of Dniester River water.

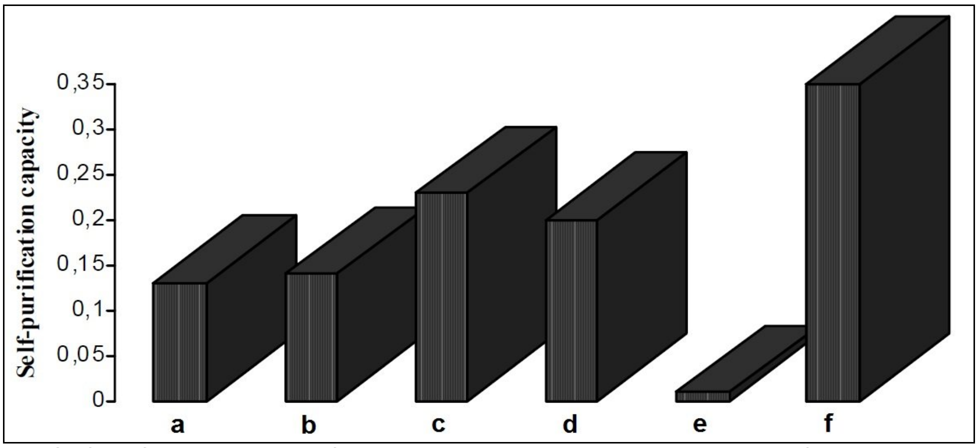

Fig. 2. Self-purification capacity of small rivers water in comparison with that of the Dniester river.

Note. a – river Cainari (Gura Cainari village); **b** – river Ikel (Ratus village); **c** – river Camenca (Gura Camenca village); **d** – river Cubolta (Mandac village); **e** – streamlet (Sangerei town); **f** – river Dniester (Otaci town).

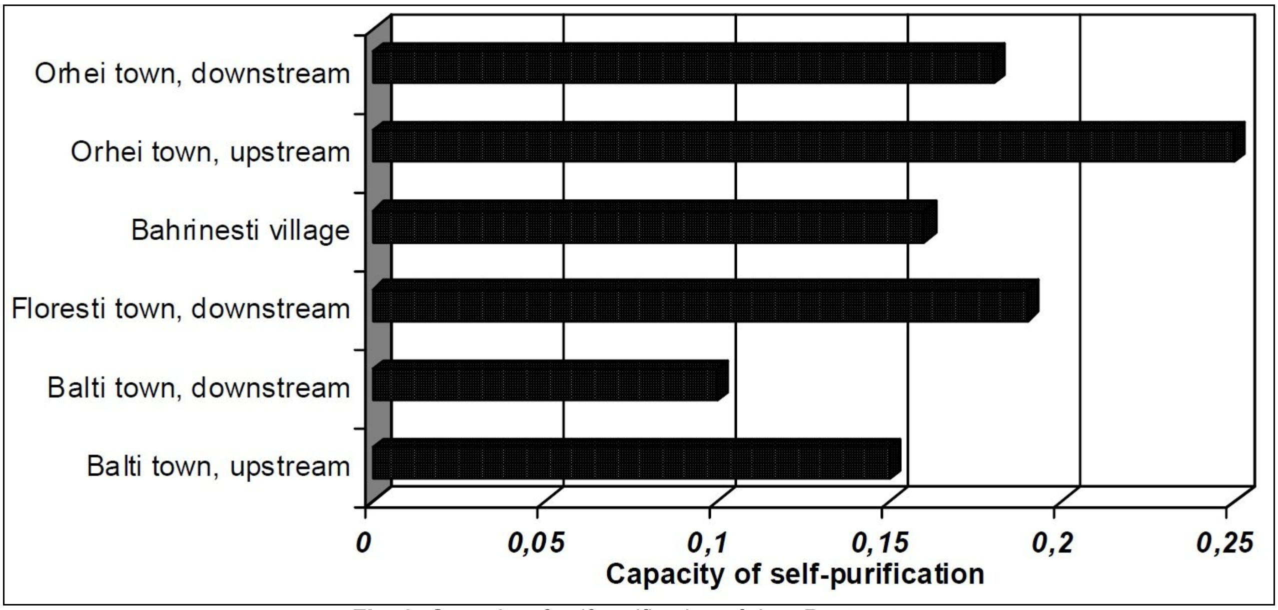

Fig. 3. Capacity of self-purification of river Raut water.

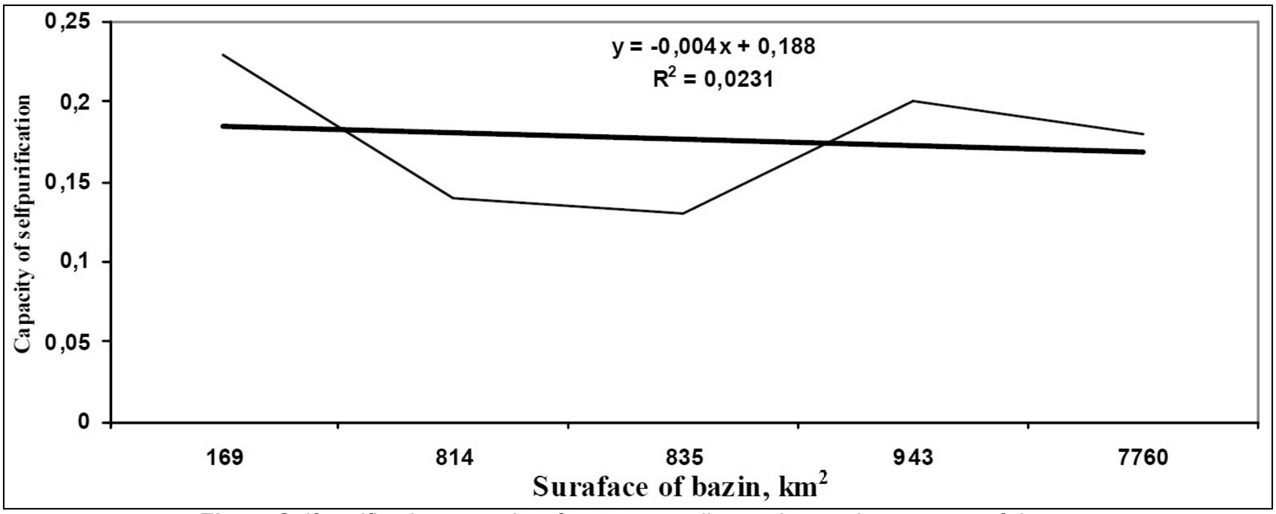

Fig. 4. Self-purification capacity of water according to the catchment area of rivers.

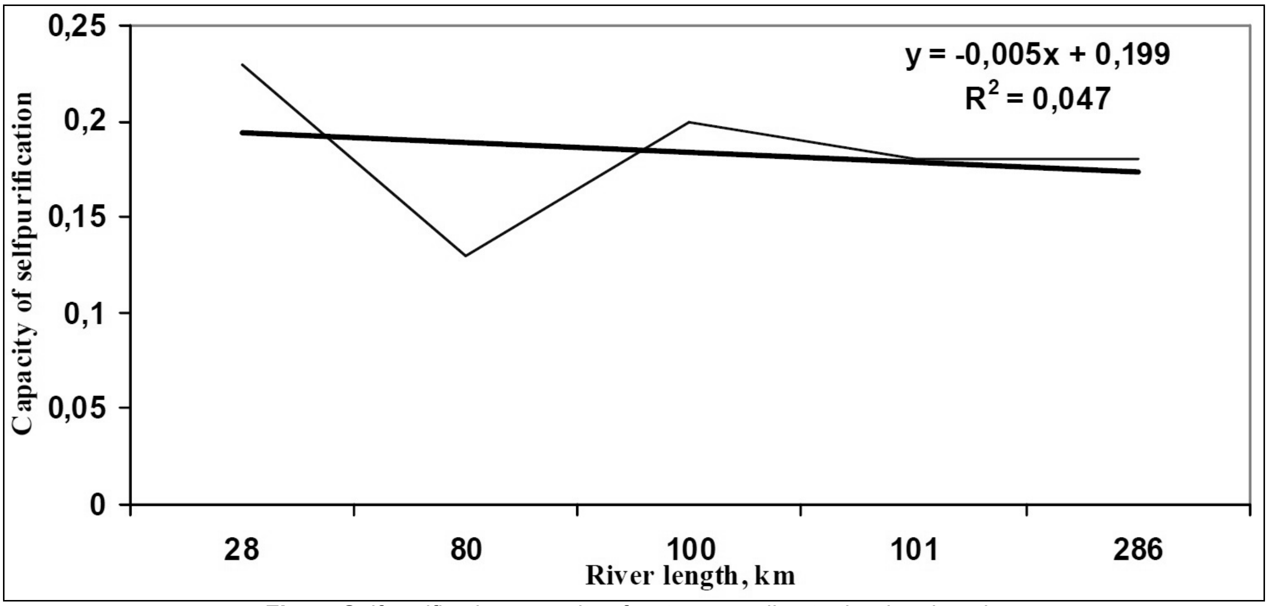

Fig. 5. Self-purification capacity of water according to the river length.

Note. river Camenca - 28 km; river Cainari – 80 km; river Cubolta – 100 km; river Ikel – 101 km; river Raut - 286 km.

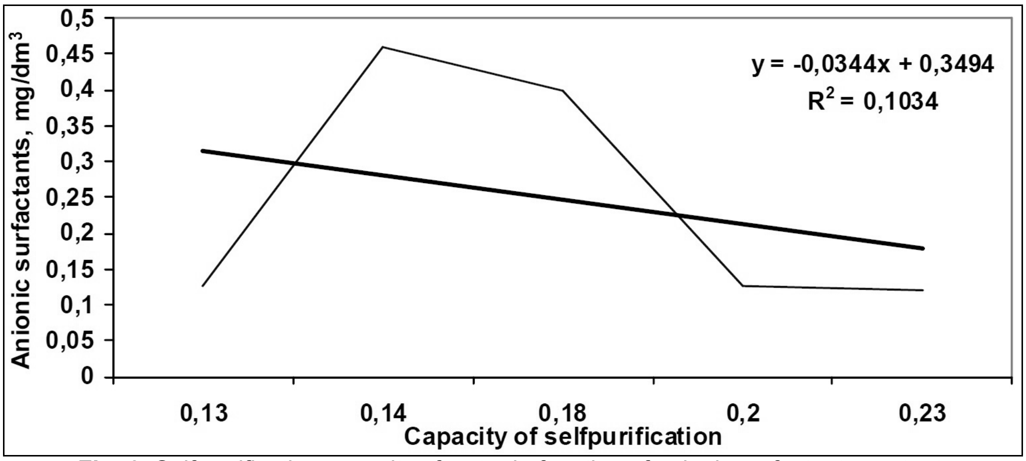

Fig. 6. Self-purification capacity of water in function of anionic surfactants content.

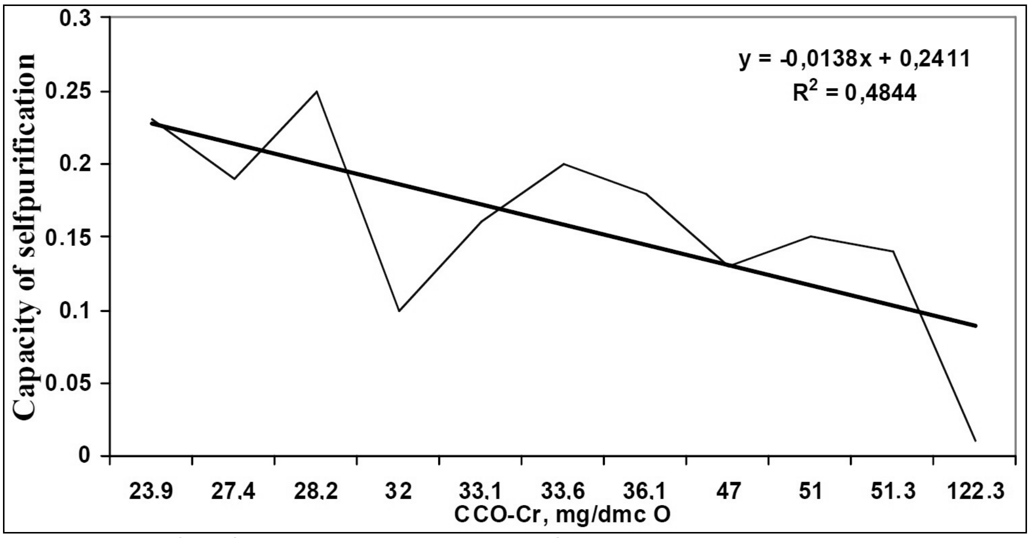

Fig. 7. Correlation between self-purification capacity and content of readily biochemically degradable substances in small river water.

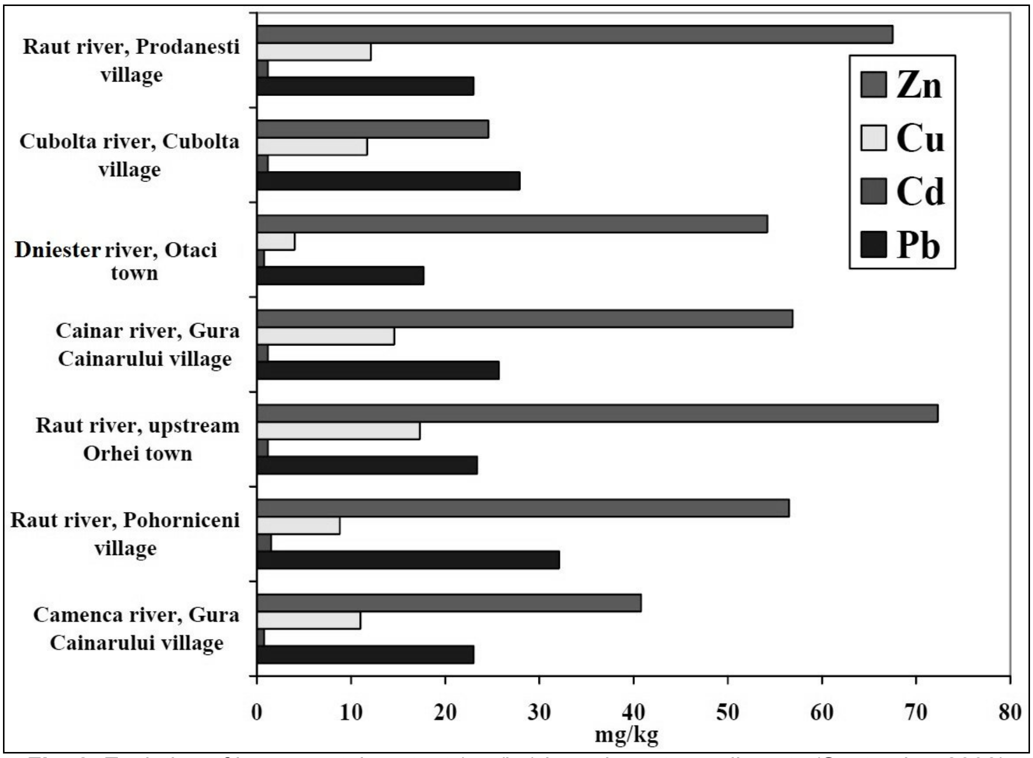

Fig. 8. Evolution of heavy metal content (mg/kg) in underwater sediments (September 2008)

The performed research shows a strict correlation between self-purification capacity and river basin area, river length and number of villages in the basin (**Fig. 4** and **Fig. 5**).

Self-purification capacity of water correlates with the anionic surfactants content (**Fig. 6**).

A clear correlation is found between self-purification capacity and content of readily biochemically degradable substances in small river water (**Fig. 7**).

Determination of heavy metals in underwater sediments

Seasonal dynamics of heavy metal content in underwater deposits collected from studied rivers are presented in **Fig. 8**.

The obtained results (content of heavy metals) indicate quantities that are below their background concentrations in soil.

CONCLUSIONS

1. Evacuation downstream of water from deep level of Novodnestrovsk (Ukraine) lake with a low temperature during spring and summer and relatively warm in winter, radically disordered thermal regime of water in Dniester river;
2. Content of anionic surface-active substances (0.04 – 0.52 mg/dm^3) in Dniester river water remains high which demonstrates domestic pollution of its water;
3. Waters of small rivers (right-side tributaries of Dniester river) are polluted both readily biodegradable substances and chemicals;
4. The content of copper compounds from river water correlates with the length of the river and its basin area;
5. Water self-purification capacity in right tributaries of Dniester river varies between 0.1 and 0.4 and is correlated with biochemical content of hardly biochemical degradable pollutants. The process has an average speed in Dniester river water (Otaci, Cosauti, Varancau), Camenca and Raut river, upstream Orhei town and below 0.2 it is slow in most small rivers;
6. A clear correlation is found between the self-purification capacity and content of biochemical readily degradable substances in waters of small rivers. Contents of biochemically hardly degradable pollutants in water of small rivers correlate with the length of the river, which shows that the major pollution source is housework.

REZUMAT (SUMMARY IN ROMANIAN LANGUAGE). **Calitatea apelor curgătoare din bazinul hidrografic al râului Nistru (în limitele Republicii Moldova).** În articol sunt prezentate rezultatele privind parametrii de calitate a apelor curgătoare din bazinul hidrografic al fluviului Nistru. Capacitatea de autoepurare (CA) a apelor de suprafaţă din arealul cercetat au valori medii de 0,30 - 0,35. Apa râului Răut (amonte orașul Orhei) are CA = 0,25, în aval CA = 0,16, fapt ce confirmă impactul masiv al apelor reziduale deversate în râu. Apele de suprafaţă, după concentraţia substanţelor organice (CCO-Cr şi CBO_5) sunt de clasa I (foarte bună) - III (moderat poluată) de calitate, iar cea a râului Răut de clasa II (bună) – IV (poluată) de calitate. Apa după conţinutul de Fe şi Zn este de clasa I (foarte bună) / clasa II (bună) de calitate. Conţinutul de Cu, Cd şi Pb clasează apa în clasele II (bună) / III (moderat poluată) de calitate, cu excepţia apei din râul Răut care este de clasa II (bună) > V de calitate (foarte poluată/degradată). Conţinutul de metale grele din sedimentele subacvatice este (în majoritatea cazurilor) în limitele admise, doar conţinutul Pb în sedimentele râului Răut (amonte şi aval de orașul Orhei) depăşeşte de 2 ori limita acestuia în sedimente.

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