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9. Interdependency of underground water – surface water in the Prut river hydrographic basin

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ABSTRACT. The article presents the data on the evolution of water quality parameters of the Prut river, taking into account the results of samplings performed in sites (on the side of Republic of Moldova) of several sections of Prut river (Criva, Sirăuți, Brânișteni, Valea Rusului, Sculeni, Ungheni, Valea Mare, Cotul Morii, Leuseni, Leova, Cantemir, Cahul and Giurgulești), respectively at Costești dam. The results show higher concentration of pollutants both downstream of cities that do not have waste water treatment stations and at the confluence of Prut with its tributaries. It was stated exceeding values of the maximum admissible concentration - about 1.7 times, downstream of the Leova city (Republic of Moldova) where insufficiently treated waste water is discharged. Content of Dissolved oxygen is satisfactory, reaching the minimum value of 6.3 mg / dm^3 at Giurgiulesti (Cahul district, Republic of Moldova). Total content of organic substances is increasing downstream of the river, at the same times content of petroleum products recorded variations between 0.036 and 0.137 mg / dm^3. Thus, the Prut river water quality was within the limits for a Class II (clean) – Lipcani – Şirăuţi section (northern part of the Republic of Moldova) and Class III (moderately polluted) – Leova sampling section (southern part of the Republic of Moldova).

Key words: surface water, maximal admissible concentration, water quality classes, Prut river basin, Republic of Moldova

INTRODUCTION

In the context of socio-economic situation, which would increase the requirement for qualitative water, and in conditions of climate change (extreme conditions - drought and floods), both surface water and groundwater in particular represents strategic water resources for most countries ([***1***]; [***2***]). As aquifers are not quit natural water bodies, but are always subject to human impact, their protection in terms of quantity and quality has become very important ([***3***]; [***4***]; [***5***]). The efficiency and specific character of protection measures depends on the evaluation and assessment mode of their vulnerability to human impact. For any locality the potential drinking water sources typically fall into three categories: (1) water from the atmosphere; (2) surface water and (3) the underground water.

Groundwaters are the major source of drinking water, the use of which is constantly increasing, especially in the context of climate change and substantial reduction of drinking water sources, both at European [***10***] and national level [***12***].

In condition of intense anthropogenic factor influence on the water sources, their pollution is an actual problem ([***6***]; [***9***]; [***10***]) with consequences more or less severe on the population. Therefore, the monitoring of water quality both of the surface and groundwater is increasingly important ([***7***]; [***8***]; [***11***]). Water quality can be defined as a set of conventional physical, chemical, biological and bacteriological terms marked in values, allowing inclusion of a water sample in a particular category, it thus acquiring ownership to serve particular scopes.

MATERIALS AND METHODS

The research methodology of water bodies (in terms of their chemistry and water quality) does not take into account their origin, so that it can be applied to study the known means and methods, or those recommended by the European Environment Agency.

Water samples were collected in compliance with the necessary requirements ([***7***]; [***8***]; [***11***]), conducting field observations and laboratory measurements. Water samples were analyzed without previous conservation of the samples. The chemical and quality parameters of water are established in accordance with the requirements of the Water Framework Directive [***9***]. Thus, some physical-chemical parameters lists the nitrates, nitrites, mineral nitrogen, total nitrogen, phosphates and total phosphorus, dissolved oxygen and organic substances, expressed as BOD5 (biochemical oxygen demand).

Water quality monitoring is the activity of standardized observations and measurements and continues for long term for knowing and evaluating characteristic parameters to management and highlight trends in its quality. In this context, it was performed a qualitative assessment of the Prut river water and of some groundwater's (springs, fountains) from it hydrographical basin (Glodeni and Fălești administrative territories). For each surface water body (Prut River and its tributaries) were identified pressures in terms of pollution and realized an assessment of human impact through analysis of five groups of chemical indicators: regime of oxygen, general ions, regime of biogenic elements, heavy metals, specific pollutants, establishing class of quality that each falls and ecological state of rivers water. Equipments used during the study: DR/2500 Spectrophotometer, pH meter, analytical balance, centrifuge.

RESULTS AND DISCUSSION

To assess the anthropogenic impact on surface water during the years 2013 - 2014 there were collected water samples from the Prut river and its left tributaries, according to regulatory requirements by respecting cheerful type, frequency of collection, conditions of storage and performance of analysis. Water sampling was performed seasonally.

The results of chemical analyzes as to the evolution of the Prut river water quality indicators (sections) show a higher concentration of pollutants downstream cities which have sewage treatment plants, but basically does not work and in confluence with the tributaries it certifies nitrates exceeding the maximum admissible concentration (about 1,7 times) or downstream Leova town where insufficiently treated wastewater is discharged directly into the river Prut (**Fig. 1**).

Dissolved oxygen content is satisfactory, the minimum value being equal to 6.3 mg/dm3 in Giurgiulesti section (**Fig. 2**).

Variation of quality indicator - oxidability, showing the overall content of organic substances, determined by the necessary quantity of oxygen to the oxidation of them is shown in **Table 1**.

On the river flow is observed the increasing of total organic matter content (**Table 1**), while that of petroleum products recorded variations between 0,036 and 0,137 mg/dm3 (**Fig. 3**).

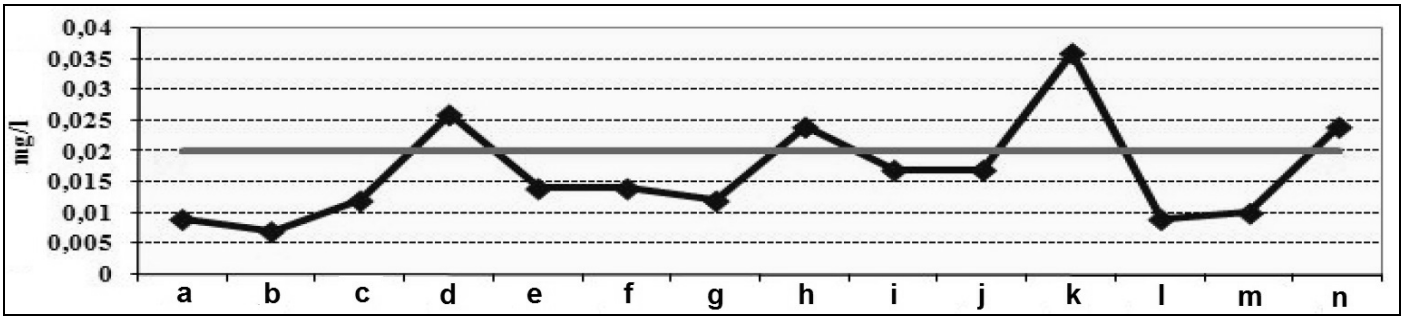


Fig. 1. Evolution of nitrites content in the Prut river water on sections.

Note. Sampling sites: a - Criva (Prut river); b - Sirăuți (Prut river); c - Costești dam (Costești river bazin); d - Braniște (Prut river); e - Valea Rusului (Prut river); f - Sculeni (Prut river); g - Ungheni (Prut river); h - Valea Mare (Prut river); i - Cotul Morii (Prut river); j - Leuseni (Prut river); k - Leova (Prut river); l - Cantemir (Prut river); m - Cahul (Prut river); n - Giurgulești (Prut river).

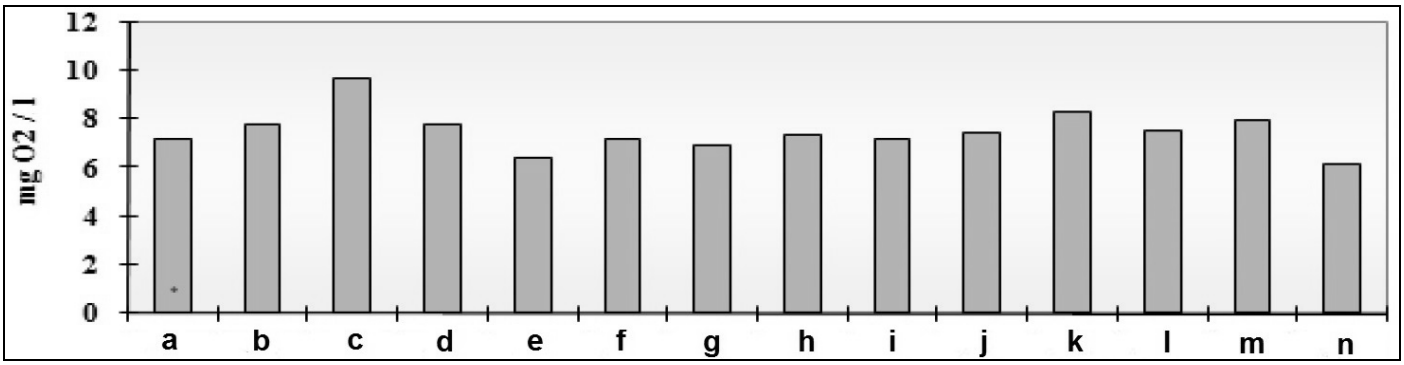


Fig. 2. Evolution of dissolved oxygen content in water of river Prut, august 2013.

Note. Sampling sites are similar to the ones indicated in **Fig. 1**.

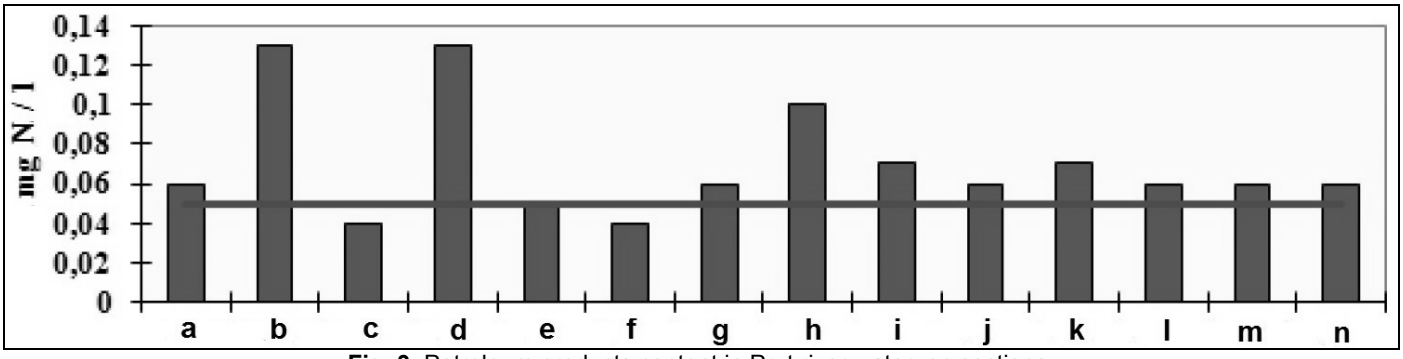


Fig. 3. Petroleum products content in Prut river water, on sections.

Note. Sampling sites are similar to the ones indicated in **Fig. 1**.

According to the results of our study, the quality of river Prut water was within the limits for a class **II of quality (clean)** in the Lipcani-Sirauti section and **class III (moderately polluted)** in the Leova section.

Ground waters are most vulnerable to anthropogenic impact. Specter of natural and artificial pollutants is very broad (nitrogen compounds, pesticides, sulfates, etc.) and they are the consequences of practicing intensive agriculture and of unhealthy land.

The causes of nitrate contamination are multiple and have a cumulative character. Two sources have significant share in the contamination of groundwater with nitrates. They are: constantly washing of polluted with nitrate soil by rainfall and irrigation water and surface water (rivers, lakes) that were discharged wastewater loaded with nitrogen compounds.

To minimize the degree of inorganic and organic compounds accumulation in springs water it are necessary urgent measures that prevent pollution, including metamorphose of water composition.

The process of fitting and cleaning of open water supply sources is a long-term, the main problem being the attitude and mentality changing of our citizens to water.

To reduce pollution of drinking water sources (wells and springs) are recommended:
- Development of a sanitary protection zones around the source of water of not less than 25 m and respect regime of protection;
- In the sanitary area of protection shall be banned: waste disposal, placing of stables, washing of laundry and cars, discharged of sewage waters and so on;
- Arrange for keeping green areas representing some natural filters around water sources;
- Regular control of water quality (well or spring).

In terms of quality, groundwaters are considered clean and enroll in normative for drinking properties or for less demanding uses. But groundwaters may contain chemicals elements whose concentrations exceed the permissible standards for drinking or industrial use.

Table 1

The evolution of oxygen regime indicators in the Prut river water, on sections, averages, September-November 2013

Section	O2	CBO5	CCO-Cr	CCO-Mn
Lipcani-Şirăuţi	9,7	2,9	12,3	4,2
Costeşti-Stânca	8,9	4,6	18,9	6,3
Ungheni	9,6	2,9	14,4	3,9
Valea Mare	7,9	5,7	24,7	7,9
Leuşeni	9,7	5,8	25,4	8,1
Leova	7,8	6,2	27,3	8,8
Cahul	9.9	3,9	29,2	8,6
Ciurgiuleşti	7,8	4,3	29,9	8,8

Table 2

Hardness and mineralization of groundwater

Hardness, me/dm^3	District			
	Făleşti		Glodeni	
	Nr. of springs	Quota, %	Nr. of springs	Quota, %
< 7	1	7	7	24
7 - 10	9	56	18	62
> 10	6	37	3	10
Mineralization, mg/dm^3				
< 1 000	10	63	21	72
> 1 000	6	37	7	28

Table 3

Type of groundwater in localities of Făleşti and Glodeni districts

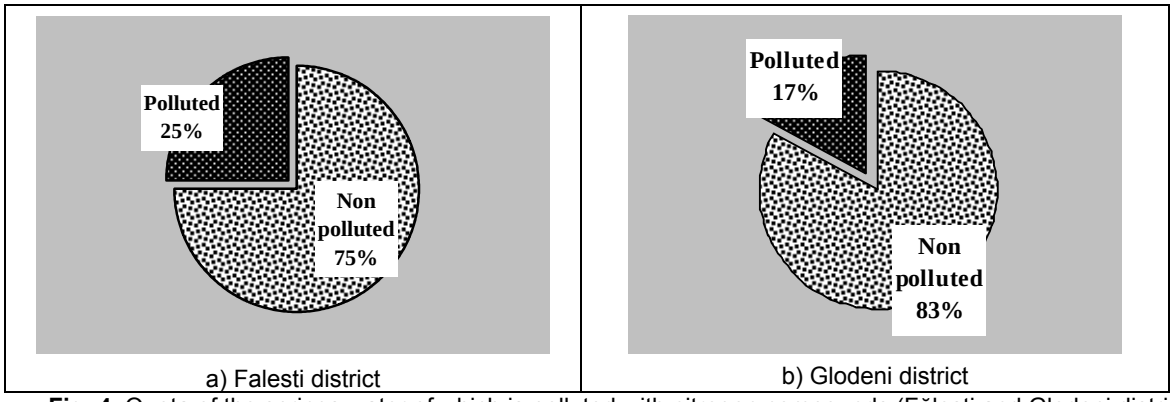
Type of groundwater	District			
	Făleşti		Glodeni	
	Nr. of springs	Quota, %	Nr. of springs	Quota, %
HCO3;	1	6	1	3
HCO3 – NO3	1	6	-	-
HCO3 – SO4;	2	13	15	52
HCO3 – SO4 / Cl;	7	44	8	28
HCO3 – SO4/Cl - NO3	1	6	2	7
HCO3 –Cl;	4	25	-	-
SO4 - HCO3 / Cl;	-	-	3	10
Na – Mg - Ca	10	63	-	-
Mg – Na / Ca	5	31	7	24
Ca – Mg / Na	-	-	1	3
Na	1	6	20	70
NH4 – Mg – Ca - Na	-	-	1	3

By determining the chemical composition of water from investigated springs and fountains it was found that in Făleşti district from total of investigated 16 springs and fountains, 25 % (4 sources) are polluted with nitrogen compounds (**Fig. 4**).

The total content of dissolved substances in monitoring water sources has a distribution that takes into account the nature of the drained substrate. The longer are routes crossed by storm water that falls and seeps underground, the dissolving of substrate by it is more advanced. Thus the content of dissolved substances (mineralization) in water sources in this study varied, and quota of probes with the mineralization exceeding the permissible limit for this parameter reaches 37% (Făleşti) and 28% (Glodeni) (**Table 2**).

In terms of ionic composition, water of springs and fountains, monitored in the area of study, is characterized by the predominance of HCO3-ions, than sulfate ions or chloride with sodium or magnesium ions dominance. It is meeting and groundwater

bicarbonate- sulfates as anions and **sodium-magnesium** after cations. This hydro chemical diversity is closely related with changing of natural conditions (precipitations, evapotranspiration and groundwater level depth). **Table 3**.



a) Falesti district b) Glodeni district

Fig. 4. Quota of the springs water of which is polluted with nitrogen compounds (Făleşti and Glodeni districts).

CONCLUSIONS

1. For each surface water body (Prut River, its left tributaries) were identified pressures in terms of pollution and it was realized the assessment of anthropogenic impact by determining the five groups of chemical indicators.
2. Nitrite content in water of Prut River (downstream of the town Leova), where are discharged insufficiently treated wastewater directly into the river Prut, exceeds approx. 1.7 MAC. The content of dissolved oxygen (BOD5) satisfies the minimum value equal to 6.3 s mg/dm3 in section Giurgiulesti (Cahul).
3. On River flow it is attests the growing on total content of organic matter, and of oil products recorded variations between 0,036 and 0,137 mg/dm^3 .
4. Water quality in Prut River was within the limits of class II of quality (clean) in the Lipcani - Sirauti and class III (moderately polluted) in the Leova section.
5. The content of dissolved substances (mineralization) in springs water vary and quota of samples with mineralization exceeding the permissible limit for this parameter reaches 37 % (Făleşti) and 28 % (Glodeni).
6. From point of view of ionic composition, water of springs and fountains monitored in the study area is characterized by the predominance of HCO3 - ions, than sulfate ions or chloride with sodium or magnesium ions dominance. It meets groundwater **"bicarbonate-sulfates"** after anion and **"sodium-magnesium"** as cations.
7. For reducing of water sources pollution it is recommended fittings of sanitary zone and keep to the protection regime with band of wastes disposal, placing of stables, washing of laundry and cars, discharged of sewage waters and so on.
8. Lately has been established a downward trend in the pollution sources influence on water due to the significant reduction of the industrial production and agro-breeding volume in recent years, but also by implementing of wastewater treatment measures. However, surface water quality due to the slow self-purification remains inadequate and the content of chemical indicators in groundwater exceeds MAC.

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