CONTROL OF SOME QUALITY INDICATORS OF PRUT RIVER IN TWO MONITORING SECTIONS (RĂDĂUȚI AND DARABANI) (SPRING SEASON)

CONTROLUL UNOR INDICATORI DE CALITATE AI RÂULUI PRUT ÎN DOUĂ SECȚIUNI DE MONITORING (RĂDĂUȚI ŞI DARABANI) (SEZONUL DE PRIMĂVARĂ)

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Abstract. *The paper describes proper experimental results concerning the control and analysis of some important quality indicators (i.e. general physical-chemical indicators, oxygen regime indicators, and some specific and/or toxic chemical indicators) during the spring season (March-May, 2009), in two monitoring sections of Prut River (i.e. Rădăuți-Prut and Darabani-Prut), together with its local potential pollution sources. The performed results permitted the evaluation of water quality, integration of each analyzed quality indicator in a specific quality category, in each monitoring section, and estimation of pollution level in spring season, but also of further actions for protection and conservation of this natural water resource.*
Key words: *monitoring section, pollution level, surface water categories, quality indicator, Prut River, spring*

Rezumat. *Lucrarea descrie rezultatele experimentale proprii privind controlul şi analiza unor indicatori de calitate importanți (i.e. indicatori fizico-chimici generali, indicatori ai regimului de oxigen şi câțiva indicatori chimici specifici şi toxici) în timpul primăverii (martie-mai, 2009) în două secțiuni de monitoring ale râului Prut (i.e. Rădăuți-Prut şi Darabani-Prut), împreună cu sursele locale potențiale de poluare. Rezultatele obținute au permis evaluarea calității apei, încadrarea fiecărui indicator de calitate analizat într-o categorie de calitate specifică, în fiecare secțiune de monitoring şi estimarea nivelului de poluare în anotimpul de primăvară, dar şi acțiuni viitoare pentru protecția şi conservarea acestei resurse naturale de apă.*
Cuvinte cheie: *secțiune de monitoring, nivel de poluare, categorii de apă de suprafață, indicator de calitate, râul Prut, primăvară*

INTRODUCTION

The water importance in the existence of human species and, in general, of vegetal and animal living world must be understood and accepted as a definitory element of our whole planet sustainable development in conditions of diminishing the natural resources of fresh water, and manifesting of some pollution episodes more and more various as form and complexity. The accumulation of pollutants in the natural water resources, self-purification or insufficient self-treat-

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ment of them, the necessity of new modern technologies more and more complex, and also expensive for treatment of natural water resources for different purposes are realities of modern world pointed out by majority of specialists in the field.

The definition of aquatic environment quality is made priority by appreciation of natural water resource quality with which is contacting, or wishes to consume. From international statistical estimation, the fresh water proportion is relatively low in comparison with salty water from seas, oceans, and is accessible as surface water in a percentage lower than 0.2 % from the total water resources of Earth (Zaharia, 2011). As result, the importance of water must be evaluated taking in consideration the repartition or distribution of natural water resources, composition of substances and organisms present in water as well its utilizations in different activities as industrial, agricultural or zoo-technical productive activities, domestic consumption, transport or energetically use (*i.e.* global utilization of water constitutes of an average 250 m^3/year. inhabitant, with extreme discordances in different geographic zones) (Surpățeanu, 2007; Teodosiu et al., 2010).

The quality of water varies also very much in different geographical regions, and are numerous organoleptic, physical-mechanical, chemical and microbiological aspects which must be considered in determination of its acceptability and viability as pure resource of consuming water (Zaharia, 2011).

The control and analysis of water quality represents one of important tools of water resource management for conservation, assuring the natural vital resource for present and future generations. This fact imposes the maintaining of specific normal physical-chemical-biological (microbiological) balances, and avoiding/reduction of more and more various pollution episodes of a higher number of rivers and lacks.

The water quality is usually appreciated by general, specific and/or toxic quality indicators of physical, chemical, biological (especially microbiological) origin, or ecotoxicological indicators (Zaharia, 2011; Zaharia and Teslaru, 2012).

The crossing through some urban and rural locations of different watercourses leads to them loading with numerous pollutants as a result of different productive activities, in general, of local socio-economical development. Therefore, the watercourse quality experiences modifications, negative from qualitative point of view, and needs different types of monitoring programs, and also hydro-fitting out for making its better. The population concern (*i.e.* citizens with different ages) but firstly of reknown, and/or in formation specialists (*i.e.* students at Bachelor, Master, PhD programs), and also the real need of certainty and/or clarifying of noticed vagueness, initiated numerous individual studies for control of some pollutants in different monitoring sections alongside some important watercourses (*e.g.*, Prut River) for evaluation of pollution level, initiation of some advanced monitoring programs, and also depollution actions for solving of different environmental and hydrological problems in different urban zones (Danalache, 2009).

This paper proposes the presentation of proper experimental results, obtained by laboratory analysis and its interpretation, for appreciation of water quality of Prut River in two monitoring sections (*i.e.* Rădăuți-Prut and Darabani-Prut). Some general physical-chemical quality indicators (*i.e.* color, pH, tempera-

ture, turbidity, suspended solids, total hardness, indicators for oxygen regime (*i.e.* dissolved oxygen, chemical oxygen demand-COD_{Mn} or permanganate index-I_{Mn}, biochemical oxygen demand-BOD_5), salty indicators (fixed residues), specific indicators for the content of some anionic and cationic representative constituients (nitrites, nitrates, phosphates, chlorides, sulphates, ammonia), and some toxic chemical indicators (phenol derivates, extractible substances in organic solvents) were controlled by periodic analysis in spring season (March-May, 2009).

MATERIAL AND METHOD

1. Characterization of Prut River and the two monitoring sections

Prut River (953 Km length) springs from Wood Carpatian (Ukraine), and flows into Danube nearly Reni (at East of Galați), disposing of a hydrographic basin of 27,500 km^2 spreading on territory of three states: Ukraine, Romania (10,990 km^2), and Republic of Moldova. On Romanian territory has a length of 742 km, an average multi-annual flow of 110 m^2/s (before springing), and disposes of a hydroenergetic fitting out at Stânca-Costeşti, built together with Republic of Moldova.

Prut River is controlling in 10 monitoring sections (*i.e.*, monitoring sections in monthly, weekly, and daily rapid monitoring sections) for supervision (S), operative (O), and reference (R) actions (*e.g.*, the best available monitoring section, or international monitoring sections together with Republic of Moldova, and also Ukraine, or TNMN transnational monitoring network, EIONET network, etc.). Data from annual statistic reports indicate a framing of Prut River in II^{nd} and III^{rd} quality category (from physical-chemical and biological point of view), with small exceptions.

Darabani-Prut control section is considered the best available section, water quality of Prut River being maintained in this section of II^{nd} quality category (since 2006, relatively clean water), with improvements of physical-chemical indicators concerning oxygen regime, nutrients, salinity, and biological indicators (biological indicators quarterly controlled for phytoplankton, microfitobentos, and macrozoobentos; absence of aquatic macrofites and halophytes) (Danalache A.E., 2009).

Rădăuți-Prut control section is considered as an operative supervision section, placed at a distance of 27 km from the previous one, qualitatively and quantitatively analyzed in the frame of Protocol between Romania and Republic of Moldova. The water quality of Prut River is maintained in this section of II^{nd} quality category refering to oxygen regime, salinity, heavy metal ions (Cd^{2+}, total Cr^{3+} and CrO_4^{2-}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}), and biological indicators (phytoplankton, microfitobentos and macrozoobentos; absence of aquatic macrofites and halophytes, quarterly control).

2. Materials and physical-chemical analysis methods

In this paper are analyzed only few physical-chemical indicators, the applied analysis methods being Romanian standard (SR) methods internationally approved (ISO or EN), as well as the reference materials, chemical reagents, stock solutions, and operating parameters for gravimetric, titrimetric, or spectrophotometrical analyses used (Surpateanu and Zaharia, 1999, 2002; Zaharia and Teslaru, 2012):

- *General indicators* of physical-chemical nature: hydrogen ions concentration – pH (SR ISO 10523-97, HACH OneLine Laboratory pH-meter, with reference electrode); temperature (thermometer); color (SR ISO 7887/1997, absorbance or Hazen color units, HU); turbidity (SR EN ISO 7027: 2001), suspended solids (STAS 6963-81); total hardness; oxygen regime as dissolved oxygen (SR EN 25814/1999), chemical oxygen demand (COD_{Mn}) (SR EN 1484/2001, SR ISO

6060/1996), biochemical oxygen demand (BOD_5) (SR EN 1899/2002); salinity indicators as fixed residues (STAS 6963-81);
- *Specific chemical indicators* for the content of some anions and cations as nitrites (STAS 3048/1-96), nitrates (STAS 8900/1,2-96), phosphates (SR EN 1189/2000);
- *Specific toxic indicators* as phenol and phenol derivates (SR ISO 6439/2001 or SR ISO 8165-1/2000) and extractible substances in organic solvents (SR 7587/1996).

All chemical reagents used have high purity degree (p.a.). The pH adjustment was done using 0.1M HCl, and 0.1M NaOH solutions. The analytical control of water sample quality was performed with help of different individual and multifunctional apparatuses (Hach One-Laboratory pH-meter; DRELL DR/2000 spectrophotometer, Hach Company), conventional methods for COD_{Mn}/I_{Mn}, BOD_5, sulphates, total hardness, extractibile substances, fixed residues, as well as spectrophotometrical methods for nitrates, nitrites, phosphates, and phenol derivates (Zaharia and Teslaru, 2012).

The collected samples were kept in specific conservation and storage conditions (refrigeration) more than 7 days for data validation. The analysis method sensibility depends of type, standard materials, used apparatuses, and the accuracy and precision are good enough for evaluation of water quality (0.01-0.0001 M).

RESULTS AND DISCUSSIONS

For the water quality control of Prut River were weekly collected water samples (March-May, 2009) which were preserved (for determination of extractible substances and nitrites, using specific chemical reagents) (Surpățeanu and Zaharia, 1999, 2002), transported to the environmental analysis laboratory, and refrigerated for subsequent laboratory analysis. The analysis of studied physical-chemical indicators facilitated the evaluation of water pollution status in the two control sections, and the specific framing in the corresponding quality categories.

The performed experimental results are presented in table 1(a) for the physical and salinity indicators (color, turbidity, suspended solids, and fixed residues), and in table 1(b) for some specific and toxic chemical indicators (pH, total hardness, oxygen regime indicators: COD_{Mn}, BOD_5, nitrites, nitrates, phosphates, extractible substances in oil ether, and phenol index).

The pH values are low alkaline in the studied two monitoring sections (except in April for Darabani-Prut section, and in May for Rădăuți-Prut section when were low acid, but framing in the admissible limits of 6.50-8.50).

The content of dissolved organic substances expressed by COD_{Mn} and BOD_5 exceeded frequently the admissible limits, but no more than 1.96-5.29 times, and were closed to the values registered in the last three years. The content of nitrites and nitrates as an indicator of oxidative transformations of nitrogen, and its derivates (NO_2^- transformed in the most stable oxidizing form of NO_3^-) is higher in the Rădăuți-Prut section exceeding of 2.4-38 times the admissible limits for nitrites, those for nitrates being generally in the admissible limits. Also, the content of phosphates is extremely high exceeding with more than 7.02-33 times the admissible limits in Darabani-Prut section, and 0.2-430 times in Rădăuți-Prut section, respectively (sign of wastewater discharges loaded with high quantities of phosphorus derivates as o-phosphates, tensioactive constituents from different cleaning, washing services etc., as well as organic phosphorus). In April and May

months were presented more extractible substances in organic solvents as a presence sign of oils and greases, and phenol derivates in much higher content than the admissible limit (exceeding of 150-890 times) in each spring month.

Table 1

The values of physical-chemical quality indicators of Prut River in the two studied monitoring sections (March-May, 2009)

Quality indicator	Measured value *(average value of weekly analysis results)*						M.A.C.*(I)
	P_1(*bridge*) – Darabani-Prut			P_2 (*bridge*) – Rădăuți-Prut			
	March	*April*	*May*	*March*	*April*	*May*	
(a) General physical-chemical indicators							
Color A436	0.125	0.042	0.024	0.093	0.048	0.022	< 50
A525	0.105	0.030	0.016	0.076	0.060	0.018	
A620	0.084	0.028	0.015	0.060	0.038	0.013	
HU (456)	90.00	32.50	13.30	59.16	40.00	15	
Turbidity, FTU	17	17	2	8	8	2	-
Suspended solids, mg/L	139	59	35	70	27	21	30 (60)
Fixed residues, mg/L	530	1060	340	420	100	180	500
(b) Specific and toxic chemical indicators							
pH	6.60	7.67	7.37	7.39	7.39	6.91	6.50-8.50
COD_{Mn}, mg O_2/L	9.76	9.64	9.48	19.52	16.48	4.56	5
BOD_5, mg O_2/L	2.023	6.401	7.232	15.480	15.871	3.283	3
Total hardness, °G	18.48	10.19	8.74	17.70	9.18	8.40	> 5
Nitrites, mg/L $N\text{-}NO_2^-$	0.094	0.029	0.024	0.061	0.039	0.031	0.01
Nitrates, mg/L $N\text{-}NO_3^-$	1.036	0.959	0.383	1.177	1.241	0.485	1
Phosphates, mg/L P	0.351	0.40	1.694	0.010	0.50	2.148	0.05
Extractible substances, mg/L	3.33	2	2	2	5	5	-
Phenol index, mg/L phenol	0.876	0.547	0.275	0.624	0.896	0.159	< 0.001
M.A.C.*(I) – maximum admissible concentration, Ist quality category, MO No. 161/2006							

Table 2

Water quality categories of Prut River for the studied physical-chemical indicators

Quality indicator	Water quality categories of Prut River						
	P_1(*bridge*) – Darabani-Prut			P_2(*bridge*) – Rădăuți-Prut			General observations
	March	*April*	*May*	*March*	*April*	*May*	
pH	I	I	I	I	I	I	I, in all months
COD_{Mn}	II	II	II	II	III	III	II, in P_1 all months II-III, in P_2
BOD_5	I	II	III	III	III	II	I-III, in P_1, all months II-III, in P_2,all months
Nitrites	III	II	II	II	II	II	II, in all months, except in March, in P_1
Nitrates	II	I	I	II	II	I	I, in P_1, all months, except in March, and in P_2, all months
Phosphates	III	III	D	I	II	III	III, in P_1, all months, except March (D) I-III, in P_2, all months
Phenol Index	D	D	D	D	D	D	D, in P_1 and P_2, all months
Fixed residues	III	III	I	II	I	I	I-III, in P_1, all months I-II, in P_2, all months
D – degraded water; I-III quality categories of water bodies (I-drinking water, II-irrigation/bathing, III-affected by anthropogenic uses in different ways)							

The framing of indicators in the corresponding quality categories (referring to Environmental Ministry Ordinance No.161/2006, and No.1146/2002), is synthetically presented in table 2, and permits the estimation of real situation of surface water quality in the two studied monitoring sections, in spring (2009).

For the majority of quality indicators in the two investigated monitoring sections, the highest values were obtained in March. The water quality of Prut River can be generally framed in IInd quality category for COD_{Mn}, BOD_5, nitrites, nitrates, fixed residues, or in IIIrd quality category for phosphates, and D-degraded for phenol index. A strict and efficient control, preventive treatment measures of all effluents discharged in Prut River, as well as the penalizations for local throwing of solid wastes and liquid residues must be always considered.

Moreover, our practice analysis concludes that the principal pollution source of Prut River in the representative influence zone of the two studied monitoring sections is SC Apa Grup SA Botoşani, Darabani sector, and few local individual housekeepings, and farms.

CONCLUSIONS

1. There were analyzed at laboratory scale set-up some physical-chemical quality indicators using standard methods internationally approved, as well as certified and abroad recognized apparatuses.
2. In the first spring month (March) were registered the highest values of the analyzed quality indicators which permitted the framing of each indicator in a proper quality category.
3. The Prut River quality in the two monitoring sections is evaluated to be of IInd quality category, with two exceptions (for content of phosphates, and also phenol derivates). As result, it is imposing the permanent monitoring of water quality in the two studied monitoring sections for identification of local potential pollution episodes.

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