Assessment Pollution of Lotic Aquatic Ecosystems of Dambovnic Catchement

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This article presents an extensive investigation of physical-chemical parameters of water samples in the Dambovnic catchment, during 2007-2010. Parameters used to assess pollution levels in the Dambovnic river are: pH, dissolved oxygen, total and inorganic species of nitrogen and phosphorus and heavy metals (Cd, total Cr, total Mn). A serious problem of pollution in the river is the level of ammonia, corresponding to the last chemical quality class, degraded, in Dambovnic and Suseni lake area. It is interesting to study the mean concentrations of nitrogen compounds and phosphorus main level control sections of Dâmbovnic river, no possible differentiation graded sediment (in terms of their nutrient content). The largest transfer rates of cadmium are made between sediment and macroinvertebrates, followed by those between water and vegetation. In addition, manganese is the most mobilized from water by aquatic vegetation, but important factors of transfer were obtained from sediment and vegetation.

Keywords: freshwater bodies, physico-chemical parameters, water quality, pollution status

Life in the aquatic environment is largely governed by the physico-chemical characteristics and their stability. Fresh water is essential for agriculture, industry, human existence, energy production [1, 11] but it is still a limited resource of the Earth [20]. Water quality is affected by human activities such as industrialization, urbanization, tourism and garbage production and by natural events like rainfall, erosion and climate change [2-3, 17, 19] . Thus, the potential of the water drops from day to day [5, 11].

The damage of internal water resources is one of the most important environmental problems of the last century [18]. Surface water and wastewater discharges are the main factors causing portal nutrients into rivers and water pollution [11).

Nitrogen pollution is a global problem [10]. The concentrations of nitrogen and phosphorus plays a key role in the determining of the ecological status of water systems. Essential for biochemical cycle, these elements enter the water usually with anthropogenic activities such as domestic sewage, industrial and unknown source spills. Excessive nitrogen and phosphorus are often considered to be the major cause of eutrophication. Eutrophication is one of the most serious environmental threats to aquatic ecosystems. As a result of eutrophication and algal blooms there occur many problems such as reducing oxygen, taste and odor problems, death of fish and biodiversity loss. Therefore, the understanding of the dynamics of nutrients transported by rivers is critical for resource management and prevention of eutrophication [12]. Because of increasing problems concerning water quality and quantity in Europe was regulated by Water Framework Directive [21]. One of the most important objectives of the Directive is to protect the current status of water bodies and do all the bodies of the European Union to achieve *good ecological status* by 2015 through an integrated approach to water management [16].

Metal ions have a partial effect on physico-chemical parameters and a direct effect on the survival of the microorganisms [7]. Data correlation between metals and chemical parameters showed both positive and negative responses while between metals and microbial population showed negative correlation [7].

In the following study we will submit the evaluation results of nutrients and the heavy metals, which are different items used in the assessing of physico-chemical state of surface waters.

Experimental part

Samples preparation

Activities in the field, along Dâmbovnic river, formed the basis of the research program, whereas after field trips, to observe local characteristics, there were chosen points / stations for sampling.

Sampling was done monthly during 2007-2010 in the following checkpoints: Dambovnic Lake (D1), Suseni Lake (D2) Slobozia (D3), Roata (D4) and Vadu Lat (D5). We analyzed the *p*H, conductivity (μS/cm), temperature (^{0}C), dissolved oxygen (mg/L), ammonia (N-NH_4^+), nitrite (N-NO_2^{--}), nitrate (N-NO_3^-), total nitrogen (TN), dissolved phosphate (P-PO_4^{3-}), total phosphorus (TP) [13, 15]. The metals for which were carried out complete analysis in all compartments (water and sediment [9], vegetation and macroinvertebrates [8, 14], and thus they allowed an integrated analysis are: Cd, Cr total (Cr^{+3}, Cr^{+6}) and total Mn (Mn^{+2}, Mn^{+6}).

In order to assess the pollution of Dâmbovnic river, the values of the parameters mentioned above have been reported to the chemical and physico-chemical quality standards, for the establishment of the ecological status of surface water regulated by Order No. 161 of 16.02.2006 for approval of the *Norms on the classification of surface water quality to determine the ecological status of water bodies.*

Results and discussions

To evaluate the degree of pollution of the river Dambovnic were analyzed term average concentrations of nutrients and heavy metals, obtained in each control sections (according to the Norms on surface water quality classification) in 2007-2010.

Each control section of Dambovnic river was placed in the appropriate chemical quality class appropriate standards in force

Regarding nutrients, one of the most critical issues of the river is the ammonium levels, which in the upper river

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No.	Quality indicator	U/M	Quality class				
			I v.good	II good	III moderate	IV acceptable	V bad
C.5. Specific toxic pollutants of natural origin							
1.	Cadmium (Cd)	µg/l	0.5	1	2	5	>5
2.	Total Chromium (Cr^{3+}, Cr^{6+})	µg/l	25	50	100	250	>250
3.	Total Mangan (Mn^{2+}, Mn^{7+})	mg/l	0.05	0.1	0.3	1	>1

Table 1
ELEMENTS AND STANDARDS OF CHEMICAL AND PHYSICO-CHEMICAL QUALITY FOR SURFACE WATERS TO ASSESS HEAVY METAL POLLUTION

Station / Parameter	Dâmbovnic Lake (D1)	Suseni Lake (D2)	Slobozia (D3)	Roata (D4)	Vadu Lat (D5)
Cd^{2+} (ppb)	0.23	0.12	0.07	0.16	0.06
Quality class	I	I	I	I	I
Cr (Cr^{3+}+Cr^{6+}) (ppb)	1.98	2.04	1.31	1.14	1.10
Quality class	I	I	I	I	I
Mn (Mn^{2+}+Mn^{4+}) (ppb)	41.56	38.34	86.11	77.24	50.01
Quality class	I	I	II	II	I

Table 2
ANNUAL AVERAGE VALUES OF CHEMICAL PARAMETERS CHARACTERIZING SPECIFIC TOXIC POLLUTANTS (METALS) IN WATER TO MONITORING SECTIONS IN DAMBOVNIC RIVER (2007-2010)

(Dambovnic and Suseni lakes) correspond to the quality class *very bad*. Water quality is gradually improving by downstream as a result of dilution, conversion of ammonia and storage processes, reaching the best class in the last control station (Vadu Lat). Nitrite levels are large and very large throughout the entire river, with values specific to quality classes *moderate and poor*. Regarding nitrate and total nitrogen values, the monitoring stations are included in classes as *moderate and good*. Storage and degradation processes fail to buffer anthropogenic nitrogen inflows. Phosphorus and total phosphorus concentrations show small variations between monitoring stations, placing in the second and third class quality [13].

To assess the level of heavy metal pollution of Dambovnic river it used the same quality standards, limits of placing in the various classes of quality for analyzed elements being selected and presented in table 1.

From the viewpoint of the load of heavy metals, water in the Dâmbovnic river is placed in very good class for both Cd and Cr (table 2).

Only for manganese the chemical status of water bodies was characterized as good in the monitoring sections Slobozia and Roata, the decrease being due to some bigger inflows in areas with higher activity / more traffic.

For assessing the chemical status of an aquatic ecosystem is not enough monitoring / analysis of physical-chemical parameters of water in the control sections, but also observing the quality of sediments, knowing that exchanges between these departments is important. The sediments are considered *fingerprint* [4] of activities performed at a catchment level, they sometimes adsorbing significant amounts of compounds emitted into the aquatic ecosystem, which remain long time at this department by the burial sediment phenomenon.

Chemical quality standards for sediment did not set limits regarding their nutrient content but only the threshold values for metals, polynuclear and mononuclear aromatic compounds, PCBs and pesticides.

In table 3 were selected items and chemical and physico-chemical quality standards for sediment, to assess the heavy metals pollution (Norms on classification of surface water quality). Based on data contained in this table, there have been able to determine whether sediment in control sections of the river Dambovnic are a risk of polluting the river.

The average concentrations of metals in river sediments, obtained for control sections (table 4) shows values that indicate that there is no risk of pollution of Cd and Cr. For Mn are not set limits, it naturally finding themselves in this position in appreciable concentrations.

National standards for quality sediment do not allow the placing in different quality classes of water bodies, but only qualitatively assess of the risk of pollution.

But in literature there were found systems of classification of surface water quality based on the level of metals in sediments. The Norwegian Institute for Water Research (NIVA) use a system for determining the quality of surface waters with five classes, which take into account the heavy metal content of both water and sediment (table 5).

No.	Indicator	UM	Quality standard
B.1. Metals			
1	Arsenic (As^{3+})	mg/kg	29
2	Cadmium (Cd^{2+})	mg/kg	0,8
3	Total Chromium (Cr^{3+}+Cr^{6+})	mg/kg	100
4	Copper (Cu^{2+})	mg/kg	40
5	Lead (Pb^{2+})	mg/kg	85
6	Mercury (Hg^{2+})	mg/kg	0,3
7	Zinc (Zn^{2+})	mg/kg	150
8	Nickel (Ni^{2+})	mg/kg	35

Table 3

Station / Parameter	Dâmbovnic Lake (D1)	Suseni Lake (D2)	Slobozia (D3)	Roata (D4)	Vadu Lat (D5)
Cd^{2+} (µg/g d.s.)	0.52	0.16	0.10	0.17	0.16
Quality class	No risk				
Cr (Cr^{3+}+Cr^{6+}) (µg/g d.s.)	74.86	55,69	39.63	52.18	47.52
Quality class	No risk				
Mn (Mn^{2+}+Mn^{4+}) (µg/g d.s.)	195.43	164.28	68.88	270.02	187,60
Quality class	Unspecified				

Table 4
ANNUAL AVERAGE VALUES (µg/g DRY SUBSTANCE) OF CHEMICAL PARAMETERS CHARACTERIZING SPECIFIC TOXIC POLLUTANTS (METALS) OF SEDIMENT IN CONTROL SECTIONS OF DAMBOVNIC RIVER (2007-2010)

Sample type	Metals	Quality class				
		I slightly polluted	II moderate polluted	III poluted	IV heavily polluted	V Very heavily polluted
Water (µg/l)	Cu	<0.6	0.6-1.5	1.5-3	3-6	>6
	Zn	<5	5-20	20-50	50-100	>100
	Cd	<0.04	0.04-0.1	0.1-0.2	0.2-0.4	>0.4
	Pb	<0.5	0.5-1.2	1.2-2.5	2.5-5	>5
	Ni	<0.5	0.5-2.5	2.5-5	5-10	>10
	Cr	<0.2	0.2-2.5	2.5-10	10-50	>50
	Hg	<0.002	0.002-0.005	0,005-0.01	0.01-0.02	>0.02
Sediment (mg/kg)	Cu	<30	30-150	150-600	600-1800	>1800
	Zn	<150	150-750	750-3000	3000-9000	>9000
	Cd	<0.5	0.5-2.5	2.5-10	10-20	>20
	Pb	<50	50-250	250-1000	1000-3000	>3000
	Ni	<50	50-250	250-1000	1000-3000	>3000
	As	<5	5-25	25-100	100-200	>200
	Hg	<0.15	0.15-0.6	0.6-1.5	1.5-3	>3

Table 5
WATER QUALITY CLASSIFICATION BASED ON THE METAL CONTENT OF THE WATER AND SEDIMENTS (BASED ON NIVA, [6]

Station / Parameter	Dâmbovnic Lake (D1)	Suseni Lake (D2)	Slobozia (D3)	Roata (D4)	Vadu Lat (D5)
pH	6.79	7.14	6.58	7.11	6.78
OM (%)	18.7	2.07	0.78	1.94	2.21
N-NH_4^+ (mg/g. d.s.)	89.85	13.67	4.84	10.05	8.93
N-NO_2^- (mg/g. d.s.)	1.22	0.79	0.21	0.59	0.69
N-NO_3^- (mg/g. d.s.)	5.17	2.41	2.51	2.14	2.86
P-PO_4^{3-} (mg/g. d.s.)	32.74	13.12	11.73	18.33	22.11

Table 6
ANNUAL AVERAGE VALUES OF CHEMICAL PARAMETERS CHARACTERIZING NUTRIENTS IN SEDIMENT, IN CONTROL SECTIONS OF DAMBOVNIC RIVER (2007-2010)

According to these standards, it can be noted that calcium levels in sediments corresponding to quality classes I and II (D1) but concentrations in water place the monitoring sections in quality classes II (D3, D5), III (D2, D4) and IV (D1). But the control stations on the Dambovnic river are palced in quality class II (medium polluted) regarding chromium.

Without being able to distinguish the sediment on quality classes in terms of their nutrient content, it is interesting the average level of main compounds of nitrogen and phosphorus at the level of control sections in the river Dambovnic (table 6).

It notes that the station D1 (Dambovnic Lake) stands out by the high contents of all the compounds analyzed, which is characterized by the most important anthropogenic impact in the form of wastewater from ARPECHIM.

Following an aquatic ecosystem pollution, also there occurs the transfer of pollutants to biota, with final opening to the human population. Therefore it is also important the factor analysis of heavy metals transfer between abiotic and biotic compartments for ecotoxicological risk assessment that these represent. They are synthesized for analyzed metals (Cd, Cr, Mn) in the tables 7-9.

The largest transfer rates of cadmium are between sediment and macroinvertebrates, followed by those between water and vegetation (table 7).

Cd tends to accumulate in sediment, therefore among the aquatic organisms, the benthic macroinvertebrates are the most exposed to the contamination with this item.

Chromium accumulates in sediments more than cadmium (one order of magnitude) and the most intense taking over rates are presented by the primary producers (table 8).

Taking over this metal by biota in sediments is insignificant, as indicated also by the subunit factors of transfer.

In water, manganese is the most mobilized by aquatic vegetation, but important factors of transfer were also obtained between sediment and vegetation. So most exposed organisms are vegetal, without neglecting the risk of contamination of benthic macroinvertebrates (table 9).

Station	water ↓ sediment	water ↓ vegetation	sediment ↓ vegetation	sediment ↓ macroinvertebrates
Dâmbovnic Lake (D1)	2.24		0.33	
Suseni Lake (D2)	1.31	3.12	3.90	2.85
Slobozia (D3)	1.44	6.82	7.49	11.21
Roata (D4)	1.05	3.40	1.19	9.57
Vadu Lat (D5)	2.94	8.78	1.04	11.06

Table 7
FACTORS OF CADMIUM TRANSFER BETWEEN ABIOTIC AND BIOTIC COMPARTMENTS, IN DAMBOVNIC RIVER, IN CONTROL SECTIONS D1-D5.

Station	water ↓ sediment	water ↓ vegetation	sediment ↓ vegetation	sediment ↓ macroinvertebrates
Dâmbovnic Lake (D1)	37.86		0.11	
Suseni Lake (D2)	26.38	13.36	0.24	0.25
Slobozia (D3)	30.32	10.43	0.18	0.40
Roata (D4)	45.90	11.08	0.19	0.38
Vadu Lat (D5)	43.03	7.77	0.28	0.46

Table 8
FACTORS OF CHROMIUM TRANSFER BETWEEN ABIOTIC AND BIOTIC COMPARTMENTS, IN DAMBOVNIC RIVER, IN CONTROL SECTIONS D1-D5

Station	water ↓ sediment	water ↓ vegetation	sediment ↓ vegetation	sediment ↓ macroinvertebrates
Dâmbovnic Lake (D1)	4.70		2.83	
Suseni Lake (D2)	4.51	176.03	6.07	4.09
Slobozia (D3)	0.80	79.08	32.14	14.66
Roata (D4)	3.50	83.90	6.37	5.21
Vadu Lat (D5)	3.75	38.13	16.72	5.76

Table 9
FACTORS OF MANGANESE TRANSFER BETWEEN ABIOTIC AND BIOTIC COMPARTMENTS, IN THE RIVER DAMBOVNIC, IN CONTROL SECTIONS D1-D5

Based on the presented data, it can say that Dambovnic river has a medium to intense pollution by nutrients, especially compounds of nitrogen, which determines the classification of water in quality classes II-V for some parameters (nitrogen, ammonia). We can not speak of a heavy metal pollution of river water, and sediment do not have concentrations of analyzed metals that present a pollution risk for surface water [13].

Conclusions

Analysis of the results obtained during of field monitoring program allowed the assessment of pollution with nutrients and heavy metals in Dambovnic river waters.

With respect to nutrients, various sections of the river were classified into quality classes from II (good) to V (bad). Sections in upstream (Dambovnic and Suseni lakes) are placed in Class V regarding ammonia and nitrite levels. Sections in downstream are characterized by a better classification of these parameters, in classes III-I for ammonium and classes IV-III for nitrite. Moreover, nitrogen pollution is one of the most critical on Dambovnic river. Nitrate and total nitrogen ensure compliance with the Class II (good) and III (modern) of all control sections. And in terms of phosphorus, so that the orthophosphate and total phosphorus, Dambovnic river waters are constant classified in categories III (moderate) and II (better).

Regarding heavy metals Cd, Cr, Mn, almost all control sections are characterized by a very good state (first class quality), except manganese, which have concentrations specific to class II (good) of chimical quality in stations Slobozia and Suseni. Sediments do not present any risk of pollution with the metals analyzed.

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