ANALELE ŞTIINŢIFICE ALE UNIVERSITĂŢII „AL. I. CUZA" IAŞI
Geologie. Tomul LVI, nr. 1, 2010

SPATIAL AND TEMPORAL CHANGES OF POLLUTION INDICATORS IN THE SURFACE WATERS OF THE BISTRIȚA BASIN (DOWNSTREAM IZVORUL MUNTELUI LAKE)

VALENTIN GRIGORAS[1], META DOBNIKAR[2]

[1] "Stejarul" Research Centre for Biological Sciences, Alexandru cel Bun 6, 610004, Piatra Neamț, Romania
[2] University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Askerceva 012, 1000 Ljubljana, Slovenia

Abstract

Unlike the upper sectors of the Bistrița River, in the sector downstream Izvorul Muntelui Lake the surface water quality was/is strongly influenced by the industrial activity. After several decades of intense pollution, the reduction of the anthropogenic impact during the past 20 years has led to an obvious improvement in water quality. From August 2007 to August 2009, samples from Bistrița and its tributaries were systematically collected and analyzed; the values determined in different seasons (DO, BOD_5, COD-Mn, NH_4^+, NO_3^-, NO_2^-) show very slight variations; the present paper is based on the first set of data (August 2007). Although in the center part of the studied area the water shows a slight degradation, the characteristic values of the oxygen regime fit water in the first two classes of Romanian surface water quality. However, the historical pollution that characterizes the whole inferior Bistrița basin manifests itself through a significant increase in the amounts of nitrates, whose source is primarily the groundwater. Moreover, nitrite has been identified in all samples, higher amounts being reported in the lower sector of the basin.

Keywords: pollution indicators, oxygen regime, nitrogen compounds, Bistrița River.

Introduction

Bistrița River is located in the central-north-eastern part of Romania (fig. 1). The lower sector of the basin, located downstream Izvorul Muntelui Lake, is the area studied in the present paper; the basin covers approximately 2960 km^2 (42% of the Bistrița basin) and the

[1] e-mail: valygrigoras@yahoo.com

river length is 114 km (40% of the Bistrița River). The geological background consists only of sedimentary formations, more or less consolidated (details can be found in Grasu et al., 1988; 1996).

In this sector, the river water is a mix of runoff water from Izvorul Muntelui Lake (details about its features in Apetroaei, 2003; Gassama et al., 2009) and a number of tributaries with variable river flows.

Over time, the surface water quality has strongly been influenced by two factors (Mazareanu et al., 1974): the first one – the city of Piatra Neamț, with its related wastewater treatment plant WWTP (a punctual pollution), and the second one – the Savinesti chemical plant (diffuse pollution). Unlike 20 years ago, a new WWTP is operating today and the industrial plant has reduced its activity almost completely; nevertheless, its operation for several decades had among its secondary effects the exhaustion of huge amounts of nitrogen, primarily as NO_2 (gas), which finally reached the soil where it was incorporated in various forms.

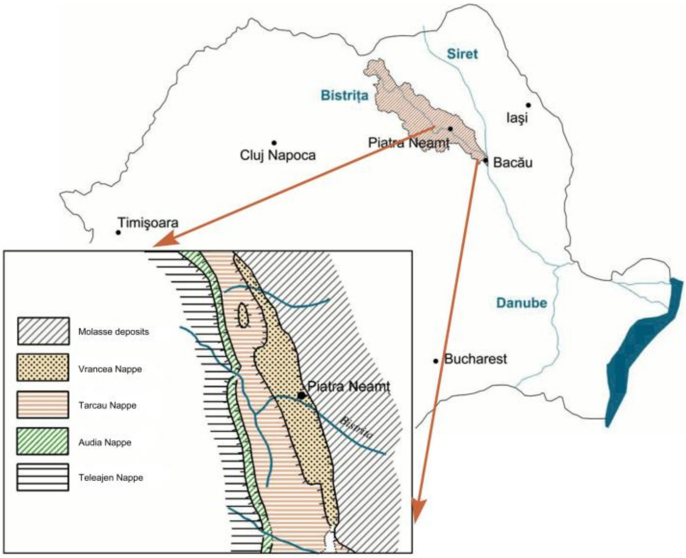

Fig. 1 Location of the studied area and geological background (modified from Grasu et al., 1988)

Materials and methods

Where the riverbed profile allowed, the samples were collected from the central part of the watercourse; otherwise, the samples were collected from a riverbank, the one with the strongest river flow. The water samples were collected in PET containers and kept cold until the analysis (no later than 24 hours). A series of recordings of certain physical and chemical parameters (temperature, pH, Eh, dissolved oxygen, conductivity etc.) were carried out *in-situ* using a Hanna HI9828 multiparameter. All records were made by placing the sensors directly into the water body.

The quantitative determination of the main pollution indicators has been performed through spectrophotometry (using a Jenway 6300 spectrophotometer - visible spectrum) according to the methodology described by Manescu et al. (1978):

- ammonium = with Nessler reagent at 425 nm;
- nitrates = with phenoldisulfonic acid at 410 nm;
- nitrites = with α-naphthylamine and sulphanilic acid at 540 nm.

The distribution of the sampling sites is shown in figure 2. All determinations were made in the ecology laboratory of "Stejarul" RCBS – Piatra Neamț.

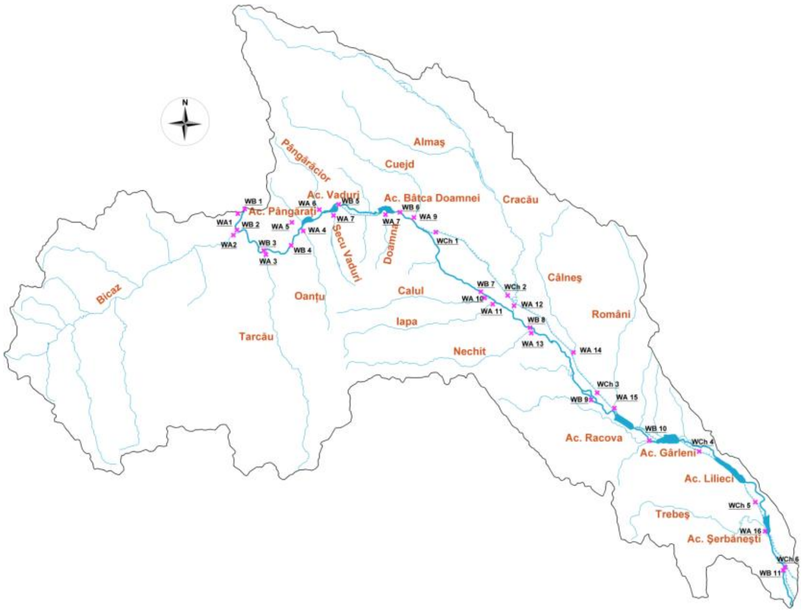

Fig. 2 Location of the sampling sites

The quality classes of the surface waters were determined in agreement with the current Romanian legislation (MMGA Ord. No. 161/16.02.2006), which stipulates 6 categories of parameters:

1. thermal and acidification regime (2 parameters);
2. oxygen regime (5 parameters);
3. nutrients (9 parameters);
4. salinity (7 parameters);
5. specific toxic pollutants with natural origin (13 parameters);

6. other relevant chemical indicators (3 parameters).

Depending on the concentration determined in the case of each parameter, surface water can be placed in one of five classes (the 1st class has the best quality). The variations highlighted in the present paper are based on some of these parameters (oxygen regime: dissolved oxygen, BOD and COD-Mn; nitrogen regime: nitrate, nitrite and ammonium contents) - limitations were mainly imposed by the data collected over the last two decades.

Results

Oxigen regime

Dissolved oxygen (DO) is one of the most important indicators of pollution; its importance involves a quantitative aspect (related to the concentration of DO in water) and a qualitative one, as well (spatial distribution, which means relatively sudden changes in concentration values). The values measured in the main river (fig. 3) indicate high contents of DO, with values above 10 mg O_2/l (corresponding to a saturation of 90-120%). The amount of DO identified downstream Piatra Neamț was 8.8 mg O_2/l, but the riverbed profile increases the DO to more than 10 mg O_2/l in just a few kilometres. Extremely low values were recorded downstream Bacau, in the old riverbed: 4.13 mg O_2/l. In all the tributaries the water shows high DO contents (9.7-13.3 mg O_2/l), the main cause being the mountain basin profile.

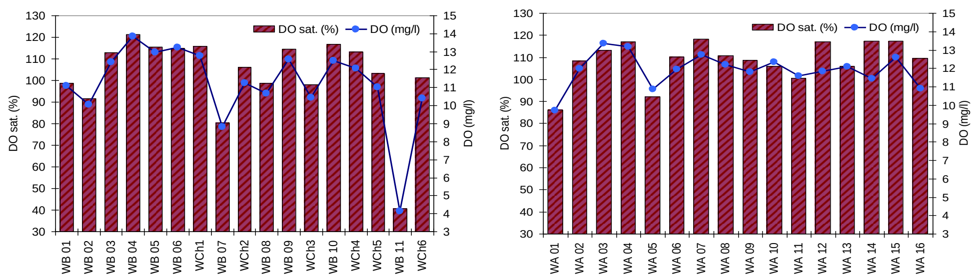

Fig. 3 Spatial distribution of DO in Bistrița and its tributaries

BOD (mg O_2/l)	
WB6	1.8
WB7	3.6
WCh4	3.2

The *biochemical oxygen demand* (BOD) in water (determined by the standard of five days and 20° C) was measured only in three points: WB6, WCh4 and WB7. The values obtained (fig. 4) indicate a slight degradation of the water upstream Piatra Neamț, followed by a slow growth downstream.

Upstream Piatra Neamț, the *chemical oxygen demand* (determined as COD-Mn) is below the limit of 9 mg $KMnO_4$/l, water self-purification processes making the concentration of organic matter slightly decrease downstream. The values measured downstream Piatra Neamț are higher, exceeding 11 mg $KMnO_4$/l, without any trend being discernable in the variation of the values. Downstream Bacau, the value determined was 25.9 mg $KMnO_4$/l. In the tributaries, the values measured were between 5.3-8.0 mg $KMnO_4$/l upstream Piatra Neamț and 8.0-14.5 mg $KMnO_4$/l downstream it (in the Calnes River the COD content was 21.8 mg $KMnO_4$/l).

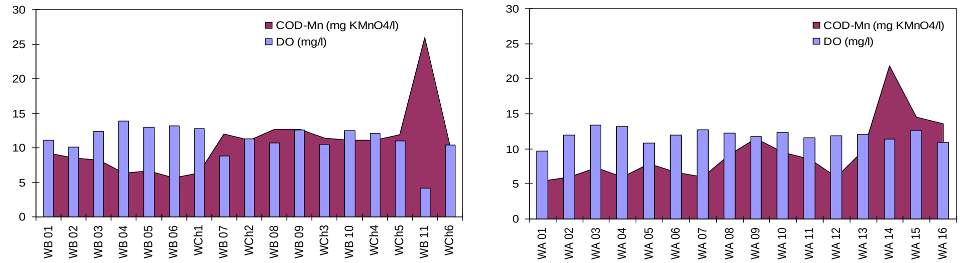

Fig. 4 Spatial distribution of COD-Mn related to DO contents

Nitrogen nutrient regime

In the longitudinal profile of Bistrița (fig. 5a), the amount of nitrogen bound in *nitrate* (N-NO_3) increases relatively constantly from 0.15 mg N-NO_3/l in the sample WB1 to more than 1.10 mg N-NO_3/l close to the Siret River. In the tributaries (fig. 5c), the content values vary slightly around 0.5 mg N-NO_3/l, a significant increase being recorded in the tributaries downstream Buhusi city.

Nitrites have been identified in all samples analyzed, both from Bistrița and its tributaries. If upstream Piatra Neamț (in the case of Bistrița) and Buhusi (in the case of the tributaries) the values determined are below 0.02 mg N-NO_2/l, downstream these two marks nitrites are present in higher amounts, up to 0.08 mg N-NO_2/l (in Bistrița) and 0.12 mg N-NO_2/l (in the tributaries).

Tab. 1 Minimum, maximum and average values of nitrogen compounds

mg/l	N-NO_3		N-NO_2		N-NH_4	
	Bistrița	tributaries	Bistrița	tributaries	Bistrița	tributaries
min.	0.154	0.170	0.003	0.001	0.005	0.022
max.	1.166	2.646	0.071	0.125	0.108*	0.249
avg.	0.503	0.783	0.032	0.032	0.042*	0.089

*the value determined in WB11 (2.933 mg N-NH_4/l) was not included among the max. and avg. values

In the case of Bistrița, the *ammonium* content variation is similar to that of nitrites: a slight increase downstream. In the tributaries, the values are constant, around 0.10-0.15 mg N-NH_4/l. In the sample WB11 the high content determined (2.93 mg N-NH_4/l) is due to some characteristics of the last segment of riverbed: a reduced river flow and a very small slope, with a range of effluents from Bacau.

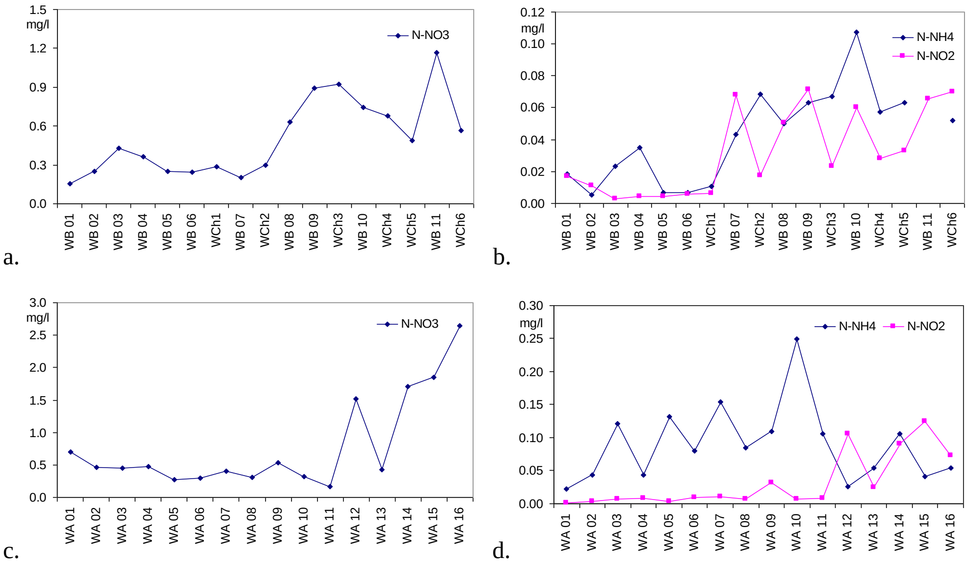

Fig. 5 Distribution of $N\text{-}NO_3$, $N\text{-}NO_2$ and $N\text{-}NH_4$ contents

Discussions

In terms of oxygen regime (DO, BOD_5, COD-Mn), the most vulnerable section of Bistrița is downstream Piatra Neamț, at a length of about 15 km; up to 1990, the water in this section was virtually “dead water,” but present data indicate only a slight decrease in quality. Still, the main polluter is Piatra Neamț WWTP. Nevertheless, compared with 1990 data, the situation is much better (fig. 6). The data presented in table 2 show that pollution indicators from the entire Bistrița River have stabilized over the last 5 years, reaching relatively constant values.

Unlike the oxygen regime, whose values appear to have stabilized, the nutrient nitrogen regime has a different behaviour.

The ammonium content places the Bistrița River in the first class of surface water quality; a major improvement is evident in the central part of the basin, where, compared to a concentration of 9.75 mg NH_4/l recorded in 1990, a value of only 0.08 mg/l has now been measured. Although the amount of ammonium increases slightly downstream, the river remains in the 1st quality class.

The temporal variation of nitrate is different: since 1990, in the upper section the values have been relatively constant (around 3-4 mg NO_3/l); in the central part, the nitrate content has dropped from 7 to 3 mg NO_3/l, while in the lower section it has increased from 4 to 7 mg NO_3/l. The variation in the first two sections is normal, since in the upper section there has never been any significant industrial activity, and in the central one the human pressure has decreased. The situation is "atypical" in the lower sector: the inputs through tributaries are too low to explain the high concentrations of nitrates from Bistrița. This situation must be linked to the nitrite concentrations. In water with a high dissolved oxygen content, nitrite is a chemical species with a very low stability, quickly oxidizing into nitrate (and/or ammonium). The presence of nitrite in all the samples determined, both in Bistrița and its tributaries (including the mountainous ones, where the human impact is much more limited), suggests a continuous supply of the surface water with nitrite from the sediments and/or soils and/or the groundwater. Although some of the Bistrița nitrite is certainly generated in the bottom sediments, at least in the mountainous tributaries – where the role of the sediment is reduced – the source is represented by the other two factors.

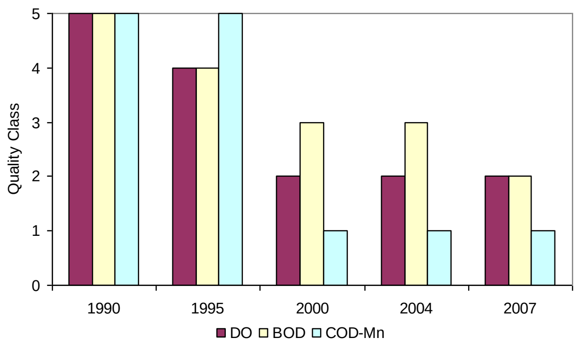

Fig. 6 The evolution of quality classes (oxygen regime) in the middle sector of the Bistrița River during 1990-2007

Firstly, almost the entire area from the Bistrița basin downstream Piatra Neamț has been declared *area vulnerable to nutrients* (INHGA, 2003); thus, the soil is a significant source of nitrogen nutrients.

Furthermore, determinations made by the authors (unpublished data) on water samples taken from shallow groundwater in the Calnes and Bicaz basins and from a small spring located in the minor riverbed of Bistrița have shown significant amounts of nitrite (up to 0.2 mg NO_2/l). Moreover, Bucuresteanu (2006) reports that the shallow groundwater downstream Piatra Neamț has nitrite contents that exceed the maximum accepted values 7 up to 35 times (according to STAS 1342-84 revised in 1991, this means up to 10 mg NO_2/l). Therefore, most of the shallow groundwater in the Bistrița basin is contaminated with nitrites, the contamination being more significant in the last section of the river. The existence of many springs close to river-courses makes it possible for those nitrites to be found in these rivers as well.

Tab. 2 Analytical results of the oxygen regime during 1990 – 2007 (data from Apetroaei et al., 2005; Japa and Tarus, 2005; unpublished data from the archive of "Stejarul" RCBS Piatra Neamț)

		1990	1995	2000	2004	2007
DO (mg O_2/l)	upper section	11.01	11.08	10.38	11.64	11.56
	middle section	0.92	4.30	8.46	8.98	8.80
	lower section	9.62	9.86	9.73	10.79	10.67
BOD_5 (mg O_2/l)	upper section	2.80	2.32	2.16	1.97	1.82
	middle section	80.80	18.98	6.60	6.30	4.70
	lower section	8.65	3.21	2.36	4.61	3.32
COD-Mn (mg O_2/l)	upper section	2.56	2.31	2.07	2.28	1.44
	middle section	179.96	80.33	3.58	3.33	3.04
	lower section	2.42	2.26	2.00	3.70	2.80

Under the new redox condition from the surface water, nitrite oxidizes to nitrate, which is a stable form, and thus, its concentration will increase with the advance in the water stream.

According to existing data, the evolution in each of the three sections of Bistrița is different (fig. 7).

- upstream Piatra Neamț, the nitrate and nitrite contents in the Bistrița River kept the river in the 1st quality class;
- in the central section, the nitrate content places the river water in the 1st quality class once again, but there is a degradation from 2nd to 3rd-4th quality class as far as nitrite contents are concerned;

Tab. 3 Analytical results of nitrogen compounds during 1990 – 2007 (data from Apetroaei et al., 2005; Japa and Tarus, 2005; unpublished data from the archive of "Stejarul" RCBS Piatra Neamț)

		1990	1995	2000	2004	2007
upper section	NH_4 (mg/l)	0.97	0.65	0.116	0.079	0.0235
	NO_3 (mg/l)	3.425	4.326	3.366	3.311	3.268
	NO_2 (mg/l)	0.016	0.019	0.020	0.015	0.024
middle section	NH_4 (mg/l)	9.75	3.24	0.282	0.112	0.0867
	NO_3 (mg/l)	7.360	6.652	5.137	3.874	2.562
	NO_2 (mg/l)	---	0.038	0.039	0.123	0.207
lower section	NH_4 (mg/l)	1.12	0.874	0.758	0.266	0.170
	NO_3 (mg/l)	4.560	5.341	4.473	5.236	7.332
	NO_2 (mg/l)	0.039	0.033	0.033	0.052	0.172

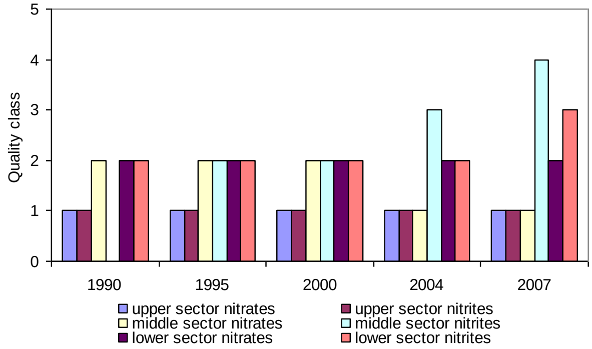

Fig. 7 Evolution of quality classes (NO_2 and NO_3 regime) in the central part of the Bistrița River during 1990-2007

-the nitrates keep the lower section in the 3rd quality class (with a significant increase of the concentration, however), while the amount of nitrites lowers the water quality from the 2nd to the 3rd class.

Conclusions

The spatial and temporal analysis of the pollution indicators points towards the existence of three distinct sections: an upper one (upstream Piatra Neamț), a middle one (between Piatra Neamț and Buhusi city) and a lower one (downstream Buhusi). Each section is currently characterized by specific values that seem to have stabilized over the past 5 years (with the exception of nitrate and nitrite contents).

Bistrița shows a slight degradation of the water quality in the central part, but self-purification processes keep the river in good conditions.

Independent of its form (nitrate, nitrite or ammonium), the nitrogen content shows a significant increase with the advance towards confluence. Nitrites have been identified in all samples analysed, both the literature and the data gathered by the authors suggesting that the sources are the soils (with their percolative water) and the shallow underground water.

Although the Savinesti chemical platform has nearly stopped its activity, the effects of the several decades of diffuse polluting are now fully felt.

Over time, increasing amounts of nitrates and nitrites (up to 2-5 times) can be observed if we compare present data to those of 1990-1995.

Acknowledgments

The present research was partially funded by the Romanian Ministry of Education, Research, Youth and Sports, through the National University Research Council (BD-type fellowship).

References

Apetroaei, N., 2003. Sediments from the dam Lake Izvorul Muntelui–Bicaz. Geochemical study. Ed. Academiei Române, Bucureşti. (In Romanian).

Apetroaei, N., Apetroaei, M., Jăpa, F., Nechita, N., Pralea, F., Ţăruş, T., Vasiliu, M., 2005. Hidrogeochemical and hidrobiological characteristics of some dam reservoirs on the Bistriţa River. St. Cerc. Muz. Şt. Nat., Piatra Neamţ, **X**. (In Romanian).

Bucuresteanu, M., 2006. The impact of the industrial decrease on the underground waters from the inferiour Bistriţa Valley. Romanian Biological Sciences, **IV**(3-4), 94–103.

Gassama, N., Cocîrţă, C., Kasper, H.U., 2009. Hydrodynamics of the Bicaz Lake. Considerations based on selected major and trace elements. Anal. Şt. Univ. "Al. I. Cuza" Iaşi, Geologie, **LV**, 39–64.

Grasu, C., Catană, C., Grinea, D., 1988. The Carpathian Flysch. Petrography and economical considerations. Ed. Tehnică, Bucureşti. (In Romanian).

Grasu, C., Catană, C., Boboş, I., 1996. Petrography of the formations from the internal Carpathian flysch. Ed. Tehnică, Bucureşti. (In Romanian).

Institutul National de Hidrologie si Gospodarire a Apelor, 2003. The involvement of water users in solving problems of nutrient pollution in the river Bistriţa. Project LIFE03 ENV/RO/000539. (In Romanian).

Jăpa, F., Ţăruş, T., 2005. Evaluation of the water quality of the Bistriţa River in the Batca Doamnei–Lilieci sector, on the basis of microbiological and chemical criteria. St. Cerc. Muz. Şt. Nat., Piatra Neamţ, **X**. (In Romanian).

Mazareanu, C., Caraus, I., Porumb, M., Rujinschi, C., Rujinschi, R., Simalcsik, F., Ţăruş, T., 1974. Influence of industrial and urban pollution on the quality of Bistriţa river water, and the artificial lakes from the downstream Bistriţa system. Research grant, Archives St. "Stejarul" Piatra Neamţ. (In Romanian).

Mănescu, S., Cucu, M., Diaconescu, M.L., 1978. Environmental health chemistry. Water and air. Ed. Medicală, Bucureşti. (In Romanian).

Received: April, 2010
Revised: May, 2010
Accepted: May, 2010