Studia Universitatis "Vasile Goldiş", Seria Ştiinţele Vieţii
Vol. 23, issue 3, 2013, pp. 271-281

POLLUTION VALUES IN TUR AND BARCĂU WATERS

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ABSTRACT. The researches which have been conducted up to now, have not approached stringently enough, the distinctive values of pollution in Tur (heavy metals) and Barcău (petroleum products), which is exactly what this paper intends to do. Consequently, water assays from the two rivers have been analysed, which showed the deterioration of water quality due to the industrial, agrarian, and urban pollutants from the aria. The assays proved the pollution downstream brook Tur inflow with heavy metals, especially Zinc, and of the Barcău waters with petroleum products, downstream the extraction and refining sector in Suplac – Marghita, especially with phenols. Owing to the analysis of the pollution values, it appears that the Tur waters are slightly altered, while the Barcău waters are heavily polluted, being strongly recommended, especially in the Barcau case, firm and vast actions of ecological reconstruction, for a constant discharge and improvement in the water quality through purification.

Keywords: assey, chemical quality of water, pollution value, estimation notes of water quality

INTRODUCTION

An important number of scientific researches relates to the anthropic impact on the waters of Tur and Barcău (N - W of Romania).

Ujvari (1972) creates a vast hydrographic characterization of Romania's waters, including Tur and Barcău. Hydrographic references to Tur are given also, by Velcea (1964) and Fazekas (1992-1993), and for the lower reach, the Hungarian section (Konecsny et al., 2001). The hydrographic of Barcău is completed by the works of Marosi and Szilard (1968), Harka et al., (1998), Wilhelm (2002) and Şumălan (2010).

The anthropic pressure on Tur and its inflows is given in the works of Mereuţă et al., (2000), Bănărescu (2004), Fazekas (2008) and Andrişca (2011), and the one on Barcău, by Sarkány-Kiss et al., (1999), Andrikovics et al., (2001), and Wilhelm (2002).

There are references to the quality of Tur waters in: Ardelean (1997, 1999), Ardelean and Duma (1997), Mereuţă et al., (2000), Breugel et al., (2005), Nagy et al., (2008), Roşu and Domşa (2011), and the quality of Barcău waters, is found in the works of: Andrikovics et al., (2001), Wilhelm (2002) and Andrişca (2011). With reference to the quality of the waters in the two rivers we have references from Roşu and Domşa (2011) for Tur and from István (2010) for Barcău.

In spite of all the numerous references, our research is justified by the fact that up to now, the analysis of the waters quality was based only on routine asseys, while a series of important factors have been omitted (heavy metals for Tur and petrolium products for Barcău). What is more, we have made a comparative study between Tur and Barcău regarding the pollution value, a revelatory factor for the water quality of a river.

MATERIALS AND METHODS

Water assays taken from the two rivers for studying the quality of the water.

Places for sampling the water assays – decided in the places with significant anthropic impact on the rivers – are showed in tabels 1 and 2 and on the maps 1 and 2.

Analysis of the physical and chemical values of the two rivers have been made, based on the assay taken, which are presented in tabel 3.

The counting of the pollution value was made using the following formula:

$$I_p = C^{max} / CMA$$

in which C_{max} – the maximum concentration of the pollutant; CMA – the maximum concentration permitted to the pollutant.

The quality of an element/ factor of the environment comes under the admitted limits (in STAS or Normative), in an estimation scale, between 1 -10, which expresses the degree of analysed environmental degradation as compared to the initial (natural) state, unaffected by the human activity. The average estimation scale (Nbm) results from the estimation scales sums for all the pollutants, divided to the number of pollutants.

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Article received: June 2013; published: September 2013

Tabel 1. Places for sampling water assays – Tur

Nr. crt.	Place for sampling	GPS coordonates	Identity code Water and sediment	Conditions for sampling	Water source
1	Upstream Negreşti Oaş (town entrance)[1]	N 47°52'09'' E 23°07'41''	Tur – A – 1	Air T. = 26°C Humid. rel. = 48% Wind speed = 0,4 m/s Water T. = 19°C Water Speed = 2 m/s O_2 dilluted = 12,6%	Natural waters, not polluted
2	Downstream Negreşti Oaş (Tur neighbourhood), upstream Călineşti Oaş Lake	N 47°55'18'' E 23°207'44''	Tur – A – 2	Air T. = 31°C Humid. rel. = 40% Wind speed = 0,8 m/s Water T. = 21°C Water speed = - O_2 dilluted = 6,4%	Local and industrial waters
3	Downstream Călineşti Oaş Lake, Turulung Vii area, upstream Turţ inflow	N 47°55'56'' E 23°09'22''	Tur – A – 3	Air T. = 29°C Humid. rel. = 36% Wind speed = 1,1 m/s Water T. = 21°C Water speed = 1,2 m/s O_2 dilluted = 9,8%	Little discharge, local waters
4	Downstream Turulung bridge – hydrometric point, downstream Turţ inflow	N 47°55'43'' E 23°05'02''	Tur – A – 4	Air T. = 31°C Humid. rel. = 40% Wind speed = 0,6 m/s Water T. = 21,5°C Water speed = 1,0 m/s O_2 dilluted = 7,4,2%	Effluents from Turţ mine
5	Downstream railway bridge Porumbeşti – Micula	N 47°56'24'' E 22°58'51''	Tur – A – 5 / TUR-S-5	Air T. = 32°C Humid. rel. = 38% Wind speed = 0,3 m/s Water T. = 22°C Water speed = 0,5 m/s O_2 dilluted = 8,2%	Local waters, fertilizers

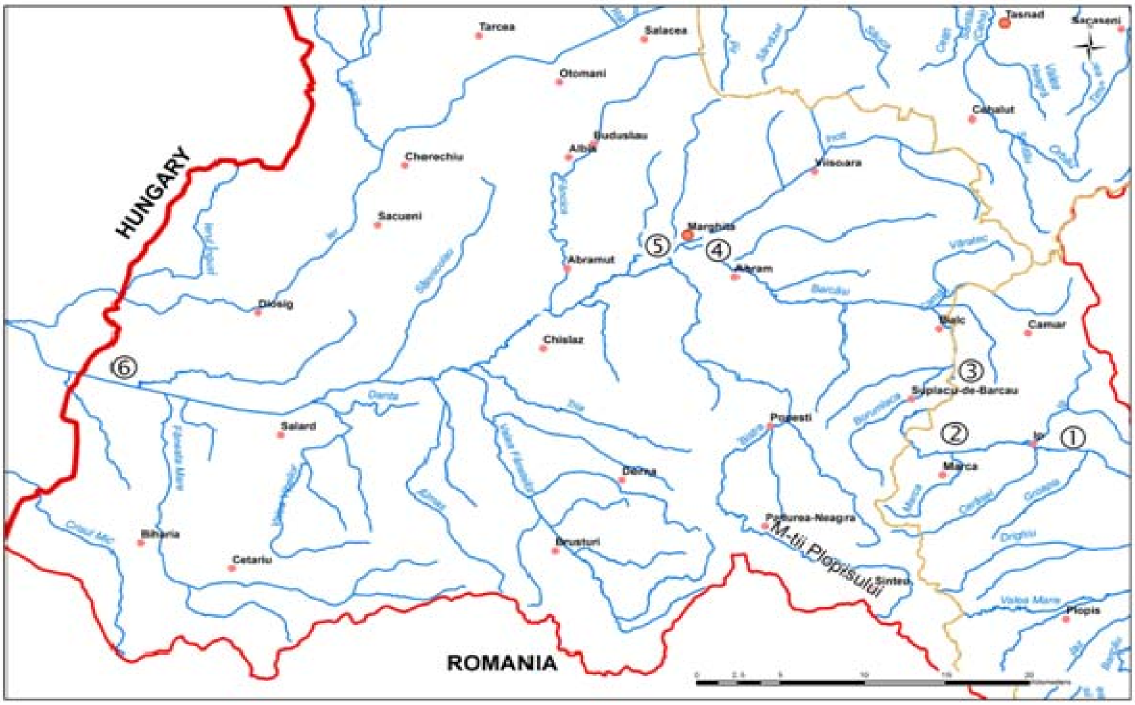
Note: the sampling place nr. 1 is the basis (reference point), less affected by the pollution, from which the effect of the anthropic impact on the waters and fish on Tur course, has been assessed.

Map 1. Sampling points on the Tur river

Tabel 2. Places for sampling water assays - Barcău

Nr. crt.	Sampling places	GPS Coordonates	Identity code	Conditions for sampling	Water source
1	Upstream loc. Subcetate	N 47°06'03" E 22°41'28"	BRC-A-1	Air T. = 19,0°C Humid. rel = 71% Wind speed = 0,2 m/s Water T. = 11°C Water speed = 1,5 m/s O_2 dilluted = 14,6%	Muddy waters
2	Upstream Suplacu de Barcău/ storage entrance Suplacu de Barcău	N 47°14'37" E 22°31'28"	BRC-A-2	Air T. = 26,1°C Humid. rel.= 40,8% Wind speed = 0,6 m/s Water T. = 21°C Water speed = 0,5 m/s O_2 dilluted = 8,0%	industrial waters
3	Downstream Suplacu de Barcău/ Upstream Refinery (loc. Cohani)	N 47°17'05" E 22°33'09"	BRC-A-3	Air T. = 28,3°C Humid. rel.= 35,8% Wind speed = 0,2 m/s Water T. = 22°C Water speed = 0,5 m/s O_2 dilluted = 5,8%	industrial waters
4	Downstream Marghita/ upstream Inot brook inflow	N 47°20'19" E 22°20'02"	BRC-A-4	Air T. = 22,6°C Humid. rel. = 50,1% Wind speed = 0,6 m/s Water T. = 20°C Water speed = 0,5 m/s O_2 dilluted = 5,2%	industrial waters
5	Downstream Marghita, 150 m downstream water – purification plant	N 47°19'47" E 22°19'19"	BRC-A-5	Air T. = 24,3°C Humid. rel = 50,9% Wind speed = 0,5 m/s Water T. = 20°C Water speed = 0,4 m/s O_2 dilluted = 6,8%	Local waters
6	Roşiori, 200 m downstream bridge national road Satu Mare-Oradea	N 47°14'16" E 21°56'20"	BRC-A-6	Air T. = 35,5°C Humid. rel = 31,2% Wind speed = 0,1 m/s Water T. = 21°C Water speed = 0,3 m/s O_2 dilluted = 7,5%	Local waters

Note: Sampling place nr. 1 is the basis (reference point) for assessing the anthropic impact on Barcău waters for the parts situated downstream.



Map 2. Sampling points on Barcău river

Tabel 3. Research methods used in assessing the anthropic impact on the water quality in Tur and Barcău rivers

Method:	Method regulation:
The analysing and assessment of the physical, chemical and biological values of the aquatic habitats in the sampling points.	- 2008/105/CE of the European Parliament and of the European council regarding the standards for the environmental quality
A. PSYSICAL VALUES	
1. Determining temperature (°C)	- measurements with special thermometres in liquid environment
2. Determining conductivity at 20°C	- Electrometry
3. Water hardness (° german)	- *The complexometric method* (Ca şi Mg ions have the capacity to form chelate compound)
4. Determining radioactivity	- *Analysing methods of the gamma mix nucleides*
B. CHEMICAL VALUES	
5. Determining the Hydrogen ions concentration (pH)	- *Electrometry*: measured „in situ" - the sampling moment (without pre-treating the samples) with pH-metre type Metler Toledo MP 230
6. The dozage of the Oxygen dilluted in the water	- *Iodometrical Method*
7. Determining the biochemical consumption of Oxygen, every 5 days (CBO_5) (mg O_2/l)	- *Determining CBO after n days* (CBO_n)
8. Chemical Oxygen consumption (CCO_{Cr}) (mg O_2/l)	- *Potassium Dichromate Method* (CCO_{Cr})
9. Determining total Nitrogen(mg/l)	- *Spectrophotometric Method of molecular absorption* – colorimetric dosage of the yellow nitrocompounds, due to the reaction between the nitrates and the phenylic- disulphonic acid
10. Determining total Phosphorus (P) (mg/l)	- *Spectrometric with Molybdate ammonium*
11. Determining the distillable substances with petroluem ether (mg/l)	- Gravimetric method
12. Determining oil products (mg/l)	– Gravimetric method.
13. Determining the phenol value (mg/l)	- Spectrometric Method with 4-aminoantipyrine after distillating
14. Determining the heavy metals (µg/l)	- Spectrometric method of atomic absorption in flame
15. Primar investigation (metal content in the sediment assay screening)	- Spectrofotometry based on the X-Rays fluorescence (XRF Metod)
16. Determining the total Oil Hydrocarbons	*Determining the content of the distillable substances from oil method.*
17. Determining the organic substances expressed through organic Carbon	*Determining the organic Carbon through sulfocromic oxidation method*

RESULTS AND DICUSSIONS

The samples were taken in September 2012. The results were compared with the limits regulated by the O.M. 1146/2002, being included in the tables 4 and 5, and the interpretation is given in the images 1-2.

With little exceptions, the indicators for water quality from the two rivers from the sampling point nr. 1 shows a natural type of water, untainted, representing a good basis for the evaluation of the anthropic impact downstream, where higher or lower alteration of the quality of water can be found.

On river Tur the following classes of water quality have been established:

- CCO-Cr and CBO5: upstream. Negreşti Oaş – cl. I, downstream cl. II;
- N-all: cl. I (exception being the section downstream brook Turţ inflow cl. II);
- P-all. cl. I – upstream Negreşti Oaş; cl. II – upstream brook Turţ inflow and Micula; cl. III downstream brook Turţ inflow; cl. IV – downstream Negreşti Oaş;
- Phenols: cl. II – all Tur;
- Fe: cl. II, exception upstream Turţ inflow – cl. III;
- Mn and Pb: cl. I – all the river;
- Cu, Cd, Ni and Cr. - cl. II all the river;
- Zn: cl. II, exception downstream brook Turţ inflow – cl. III.

Barcău waters are included in the following class quality:

- CCO-Cr: cl. II-V;
- CBO5: cl. II – IV;
- N-all: cl. I – downstream; cl. II – downstream Marghita and Roşiori; cl. III – upstream Suplac and downstream Marghita;
- Oil products (benzene): cl. II – downstream Subcetate and Roşiori; cl. III – upstream Suplac; cl. IV and V – downstream Suplac;
- Phenols; cl. II – downstream Subcetate; cl. III – Roşiori; cl. V. – the rest of the sections.

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Tabel 4. The results obtained for the Tur water samples, compared to the limits regulated by Ordin MAPM nr. 1.146/2002 (15-22.IX.2012)

Sample code / Regulated limit	pH	CCO Cr mgO/l	CBO_5 mg/l	Total Nitrogen mgN/l	Total Phosphorus mgP/l	Oil Hydrocarbons (µg/l)	Phenols (Phenolic index) (µg/l)	Fe mg/l	Mn mg/l	Pb µg/l	Cr µg/l	Ni µg/l	Zn µg/l	Cd µg/l	Cu µg/l
Cl. Quality. I	6,5 – 8,5	10	3	1,5	0,1	fund	fund	fund	fund	fund	fund	fund	fund	fund	fund
Cl. Quality. II		25	5	4	0,2	100	1	0,1	0,05	5	50	50	100	1	20
Cl. Quality. III		50	10	8	0,4	200	20	0,3	0,1	10	100	100	200	2	40
Cl. Quality. IV		125	25	20	1	500	50	1,0	0,3	25	250	250	500	5	100
Cl. Quality. V		>125	>25	>20	>1	>500	>50	>1,0	>0,3	>25	>250	>250	>500	>5	>100
TUR-A-1 Upstream Negreşti	7,29	7,6	2,21	0,7	0,09	0,0	3,4	0,024	0,008	<0,5	15,55	22,01	58,2	0,277	0,63
TUR-A-2 Downstream Negreşti, upstream Călineşti	7,23	12,3	4,82	1,3	0,48	0,0	3,5	0,054	0,011	<0,5	10,67	32,65	68,9	<0,01	1,58
TUR-A-3 Downstream Călineşti Upstream Turţ inflow	7,33	12,6	4,25	1,2	0,18	0,0	3,5	0,109	0,007	<0,5	8,23	25,01	74,6	<0,01	0,99
TUR-A-4 Downstream Turţ inflow Turulung	7,26	14,2	3,64	1,8	0,21	0,0	4,1	0,048	0,005	<0,5	7,85	17,11	116,2	0,067	0,93
TUR-A-5 Micula – Porumbeşti	7,42	12,3	3,41	1,3	0,19	0,0	4,1	0,078	0,010	<0,5	6,63	27,84	104,3	0,227	1,22

Note: Quality – Cl. I qual. (green color) – water of a very high quality, untainted or with minor anthropic tainting; Cl. II qual. (blue color) – water of good quality, with small deflection compared with the untainted waters; Cl. III qual. (red color) – water of average, with average deflection compared to the untainted waters; Cl. IV qual. (purple color) – water of low quality, with significant deflection compared to the untainted waters; Cl. V qual. (grey color) – poor quality waters, with severe deflection compared to the untainted waters (Water Framework Directive)

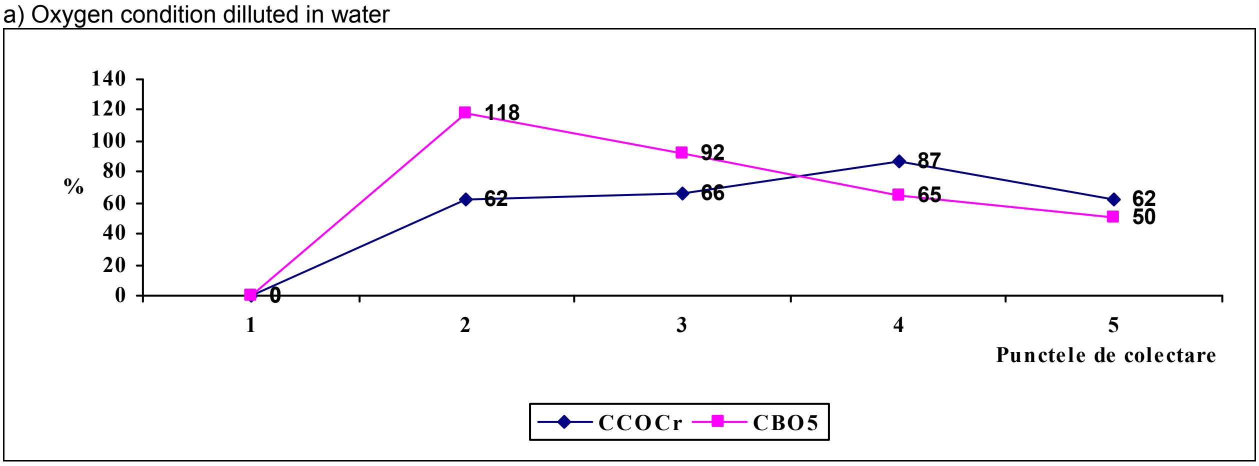
The chemical state of Tur waters is deteriorated especially by the three heavy metals: Ni, Cu and Zi. But, the most important pollution problems are still those with Zinc. It is clear from the results of the water analysis that the most importantly polluted sections on Tur river are a) downstream Negreşti Oaş, with sewage and industrial waters insuficiently purified (especially with Phosphopous); b) in Micula, on the lower reach, because of the fertilizers and animal dejections (especially with N); c) downstream brook Turţ inflow in Tur (it brings waters from the mine with high concentrations of heavy metals – especially Zinc).

Tabel 5. The results obtained for the Barcău water samples, compared to the limits regulated by Ordin MAPM nr. 1.146/2002 (17 and 23.09.2012)

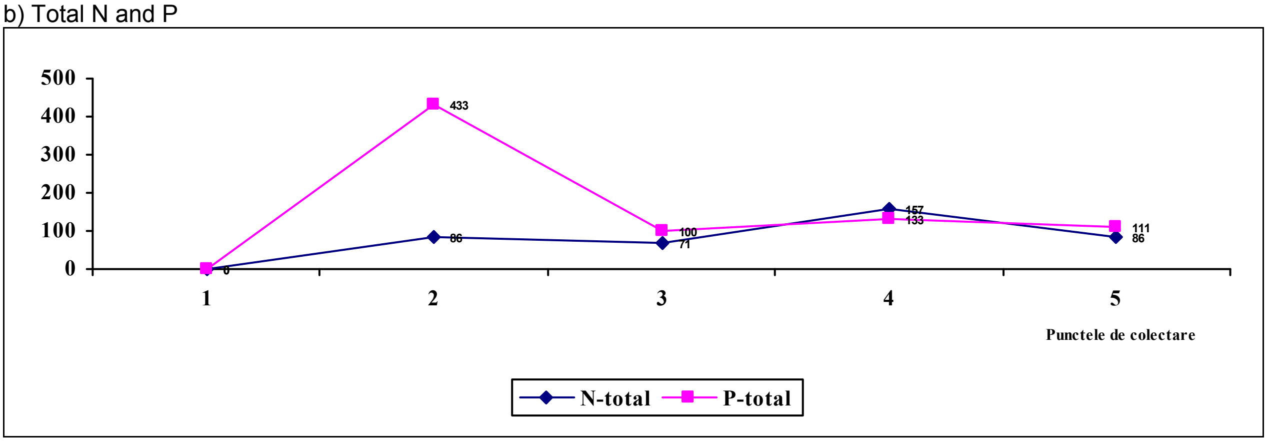
Sample code / Regulated limit	pH	CCO-Cr mgO/l	CBO5 mg/l	Total Nitrogen mgN/l	Total Phosphorus mgP/l	Oil Hydrocarbons (µg/l)	Phenols (Phenolic index) (µg/l)	Total Nitrogen mgN/l	Fe mg/l	Mn mg/l	Pb µg/l	Cr µg/l	Ni µg/l	Zn µg/l	Cd µg/l	Cu µg/l
Cl qual. I	6,5 – 8,5	10	3	1,5	0,1	-	fund	fund	fund	fund	fund	fund	fund	fund	fund	fund
Cl qual. II		25	5	4	0,2	-	100	1	0,1	0,05	5	50	50	100	1	20
Cl qual. III		50	10	8	0,4	-	200	20	0,3	0,1	10	100	100	200	2	40
Cl qual. IV		125	25	20	1	-	500	50	1,0	0,3	25	250	250	500	5	100
Cl qual. V		>125	>25	>20	>1	20*	>500	>50	>1,0	>0,3	>25	>250	>250	>500	>5	>100
BRC-A-1 Upstream Subcetate	6,6 6,4	10,6	2,23	0,9	0,05	2,11	<10	2,5	0,020	0,007	<0,5	1,61	2,20	0,427	<0,01	0,61
BRC-A-2 Upstream Suplacu de Barcău	6,6 7,2	12,6	4,8	0,8	0,09	-	460	98	0,071	0,011	1,209	0,35	<0,5	0,243	<0,01	1,81
BRC-A-3 Downstream Suplacu de Barcău	6,2 6,4	53,6 52,8	11,4	4,9 4,5	0,13 0,15	10,31	520 340	732 31,4	0,062	0,061	<0,5	0,84	2,26	0,631	<0,01	2,58
BRC-A-4 Downstream Marghita	7,2 7,2	51,2 396,0	8,2	1,9 3,8	0,35 0,38	134	322 870	418 598	0,154	0,055	<0,5	1,09	<0,5	0,589	<0,01	3,77
BRC-A-5 Upstream Marghita	6,1 7,0	54,0 184,8	12,1	4,1 5,7	0,45 0,40	66,60	1024 436	837 84,6	0,148	0,031	<0,5	1,08	<0,5	0,355	<0,01	3,55
BRC-A-6 Roşiori	7,1 6,6	24,5 94,4	8,6	3,5 3,1	0,14 0,17	55,20	766 84	942 37,3	0,082	0,007	0,728	0,37	<0,5	0,274	<0,01	2,01

Note:
- There are two values mentioned for each indicator representing the values of the samples taken on the 17th and 23rd of September 2012;
- The rest of the explanations are those mentioned in Table 4;
- The regulated values according to NTPA 001/2001 – the maximum values the waters filled with industrial and local effluents, evacuated in the natural receptors

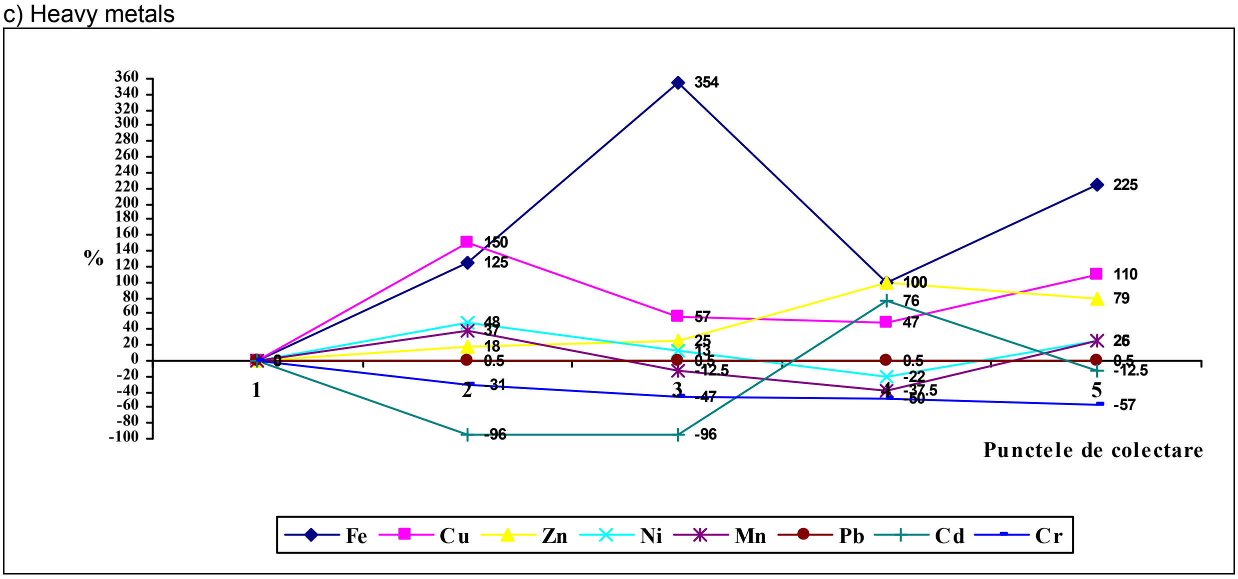
a) Oxygen condition dilluted in water



b) Total N and P

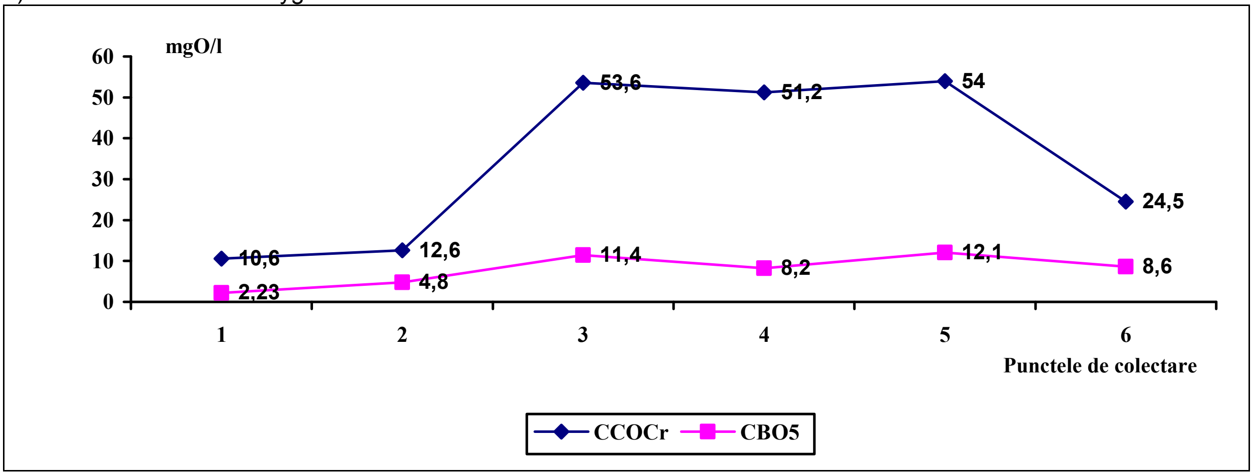


c) Heavy metals

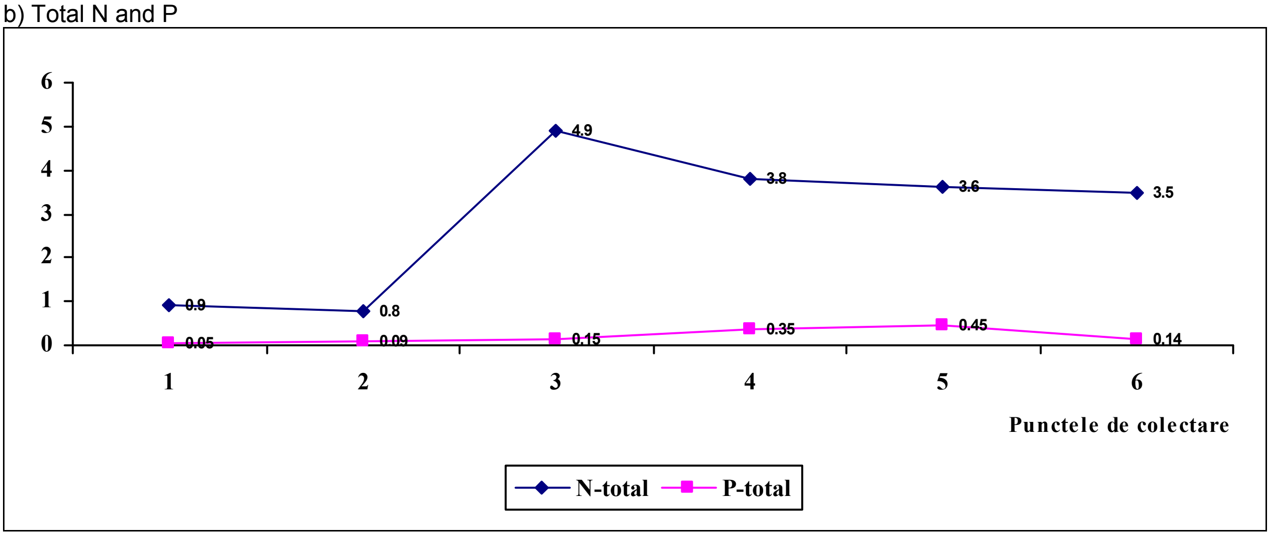


Picture **1**. The evolution of Tur's waters parametres in Autumn 2012

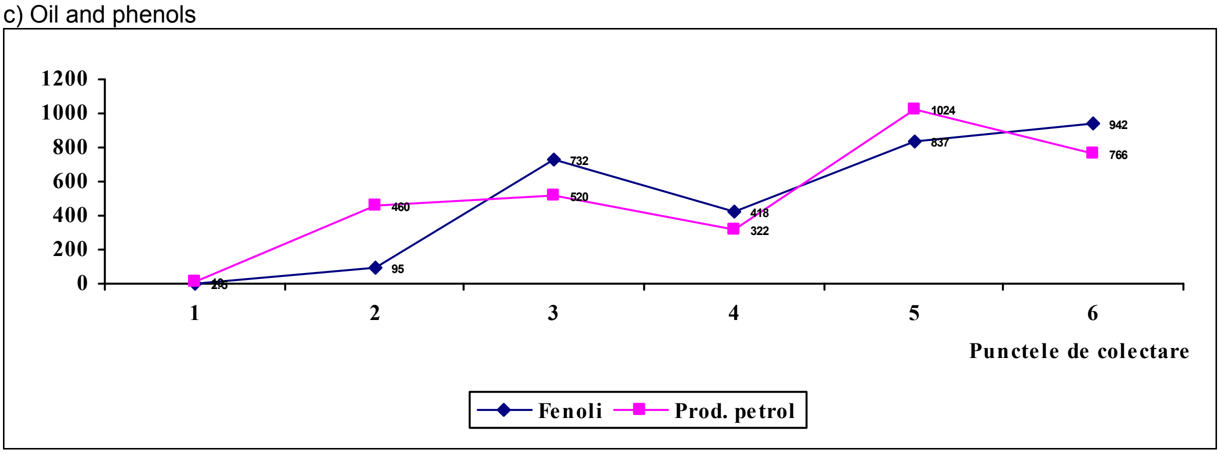
a) The condition of the Oxygen dilluted in water



b) Total N and P



c) Oil and phenols



Picture 2: The evolution of Barcău's waters parametres in Autumn 2012

On Barcău, the specific pollutants are: a) oil products in Suplac - Marghita area (benzene and phenols), due to the exploaration and refining of oil; b) sewage and industrial waters from Marghita town (filled with organic substances); c) the waters filled with fertilizers downstream, at Roşiori.

It is also worth mentioning that on both rivers, the severe specific pollutions, cause on their middle course an "ecological void", on 1-2 kilometres downstream (where there are no aquatic animals, including fish): on Tur, downstream Brook Turţ inflow, because of the heavy metal discharges, while on Barcău, downstream

Suplac refinery, because of the high values of petroleum products.

Lastly, it can be noticed that pollution with benzene and phenols on Barcău river is more severe and large than the pollution with heavy metals on Tur river.

For establishing the pollution coefficient of the water on both rivers, we kept in mind, according to the methodology for global quality water evaluation, the pollutant with the higher concentration, and, based on this, the estimation for waters. The concrete data of calculating for establishing Ip and the estimation note are presented in tables 6 and 7.

Tabel 6. Data for calculating the pollution coefficient (Ip) and the estimation note for Tur waters

The research section on river Tur	Pollutant with max. conc.	Cmax	CMA	Ip	Ip/100	Estimation note
0	1	2	3	4	5	6
TUR-A-1 (upst. Negreşti Oaş)	-	-	-	0,000	0,000	10
TUR-A-2 (downst. Negreşti Oaş)	P-total	0,480	0,10	4,800	0,048	9
TUR-A-3 (downst. Călineşti Oaş)	Fe	0,109	0,09	5,333	0,053	9
TUR-A-4 (Turulung)	Zn	116,2	99,0	1,173	0,053	9
TUR-A-5 (Micula)	Zn	104,3	99,0	1,053	0,010	9

Tabel 7. Data for calculating the pollution coefficient (Ip) and the estimation note for Barcău waters

The research section on river Barcău	Pollutant with max. conc.	Cmax	CMA	Ip	Ip/100	Estimation note
0	1	2	3	4	5	6
Upstr. Subcetate	Phenols	2,5	1	2,50	0,025	8
Upstr. Suplacu de Barcău	Phenols	98	1	98,00	0,98	7
Downstr. Suplacu de Barcău	Phenols	520	1	520,00	5,20	4
Upstr. Marghita	Phenols	598	1	598,00	5,98	4
Downstr. Marghita	Petroleum Prod.	1024	99	10,34	0,103	9
Roşiori	Phenols	942	1	942,00	9,42	3

Based on the data from the first 3 columns of Table 6, the Ip could be calculated, and the results can be seen in column 4. If we divide the Ip to 100, the values from column 5 will be obtained, to which the estimation notes from column 6 are corresponding – on an estimation note scale from 1 -10. Each estimation note is characterized by some effects of the pollutant on people and the environment. (I.C.I.M., 2006)

The estimation notes for Tur waters are: 10 for the section upstream Negreşti Oaş and 9 for the rest of the sections. The estimation note 10 for the upper course of the river Tur, upstream Negreşti Oaş, corresponds to an environment unaffected by human activity, and the environment's condition is a natural one, while the estimation note 9 for the rest of the river Tur shows that the environment is affected by the human activity, but the condition of the environment is close to natural, without visible effects (this is also the average estimation note for Tur waters (Nbm).

On the whole Tur, the coefficient for pollution of the water is 9, which represents a course of water affected by the contemporary anthropic pressure, which needs some decisions for ecological reconstruction.

The conclusion of the analysis of the data for the river Barcău, is that this river is polluted starting from the upper course, especially with phenols. As a consequence, in Subcetate the environment is affected within the accepted limits (level 1), and with possible effects on the quality of the water. Upstream Suplac the water is affected within accepted limits (level 2), showing a level of intervention with significant effects. Downstream Suplac and upstream Marghita, the water is affected over the accepted limit (level 3), being detected serious harmful effects - as well as the total disapearance of the fish from the river waters. Downstream Marghita, the waters are getting better. Still, they are affected by human activity, but without clear effects. At Roşiori, Barcău waters (on their lower course) is degraded, still due to the phenols (level 1), and their effects are deadly if exposed for longer time.

In conclusion, the water and sediments analysis from Barcău show that this river is severely affected by the incontrollable evacuations and controlled by the oilry fractions from Suplac and Marghita area, and less importantly by the heavy metals coming from the urban sewage from Marghita. On the whole, after some quality coefficients, Barcău is a polluted water course, degraded (class V of quality).

Based on the data from the tables 6 (for Tur) and 7 (for Barcău), gathered in table 8 and in the chart from the fig. 3, the estimation notes of the waters in the two rivers have been compared.

Tabel 8. The estimation notes from Tur and Barcău rivers

Rivers / Estimation notes on sections	Section 1	Section 2	Section 3	Section 4	Section 5	Section 6
Tur	10	9	9	9	9	-
Barcău	8	7	4	4	9	3

From Table 8 and fig. 3 results that the petroleum products and phenols create a severe pressure on the chemical quality of Barcău as compared to the pressure created by the heavy metals on river Tur (downfall) due to the reduction of the activities of oil exploitation and refining.

Taking into consideration the estimation classes, especially for Barcău, it is easily understood which are the negative consequences of the aquatic environment degradation (Gheorghe, 2009):

a) the reduction of the biodiversity, including the ichthyologic one, for both rivers;

b) the reduction of the natural productivity of the aquatic ecosystems, including the number of fish and of the annual rate of catchings for both rivers;

c) the degradation of the ecological balance to the point where the life quality of the ecosystems is affected, on both Tur, but more specific on Barcău;

d) the over exploitation of the aquatic resources, especially fishy, through poaching and by allowing too many fishing permits for Tur river.

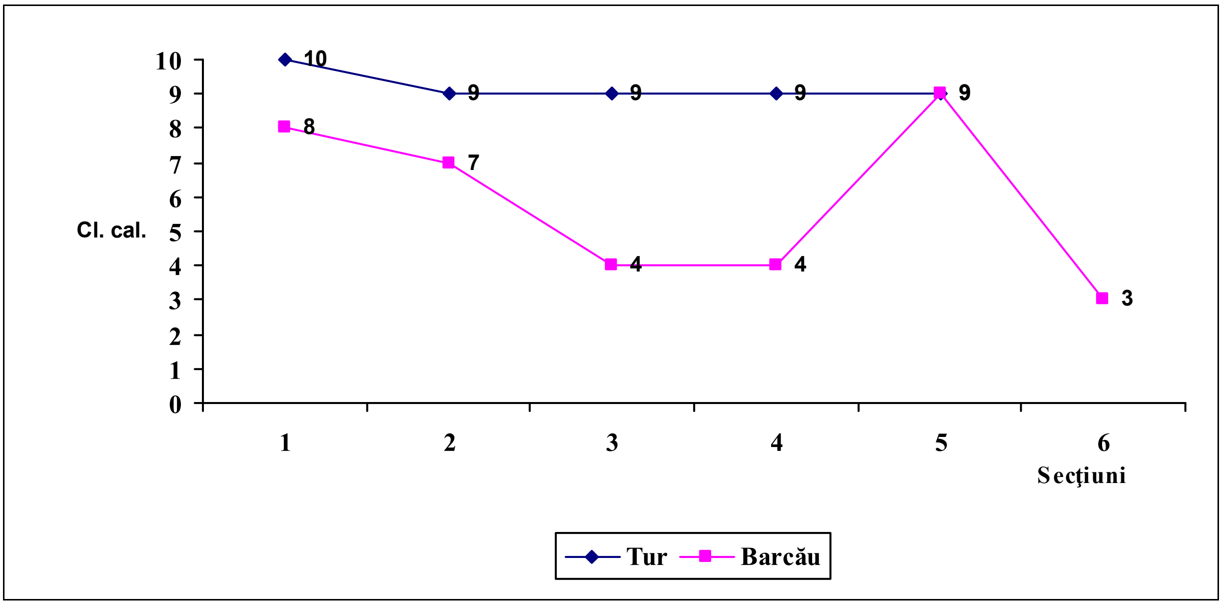


Fig. 3. The estimation notes for Tur and Barcău waters, on sections

CONCLUSIONS

The value for pollution for Tur waters, which determines the note for pollution 9, shows a course slightly affected by the contemporary anthropic pressure and which would benefit from some measurements of ecological restauration.

The value for pollution of Barcău waters which determines the estimation notes between 3 and 8, shows that the waters are clearly polluted, almost from the higher course, especially with phenols, being distinguised degradations of the quality of the water, even with deadly effects for animals, downstream Suplac.

When comparing the estimation notes of water quality of the two rivers, it can be noticed that the petroleum products and phenols determine a more severe pressure on the Barcău water quality than the heavy metals on river Tur.

The industrial regression in the last two decades has reduced significantly the pollution values of the waters.

Specials measures for ecological rehabilitation are needed to improve the quality of waters in the two rivers, focused on the constant water discharge reducing of the polluting sources (heavy metals on Tur; petroleum products on Barcău) and the creation of a some water- purifying plant which can retain the pollutants.

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