Studia Universitatis "Vasile Goldiş", Seria Ştiinţele Vieţii
Vol. 23, issue 2, 2013, pp. 195-207

THE ANTHROPOGENIC IMPACT ON THE WATER QUALITY OF TUR RIVER (SATU MARE COUNTY)

Doru Ioan ARDELEAN
"Vasile Goldiş" Western University Arad

ABSTRACT. Tur is a river of medium size that springs from Gutâi Mountains and it flows into Tisa, in Hungary. It is polluted by the waters discharged by the neighbouring localities, by the mine waters discharged by Turţ brook and by the agricultural fertilizers, used mainly in their inferior course. Samples of water and mud were taken from many points from the river. More indicators of water and mud quality at the oxygen consumption, biogenic elements (total Hydrogen and Phosphorus) and heavy metals were analysed. The analysed water samples indicate a water of good quality, less at Zinc, and the mud samples show the accumulation of some pollutants over the admitted quota at Zinc, Titanium and Arsenic. The accumulation of heavy metals in the mud is bigger than in the water. The pollution indicator (Ip) for the Tur's water was calculated, establishing the 9 grade of estimation which means almost natural water, but slightly affected by the anthropic impact, requiring some measures of ecological reconstruction.

Keywords: anthropogenic impact; heavy metals; water quality; mud quality; pollution indicator

INTRODUCTION

Tur is a river of medium to small size (102 kilometres) from the north-western part of Romania. It springs from the Gutai Mountains (986 meters altitude) and it flows into Tisa, in Hungary. It crosses the Oaş Depression and the Satu Mare Plain, in proportion of 35%, respectively 65%, tempering its slope step-by-step (from 20% to only 1%). Its minor channel is strongly meandered, being initially strewed with boulders, and with gravel and even mud down the river. The inferior course is totally channelled and embanked, losing its natural shores, its meanders and meadows.

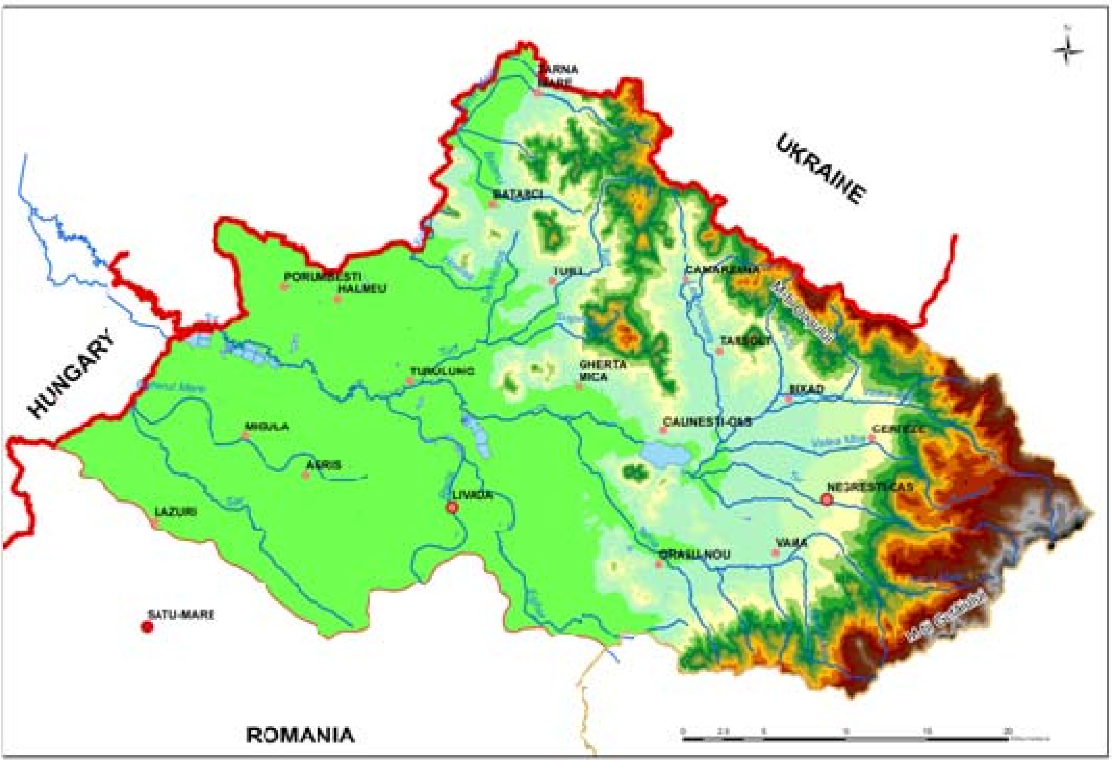
The main characteristics of the Tur water are: the feed is ensured mainly from rains (73%), from which cause its debit is evidently fluctuating; the debit is modest, especially until the entrance in the plain (7,16 cubic meters/second); the weight of the multi-annual season leaks is unequal: in spring – 33%, in summer – 17%, in autumn – 11% and in winter 36%; the maximum medium monthly leak is in February (13,93 cubic meters/second) – when, often, heavy, even catastrophic flows occur (13 May 1970 – 743 cubic meters/s, at Turulung) – and the minimum one in August (2,41 cubic meters/second), frequently the consequence of some long periods of drought; the water temperature maintains itself at +5 degrees Celsius all year long, and in summer it registers even +30 degrees Celsius, generating a visible discomfort of the aquatic fauna; the ice bridge can last between 10-75 days, depending on the air temperature; the water turbidity and mineralization, as well as the solid leak are reduced (100-300 g/cubic meter, 80 mg/litter, respectively under 2 tons/hectare/year) because of the eruptive rocks little soluble that represent the bed of the river's bank (Ujvari, 1972).

In the Tur valley there are many relatively big localities and extended surfaces of land on which a semi-intensive agriculture is practiced, especially the horticulture.

More works (Velcea, 1964; Ujvari, 1972; Fazekas, 1992-1993) realize an almost complete characterization of the Tur's hidrography, other (Bănărescu, 2004; Andrişca, 2011) notice the pollution sources from the river, some, more recent, reference to the qualitz of its water (Ardelean, 1997 and 1999; Ardelean and Duma, 1997; Mereuţă and colleagues, 2000; Breugel and colleagues, 2005; Nagy and colleagues, 2008; Roşu and Domşa, 2011). The named works give a brief summary of the anthropic impact on Tur: a) the debit's reduction, as a result of the diverse water samplings; b) the pollution with waste waters (filled with organic substances) and used mine waters (with heavy metals) or deriving from various commercial agents; c) the eutrophication of the water following the diminishing of the debits and/or the warming of the water; d) the crossing of the river (the embankment from Călineşti Oaş) that blocks the fish circulation; e) the over-fishing, including the trespass. Also, the more recent works point out the fact that the economical rebuff from the last 20 years, as well as the harshening of the legislation regarding the protection of the environment ameliorated, in a certain extent, the Tur ecological state, as its water is almost clean up to Turţ brook's affluence on (which discharges mine waters upstream, medium polluted water (with heavy metals and organic substances).

The present work proposes itself to evaluate the new situation regarding the pollution sources and the quality of Tur water in view of formulating some efficient measures of hydrological and ecological management of the river.

***Correspondence:** *Doru Ioan Ardelean, "Vasile Goldiş" Western University Arad*
Article received: February 2013; published: May 2013



The physical map of the hydrographical basin of the river Tur

The river Tur, superior course, upstream Negreşti-Oaş

The river Tur, middle course, down the river Călineşti Oaş Lake (original photo)

The downstream tour Negreşti-Oaş – bridge over the river

The Tur at Porumbeşti – invaded by water plants

Studia Universitatis "Vasile Goldiş", Seria Ştiinţele Vieţii
Vol. 23, issue 2, 2013, pp. 195-207

MATERIALS AND METHODS

Water and mud samples were taken from the river Tur.

- **Water samples**
- *Potential sources of water pollution*

- The evacuation of the used waters purged by the purification station of Negreşti Oaş city;
- The storage of the waste processing near the water course;
- Uncontrolled evacuations of used waters from the localities without commune sewerage;
- Activities connected to mining (Turţ brook overtakes the waters from the ex-mining exploitation Turţ-Socea).

- *The followed pollutants*

The concentrations of the following quality indicators were determined for the establishment of the concentration of the pollutants in the water of Tur's river:

- The concentration of the hydrogen ions (pH): potentiometric (SR ISO 10523/2009);
- The chemical consumption of oxygen (CCO-Cr): titrimetrical (SR ISO 6060-1996);
- The biochemical consumption of oxygen (CBO5): incubation-titrimetry (SR EN ISO 9408-2004; SR EN 1899-2/2003);
- The oxygen dissolved in water: „in situ" – electrochemical with WRW oxicontact sensor (SR EN 25814/1999);
- Total nitrogen (N-tot.): mineralization – colourimetry (SR EN 25663/2000);
- Total phosphorus (P-tot.): mineralization – colourimetry (SR EN 6878/2005);
- Heavy metals (Chrome, Nickel, Cadmium, Led, Zinc, Copper, Manganese, Iron): spectrophotometry of atomic absorption (SR EN ISO 15586/2004).

- *The placement of the points of sampling of the water and mud samples*
- *Sampling techniques of the water samples*

Table 1

The points of sampling of the water and mud samples

No.	Sampling place	GPS coordinates	Identity code	Sampling conditions
1	Upstream Negreşti Oaş, the footbridge from over the river	N 47°52'09" E 23°27'41"	Tur – A – 1	Air temperature = 26°C Relative humidity = 48% Air speed = 0,4 m/s Water temperature = 19°C Water speed = 2 m/s Dissolved O_2 = 12,6%
2	Upstream Negreşti Oaş (Tur neighbourhood), upstream Călineşti Oaş Lake	N 47°55'18" E 23°207'44"	Tur – A – 2	Air temperature = 31°C Relative humidity = 40% Air speed = 0,8 m/s Water temperature = 21°C Water speed = - Dissolved O_2 = 6,4%
3	Upstream Călineşti Oaş, Viile Turulung zone	N 47°55'56" E 23°09'22"	Tur – A – 3	Air temperature = 29°C Relative humidity = 36% Air speed = 1,1 m/s Water temperature = 21°C Water speed = 1,2 m/s Dissolved O_2 = 9,8%
4	Upstream bridge Turulung – hydrometrical point	N 47°55'43" E 23°05'02"	Tur – A – 4	Air temperature = 31°C Relative humidity = 40% Air speed = 0,6 m/s Water temperature = 21,5°C Water speed = 1,0 m/s Dissolved O_2 = 7,4,2%
5	Upstream bridge CF Porumbeşti – Micula	N 47°56'24" E 22°58'51"	Tur – A – 5	Air temperature = 32°C Relative humidity = 38% Air speed = 0,3 m/s Water temperature = 22°C Water speed = 0,5 m/s Dissolved O_2 = 8,2%

- Samples were taken for the characterization of the water quality from the river according to SR ISO 5667-6/2009 „The quality of the sampled water"
- The conservation, the transport and the storage of the samples was made according to the methodology from SR EN ISO 5667-3/2004; the water samples were taken in recipients of polyethylene
- The water samples were processed and analyzed according to the methods afore mentioned at the establishment of the quality indicators of the water.

- *The analysis of the results in rapport with the regulated limits*

- The obtained results for the water samples were compared to the limits regulated by O.M. 1146/2002, in which sense the table 2 was made.

- **The mud samples**
- *The potential sources of the mud pollution*

- The precipitation and the deposition of the non-organic pollutants (dissolved metals) from the river's water

- *The followed pollutants*

- Heavy metals (Chrome, Nickel, Cadmium, Plumbum, Zinc, Copper, Manganese, Iron): spectrophotometry of atomic absorption (SR EN 15309/2007; SR ISO 11047/1999)

- *The placement of the points of sampling of the water and mud samples (the same as in the case of the water)*
- *Sampling techniques of the mud samples*

- The samppling of the mud samples was made by manual drilling with soil plunger; from the superior layer of mud (5-20 cm), according to SR ISO 5667-12/2001. The mud samplings, as those of water, were made on 04.08.2012.
- The samples were packed in polyethylene bags, according to the SR EN ISO 5667-15/2010 requests.
- The preparation of the mud samples was made through the following lab operations: drying at 105 degrees Celsius in dying oven type Aprilie ES25; the dried samples were minced through grinding mortar and passed through a shingle with = 0,64 mm; the prepared samples were analyzed through techniques of determination of the content of heavy metals.
- The primary investigation (screening) of the content of metals in the mud samples was made with the help of a portable spectrometer type NITON XL3t – 90 – GOLDD that is based on the fluorescence of the X rays (XRT Method). The device is able to detect and quantify the concentrations of metals in a few seconds. That is why, the determinations with the XRF analyzer are very useful and recommendable in the investigation of the polluted zones.
- The determined values are stocked in the memory of the device that can be transferred to a PC with the help of the NITON Data Transfer NTD V.6 software. The concentrations of heavy metals that can be determined through this laboratory technique are of the ppm order (mg/kg dried sample).
- Analyses through mass spectrometry with atomic absorption were also executed for the quantification of the traces of toxic metals. The prepared mud samples were mineralized in blend of nitric acid 65% and perhidrol 30% in a system of mineralization assisted by microwaves type Milestone START D.
- The samples brought in solution were dosed with spectrophotometer with atomic absorption type GCG Avanta, equipped with system of electro-thermal vaporization (oven with blacklead GT 500 and autosampler Pal 5000).
- The results of the made analyses in rapport with the regulated limits

The quality indicators of the sediments (mud samples) were compared to the limits regulated by O.M. 1146/2002 (table 2).

RESULTS AND DICUSSIONS

They regard the current sources of pollution, as well as the results of the chemical analysis of the water and mud samples from Tur.

The main current sources of pollution of the water and mud from Tur. Following the displacements on the valley of the river Tur, in the summer of the years 2011 and 2012, the author noticed the current sources of pollution – depending on which the sampling points were set – which are presented as follows.

a) the Tur's channelling and the innings of the afferent swamps that transformed the river into a channel with more accelerated leak and destroyed the afferent wet habitats (with the specific flora and fauna);

b) the water sampling from Tur and its tributaries for various destinations (especially as water) that determined the debit's obvious reduction and the water's warming;

c) the evacuation of the commune and industrial waters from Negreşti Oaş city (waters from the city purification Station, whose capacity is surpassed, are discharged daily in Tur);

d) uncontrolled evacuations of used waters from the localities without commune sewerage (most of the localities from the investigated zone are in this situation);

e) the deposition of the railings/wastes near the water course;

f) the embankment and the reservoir over Tur from Călineşti Oaş (blocks the fish migration on the river, especially for reproduction; eutrophication phenomena appear on the lake; the debit of the water course is very diminished upstream the embankment);

g) the water mine discharge in Tur by the stream Turţ which gathers the residual waters from R.M. Turţ-Socea (contaminated with heavy metals, even after the cease of the mining activity)ş

h) the fishery lakes from Adrian and Bercu Nou that overtake important quantities of water (the effect is more obvious in summer, in the periods with prolonged drought);

Studia Universitatis "Vasile Goldiş", Seria Ştiinţele Vieţii
Vol. 23, issue 2, 2013, pp. 195-207

i) the accumulation of fertilizers from the agricultural exploitations (manures, pesticides and animal husbandry dejections).

A more complete table of the current sources of pollution from Tur is presented compared to the data mentioned in the specialty literature. A few differences regarding the geographical distribution and the pollution intensity on this river emerge from their presentation such as: a) the apparition of some new purification stations (Halmeu, Turulung) that diminish the load of organic substances; b) the water sampling increased, respectively the river's water debit decreased, especially upstream from Negreşti Oaş; c) the discharges of mine water by Turţ brook decreased after the closing of the exploitation of non-ferrous from the upstream; d) the presence on the river of more artificial lakes diminishes the debits from the downstream (especially from Călineşti Oaş Lake with the capacity of over 28 million cubic meters); e) the over-fishing amplified (authorisations of sport fishing are sources of incomes for the fishery associations), including the poaching (the lack of systematic and severe control).

The quality of Tur's water. The results obtained at the chemical analysis of Tur's water from the sampling points are presented in table 2. They give us a complete image regarding the quality indicators of these river's water.

The Tur's waters, at the date of the prelevation of the samples, had the temperature of 19-22 degrees Celsius (it rises down the river), the water speed of 2,0 – 0,5 meters/second (it decreases down the river), and the organoleptic characteristics are altered insignificantly. The other parameters of the water quality, followed in the present study, are presented as follows.

The oxygen dissolved in water, the inverse ratio expression of the accumulation of organic substances registers, across Tur, values between 12,6 and 6,4%. The first value corresponds to the water generally, well oxygenate, and from the biggest part of the course, and the second represents the exception from this situation, the section downstream from Negreşti Oaş where waters with many organic substances are discharged. The viability of the inverse ratio rapport between the water's temperature and the quantity of the oxygen dissolved in it is also confirmed in this study (Hedley, 1998). But, the analysis of the indicators regarding the consumption of oxygen in water will clear even more substantially the oxygen regime in Tur's waters.

Table 2 presents us first the water's active reaction (the pH) which notices the deviations of the biological processes from the water and the toxicity of the intermediate compounds of N and P. By the pH between 7.23 – 7.42, Tur's waters are part of the category neutral waters – weakly alkaline which is in accord with the appreciation of Transylvania's waters by Hegedus (2010). These are waters that offer good living conditions, including for fish fauna, with the exception of some sections where small local oscillations are noticed. So, the water is slightly more acid at the affluence of Turţ brook where the acid mine waters totally annihilate the aquatic biocenosis over Tur on more than 500 metres downstream or, on the contrary, slightly alkaline in the inferior course (Micula locality) where un purified commune waters and agricultural fertilizers are discharged.

On the other hand, it also results from this table that Tur's water from the superior course (upstream Negreşti Oaş) inscribes itself in class I of quality at all determined chemical indicators which assimilates to an unaffected natural water. For this reason, we considered this section the reference base towards which the deviations of the quakity parameters from the sections situated downstream will be calculated thenceforth.

The biochemical consumption of oxygen (CCO-Cr) for the oxidation of the substances from the water has small values only upstream from Negreşti Oaş (7.6 mgO/l). This value frames Tur's water in class I of quality, meaning at unaltered natural waters. In the other sections, CCO-Cr increases at 12.3 – 14.2 mgO/l, framing Tur's water at this parameter in class II of quality, meaning waters with small deviations compared to the natural waters. The CCO-Cr increase by at least 4.7 mgO/l upstream from Negreşti Oaş is the consequence of the discharge of insufficiently purified waters (the purification station from here requires a fast rehabilitation) or of unpurified waters discharged directly in the river. Another sudden increase pf CCO-Cr on Tur's course is registered at the affluence of Turţ brook (it increases by approximately 2 mgO/l) where the supplementary input of heavy metals in Tur requires a bigger quantity of oxygen for the deployment of the chemical processes of oxidation.

The biochemical consumption of oxygen (CBO5) for the decomposing of the organic biodegradable substances contained by the water is small only in the section upstream of Negreşti Oaş (2.21 mgO/l) which correponds to a water of the Ist class of quality. In all the sampling points downstream from Negreşti Oaş, CBO5 increases by approximately 1.20 – 2.60 mgO/l because of the discharge of un-purified or weakly purified waters, especially immediately downstream from Negreşti Oaş. CBO5 decreases, though, slightly once with the reduction of the discharges of organic substances in the water downstream from Călineşti Oaş Lake.

The 2 indicators regarding the consumption of oxygen – CCO-Cr and CBO5 – are in a complementarily rapport but which is not consequent in all the sampling points from Tur, being influenced by a multitude of factors, aspect also reflected in the graph from figure 5.

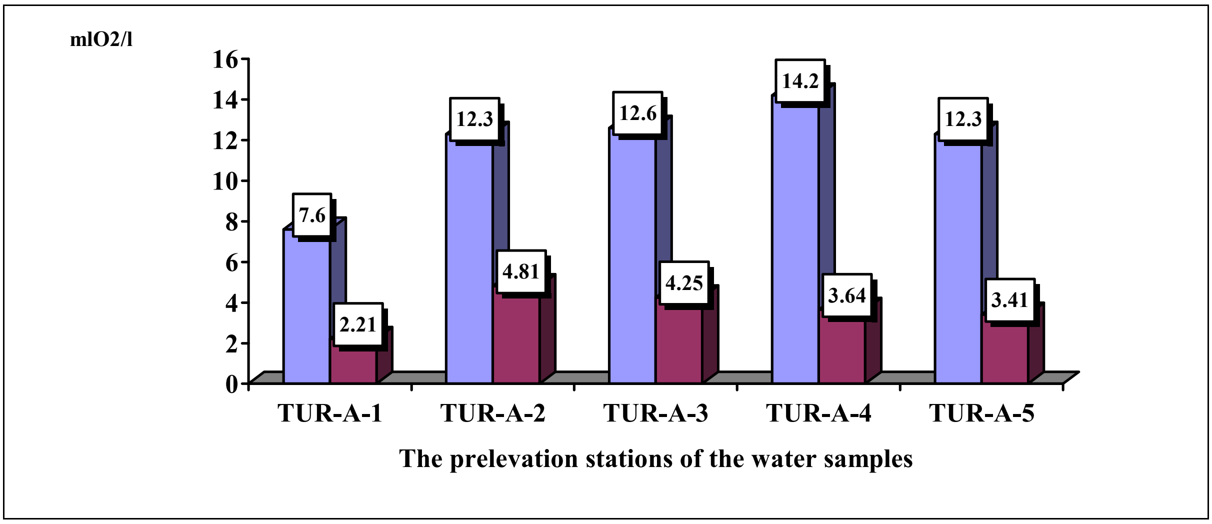


Fig. 5. The CCO-Cr/CBO5 rapport in the Tur's water, in the summer of the year 2012

Table 2

Results in setting up Tur water samples as compared to the MAPM Order no. 1.146/2002 provisions

Sample Code / The admitted limit	pH	CCOCr mgO/l	CBO_5 mg/l	Total Nitrogen mgN/l	Total Phosphorus mgP/l	Petroleum hidrocarbons (µg/l)	Phenols (index phenolsc) (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
Class quality I	6.5 – 8.5	10	3	1.5	0.1	fund	fund	fund	fund	fund	fund	fund	fund	fund	fund
Class quality II		25	5	4	0.2	100	1	0.1	0.05	5	50	50	100	1	20
Class quality III		50	10	8	0.4	200	20	0.3	0.1	10	100	100	200	2	40
Class quality IV		125	25	20	1	500	50	1.0	0.3	25	250	250	500	5	100
Class 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 Am. conf. Turţ	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 conf. Turţ 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: *The quality classes – Class Quality I (the green colour) - water of very good quality, unaltered or with minor anthropic alterations; Class Quality II (the blue colour) – water of good quality, that is with slight deviations compared to the altered waters; Class Quality III (the red colour) – water of medium quality, that is with medium deviations compared to the unaltered ones; Class Quality IV (the violet colour) – water of weak quality, that is with major deviations compared to the unaltered waters; Class Quality V (the grey colour) – water of bad quality, that is with severe deviations compared to the unaltered waters.*

The results obtained at this indicator frame Tur's waters in class I of quality (0.7 – 1.3 mgN/l), with smaller values downstream from Negreşti Oaş. The increases from downstream from the superior course, practically insignificant, are the consequence of some partial purifications or of a reduced input of nitrogen by the raw waters. Only downstream from the affluence on Turţ, N-total increases more visibly in

Tur's waters (1.8 mgN/l), framed in class II of quality. The increase is the consequence of the discharge in Tur of used mine waters and raw waste waters resulted from some bigger localities (Turţ, Halmeu and Turulung). The nitrates and the nitrites penetrate the underground water, affecting the consumption water from the people's fountains, and the overflow of the admitted quotas increases the toxicity from the water, affecting the fish fauna, accumulating themselves also in the fishes' flesh.

As carrier of energy, the phosphorus is an element that is essential to life. But, at the same time, it sets the eutrophication of the water, and, for fish, concentrations of over 1 mgP/l that are toxic (Mustaţă, 2000). We noticed a serious and surprising situation at the determination of P-total from Tur's water. It frames in the class I of quality (0.09 mgP/l) only in the reference section (upstream Negreşti Oaş). Downstream, without exception, this quality indicator registers significant increases (0,11 – 0,21 mgP/l) framing Tur's water in classes II and III of quality, increases produced by the commune waters loaded with organic substances and fertilizers used on the vegetable exploitations, especially from the area Halmeu – Turulung. The situation immediately from downstream from Negreşti Oaş is surprising, where P-total reaches the highest value from the river (0.48 mgP/l), the consequence of the bad functioning of the municipal purification station (it does not dispose of chemical batter and so it does not retain the phosphorus) but also of some industrial waters loaded with phosphorus. The phosphorus dissolved in Tur's water accumulates itself in the lake from Călineşti, where there is a significant risk for the eutrophication of its waters. I think this is the explanation why the concentration of the phosphorus downstream from the lake decreases.

Our determinations did not point out the presence of petroleum hydrocarbons in Tur's waters. Phenols are, though, present, whose concentration increases downstream (from 3,4 to 4,1 µg/l), including Tur's waters in class III of quality, being a sign that across the entire Tur's course various chemicals used by the population or by the economic agents are discharged.

Due to the remarkable toxicity, we have given a special attention to the determination of heavy metals that represent Tur's specific pollutants. These get into the water and nitrites get in the body of the fish, and by its consumption as food they also get in the human's body where it causes specific derangements of the functioning of the systems and organs. The main sources of pollution with heavy metals are the industrial activity from Negreşti Oaş and the discharge of mine waters from EM Turţ, through the Turţ brook. Undeniably, the industrial rebuff from the last 2 decades diminished the discharges of heavy metals in Tur. This explains why the water samples taken by us do not contain high concentrations of heavy metals compared to those taken during the functioning of the mine. But, although closed, the non-ferrous mines from Oaş Mountains continue to discharge in Tur, through Tur brook, used waters loaded with metals. That is why, also presently, Tur's waters frame in inferior classes of quality at more heavy elements like Manganese, Nickel, Copper and especially at Iron and Zinc.

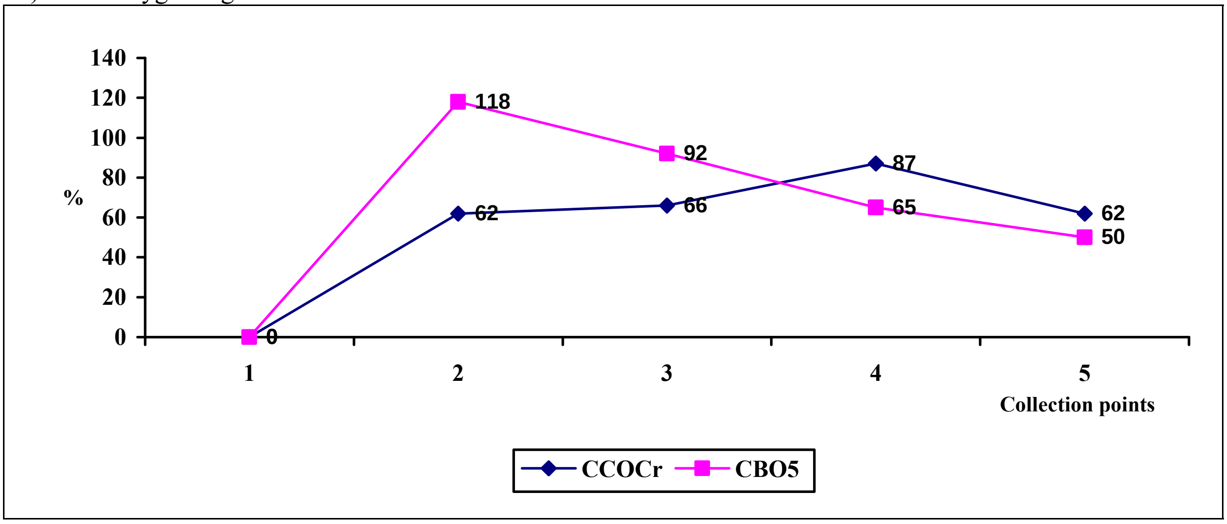
The iron (Fe), minor element that is essential for the living creatures is present in Tur's water in small concentrations, mainly due to the natural fund. Upstream Negreşti Oaş, in the reference section, Fe has the lowest concentrations from the river (0,008 mg/l). Downstream from this section in the water, supplementary quantities of iron that come from man's activity (the rust and the exploitation of chalybeate rocks) are accumulated and they increase its concentration by 2-3 times compared to the reference area (0,048 – 0,078 mg/l), framing Tur's water in class II of quality. The fact that the highest concentration of iron in Tur's water was registered downstream from Călineşti Oaş Lake (0,109 mg/l) leads to the supposition that a part of the iron accumulated in the lake is discharged in the river through a secondary channel. Generally, though, the surplus of iron from Tur's water does not cause big problems for the man's and animals' health. Only the bigger concentrations of iron (10-15 mg/l) are lethal for the fish. The other metals associated to iron have, generally, small concentrations in Tur's water that corresponds in this regard also to the class I of quality (Manganese: 0,007 – 0,011 µg/l; Nickel: 17.11 – 32,65 µg/l). Only downstream from Negreşti Oaş and in the Micula section, the Manganese and Nickel concentration increase (0,010 – 0,011 mgMn/l, respectively 25,01 – 32,65 µgNi/l), framing the water in class II of quality, being the consequence of the accumulation of some big quantities of allied metals abandoned on the shore (population, industry).

The Led (Pb), a very toxic metal, maintains itself across the entire length of the river at the level of the natural fund (under 0.5 µg/l). Consequently, following the human activity from the area, Led is not accumulated in Tur's water over the admitted limit, maintaining itself, at this metal, in class I of quality. As a result, Tur's water improved very much regarding led compared to the situation from 10-20 years ago.

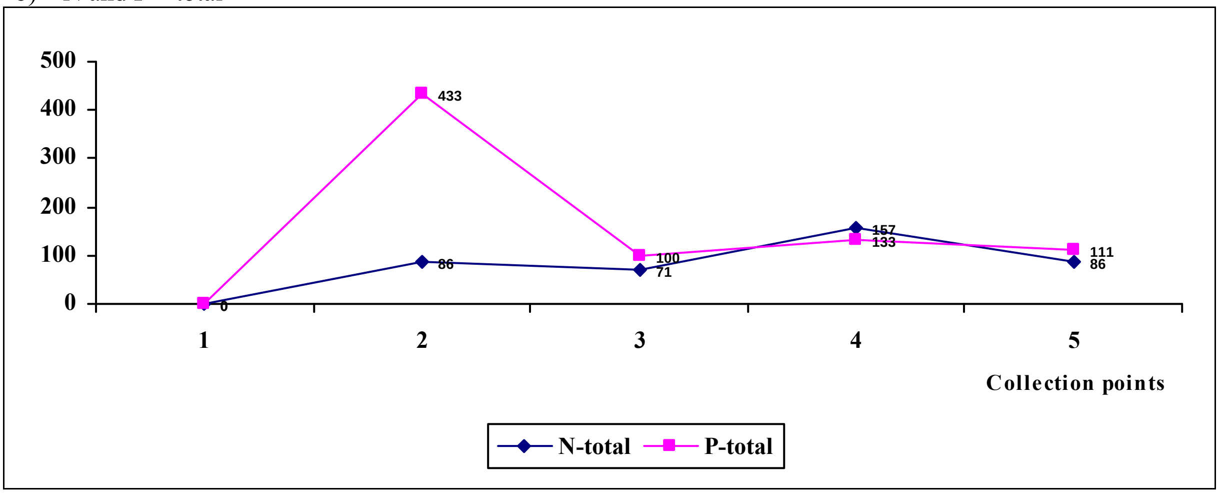
A similar situation have the metals associated to lead. The Chrome (Cr) and the Cadmium (Cd) concentration is given only by the natural fund, registering values (Cr: 6.63 – 15,55 µg/l; Cd: under 0,277 µg/l) that situate Tur's water in class I of water quality.

The Copper (Cu) accumulated itself in Tur from the used water evacuated by the industrial units. Its concentration increases a little over compared to the reference section (0.93 – 1.58 µg/l) including the river in class II of quality on 90% of its length. This water does not evidently affect the fauna, including the fish, but it can affect the fish sapling which is more sensitive to pollution.

a) The oxygen regime



b) N and P – total



c) The heavy metals

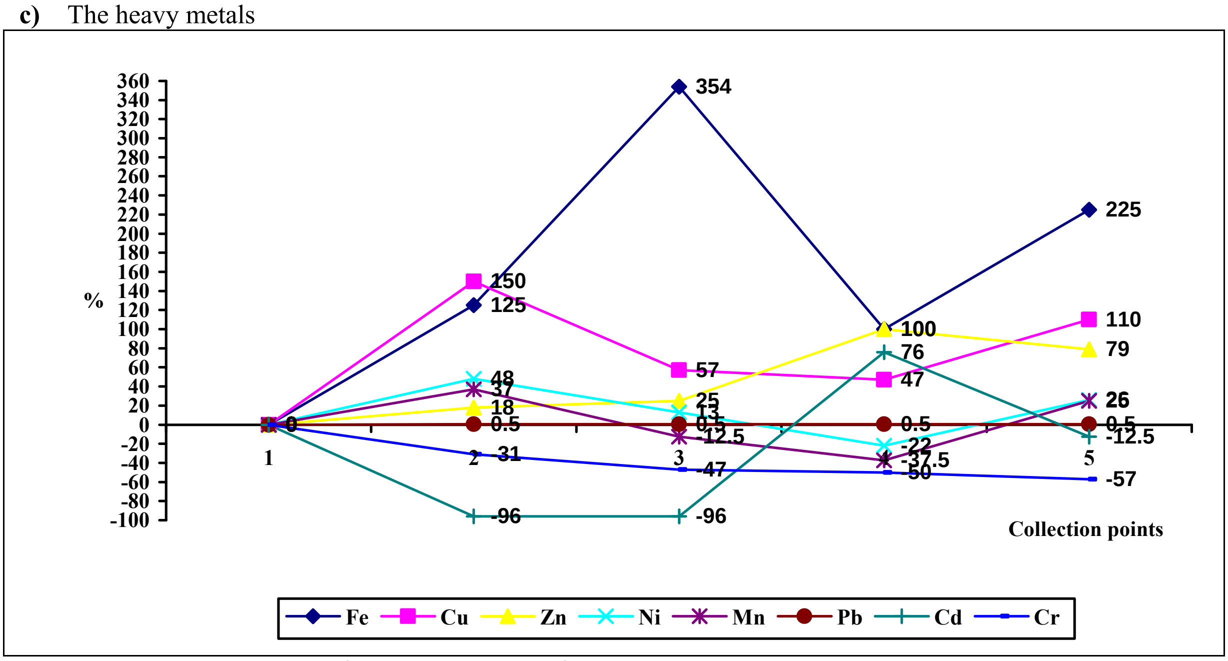


Fig. 6. The percentage increase of the concentration of the pollutants across the river in rapport with the basic structure (TUR-A-1). 1-5 – the collecting points of the samples; a – CCO-Cr and CBO5; b – N–total and P-total; c – the heavy metals

From the heavy metals the biggest problem is raised by the pollution with zinc (Zn), especially downstream from Turţ brook's affluence, with all the current tendency of diminishing of its concentration. The zinc has increased concentrations downstream, in the middle course, at 68.9, respectively 74.6 µg/l (class II of quality) and in the inferior course even more (116.2 µg/l, respectively 104.3 µg/l), where the water is of class III of quality compared to the reference point (58,2 µg/l, on the cost of the natural fund). In the middle course, Tur water loads itself with the ions of this metal from the insufficiently purified waters from Negreşti Oaş, as well as on the cost of the downstream water discharge from Călineşti Oaş Lake. In the inferior course the surplus of zinc is due to the discharge of mine waters in Tur from Turţ. The more reduced concentration of zinc at Micula – Porumbeşti is due to the water dilution and to the accumulation of heavy metals in May downstream from the sources of pollution.

The afore mentioned results regarding the accumulation of pollutants in Tur's waters are presented in the graphs from figure 6, in which the values of the indicators from the sampling points are presented as percentage increases compared to the unpolluted reference section.

The mud quality from Tur's bed. We considered necessary to take mud samples to determine in which measure the pollutants, more precisely the heavy metals accumulated themselves in the mud because some sources of pollution from the area diminished or ceased activity in the last 20 years (the industrial rebuff) and the quality of Tur's river improved. The obtained results were included in table 3 and in figures 7 and 8.

Table 3. The concentrations of metals determined in Tur's mud in the year 2012

Nr. crt.	Place of prelevation / Element	TUR-A-1 Upstream Negreşti	TUR-A-2 Downstream Negreşti, upstream Călineşti	TUR-A-3 Downstream Călineşti Am. conf. Turţ	TUR-A-4 Downstream conf. Turţ, Turulung	TUR-A-5 Micula-Porumbeşti	The admitted limit Order MAPM nr. 1.146/2002
1.	K (ppm)	10.500	9.768	11.900	12.200	14.700	-
2.	Ca (ppm)	13.600	8.645	7.824	6.026	3.511	-
3.	Fe (ppm)	39.800	51.100	30.200	27.600	28.200	-
4.	Ti (ppm)	4.382	4.888	4.547	3.836	4.674	-
5.	Zr (ppm)	250	356	300	269	398	-
6.	Sr (ppm)	154	117	141	126	109	-
7.	Mn (ppm)	971	1.970	499	1.082	1.468	-
8.	Cr (ppm)	<20	<20	44	27	<20	**90**
9.	Cd (ppm)	<10 (<0,20)	<10 (1,31)	<10 (0,96)	<10 (1,88)	<10 (2,86)	**3,5**
10.	Ni (ppm)	<20 (15,42)	<20 (16,78)	<20 (18,36)	<20 (16,37)	<20 (16,59)	-
11.	Cu (ppm)	<20 (1,45)	30 (27,01)	<20 (7,69)	<20 (14,11)	<20 (17,79)	**200**
12.	Pb (ppm)	<20 (13,31)	<20 (12,85)	<20 (10,43)	<20 (22,98)	<20 (25,17)	**90**
13.	Zn (ppm)	134	216	211	**514**	**431**	**300**
14.	Mo (ppm)	8	10	12	6	12	-
15.	Rb (ppm)	55	67	73	67	112.	-
16.	As (ppm)	15	**19**	**18**	**20**	**22**	**17**
17.	V (ppm)	<50	176	<50	52	<50	-

Note: Most of the determinations were realized through the XRF method; the values from the bracket represent determinations through the method AAS-GF

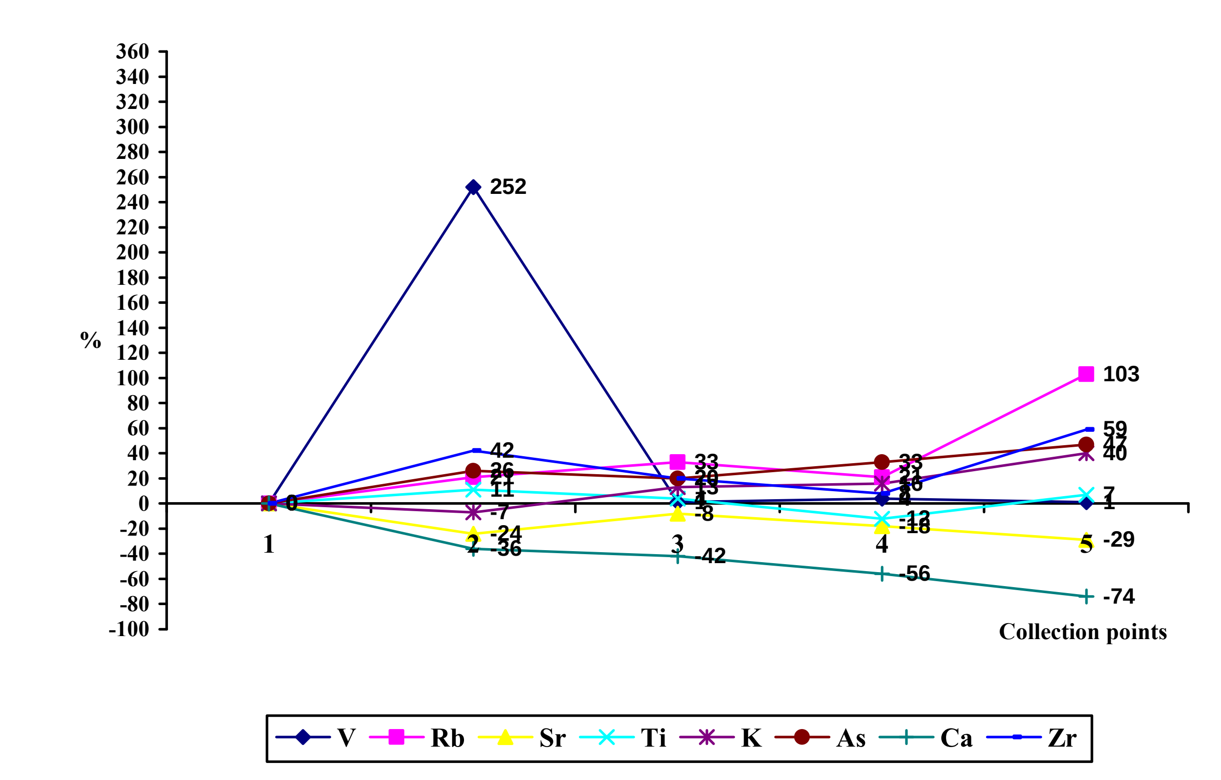


Fig. 7. The percentage increase of the concentration of some heavy metals in Tur's mud rapported to the basic structure (TUR-A-1). 1-5 the collecting points of the samples

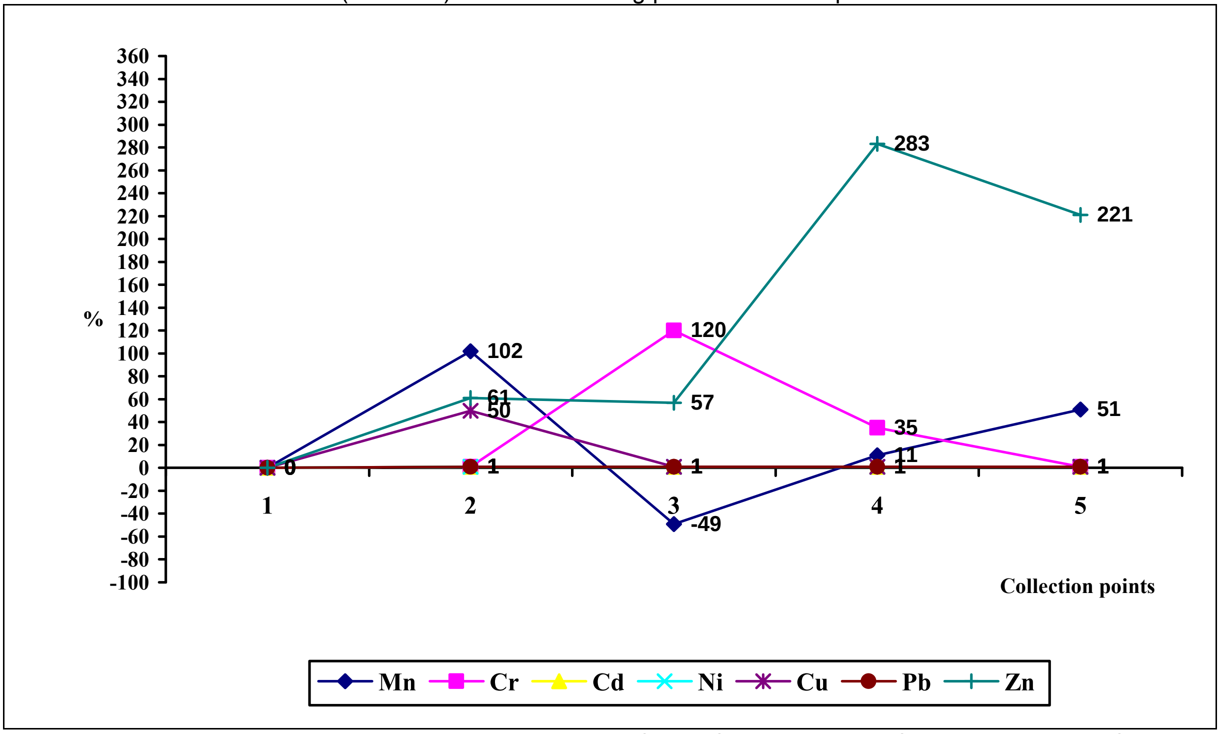


Fig. 8. The percentage increase compared to the indicators of the reference section of the concentration of the heavy metals from Tur's mud for which determinations from water samples were also realised

The interpretation of these results raise, though, the difficulty that, for more metals, O.M. nr. 1146/2006 does not set official admitted limits, from which cause the interpretation of the data was made only in rapport to the data obtained in the reference section.

We notice overflows only at Cd for the entire course of the river and at Zinc for Tur's inferior course for the heavy metals for which the admitted limit was established, on the expense of the input of the industrial used waters.

Table 3 comprises also a series of elements as Potassium, Cadmium, Titanium, Zinc, Strontium, Molybdenum, Rubidium, Arsenic, Vanadium for which samples of water were not sampled but at which we notice only very small increases compared to the reference section, increases due more to the natural fund than to man's activity.

The following aspects regarding the accumulation of metals in the alluvial mud could be formulated from the analysis of the statistical (and even graphical) data: a) Nickel, Copper, Cadmium and led have concentrations in the mud equal to those of the reference base which means that they come from the natural fund; b) Molybdenum, Chrome and especially Zinc register across the river concentrations in the mud bigger than the reference base due to the discharge of waters evacuated from Negreşti Oaş and from Turţ brook; c) Zinc registers the biggest accumulations of metal in mud – as well as in the water samples – especially downstream by the Turţ brook's affluence which discharges mine waters rich in heavy metals; d) the increase of the concentration of Titanium in mud downstream of Negreşti Oaş and especially of Arsenic, across the entire river, represent harmful pollutions, over the admitted limit, that can affect the fish populations from Tur (it represents a permanent source of risk with immediate lethal effect for the living creatures from these river's water).

Correlations of the results offered by the analysis of the water samples and the mud samples from Tur regarding the heavy metals. In table 4 the concentrations of the heavy metals from the water and mud were presented in view of noticing some possible correlations.

Table 4. Compared data regarding the Tur pollution with heavy metals in water and mud

The prelevation sections of the samples	Heavy metals:							
	Fe mg/l	Mn mg/l	Pb μg/l	Cr μg/l	Ni μg/l	Zn μg/l	Cd μg/l	Cu μg/l
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
TUR-A-1								
- water	0,024	0,008	0,5	15,55	22,01	58,2	0,2777	0,63
- mud	39800	971	13,31	<20	15,42	134	<20	1,45
TUR-A-2								
- water	0,054	0,011	0,5	10,67	32,65	68,9	<0,01	1,58
- mud	51100	1970	12,85	<20	16,78	216	1,31	27,01
TUR-A-3								
- water	0,109	0,007	0,5	8,23	25,01	74,6	<0,01	0,99
- mud	30.200	499	10,43	44	18,36	211	0,96	7,69
TUR-A-4								
- water	0,048	0,005	0,5	7,85	17,11	116,2	<0,01	0,93
- mud	27600	1082	22,98	27	16,37	514	1,88	14,11
TUR-A-5								
- water	0,078	0,010	0,5	6,63	27,84	104,3	<0,01	1,22
- mud	28200	1468	25,17	<20	16,59	431	2,86	17,79

Note: the first unit measures refer to water, and ppm to mud

From the analysis of table 4 it results that between the results of the determinations of the 2 samples there is no direct correlation for the same section of the river, eventually one can notice a similar trend regarding the evolution of the concentration of heavy metals downstream, compared to the reference section. Undoubtedly, there are different processes of accumulation of the heavy metals in water compared to the concentration ones in the mud that should represent a distinctive scientific study.

The pollution indicator of Tur water

The pollution indicator (Ip) is calculated according to the formula:

$$Ip = C_{max} / CMA$$

in which C_{max} – the maximum concentration of the pollutant (the real situation from samples); CMA – the maximum admitted concentration of the respective pollutant (the ideal situation).

For the establishment of the Ip of Tur's water, we had in view, for each section of the river, the pollutant with the highest concentration, according to table 5.

Ip, whose values are found in column 4, could be calculated on the basis of the data from the first 3 columns of table 5. The values from column 5 are obtained by dividing Ip by 100, to which a note of estimation corresponds in column 6, in a scale of estimation between 1 and 10. Each note of estimation is characterized by certain effects of the pollutant in cause on the man and the surrounding environment (The Institute of Researches of Environment Engineering, Bucharest, 2006).

Table 5. Data for the calculation of the pollution indicator (Ip) and of the estimation note for Tur's water

The research section from Tur	The pollutant with the maximum concentration	Cmax	CMA	Ip	Ip/100	Estimation note
0	1	2	3	4	5	6
TUR-A-1 (upstream Negreşti Oaş)	-	-	-	0,000	0,000	10
TUR-A-2 (downstream Negreşti Oaş)	P-total	0,480	0,10	4,800	0,048	9
TUR-A-3 (downstream 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

The estimation notes for Tur's water are: 10 for the section upstream Negreşti Oaş and 9 for the other sections. The estimation note 10 for Tur's superior course, upstream Negreşti Oaş corresponds to an environment unaffected by the human activity, and the environment's state is natural, whereas the estimation note 9 for the rest of Tur's river shows that the environment is affected by the human activity, but the environment's state is still almost natural, without special quantifiable effects (this is in fact also the medium estimation note of Tur's water (Nbm). So, in all for Tur, the indicator of water pollution is 9, meaning a water course affected by the current anthropic pressure that needs some measures of ecological restoration.

CONCLUSIONS

Following the present study, the following conclusions regarding Tur's water and mud quality from its river bed can be formulated:

- The most important sources of pollution from Tur are: a) the waters insufficiently purified or even not-purified discharged in Tur by Negreşti Oaş and the bigger localities (Bixad, Turulung, Halmeu); b) the discharge of mine waters by Turţ brook from the mines (already closed) from Oaş Mountains; c) leaks of agricultural fertilizers and dejections from the animal husbandry exploitations.
- The results obtained at the determination of some pollutants' concentrations, especially at heavy metals, at the water and mud samples, show an improvement of the ecological state of the Tur River after the economic rebuff, especially industrial, from the years 1990-2000.
- The accumulations of pollutants both in the water and in the mud increase downstream, especially downstream from Negreşti Oaş (it discharges residual and industrial water) and on the affluence of Turţ brook (it discharges mine waters).
- The accumulation of the pollutants is greater in Tur's mud than in its water. The contents of precipitated metals from Tur's sediments represent a „reservoir" of heavy metals with significant risk for the integrity of the aquatic ecosystems.
- Tur's water is clean in the section upstream Negreşti Oaş, a reason for which this section was considered reference basis for the evaluation of the pollutants from downstream.
- Tur has 2 sections where water and mud are more polluted: the section downstream of Negreşti Oaş, especially with waste and industrial water, and the section downstream by the affluence of Turţ brook where the mine waters generate „an ecological void" on at least 500 metres downstream (the lack of aquatic fauna).
- Zinc that surpasses the admitted limits on Tur's course raises special problems in the water samples. Other metals register exceeding only on some sections.
- Zinc registers the biggest accumulations of metal also in the mud samples, especially downstream of the Turţ brook's affluence. The increase of the concentration of Arsenic in the mud from Tur's entire course represents a permanent source of harmful, even lethal pollution, for the populations of aquatic animals from the river.
- There is no direct correlation between the accumulation of heavy metals in water and mud, one being able to notice only the tendency of these accumulations.
- 10 was established as general note of estimation on the basis of the pollution indicator (Ip) for the section upstream from Negreşti Oaş which corresponds to a natural water unaffected by the human activity, and 9 for the other sections downstream which corresponds to a water still almost natural but slightly affected by

Studia Universitatis "Vasile Goldiş", Seria Ştiinţele Vieţii
Vol. 23, issue 2, 2013, pp. 195-207

the anthropic impact, which needs some measures of ecological reconstruction.

Measurements proposals

More technical measures are required are required to improve the ecological state of Tur's water in general and, especially, in the sections upstream Negreşti Oaş and of affluence p. Turţ:

a) the linking of all localities from Tur's Valley to sewerage networks and purification stations;

b) the increase of the capacity and the perfection of the functioning of the commune purification stations Negreşti Oaş and Turţ, as well as of that from EM Turţ;

c) the completion of the respective purification stations with mechanisms or chemical processes to retain Zinc and Arsenic to prevent the increase of the water and mud toxicity from Tur.

d) the constitution of a sewerage channel of the water in the damn from Călineşti Oaş to ensure a constant debit of water on Tur's course downstream;

e) the construction of some collateral water reservoirs on Tur's course to increase the water debit in the droughty periods;

f) the prevention of the accumulation of N-total and P-total in Tur's waters by diminishing the leak of fertilizers, animal dejections and waters filled with organic substances;

g) the organization of a system of integrated management for the monitoring of the river and the realization of some rehabilitation measures of Tur's water.

ACKNOWLEDGEMENTS

This work was supported by Structural Funds POSDRU/CPP107/DMI 1.5/S/77082"Burse doctorale de pregătire ecoeconomică şi bioeconomică complexă pentru siguranţa şi securitatea alimentelor şi furajelor din ecosisteme antropice"

REFERENCES

Andrişca Simona-Gabriela, The state of the water quality in the hydrographic basin Barcău. The summary of the doctoral thesis (scientific coordinator N. Josan, Oradea University), pp. 7-24, 2011.

Ardelean G., Ecological aspects regarding the accumulation lake Călineşti Oaş. Studia Universitatis "Vasile Goldiş" Arad, nr. 7, pp. 93-97, 1997.

Ardelean G., Aspects of the determination of Tur's water quality with the help of the species of fish, Studia Univ. „Vasile Goldiş" Arad, Ser. B, 9: 33-37, 1999.

Ardelean G., Duma Melania, Observations regarding the zooplankton of the storage lake Călineşti Oaş. Studia Universitatis „Vasile Goldiş" Arad, nr. 7, pp. 99-101, 1997.

Bănărescu P., The current situation of Romania's fish fauna of fresh water of Romania under fauna, taxonomical and of protection aspect, Studia Universitatis „Vasile Goldiş" Arad, The Series Sciences of Life, „Vasile Goldiş" University Press, Arad, 14: 7-11, 2004.

Dima M., The purification of the urban used water, Junimea Publishing House, Iaşi, pp. 17-43, 1998.

Fazekas L., The Tur hidrographic basin. The general hidrological characteristics. Satu Mare. Studies and Communications, Western Printing House, Oradea, IX-X: 331-339, 1992-1993.

Institutul de Cercetări şi Ingineria Mediului, Bucureşti, 2006

Mereuţă Rodica, Hozan Mihaela, Ardelean G., qualitative situation of the environment factors in the county of Satu Mare during 1991 – 1999. Studies and Communications, Natural Sciences edition, Satu Mare Museum Publishing house, vol. I, 433-439, 2000.

Mustaţă Gh., Hydrobiology, The Publishing House of "Al. I. Cuza" University, Iaşi, pp. 33-34, 2000.

Nagy I., Fodorpataki L., Weiszburg T., Bartha A., Preliminary Resultats on Environmental Impact of Mining Activity on the Turţ Creek, Satu Mare Country, Romania. In Sike T., Márk-Nagy J. (eds): The Flora and Fauna of the Tur River Natural Reserve, The Publishing House of the Oradea University, Oradea, Romania, Biharean Biologist Supplement 2008: 17-26, 2008.

O.M. 1146/2002 for the approval of the Normative regarding the reference objects for the classification of the quality of the surface waters, published in Monitorul Oficial 197 from 27 March 2003.

Roşu I., Domşa N., The annual synthesis regarding the quality of the water bodies in the hidrographical space Someş – Tisa pe 2010. The Basin Administration of the Waters Someş – Tisa F-Ga-30, pp. 10-164, 2011.

Ujvari I., The geography of Romania's waters, The Scientific Publishing House, Bucharest, 244-277, 1972.

van Breugel M., van Eck G., Gerlash G., The river Someş, the river Tur and the lake Porumbeşti. Rapport of fish researches. The Organisation for the Improvement of the Internal Fishing, Nilu Wegen, Nederland, pp. 9-10, 2005.

Velcea I., Ţara Oaşului, The Publishing House of the Romanian Academy, Bucharest, pp. 10-59, 1964.

SR EN 25814/1999; SR EN 25663/2000; SR EN 1899-2/2003; SR EN 15309/2007; SR EN ISO 8467:2001; SR EN ISO 15586/2004; SR EN ISO 9408-2004; SR EN ISO 6878/2005; SR ISO 11047/1999; SR ISO 6060-1996; SR ISO 5667-3:2004; SR ISO 5667-12/2010; EN ISO 5667-15/2010; SR ISO 5667-6/2009; SR ISO 10523/2009.