# THE TOXICITY LEVEL OF THE LOWER JIU WATER

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**Abstract.** In accordance with Article 8 (1) of the Water Framework Directive (2000/60/EC), European Union Member States have established monitoring programs for surface waters, groundwater and protected areas in order to know and classify the „status" within each basin (HATTON-ELLIS, 2008). In Romania, the established monitoring programs became operational on December 22, 2006 and are applied on surface water bodies, groundwater bodies and protected areas. The lower Jiu is part of this category, respectively Răcari and Podari sections. There have been monitored biological (macrobenthos, phytoplankton) and physico-chemical parameters (oxygen regime, biotic substances, toxic substances, general ions). Following the analysis, Răcari section belongs to the II quality class from the biological point of view and to the IV quality class regarding the physico-chemical parameters. Podari section was framed, from the biological point of view, in the II and III quality class, in the II quality class in terms of chemical indicators and in the IV quality class regarding the toxic substances.

**Keywords:** lower Jiu, biological and physico-chemical indicators, saprobic index, quality class.

**Rezumat. Nivelul de toxicitate al apei Jiului inferior.** În conformitate cu Articolul 8 (1) al Directivei Cadru din domeniul apelor (2000/60/EC), Statele Membre ale Uniunii Europene au stabilit programele de monitorizare pentru apele de suprafaţă, apele subterane şi zonele protejate în scopul cunoaşterii şi clasificării „stării" acestora în cadrul fiecărui bazin hidrografic (HATTON-ELLIS, 2008). În România programele de monitorizare stabilite au devenit operaţionale la 22 decembrie 2006, aplicându-se corpurilor de apă de suprafaţă, corpurilor de apă subterane şi zonelor protejate. Din această categorie face parte şi râul Jiul inferior respectiv, secţiunile Răcari şi Podari. Au fost monitorizaţi parametrii biologici (macrobentosul, fitoplanctonul), şi fizico-chimici (regimul de oxigen, substanţele biotice, substanţele toxice, ionii generali). În urma analizelor, secţiunea Răcari se încadrează, din punct de vedere biologic, în clasa a II-a de calitate şi, din punct de vedere fizico - chimic, în clasa a IV-a de calitate. Secţiunea Podari a fost încadrată, din punct de vedere biologic, în clasa a II şi a III-a de calitate, iar în ceea ce priveşte indicatorii chimici în categoria a II -a de calitate şi substanţele toxice, în categoria a IV-a de calitate.

**Cuvinte cheie:** Jiu inferior, indicatori biologici şi fizico-chimici, index saprobic, clasă de calitate.

## INTRODUCTION

Integrated management of water resources is an activity that promotes the development and sustainable management of water, land and related resources, in order to obtain a maximum growth of the economic resultant and social status in a balanced manner, without affecting the sustainability of vital ecosystems (MEYBECK & VÖRÖSMARTY, 2004).

Water quality does not remain constant over time, but may vary due to natural or artificial sources of contamination (CÎRŢÎNĂ, 2010), which requires permanent control of the parameter which defines the quality of surface waters and their ability to be the power source of human settlements or of use in industrial processes and agricultural activities.

From a legal perspective, preventing degradation of the aquatic environment is a concern in Europe dating since the 70s, when it was drafted the first Water Directive (75/440/EEC) and culminated in the drafting of the Directive 2000/60/EC which establishes a framework for Community action in the field of water policy (MOSS, 2008). Entered into force in 2000, the Water Framework Directive is a bold and far-reaching instrument in the sustainable use of water resources in Europe and has as a main objective achieving and maintaining good status of water by 2015.

Initially, in our country, water quality assessment for their management was based mainly or exclusively on physico-chemical analysis, biological assessment methods become fully accepted in the 70s of last century (BALABAN & CONSTANTINESCU, 2006). Currently, in Romania, surface waters are assessed in accordance with the Normative 161/2006 by which the classification is done in terms of ecological and chemical parameters or all surface waters.

## MATERIAL AND METHODS

Surface waters quality from the lower basin of the river Jiu was evaluated during 2013, using monitoring data from two distinct areas. Water quality assessment was performed using biological, general physico-chemical and chemical indicators (heavy metals and organic micropollutants) analysed in Răcari and Podari sections.

Monitoring sections were chosen from the National Network for Monitoring and aim to highlight critical points in terms of water quality, which are located both upstream and downstream of the main pollution sources, providing information on their impact on water surface.

The characterization from the biological perspective of watercourses quality in the lower basin of the river Jiu was based on monitoring macrozoobenthos and phytoplankton. Saprobic index was calculated by the Puntle-Buck method for each section monitored and was correlated with the quality class from Normative 161/2006.

Physico-chemical quality elements used in the development of ecological status for all water bodies (natural and heavily modified) are: acidification status (pH), the oxygen regime (dissolved oxygen), nutrients (N-$NH_4^+$, N-$NO_2^-$, N-$NO_3^-$, P-$PO_4^{3-}$, $P_{total}$).

Specific pollutants are represented by synthetic and non-synthetic substances (metals: chromium, nickel, lead, mercury). For the synthetic substances were used, as evaluation limits of the ecological status, the environmental standards of Directive 105/2008.

Due to the natural existence of metals in surface waters, the natural background value was calculated first, in order to know the contribution coming from anthropogenic sources, only in situations in which the concentration obtained exceeded the quality standards of the Directive. For non-synthetic specific pollutants, high ecological status is defined by concentrations which remain within the range normally associated with background values.

Good environmental status for both specific synthetic pollutants, and for the non-synthetic, is defined by concentrations which do not exceed the environmental quality standards. The determinations were performed with the following instruments: water harvesting kit, equipped with vacuum pump, Hanna ph-meter, incubation vials for determining biochemical oxygen demand, Hach digital titrator, system Kjeldahl for determination of total nitrogen, flamephotometer model FLM-KRS, DR 2010 spectrophotometer, RQ-flex19+. Toxic substances, namely cadmium, nickel, lead and mercury were analysed using atomic absorption spectrophotometer AAS-ML-1200.

## RESULTS AND DISCUSSIONS

Although biological elements are considered integrator of all types of pressure, to assess the ecological status, analysis needed certain support elements represented by: general physico-chemical indicators, hydromorphological elements and specific pollutants (Fig. 1).

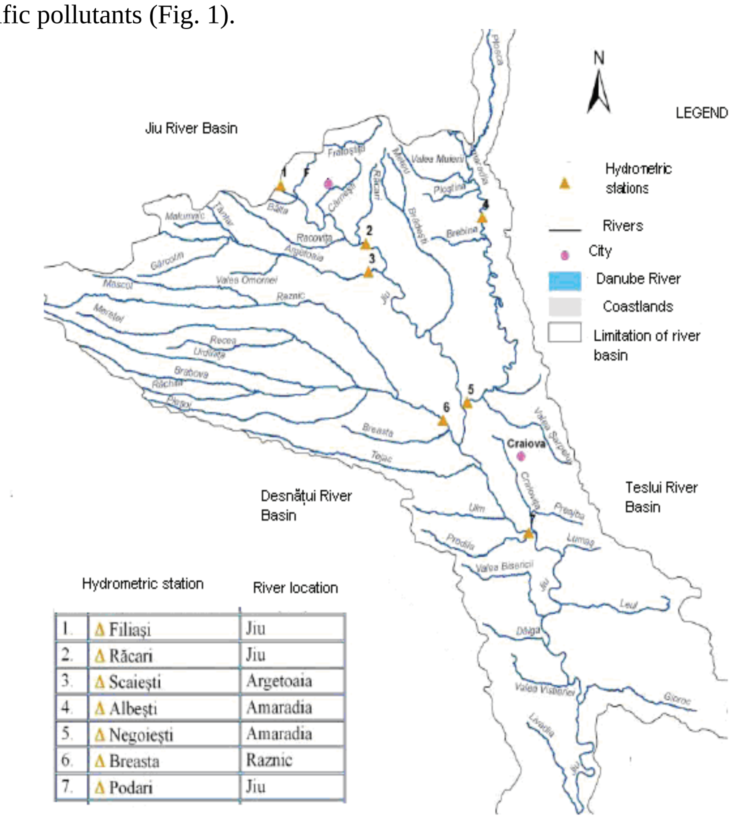


Figure 1. Delimitation of Jiu river course (Source: WBA Jiu).

On the river Jiu, in the first section monitored in terms of biological indicators (Răcari), zoobenthos samples were collected in June, August and September and phytoplankton in April, July and September 2013.

With an annual average density of 1,000 specimens/sq. m and a saprobic index of 2.135, macrozoobenthos was represented by species belonging to: Gastropoda (*Physella acuta, Sphaerium rivicola*), Amphipoda (*Gammarus fossarum*), Ephemeroptera (*Caenis macrura, Cloeon dipterum*), Odonata (*Calopteryx virgo, Coenagrion pulchelum, Gomphus vulgatissimus*), Diptera (*Corynoneura scutellata, Cricotopus bicinctus, Simulium balcanicum*), so the water body is in the II quality class according to normative 161/2006.

Phytoplankton, with an annual average density of 275,567 specimens/l and a saprobic index of 1.84, has placed this water body still in the second quality class. In this section there were identified species belonging to Bacillariophyta (*Synedra ulna, S. acus, Melosira granulata, Gomphonema constrictum, Pinnularia viridis, Diatoma vulgar, Ceratoneis arcus*) and Chlorophyta (*Closterium Navicula, Ulothrix zoned*), Cyanophyta (*Merismopedia tenuissima*).

The main indicator of quality in terms of physico-chemical characteristics is represented by the hydrogen ion concentration (pH), which may vary due to discharges of industrial and domestic wastewater. In the lower basin analysed, the variation of pH is relatively low 7.25-7.45 upH, its value being within in the permissible limits (6.5-8.5).

In river waters, soluble gases, oxygen and carbon dioxide vary within limits which depend on the solubility of the compounds in accordance with the environmental conditions. The highest content of dissolved oxygen in the river waters is not more than 15 mg/l, and the maximum amount of carbon dioxide does not exceed 20-30 mg/l. Daily and annual regime of these gases dissolved in river waters is conditioned by water temperature, intensity of photosynthesis, power sources of the rivers, as well as pollution sources. Within this class of water quality assessment (rivers category), there were analysed three indicators:

- dissolved oxygen (mg $O_2$/l) is in close relation to water temperature (inverse variation), the amount of microorganisms and oxidable substances;
- biochemical oxygen demand ($BOD_5$), expressed in mg $O_2$/l, depending on the amount and capacity of biochemical decomposition of organic substances existing in water;
- chemical oxygen demand (COD), expressed in mg $O_2$/l, represents the quantity of oxidable substances in water and can be determined using potassium dichromate (COD) or potassium permanganate (CCOMn).

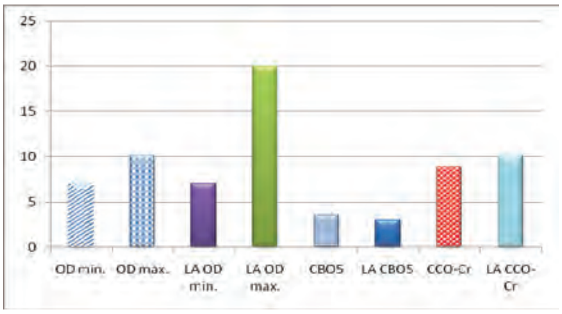


Figure 2. Variation of oxygen regime on river Jiu, section Răcari.

From figure 2, we can notice that the dissolved oxygen minimum value of 7.21 mg/l is above the allowable minimum and the maximum value of 10.13 mg/l is under the maximum limit of 20 mg $O_2$/l.

The second indicator is the biochemical oxygen demand ($BOD_5$) at which is observed a non-significant difference of 0.59 mg $O_2$/l, compared to the allowed limit. Chemical oxygen demand determined by potassium dichromate is below the permissible value of 10 mg $O_2$/l. We can conclude that water from Răcari section is part of the II quality class.

The main biogenic elements (Nutrient regime) consist of nitrogen compounds (ammonia, nitrates, nitrites, total nitrogen), phosphorus ions (orthophosphate, total phosphorus).

Ammonium ion (ammonia: $N\text{-}NH_4^+$) can occur in natural waters as a result of decomposition of organic matter under anaerobic conditions in the presence of bacteria or following the reduction of nitrites ions. In the majority of natural waters, ammonium ion predominates, because they have a pH around 7, but in alkaline waters free ammonia may reach levels that exceed the maximum allowable concentration.

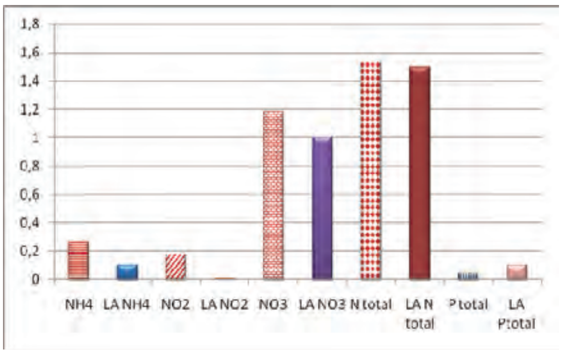


Figure 3. The content of biogenic substances in Răcari section.

In figure 3, there are represented biogenic substances from the lower basin of the Jiu river, Răcari section. There were recorded high values of the concentrations of ammonium ion 0.256 mgN/l (0.172 mg/l compared to the allowed limit 0.01 mg/l), nitrate (1.18 mg/l, at 1 mg/l), total nitrogen 1.53mg/l - 1.5 mg/l limit allowed), total phosphorus 0.043 mg/l does not exceed the limit of 0.1 mg/l.

The nitrite ion ($NO_2^-$) is the result of the nitrification process by which bacteria convert the ammonium ion into nitrite ion. In addition, nitrite ions may also occur due to the reduction in anaerobic conditions. Ions “nitrite” indicates faecal contamination of water. A possible cause could be due to partially treated sewage disposal of Filiaşi. The nitrites are found in much smaller amounts than nitrates. Nitrites occur during the normal cycle of decomposition of organic substances, typically in the late summer and fall. In case of the discharge of polluted waters, the nitrate content increases up to tenths of mg/l.

The nitrate ion ($NO_3^-$) is found in almost all water categories. Under natural conditions, surface waters are characterized by minimum variable nitrate content in summer when it is consumed by aquatic plants; in case of intense processes of photosynthesis nitrates disappear completely.

Regarding the regime "general ions – salinity", there were analysed the following chemical parameters: chloride ($Cl^-$), sulfate ($SO_4^{2+}$), calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), sodium ($Na^+$). The elements of chemical quality of this "regime" are substances of natural origin and do not indicate pollution; therefore Răcari section is part of the I quality class.

From Table 1 it is observed that the values determined for the aforementioned chemical indicators in section Răcari do not exceed the allowed limit.

Table 1. Regime "general ions - Salinity".

| Indicators | Determined Value | Allowed limit |
|---|---|---|
| Chlorides (mg/l) | 21.8 | 50 |
| Sulfates (mg/l) | 70.3 | 80 |
| Calcium (mg/l) | 59.6 | 75 |
| Magnesium (mg/l) | 21.2 | 25 |
| Sodium (mg/l) | 13.4 | 25 |

The last reviewed regime is the "specific toxic pollutants of natural origin". In this group, there were analysed total concentrations (μg/l) of the following ions: total chromium ($Cr^{3+}$, $Cr^{6+}$), copper ($Cu^{2+}$), zinc ($Zn^{2+}$), total iron ($Fe^{2+}$, $Fe^{3+}$), total manganese ($Mn^{2+}$, $Mn^{7+}$), as well as non-synthetic substances Cd – 0.1, Ni – 1.431, Pb – 0.482, Hg – 0.124 (μg/l).

Special toxicity of these heavy metals (cadmium, nickel, lead and mercury) manifested on the aquatic environment has led to the need for their separate assessment. The presence of cadmium in surface waters is due both to the natural and anthropogenic sources of pollution (chemical, mining). The main natural source is the ore containing 0.5% cadmium, but is found in the form of CdS and $CdCO_3$.

Widely spread in nature, mercury is in the form of mercurous chloride $(Hg_2Cl_2)_{3,}$ iodide mercury ($Hg_2I_2$) and mercuric sulfide, cinnabar (HgS). It may derive from anthropogenic sources as: mining, chemical industry and agriculture (GAVRILESCU & BUZATU, 2014).

The levels of these two toxic metals recorded in the lower basin of the Jiu river were below the detection limit of the device mass spectrometry with inductively coupled plasma (for cadmium) and for mercury variation interval was between 0.085 μg/l - 0.185 μg/l, with values well below the limit values set by normative 161-2006.

Nickel is a metal relatively non-toxic to humans and is rare in nature in elemental form; it is usually combined with sulfur, arsenic or antimony. In contrast, aquatic ecosystems are influenced by the presence of nickel, the concentrations lethal to fish (CALABRESE et. al., 1973) varying within very wide limits (4 mg/l - 43 mg/l). From this point of view the water falls in the IV quality class.

In Podari section, located 81 km from the confluence of the Jiu river with the Danube, zoobenthos and phytoplankton samples were collected in the months of May, July and September 2013.

The macrozoobenthos was represented by species belonging to the orders: Oligochaeta (*Chaetogaster limnaei, Dero obtusa, Nais communis, Pristina longiseta, Tubifex tubifex, Eiseniella tetraedra, Lumbriculus variegatus*), Gastropoda *(Physella acuta, Bithynia tentaculata*), Bivalvia (*Sphaerium corneum, Unio pictorum*), Amphipoda (*Gammarus fossarum*), Ephemeroptera (*Caenis macrura, Baetis vernus, Cloeon dipterum*), Odonata (*Calopteryx virgo, Gomphus flavipes, Platycnemiss pennipes*), Coleoptera (*Hydraena riparia, Platambus maculatus*), Diptera (*Brillia monilis, Orthocladius thienemmani, Chironomus thummi, Cricotopus bicinctus*). Saprobic index of 2.43 calculated in the monitoring section, as well as the annual average density of 1,835 specimens/sq. m, led to the conclusion that the water body belongs to the III quality class.

The phytoplankton, with an annual average density of 636,875 specimens/l and a saprobic index of 2.14, framed the water body in the II quality class. The representative species identified belong to the orders: Bacillariophyta (*Synedra ulna, S. acus, Melosira granulata, Gomphonema constrictum, Pinnularia viridis, Diatoma vulgare, and Ceratoneis arcus*) and Chlorophyta *(Closterium navicula, Ulothrix zonata*), Cyanophyta (*Merismopedia tenuissima*).

The value of pH determined in section Podari (average) is 7.54 upH, which can vary due to discharge of industrial and domestic wastewater. The variation interval for the pH is relatively small, the only situation in which its value is not within the allowed limits (6.5-8.5) was registered in May 2013, when it was measured a value of 6.31. The acidic nature is justified by the fact that in this body of water untreated wastewaters of Craiova are discharged.

Regarding the oxygen regime, respectively the minimum dissolved oxygen was 7.18 mg O/l and chemical oxygen demand caused by potassium dichromate exceeded the allowed limit (10 mg O/l). In Podari section, oxygen regime, represented by dissolved oxygen, $BOD_5$ and COD, exceeds the allowed maximum.

The second indicator of this analysed regime is the biochemical oxygen demand ($BOD_5$). On the lower Jiu, the range of the quality indicator $BOD_5$ is between 3.76 mg $O_2$/l (section Răcari) and 5.74 mg $O_2$/l in Podari section.

The last indicator of quality from this group is the chemical oxygen demand (COD) determined using the potassium dichromate (CCOCr) and expressed in mg $O_2$/l. On the Jiu river, the chemical oxygen demand, an indicator of pollution, varies from 9.79 mg/l recorded in Răcari section to 17.1 mg/l, Podari section (Figs. 2, 4). Higher values are due both to seasonal variation (summer is characterized by maximum values) and pollution sources.

In the plain area, oxidative processes are carried out with a low efficiency due to high temperatures and various sources of pollution - agriculture, urban wastewater, leading to an increasing amount of organic matter in surface waters.

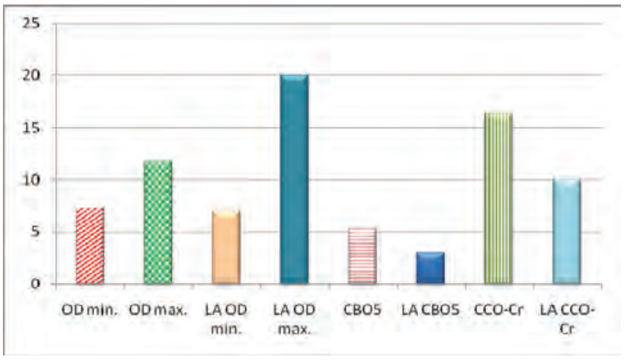


Figure 4. Variation of oxygen regime on river Jiu, section Podari.

The biogenic substances accumulated in this section exceed the maximum limit for all indicators (Fig. 5), except for the content of total phosphorus (0.038 mg/l compared to 0.1 mg/l limit allowed).

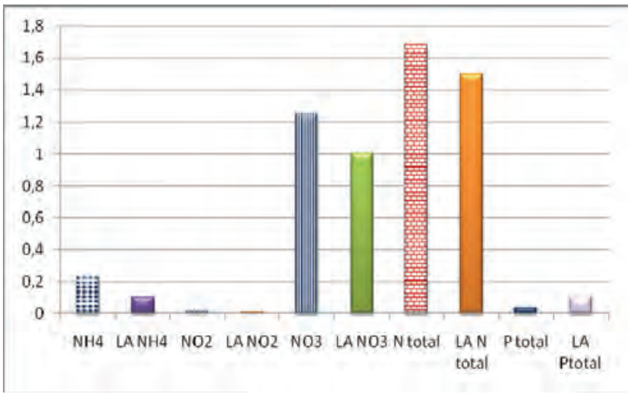


Figure 5. The content of biogenic substances in Podari section.

Ammonium ion (ammonia: N-$NH_4^+$) can occur in natural waters as a result of the decomposition of organic matter under anaerobic conditions in the presence of bacteria or following the reduction of nitrites ions. Depending on the pH of the water, ammonia in water is in the form of the ammonium ion $NH_4^+$ (low toxicity) or as free ammonia $NH_3$, which is highly toxic. Ionic form ($NH_4^+$) is 50 times less toxic than the unionized form.

Within the regime "general ions - salinity" were analysed the following chemical indicators: chloride ($Cl^-$), sulfate ($SO_4^{2+}$), calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), sodium ($Na^+$). The determined values for sodium and chlorides indicators exceed the allowed limit (Table 2); the source of these elements is of anthropogenic nature, being represented by the discharges of wastewater from Podari industrial platform.

Table 2. Regime "general ions – salinity".

| Indicators | Determined Value | Allowed limit |
|---|---|---|
| Chlorides (mg/l) | 58.3 | 50 |
| Sulfates (mg/l) | 70.3 | 80 |
| Calcium (mg/l) | 62.4 | 75 |
| Magnesium (mg/l) | 22.1 | 25 |
| Sodium (mg/l) | 27.1 | 25 |

The last reviewed regime is the "specific toxic pollutants of natural origin". In this group, there were analysed the total concentrations (µg/l) of the following ions: total chromium ($Cr^{3+}$,$Cr^{6+}$), copper ($Cu^{2+}$), zinc ($Zn^{2+}$), total iron ($Fe^{2+}$, $Fe^{3+}$), total manganese ($Mn^{2+}$, $Mn^{7+}$). The range of variation of these metal ions was relatively small and did not adversely affect the status of water bodies. According to the regime "toxic pollutants of natural origin", in 2013, Podari section belonged to the I quality class.

Table 3. Average concentrations of non-synthetic substances recorded in Podari section.

| Monitoring section | Average concentrations recorded in 2013 (µg/l) | | | |
|---|---|---|---|---|
| | Cadmium | Nickel | Lead | Mercury |
| Podari | 0.1 | 1.567 | 0.337 | 0.097 |

(shaded) Exceedances compared to the limit value

From table 3, one can observe that the values recorded for the average concentrations exceed the limit stipulated by the Regulations 161/2006 in Podari section for nickel.

## CONCLUSIONS

The Saprobic' index values calculated for the two sections of the Jiu river ranged from 2.135 to 2.43 regarding the macrozoobenthos and from 1.84 to 2.14 for phytoplankton.

On the lower Jiu, the variation of $BOD_5$ quality indicator is between 3.76 mg $O_2$/l (section Răcari) and 5.74 mg $O_2$/l in Podari section. The chemical oxygen demand, an indicator of pollution, varies from 9.79 mg/l recorded in Răcari section to 17.1 mg/l in Podari section.

The ammonium ion concentrations varied between 0.256 mg N/l in Răcari section and 0.231 mg N/l in section Podari. Ions "nitrite" indicates faecal contamination of water. On the Jiu river, the highest concentration was recorded in section Răcari (1.18 mg N/l) and the highest average concentration of the nitrate ion is found in section Podari (1.25 mg N/l). In the "toxic pollutants specific natural origin" group, there were analysed total concentrations (µg/l) of the following ions: total chromium ($Cr^{3+}$, $Cr^{6+}$), copper ($Cu^{2+}$), zinc ($Zn^{2+}$), total iron ($Fe^{2+}$, $Fe^{3+}$) and total manganese ($Mn^{2+}$, $Mn^{7+}$). The variation of these metal ions was relatively small and did not affect the status of water bodies in a negative way.

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Received: March 17, 2014
Accepted: May 25, 2014