DISTRIBUTION OF DISSOLVED AND PARTICULATE HEAVY METALS IN SURFACE WATER FROM AN AREA AFFECTED BY MINING ACTIVITIES

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Abstract. Among all pollution types, the presence of metals in water and sediments, due to the pursuit of activities of mining and ore processing for long periods is experiencing a relatively high prevalence and a serious difficulty to correct. Of all the other contaminants, heavy metals detach themselves by their high toxicity, having a direct impact on ecosystems and by their capacity to accumulate both in sediments and in aquatic organisms. This paper presents the investigations carried out on sediment quality and surface water collected in 10 control sections during 2 sampling campaigns (summer, autumn), sections located in an area polluted by the mining activities (discharges of mine water, drains from sterile storage ponds). Water and sediment samples collected in the 2 campaigns were subjected to *in situ* analysis of physical parameters: pH, conductivity, redox potential, and in laboratory for determining the total content of metals: copper, manganese, zinc, iron, cadmium and of other pollutants (anions, organic loading) in order to establish correlations between them and to identify the forms of heavy metals presence in the environment. For metals there were determined both dissolved fraction and total metal content, when following the ratio of total metal/dissolved metal and their correlation with pH values, in order to measure the bioavailable metal fraction. Analytical test results bring meaningful contributions to the knowledge of modalities by which environment quality components close to pollution sources are affected, and of the contribution of pollutants transport in space.

Keywords: heavy metals, mining activities, surface waters, pollutant partitioning.

AIMS AND BACKGROUND

River water is a complex matrix, vulnerable and constantly moving, depending on the interactions with the environment. It is an environment characterised by large fluctuations of physicochemical parameters and in most cases was strongly affected by anthropogenic activities, industrial, agricultural and household waste resulting from spills, thus strongly influencing these processes and interactions.

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Existing elements in the aquatic environment, with or without anthropogenic origin, including heavy metals, are transported to long distances by rivers, stored and transferred to biota. Among the many environmental contaminants, metals require special attention because, although some of them – Mn, Cu, Zn, Fe – are biological micronutrients essential to normal development of many species, can become toxic at too high concentrations by presenting persistence in the environment, mobility, bioavailability, therefore being ecological risks[1].

European Framework Directive 2000/60/EC amended by Directive 2008/32/EC establishes limit values for metal pollutants in water quality standards, limits that refer to the dissolved concentrations (dissolved phase obtained by filtration through 0.45 mm or any equivalent treatment)[2]. For this reason, when analysing the environmental pollution, it is indicated to use analytical methods able to determine the quantities of metals dissolved in different types of water.

Metals are present in surface water as different species, ranging between the pure form and metal ion covalently bound. In addition, elements can occur as dissolved species or adsorbed on suspended particles. The smaller the particles are, the slower they settle, therefore the adsorbed elements will be treated as dissolved in this case. The total amount of metal is the sum of its species and because they may have different toxicity, knowledge of speciation is necessary in order to determine hazards induced by metallic pollutants[3].

It is well known that suspended solids play an important role in controlling the metals speciation and their bioavailability. Particles in natural waters are characterised by a great diversity and generally include minerals, clays, organic particles, organic debris and inorganic particles covered by organic material[4].

At the interface between the dissolved phase and the suspended particles heterogeneous processes occur, therefore the speciation can be affected by different environmental conditions. The chemical composition of suspended particles matter is in relation to chemical and mineralogical composition of sediments and soils – the main source of particles matter in the system. Because of particle/solution interaction, floculation, coagulation and sedimentation of particles loaded with metal, the water 'filtration' takes place. Also, in certain circumstances, reverse processes of engagement of sediments and desorption of metal from particles take place.

This study has proposed the investigation of metallic elements distribution in traces (mg/l) – manganese, copper, zinc, cadmium, iron, in various aqueous fractions, by their determination in filtered and unfiltered river water samples in order to distinguish between elements transported by fine particles or carried in solution. The results allow the assessment of elements, scattering which is important when inputs of toxic substances occur in the ecosystem[5].

EXPERIMENTAL

The investigated area. The investigation took place in the Apuseni mountains, the Alba county, Romania (Fig. 1), in a mining area where the main collector of surface water is the Abrud river, right tributary of Aries. The Abrud river, together with the Rosia stream (Foies), drain the northern slopes of mountains located in the central part of the Metalliferous mountains. The Foies stream collects along its course mine water from a network of underground galleries and drip water from some areas overburden and exposed to impact of external factors. The area is also studied with semi-permanent rivers (torrential), namely waters tributary to Abrud or to its tributaries, which have an increased transport capacity. As a consequence of this flow regime, the quantity of matter in suspension varies significantly depending on hydrometeorological conditions.
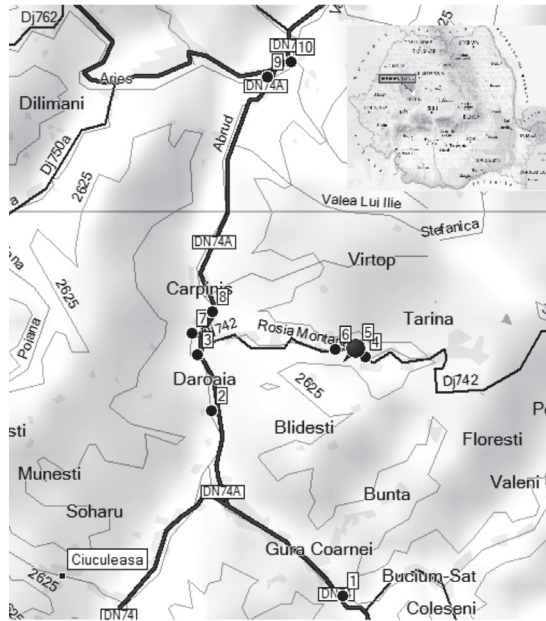

Fig. 1. Location of control sections

Sampling and analysis. For an accurate assessment of the effects of climate change on water quality and their correlation with the concentrations, water samples were taken in different seasons – summer, autumn. Fieldwork was conducted in 2009 in 2 periods: June and September. Using a GPS (Garmin) the coordinates were recorded for each of the 10 control sections (1–10) considered to be representative for the investigated area.

Surface water samples were collected according to standardised rules. There were taken 2 sets of liquid samples of 2 l for each sampling point, one for laboratory

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analysis and the other to achieve land determinations: pH, electrical conductivity, redox potential, temperature, using a multiparameter portable type equipment (Mettler Toledo and Hanna).

To assess the investigated water quality conditions there were selected for laboratory analysis those chemical indicators considered relevant (anions: sulphate, chloride, phosphate, nitrate; cations: manganese, copper, zinc, cadmium, iron, sodium, calcium, potassium, magnesium and total suspended solids).

Water samples were filtered through Whatman membrane filters (mixed cellulose ester) with a pore diameter of 0.45 mm using a Millipore filter assembly. Analytical laboratory determinations necessary to assess the anion/cation content of surface collected water samples were made by ISO standard methods. Concentrations of heavy metals – Cu, Mn, Fe, Cd, Zn – in homogeneous and filtered samples were measured with an atomic absorption spectrometer with oxyacetylene flame NOVA 300AnalytikJena. All materials needed for these analytical determinations were imposed by quality methodology in force.

The purpose of determination of both forms of metals present in analysed water samples is to assess the total metal/dissolved metal ratio and their correlation with pH value because the metals present in the solution in precipitated state could be re-precipitated if the pH value or other water quality conditions change throughout the route of investigated waters.

RESULTS AND DISCUSSION

Chemical species concentrations determined in surface water samples and acid mine water can be found in Tables 1 and 2.

For a better correlation of the results we processed the hydrochemical information in order to calculate the Pearson correlation coefficient. There were emphasised positive correlation factors greater than 0.9 for the following pairs of variables: metal (Cu, Mn, Zn, Cd and Fe) with phosphates, sulphates, TDS and metal pairs together.

By analysing the evolution of pH quality parameter in the 2 sampling campaigns we can see that, for most control sections, the values are outside the range of allowed values from 6.5 to 8.5, having an acidic and strongly acidic pH (sections **5** and **6**), except the control sections **3** and **8** in June campaign, control sections **2**, **3** and **9** in September, and control section **10** in both campaigns, sections which show values in the range allowed by the legislation in force; there is also observed a good correlation between pH values and concentration variation of sulphate anions which are responsible for the acidic character (soluble sulphides from mineral pyrite composition get oxidised in an aerobic environment and lead to formation of sulphuric acid) .

Table 1. Concentrations of major ions and metal species in filtered fraction

Sample code	pH	EC (µS/cm)	TDS	SO$_4^{2-}$	Cl$^-$	PO$_4^{3-}$	NO$_3^-$	Cu	Mn	Zn	Cd	Fe	Na	Ca	Mg
								(mg l^{-1})							
Summer															
1	4.3	548	436	270	12.3	0.06	1.52	0.45	0.81	0.58	0.006	0.03	9.17	49.00	12.13
2	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a
3	6.9	474	336	141	15.8	0.07	4.90	0.01	0.13	0.01	0.002	0.04	9.78	76.21	7.44
4	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a
AMW	2.6	4280	6672	4279	861.1	9.5	0.88	1.60	272.3	41.28	0.242	339.2	19.62	76.85	94.28
6	2.8	2090	2012	1253	544.7	0.14	2.14	0.42	31.51	8.46	0.065	11.99	17.91	66.38	30.43
7	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a
8	7.0	308	258	80	17.6	0.02	3.44	0.005	0.004	0.004	0.003	0.03	0.85	14.30	9.09
9	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a
10	6.9	189	114	29	10.5	0.04	3.25	0.003	0.008	0.007	0.003	0.03	4.62	9.90	5.48
Autumn															
1	5.6	593	474	300	14.1	0.05	1.02	0.053	0.92	0.679	0.006	0.05	8.57	70.44	14.16
2	6.9	633	436	242	22.8	0.19	2.37	b	b	b	0.002	0.04	11.52	29.47	8.25
3	6.3	680	528	289	21.1	0.21	2.10	b	2.06	0.04	0.003	0.07	13.91	70.98	11.75
4	4.3	930	862	493	207.4	0.46	4.25	0.157	13.76	0.72	0.007	0.05	13.88	92.50	16.67
AMW	2.7	4140	14071	4540	8259.0	11.2	0.41	1.31	251.5	36.64	0.261	339.5	12.35	34.95	84.38
6	2.8	3240	4574	2857	1054.0	3.81	1.77	0.65	114.9	16.23	0.123	169.8	8.64	29.16	43.44
7	6.4	707	624	318	35.1	0.009	2.45	b	b	0.023	0.004	0.04	14.62	101.4	13.53
8	4.2	930	856	499	158.2	0.049	2.19	0.074	16.55	2.01	0.017	0.04	12.39	87.55	15.30
9	7.1	196	142	21	14.1	0.039	0.96	b	b	0.001	0.003	0.05	3.36	27.22	3.15
10	6.9	247	178	52	14.1	0.052	1.04	b	b	0.011	0.003	0.07	4.069	39.44	4.05

^{a} Not been sampled; ^{b} <LOD.

Table 2. TSS concentrations and metal species in homogeneous fractions

Sample code	Summer						Autumn					
	MTS⁻	Cu	Mn	Zn	Cd	Fe	MTS	Cu	Mn	Zn	Cd	Fe
	(mg l⁻¹)						(mg l⁻¹)					
1	114	0.50	0.87	0.71	0.007	4.14	85	0.45	0.94	0.76	0.010	3.54
2	a	a	a	a	a	a	55	b	0.17	0.014	0.003	0.05
3	67	0.07	0.80	0.12	0.0039	4.88	67	b	2.55	0.10	0.004	16.07
4	a	a	a	a	a	a	225	0.16	14.86	0.736	0.010	11.97
5 (AMW)	843	1.59	289.45	88.78	0.2540	524.50	523	1.612	344.38	41.455	0.293	440.13
6	459	0.48	73.08	10.49	0.0702	106.08	531	0.990	199.75	26.055	0.157	199.38
7	a	a	a	a	a	a	114	0.01	4.53	0.19	0.006	18.41
8	1252	0.17	2.79	0.35	0.0067	29.05	44	0.07	21.24	2.372	0.020	10.18
9	a	a	a	a	a	a	19	b	0.04	0.009	0.004	0.35
10	983	0.04	0.54	0.11	0.0033	15.37	18	b	1.13	0.07	0.005	0.48

[a] Not been sampled; [b] <LOD.

The explanation for low pH values consists of water intake brought by mine water and by the water drained from the slopes on the right side of the river Abrud. Water samples of the Foies stream and mine water inside the Mine mouth (sections **4**, **5** and **6**) have a strong acid-induced effect due to wastewater discharge (Fig. 2).
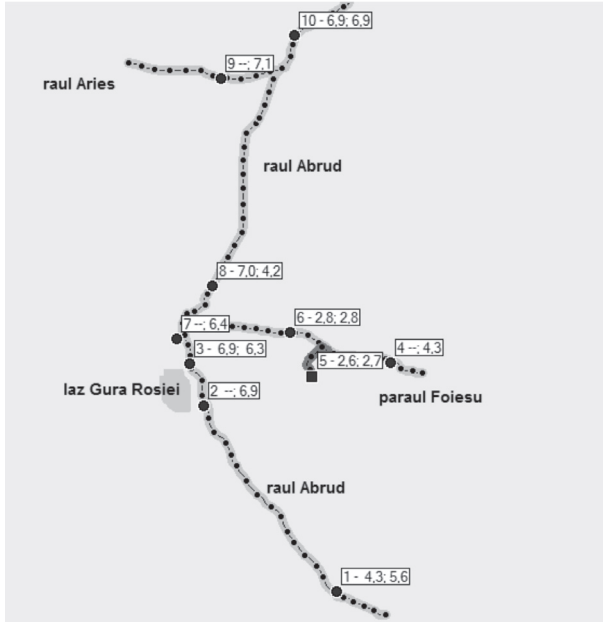
Fig. 2. pH variation in the 2 sampling campaigns

Metal partition coefficient (or distribution coefficient) k_d is used in different models to describe the distribution of metals between solid and solution phases and may be a direct indicator of metal solubility in surface waters.

Partition coefficient is calculated according to equation (1) (Ref. 5) based on total metal concentration $[M]_T$, concentrations of dissolved phase metals $[M]_D$, and concentrations of total suspended solids TSS. k_d is expressed in l/kg, $[M]_T$ and $[M]_D$ – in mg/l and TSS – in mg/l.

$$k_d = \frac{([M]_T - [M]_D)/\text{TSS}}{[M]_D} \times 10^6. \tag{1}$$

A high value of k_d shows a significant binding between the metal and the particles in suspension. The results obtained by using the formula show a clear dependency between the value of k_d and pH, in the sense that at the strong acid and acid pH values k_d values are lower, increasing greatly as the pH of the sample approaches the neutral field (Fig. 3). Thus we can say that the release of metal

related to particles is controlled by pH, retention and accumulation of metals in particles taking place in alkaline pH conditions.
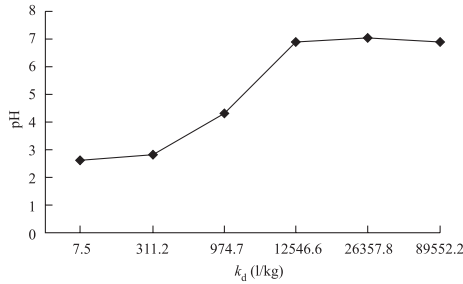
Fig. 3. k_d variation depending on pH

Copper. Reporting the results obtained for the total content of copper at normal levels, it can be seen that the investigated surface water quality is degraded in all control sections in the summer campaign, as in the autumn to fall to grade I in sections **2**, **3**, **7**, **9** and **10** and in grade V in sections **1**, **4** and **6**, in the sections affected by human activities specific to the area: **1** – Bucium Career; **4**, **6** – the Foies river upstream and downstream the Mouth mine, which collects more career waters and water flow (Fig. 4).
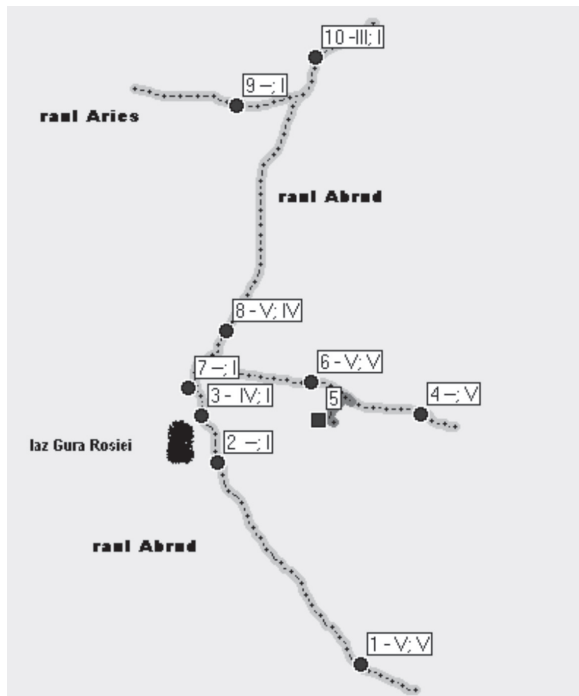
Fig. 4. Evolution of quality states for copper

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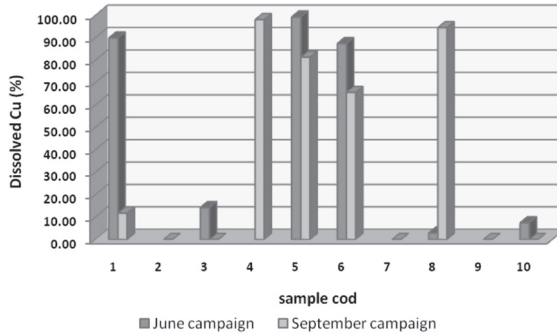
Fig. 5. Variation of dissolved copper concentration

Also, comparative analysis of determined total copper concentrations (in homogeneous samples) and dissolved copper (in the filters samples) shows that in most sections it is found in dissolved form (Fig. 5).

In summer campaign, the concentration of dissolved Cu from total are generally higher than in autumn, probably due to dilution by rain falling at the end of June, except the section **8** (the Abrud river after confluence with the Foies stream) for which in June the concentration of dissolved Cu was just 2.94% and in September 94.59%, phenomenon due to the engagement of large amounts of suspended matter by rain.

Analysing the evolution of the concentration values from control section **1** to control section **10** in the 2 sampling campaigns in relation to pollution sources, it appears that section **1** has significant loading in both campaigns, the total concentrations of homogeneous sample being virtually equal, instead in September it is mainly related to particles form of Cu – only 11.8% being dissolved.

It can also be noted a decrease in total Cu concentration from section **1** to upstream of the Red Mouth lake, because of the phenomenon of dilution, due to the fact that the Abrud river receives input streams on the left side from an area not-affected by mining activities. In copper case there is not observed any influence from the proximity to the potential anthropic pollution source – the Red Mouth lake.

High values of copper concentrations – mostly dissolved 65.7–98.1% – highlight instead very strongly the effect caused by the collection of surface runoff from waste rock dumps or from other affected areas (in section **4**) done by the natural emissary Foies river, and also caused by the discharge of mine water (**5**) resulting from mining activities (in section **6**). The results obtained for section **6** highlight punctually the load of pollutants produced by the discharge of acidic mine water (**5** – AMW) in a natural emissary. The values obtained for section **6** are much higher than those obtained for section **4**. In section **6** there is an increase of approximately 50% of the total and dissolved copper concentration values between the 2 sampling

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campaigns, in conditions of the weakening of surface water flow and maintaining relatively constant intake of water inside the mine mouth.

Manganese. Comparing the values obtained for the quality indicator manganese with the existing norms, it is found in terms of total content of manganese in both sampling campaigns, the existence of poor (IV) and bad (V) ecological states in all investigated control sections and that the samples collected in September have a manganese content higher than in June (Fig. 6).
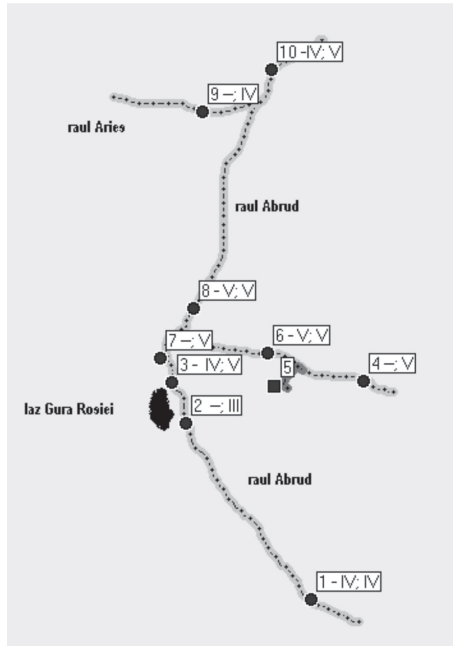
Fig. 6. Evolution of quality states for manganese
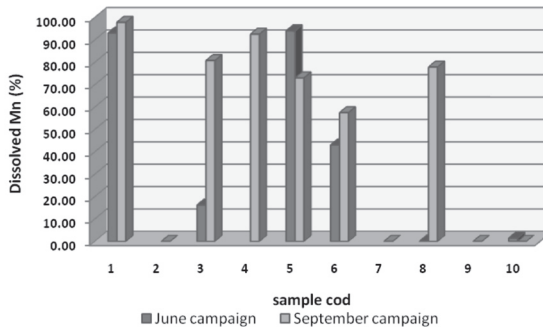
Fig. 7. Variation of dissolved manganese concentration

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Also, there can be seen a similar variation of concentration values of this quality parameter as in the case of copper, with extremely high values for the Foies river water after collecting mine water and for the Abrud river after the confluence with it. By analysing the concentrations of dissolved and total manganese we see that it is found predominantly in the dissolved state, as seen in Fig. 7.

Control section **3** stands out having only 16.25% dissolved manganese in June and 80.78% in September, because summer sampling took place immediately after several days of rainfall which engaged solid material from the pond. Also sample **8** shows that in summer, the manganese is related mainly to suspensions, and in September it is dissociated 77.92%.

The conclusion regarding the surface water quality in the area of interest of manganese quality indicator point of view is that it is found in high concentrations, values that lead to rating the entire investigated complex in poor (IV) and bad (V) ecological condition.

Zinc. Analytical results obtained for total zinc content show a variation of identified ecological states according to the regulations, for the investigated control sections. The control section **1** on the Abrud river has the ecological status IV (poor); near the tailings – upstream **2** and downstream **3** – becomes very good (I) and good (II) due to deposition and to dilution of tributaries on the left side of the Abrud river (Fig. 8). As with manganese, the total zinc content has in September concentrations higher than in June.
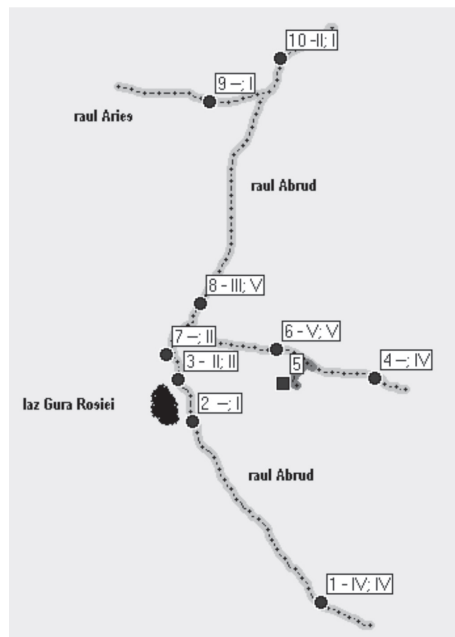

Fig. 8. Evolution of quality states for zinc

Comparing the zinc distribution in dissociated form in the 2 campaigns, we mainly see that this metal is in dissolved form, as seen in Fig. 9. Control sections **3** (downstream of the pond) and **8** (the Abrud river after the confluence with the Foies brook) must be mentioned, having in summer zinc mainly in the particles form (only 8.33 and 1.14% dissolved zinc), a phenomenon seen also for the other investigated metals, but in the fall the dissolved form prevails (40 and 84.74%).
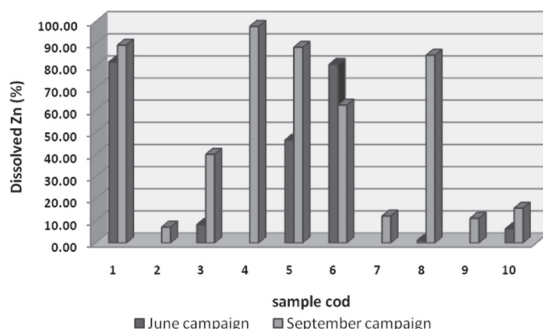

Fig. 9. Variation of dissolved zinc concentration

Also, the water sample taken in September from the control section **9** shows a low percentage of dissolved metal, the total content being probably due mainly to the engangement of the particles containing associated metals.

As with manganese, it is observed for the quality parameter zinc the influence of neighbourhood sources of pollution – the Red Mouth lake and the discharge of mine water from the inside of the mine mouth – by a significant increase of values for this indicator and such by the changing water quality states.

Cadmium. Comparing the results of analytical measurements made for quality indicator cadmium – total content, it can be found in all investigated control sections the existence of poor (IV) and bad (V) environmental states. Note also that there are not significant differences between values obtained in the 2 sampling campaigns (Fig. 10). As with copper, there stands out only a very strong anthropic influence exerted by the discharge of mine water (**5**) and by collecting wastewater from activities in the areas in section **4** by the Foies river, the proximity with the Red Mouth lake not changing the status of the Abrud river.
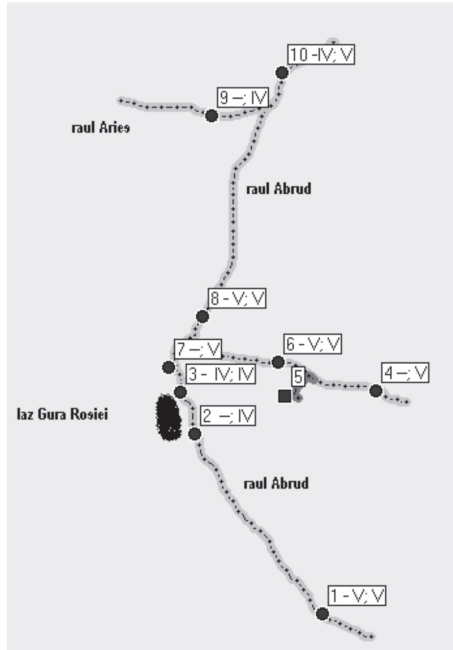
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Fig. 10. Evolution of quality states for cadmium

Regarding the form in which cadmium is found in the investigated area, very high percentages of metal in dissolved form in all sampling campaigns stand out, the lowest proportion being 45% (Fig. 11). Note also that in the summer campaign the dissociated metal percentages are higher than in September, except control sections **3** and **8** where values are lower in June than in September.
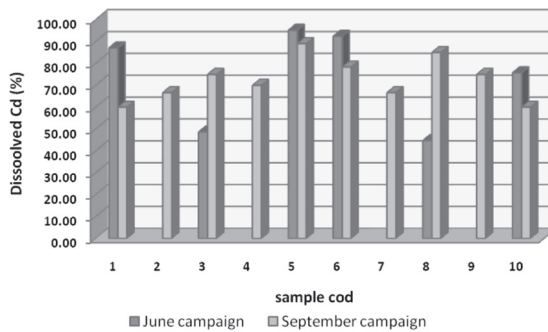

Fig. 11. Variation of dissolved cadmium concentration

Iron. For quality indicator iron, comparing the values obtained for the total metal content with values contained in Order 161, the quality state V (bad) is found in

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almost all investigated sectors, except the control section **2** – upstream dump, where the sector has a very good ecological state (I) due to dilution by the contribution made by small tributaries of Abrud and deposition phenomenon. In that metal case also, the influence of the 2 major sources of pollution in the investigated area can be seen – neighbourhood with the Red Mouth lake (significant increase in the pollutant load from upstream water – **2** to downstream – **3** by particle engagement by the tailings pond rainfall and wind – and mine and career wastewater collection – sections **4** and **6**; the red colour of the Foies river (known as the Red because of its colour) is accentuated after collecting the mine water.

The Aries river reaches the confluence with the Abrud river waters having a good ecological status (II) in section **9**, but after the confluence the condition becomes worse (V) for the summer sampling and good (II) for autumn sampling (Fig. 12). It should be noted the existence of this quality indicators primarily in the bounded iron form, as precipitate (ferric hydroxide), the percentage of dissociated iron being extremely small (less than 1% in most sections) in control sections where the water pH is approximately in the neutral range allowed. In extremely low pH sections – **5** and **6** – the percentage of dissolved iron from the total content is very high, varying in the range 64–85% (Fig. 13).
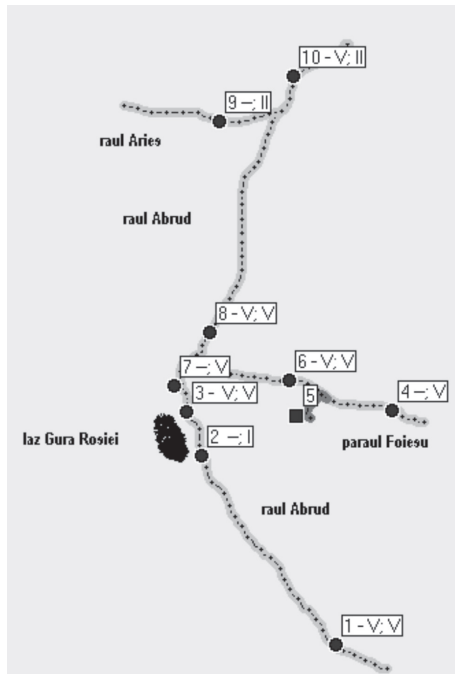

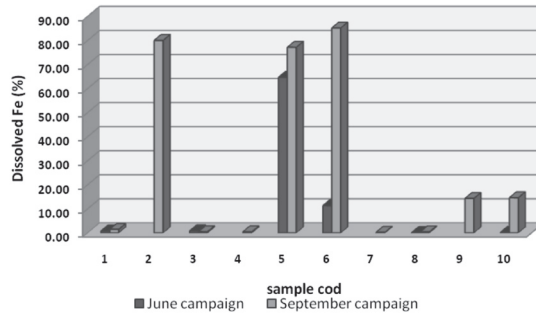**Fig. 12**. Evolution of quality states for iron

Fig. 13. Variation of dissolved iron concentration

Analysing the data obtained using Figs 14 and 15, it is found that the 5 metals whose evolution was observed on the basin subjected to chemical investigation in the 2 sampling campaigns, have different distribution depending on climatic conditions and chemical composition. This highlights the effect of summer rainfall on the concentration and ratio of dissolved metal/total metal (dissolved form growth in fall) by driving suspension in control sections **3** and **8**. It is also apparent that in control sections with very acid pH (5, 6) there are recorded the highest concentrations of dissolved metal which is confirmed by the calculated distribution coefficient k_d. It should be noted that the metals investigated have different behaviour between the 2 campaigns. During autumn, dissolved copper increses in section **1** and decreases in sections **8** and **10**. Dissolved manganese is low in the summer – it is found in the form bound on suspensions driven by rainfall – in section **3** – and increases in autumn in section **8** – because the phenomenon of submission. Zinc has a constant evolution, noting that dissolved zinc concentrations are higher in autumn than in summer. Also cadmium has a constant behaviour, with preference to dissolved form in both sampling campaigns and a slight increase of these values for the fall campaign. Iron is found mainly in bound form, only in areas with very acid pH 5, 6 being significant mentioned in dissolved form.
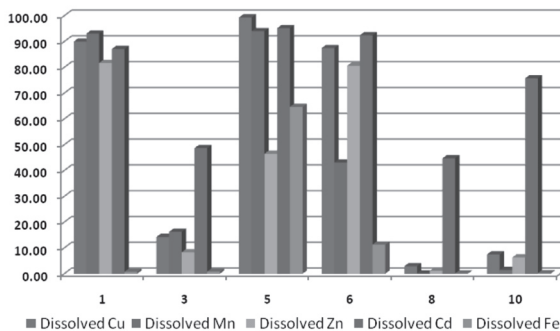

Fig. 14. Spatial distribution of dissolved forms in the summer campaign
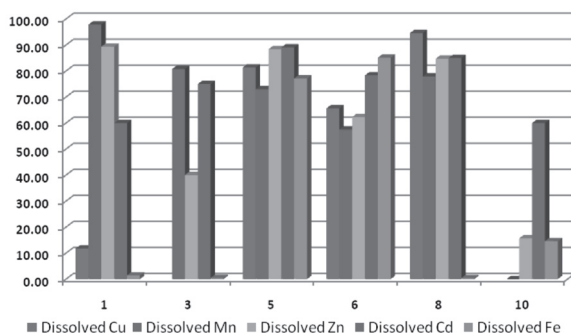
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Fig. 15. Spatial distribution of dissolved forms in the autumn campaign

CONCLUSIONS

In conclusion we can say that it is necessary not only to characterise the content of heavy metals from a watercourse, but also in terms of their partitioning to estimate the effects of climate changes on aquatic ecosystems quality states.

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