

ASSESSING THE CONTENTS OF ARSENIC AND OF SOME HEAVY METALS IN SURFACE FLOWS AND IN THE HYPORHEIC ZONE OF THE ARIEȘ STREAM CATCHMENT AREA, ROMANIA

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Abstract: By directly assessing, through atomic absorption spectrometry (AAS), the heavy metals and the arsenic contents of natural water-flows that cross regions where large-scale mining activities are carried out, there are quite accurately estimated the corresponding amounts of contamination. The present paper describes the methodology which was employed in order to assess the contents of Mn, Fe, Cu and Zn, by means of flame-AAS, and the contents of Cr, Co, Ni, Cd, Al, Pb, Sb and As, by means of direct electrothermal-AAS. The analytical methods which had been developed have been further utilized in surveying the chemical composition of an almost 110 km long stream section of Arieș river, by considering water samples collected both from the surface flow, and from the adjoining hyporheic zone. The experimental activities managed to identify two distinct regimes, one that was relatively normal in terms of contaminants distribution and, in contrast, one episode of severe pollution. Through the adopted approach there was ascertained that also the hyporheic zone was contaminated with heavy metals carried by the stream Arieș, yet the corresponding concentration levels were significantly smaller, the latter circumstance outlining the role played by that zone in the processes of self-decontamination.

Keywords: hyporheic zone, heavy metals, atomic absorption spectrometry, surface water, mining area, Arieș

1. INTRODUCTION

The contamination of surface water and of groundwater with various metals and semimetals (metalloids) derived from anthropogenic activities is an investigation field which in the recent years made the object of intensive studies, the latter circumstance being a consequence of the corresponding high toxicological potential and of the undesirable effects exerted on the associated ecosystems (Damian & Damian, 2006; Jelea et al., 2007; Bogatov & Bogatova, 2009; Custer et al., 2009), and - last but not least - of the effects exerted on the general health condition of the human communities which use of the concerned water supplies. In particular, conspicuously high pollution levels are recorded in stream-courses that flow across areas where mining activities are carried out.

The weathering of sulphide-rich mining waste causes acid mine drainage. Those effluents are characterized by low pH and contain significant quantities of sulphates, As, and heavy metals (Nordstrom, 2000; Herbert Jr., 2006; Rieuwerts et al., 2009; Casiot et al., 2009; Luís et al., 2009; Lizárraga-Mendiola et al., 2009). As a general rule however, the contamination of those stream-courses is a much more complex process, requiring that not only water was taken into account, but also the water-carried suspensions, as well as the accumulated sediments Boulton (1996); Bird et al. (2003); Kraft et al. (2006); Matache et al. (2002).

An outstandingly important part in the dynamics of the processes of contaminants transport and of surface flows self-decontamination is played by the transition zone between streams and groundwater. Orghidan (1955, 1959) was the first to

recognize the groundwater/surface water interface as a distinct zone, with a specific ecological significance, that zone being designated by him as the *hyporheic biotope*". The term "*hyporheic*" originates in the Greek roots *hypo*, meaning under, and *rheos*, meaning a stream. There is so far no unanimously accepted definition of the hyporheic zone, each of the several disciplines that investigate it making use of its own definition. Until recent times, related biology, ecology (Brunke & Gonser, 1997) or microbiology studies (Feris et al., 2003, 2004) were prevalent. During the last decade, the focus of the studies has however shifted toward investigations that addressed the hyporheic zone in terms of the surface-flows and groundwater-flows hydrology (Bencala, 2000; Sophocleous, 2002; Smith, 2005; Dogwiler & Wicks, 2006; Burkholder et al., 2008), of geochemistry (Harvey & Fuller, 1998; Jonsson, 2003; Zaramella et al., 2006) and of biogeochemistry (Bridge, 2005) of the contaminants transport, the nitrogen cycle included (Hinkle et al., 2001; Marshall & Hall Jr., 2004). A special attention was devoted to the role played by the hyporheic zone in the self-decontamination of the surface waters subject to pollutions that involved heavy metals (Gandy et al., 2007; Fuller & Harvey, 2000; Grosbois et al., 2009) and arsenic (Nagorski & Moore, 1999; Brown et al., 2007) resulted from mining activities.

Arieş ranges among the stream-courses in our country which are the most heavily affected by mining activities carried out in the associated catchment areas. The mines, the quarries, the waste dumps, the tailing ponds, the fluid pipes and the ore dressing plants - all of them are major pollution sources, especially as far as heavy metals are concerned (Luca et al., 2006). In this respect, a series of studies have already addressed the mineralogy (Neacşu et al., 2009), soil contamination (Lăcătuşu et al., 2009) and surface water pollution in that area (Forray & Hallbauer, 2000; Bird et al., 2005; Florea, 2007; Senila et al., 2007; Friedel et al., 2008).

In terms of concerned analytical techniques, assessments of the heavy metals contents are usually carried out both by atomic spectrometry including flame (F-AAS) or graphite furnace (GF-AAS) atomic absorption spectrometry, and by inductively coupled plasma mass spectrometry (ICP-MS). However, due to the high complexity of the matrices and to the low levels of the metal ions concentrations in the aquatic samples, their separation, and also the use of a pre-concentration step prior to the metal analysis are usually required. To this purpose, a multitude of separation and pre-

concentration procedures have been developed for trace metal ion determination, including: solid phase extractions (Tuzen et al., 2005; Liu et al., 2005; Tokalıoğlu et al., 2009; Shabani et al., 2009), ion exchange (Kara et al., 2005, 2006), coprecipitation (Tokalıoğlu & Yıldız, 2009) or size exclusion chromatography (Laborda et al., 2009).

In the following, there are described the direct procedures based on atomic absorption spectrometry which have been used for assessing the contents of certain metals and of arsenic in the stream-water of Arieş and in the hyporheic zone associated to the latter. To this purpose there have been employed both atomization techniques that are currently of common use, namely the flame AAS (for the assessment of the Mn, Fe, Cu, and Zn contents) and the electrothermal AAS (for the assessment of the Cr, Co, Ni, Cd, Al, Pb, Sb, As contents). The accuracy of the method was confirmed by analyzing the certified reference materials and the recovery studies. Relying on the indicated experimental approach, there were outlined the inter-relationships which existed between the surface water and the hyporheic zone.

2. THE STUDY AREA

The stream Arieş is the most important right-hand side tributary of Mureş, which at its turn is one of the main rivers in north-western Romania. The stream-flow of Arieş ranges between 5 and 63 m³/s, with the corresponding multi-annual average amounting to 24 m³/s (Forray & Hallbauer, 2000). On both sides of the valley, hill-tops reach elevations in the 1000–1200 m a.s.l. range, while the river streambed, in the neighborhood of Baia de Arieş, reaches an elevation of about 480 m a.s.l.. The catchment area of Arieş stream extends over 2540 km², the actual stream-course being directed eastward, along the northern edge of Metaliferi Mountains - a sub-unit of Romania's Western Carpathians (the latter mountains unit being designated in Romanian as "Munţii Apuseni"). Starting from its headwaters located at 1160 m a.s.l., Arieş flows mainly on a gravel-bed. Various sources of contaminants occurring along its stream-course make it one of the most polluted rivers in Romania (Friedel & Linard, 2008).

The pollution levels induced by mining activities vary as a function of the ore-type which is mined, of the type of the host-rock, and of the exploitation methods that are employed (Forray, 2002). The richest ore-potential of the Arieş River catchment area is concentrated in 20 metalliferous deposits, the most important of which are located at

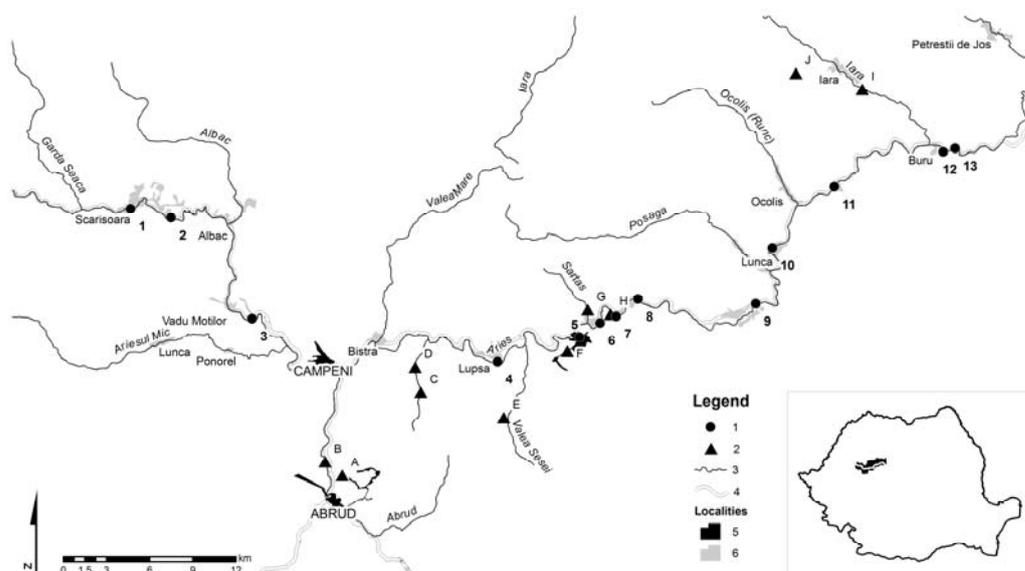


Fig. 1. Location map indicating the surface and underground water sampling sites and the main tailing ponds associated to the mining works located within the Arieș stream catchment area. Legend: 1 - Sampling point, 2 - Tailing pond, 3 - River, 4 - National road, 5 - urban and 6 - rural localities. The sampling points are: **1** - Scărișoara 1, **2** - Scărișoara 2, **3** - Vadul Moților, **4** - Pod Hădărău, **5** - Baia de Arieș, **6** - Sărtaș, **7** - Brăzești 1, **8** - Brăzești 2, **9** - Sălciua de Jos, **10** - Lunca Arieșului, **11** - Vidolm, **12** - Buru 1, **13** - Buru 2. The indicated tailing ponds are: A - Săliște, B - Gura Roșiei, C - Ștefanca 1, D - Ștefanca 2, E - Valea Șesei, F - Valea Cuții, G - Valea Sărtașului, H - Brăzești, I - Făgetu Ierii și J - Bărișoara.

Roșia Montană and at Roșia Poieni (Luca et al., 2006). Four important mines actively operate in the Arieș River catchment area: Roșia Montană, Abrud, Baia de Arieș, and Iara (Serban & Bălțeanu, 2004).

The geologic structure of the Arieș stream catchment area includes sedimentary formations, volcanogenic-sedimentary formations, igneous and volcanic rocks with different chemical compositions, from acid to basic, as well as metamorphic formations. The tectonic structure is also complex, and so is the lithology of the area (Forray, 2002). Since ancient times, large amounts of Au, Ag, Cu, Pb, Zn have been extracted from that region (Neacșu et al., 2009). Ensuing to the mining operations, phenomena of chronic and acute environmental pollution have been induced to the surface-flows and to the groundwater, which became therefore contaminated with heavy metals and with other hazardous substances. The tributaries of Arieș are small, yet some of them still underwent a severe pollution induced by the extraction industry. Baia de Arieș and Roșia Poieni are the main extractive industry centers within the Arieș stream catchment area, being at the same time responsible for the most intense pollution phenomena. The latter originate mostly in mining activities, in non-treated wastewater leakages, and to a lesser extent in sewage water discharges, in waste dumps, in settlements and in agricultural activities (Luca et al., 2006; Forray, 2001). Besides metals, the stream-water of Arieș

also contains organic pollutants, such as flocculants, surfactants, frothers and others, which all originate in ore dressing plants (Forray & Hallbauer, 2000).

3. SAMPLING AND ANALYTICAL METHODS

The present study required that 13 water-sampling stations were periodically set up along the stream-course of Arieș (Fig. 1). The sampling site occurring at the upstream extremity was set up in the area of Scărișoara village, while the one located at the downstream extremity, 108.42 km away from the first one, was set up in the village Buru. There have been collected two series of samples, the first one on 18 April 2008, and the second one on 21 and 22 July 2008. Water-samples from the stream-water of Arieș have been collected directly in HDPE Nalgene sampling bottles, at least 1m away from the stream-border, in places where the thickness of the stream-water layer exceeded 20 cm. In correspondence to the stream-water sampling sites, sampling operations have also been conducted on the stream-border, in order to collect, by means of the Bou & Rouch (1967) method, water from the hyporheic zone, from the 1–1.5 m depth range. The indicated Bou-Rouch procedure is widely used for collecting interstitial fauna, or for microbiological sampling (Guemmouh et al., 2005). Prior to sampling, every sampling bottle has been washed with Ultra-pure quality

acids, with ultra-pure water and, repeatedly, with the water that was finally meant to be sampled.

When collected, water samples were filtered *in situ* by means of a Chromatography Research Supplies filtering system, provided with a manual Nalgene vacuum pump. MCE-Millipore membranes, mixed cellulose esters, of 0.45 μm porosity and of 47 mm diameter have been used for filtering. Each membrane filter was washed in ultra-pure water before the experiment and used only once. During filtration, the first 250 mL of solution were discarded, thus allowing the saturation of the membrane surface prior collecting the filtrate. Filtered water samples were acidified with Ultrapur® 60% Nitric acid (Merck) to pH 2 and stored at 4°C. Heavy metal and arsenic concentrations were subsequently determined using atomic absorption spectroscopy.

The water temperature was measured at the sampling site by using a Crison portable thermometer TM65 with Immersion probe Pt 1000 sensor (measuring error $\leq 0.2^\circ\text{C}$, reproductibility $\pm 0.1^\circ\text{C}$). When samples were being collected, a Crison PH 25 portable instrument has been used in order to perform all pH measurements (50 51 Electrode with integrated Temperature Probes ATC, NIST-traceable pH buffer solutions pH 4.01 and 7.00), according to (Wilde et al., 2006) recommendations.

The Mn, Fe, Cu, and Zn concentrations in water samples were determined in laboratory by flame-AAS, while the Cr, Co, Ni, Cd, Al, Pb, Sb, and As concentrations were determined in laboratory by electrothermal-AAS. The determinations were carried out with a Perkin-Elmer atomic absorption spectrometer, model AAnalyst 700, with deuterium

Table 1. The operating instrumental condition for flame AAS methods.

Element	Mn	Fe	Cu	Zn
Lamp	HCL	HCL	HCL	EDL
Wavelength (nm)	279.5	248.3	324.8	213.9
Slit (nm)	0.2	0.2	0.7	0.7
Mode	AA-BG	AA-BG	AA	AA-BG
Calibration	Linear	Nonlinear	Linear	Linear
Standards (mg/L)	0.5, 1.0, 2.0	1.0, 3.0, 6.0	0.5, 1.0, 2.0	0.1, 0.3, 0.6

Table 2 – The operating instrumental condition for electrothermal AAS methods.

Element	Cr	Co	Ni	Cd
Lamp	HCL	HCL	HCL	HCL
Wavelength (nm)	357.9	240.7	232.0	228.8
Slit (nm)	0.7	0.2	0.2	0.7
Applied Current (mA)	25	30	25	8
Energy	71	29	25	35
Mode	AA	AA-BG	AA-BG	AA-BG
Calibration	Linear	Linear	Linear	Nonlinear
Standards ($\mu\text{g/L}$)	2, 6, 12	5, 15, 30	5, 15, 30	0.5, 1.5, 3.0
Matrix modifier (5 μL)	1.0% $\text{Mg}(\text{NO}_3)_2$	1.0% $\text{Mg}(\text{NO}_3)_2$	1.0% $\text{Mg}(\text{NO}_3)_2$	0.3% Pd + 0.2% $\text{Mg}(\text{NO}_3)_2$
Element	Al	Pb	Sb	As
Lamp	HCL	HCL	HCL	EDL
Wavelength (nm)	309.0	283.3	217.6	193.7
Slit (nm)	0.7	0.7	0.7	0.7
Applied current (mA)	25	10	25	380
Energy	55	42	71	29
Mode	AA-BG	AA-BG	AA-BG	AA-BG
Calibration	Nonlinear	Linear	Linear	Linear
Standards ($\mu\text{g/L}$)	10, 30, 60	3, 9, 18	10, 30, 60	10, 30, 60
Matrix modifier (5 μL)	1.0% $\text{Mg}(\text{NO}_3)_2$	4.0% $\text{NH}_4\text{H}_2\text{PO}_4$	0.3% Pd + 0.2% $\text{Mg}(\text{NO}_3)_2$	0.3% Pd + 0.2% $\text{Mg}(\text{NO}_3)_2$

arc background correction, equipped with an HGA-800 graphite furnace, an AS-800 autosampler (for GF-AAS) and S10 autosampler (for F-AAS). The calibration lines were traced using solutions prepared from standard solutions CertiPUR® (Merck). The methods accuracy, precision and sensitivity were tested by using the reference matters provided by Perkin-Elmer groundwater and wastewater pollution control certified reference materials (Trace Metals I - 15 elements - Part No. N9300211, Trace Metals II - 3 elements - Part No.

N9300212 and Trace Metals III - 6 elements - Part No. N9300213). All the solutions were prepared with ultra-pure water (TKA Ultra Pure System GenPure, electric resistance 18.2 MΩ×cm).

In F-AAS determinations, all measurements were carried out in an air/acetylene flame, at flow rates of 17 and 2.0 L/min, with a 10 cm long slot-burner head (Tab. 1). In GF-AAS determinations, pyrolytically coated graphite tubes with integrated platforms (Perkin-Elmer catalog No. B3001262) were used (Tab. 2).

Table 3. Analytical performance and validation for flame AAS methods.

Element		Mn	Fe	Cu	Zn
Method detection limit	<i>n</i>	10	10	10	10
	mg/L	0.04	0.11	0.008	0.024
	St. dev.	0.013	0.035	0.0026	0.0081
Precision-repeatability	<i>n</i>	7 (at 0.5	6 (at 1.0	8 (at 0.5	6 (at 0.2 mg/L)
		0.021	0.041	0.087	0.0054
Precision-reproductibility	<i>n</i>	24 (at 0.5	24 (at 1.0	24 (at 0.5	24 (at 0.2
		0.018	0.032	0.010	0.0132
Trueness ("bias")	<i>n</i>	24 (at 0.5	24 (at 1.0	24 (at 0.5	24 (at 0.2
	%	0.46	3.92	0.86	1.58
Experimental recovery	%	97.6–106.5	88.3–101.6	89.1–104.7	87.4–108.0

Table 4. Analytical performance and validation for electrothermal AAS methods.

Element		Cr	Co	Ni	Cd
Method detection limit	<i>n</i>	10	10	12	18
	µg/L	0.30	0.34	1.39	0.012
	St. dev.	0.099	0.112	0.462	0.040
Precision-repeatability	<i>n</i>	8 (at 10 µg/L)	5 (at 20 µg/L)	5 (at 20 µg/L)	8 (at 2 µg/L)
		0.195	0.681	0.994	0.0542
Precision-reproductibility	<i>n</i>	19 (at 10 µg/L)	12 (at 20 µg/L)	13 (at 20 µg/L)	15 (at 2 µg/L)
		0.618	0.702	1.384	0.1503
Trueness ("bias")	<i>n</i>	19 (at 10 µg/L)	12 (at 20 µg/L)	13 (at 20 µg/L)	15 (at 2 µg/L)
	%	0.65	1.85	6.21	3.06
Experimental recovery	%	86.6–98.5	91.9–105.2	89.0–103.9	93.2–107.4
Element		Al	Pb	Sb	As
Method detection limit	<i>n</i>	12	15	10	16
	µg/L	0.22	0.45	3.89	0.42
	St. dev.	0.075	0.150	1.296	0.139
Precision-repeatability	<i>n</i>	5 (at 20 µg/L)	6 (at 10 µg/L)	4 (at 40 µg/L)	5 (at 20 µg/L)
		1.924	0.390	0.587	1.924
Precision-reproductibility	<i>n</i>	12 (at 20 µg/L)	12 (at 10 µg/L)	8 (at 40 µg/L)	12 (at 20 µg/L)
		1.304	1.159	4.961	1.304
Trueness ("bias")	<i>n</i>	12 (at 20 µg/L)	12 (at 10 µg/L)	8 (at 40 µg/L)	12 (at 20 µg/L)
	%	6.58	0.65	5.38	6.58
Experimental recovery	%	93.9–100.8	89.9–105.1	86.0–105.4	93.9–100.8

The graphite furnace temperature programs were carried out according to the manufacturer recommendations. In most cases the water samples were analyzed directly, with an injected sample volume of 20 μL .

In the case of the Al determinations, certain samples required preliminary dilutions, since the dilution capability of the auto-sampler was exceeded. The atomic absorption signal was measured as a peak area mode against an analytical calibration curve. The performance of the employed analytical procedures was determined according to the International Union of Pure and Applied Chemistry (IUPAC) (Thompson et al., 1999, 2002) and EURACHEM (Ellison et al., 2000) recommendations (Tabs 3, 4).

4. RESULTS AND DISCUSSION

In Figs. 2-8 there are plotted the pH values and the values of the heavy metals and arsenic concentrations, determined for the two series of samples collected in the months of April and July

2008 from the stream-water of Arieş and from the corresponding hyporheic zone.

The acquired experimental data point to a few general conclusions. In terms of hydrochemical characteristics, two distinct sections can be separated along the stream-course of Arieş: the section extending upstream Baia de Arieş, where the pollution level is comparatively low, and the section extending further downstream, where the heavy metals concentrations amount to significant values. The two right-hand side tributaries of Arieş are responsible for the indicated setting. The first among those streams is Abrud, whose catchment area includes the mining exploitation Roşia Montană. All the tributaries of that stream, many of which are subject to stream-courses that the mining works severely disrupted, are highly polluted (Bird et al., 2005; Florea, 2007). The other Arieş tributary which poses serious contamination threats is Valea Şesei. The large tailing pond located in its area accumulates most part of the meteoric water that leaches the huge waste dumps derived from the quarry of Roşia Poieni.

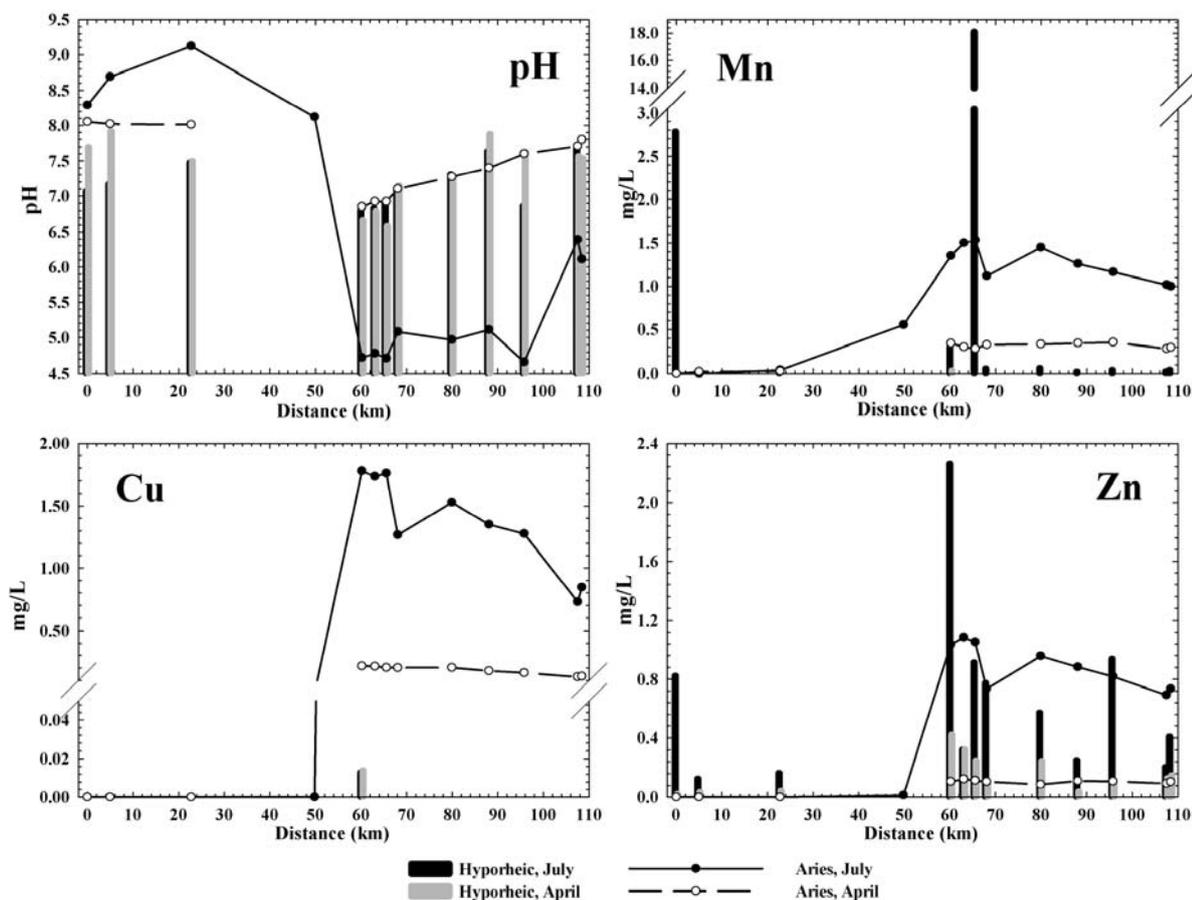


Figure 2. The variation of the pH and of the Mn, Cu and Zn concentrations along the stream-course of Arieş (lines) and at the corresponding hyporheic sampling sites (bars).

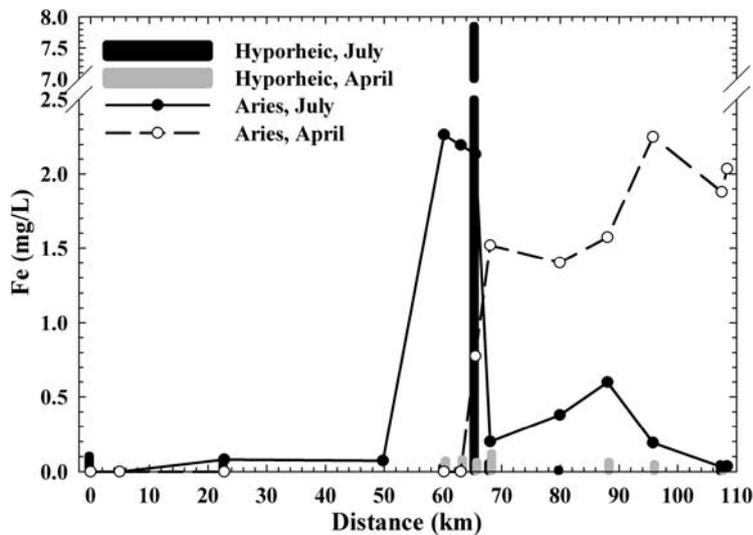


Figure 3. The variation of the Fe concentrations along the stream course of Arieș (lines) and at the hyporheic sampling sites (bars).

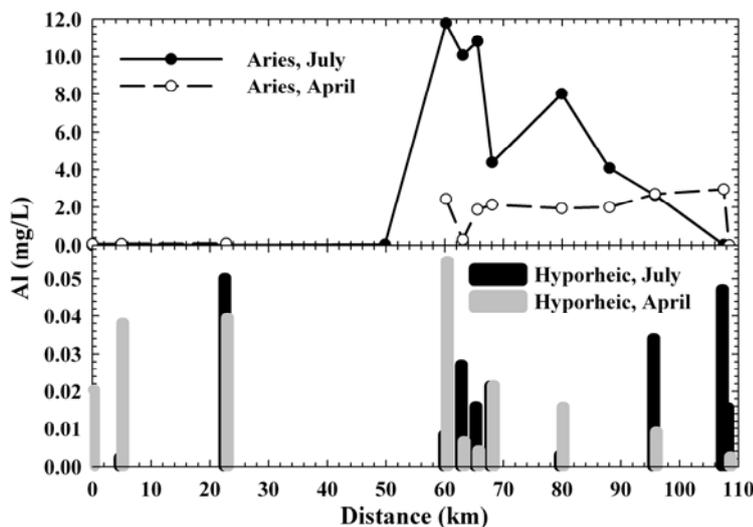


Figure 4. The variation of the Al concentrations along the stream course of Arieș (upper field of the diagram) and at the hyporheic sampling sites (lower field of the diagram).

Two distinct settings have been delineated by the two series of water samples. In April 2008, a high flow rate was discharging along the stream Arieș, being supplied mostly by snowmelt occurring in the mountainous, elevated region of the catchment area. Alternatively, the stream discharge was low in the month of July 2008, and subject to that circumstance there has occurred a severe pollution accident which originated in the Valea Șesei tailing pond, and that we detected as it evolved. Water that was strongly acid and extremely rich in heavy metals overflowed from the indicated pond and contaminated the stream water of Arieș over a distance that exceeded 50 km, resulting in pH values as low as 4.5–5.0 (Fig. 2), while the heavy metals concentrations rose significantly. By considering the heavy metals concentration distributions, there results that our sampling operation managed to detect the plume displacement prior to its arrival at

the two sites located at the downstream extremity of the sampled stream section (which are specifically located within the premises of the village Buru).

Another general observation concerns the hyporheic domain heavy metals concentrations, which in most cases are lower than those of the stream-water. That circumstance substantiates the significant role that the hyporheic zone plays in the self-decontamination processes (Brunke & Gonser, 1997; Gandy et al., 2007). Yet in the case of certain sampling stations, notable exceptions may occur: for instance, the sampling sites located within the Baia de Arieș–Brăzești section undergo obvious impacts due to the tailing ponds of Valea Sârtașului and of Brăzești.

Specifically, small iron concentrations were recorded in the hyporheic zone water for most of the analyzed cases (Fig. 3). In addition, the Co and Ni concentrations of that area ranged - except for two

sampling sites of the hyporheic zone - below the detection limits of the employed methods (Fig. 5). Analogous situations were recorded also in the case of Sb and Pb (Fig. 7). Additionally, the contaminants concentrations in the hyporheic zone appear to experience seasonal variations, a fact which was also noticed by former investigators (Herbert Jr., 2006). Those fluctuations are however subject to intense distortions, which are a result of accidental dumping of waste-water originating in the tailing ponds located within the Arieş stream catchment area. Such incidents frequently lead to excessive accumulations of contaminants. Highly illustrative in this respect are the excessive concentrations of Fe (Fig. 3), Cd (Fig. 6) or As (Fig. 8) detected in certain water samples collected from the hyporheic zone.

The hyporheic domain behavior in terms of geochemistry is closely related to the local hydrology. Reciprocal recharge relationships exist between the streams network and the groundwater accumulations. The intensity and the direction of the

water exchanges are controlled (among other) by the aquifer formations permeability and by the recharge sources of superficial or underground origin. The water exchange between the stream Arieş and the hyporheic accumulations located within the unconsolidated detritic deposits of the floodplain is controlled by the stream water-level. As a general rule, during drought periods, the streambed of Arieş is supplied by groundwater inflows provided by the deposits that build up the floodplain and the terraces. High discharge occurring during spring time, as well as summer time flash floods may induce temporary reversals in the groundwater flow direction, so that hyporheic groundwater accumulations within the floodplain start being recharged by the stream water. This is the setting which favors the pollutants transfer from the stream-course to the hyporheic water accumulations, the concerned process reaching its maximum intensity when the lower floodplain is actually flooded.

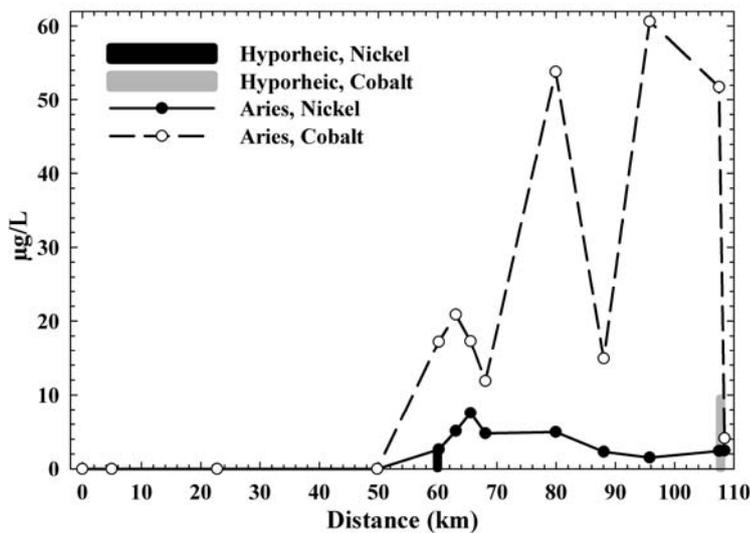


Figure 5. The variation of the Co and Ni concentrations along the stream course of Arieş (lines) and at the hyporheic sampling sites (bars).

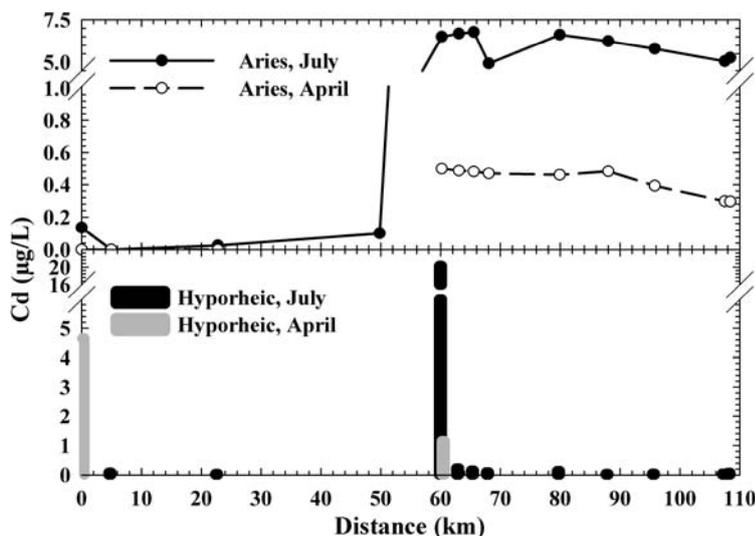


Figure 6. The variation of the Cd concentrations along the stream course of Arieş (upper field of the diagram) and at the hyporheic sampling sites (lower field of the diagram).

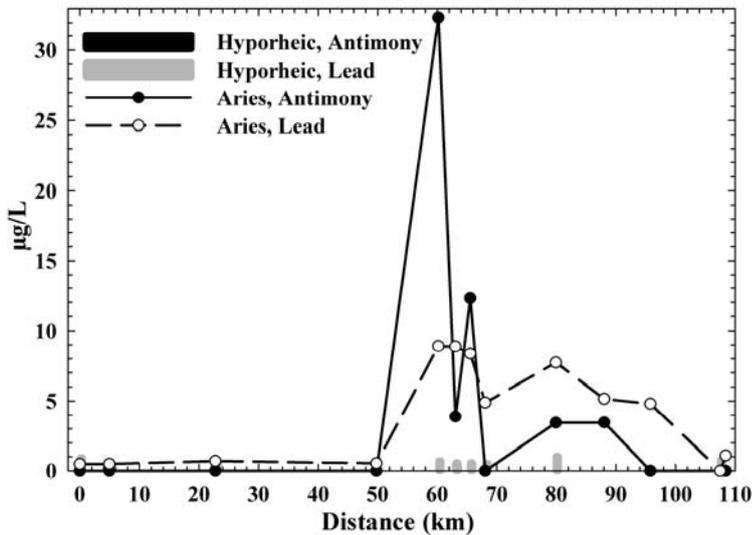


Figure 7. The variation of the Sb and Pb concentrations along the stream course of Arieş (lines) and at the hyporheic sampling sites (bars).

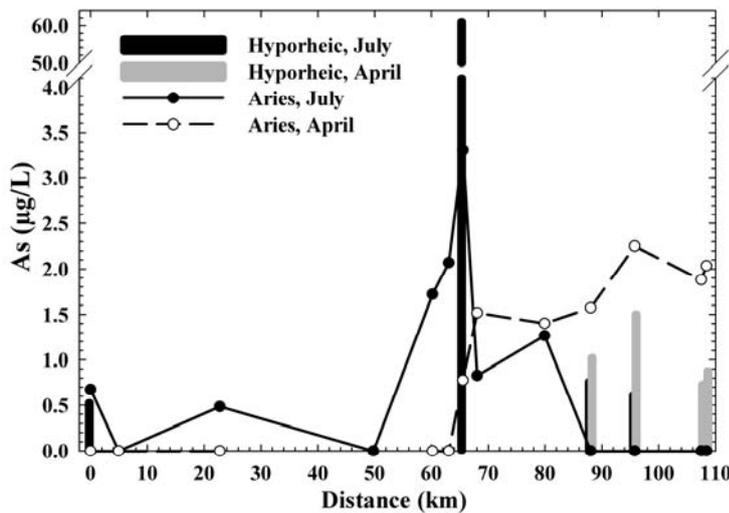


Figure 8. The variation of the As concentrations along the stream course of Arieş (lines) and at the hyporheic sampling sites (bars).

The Al, Fe, and Mn contents of groundwater which saturates the hyporheic aquifer associated to Arieş stream are about one order of magnitude smaller than the corresponding contents of the surface water (Figs. 2-4). The weaker contamination of the hyporheic domain with those elements is due to the circumstance that in solution, they are liable to precipitate as hydroxides, generating fine colloids (Gandy et al., 2007; Harvey & Fuller, 1998). The latter, although being precipitation products, behave in terms of transport mechanisms similarly to the dissolved compounds. The generation of colloids, prevalently as a result of the trivalent cations hydrolysis, has also a significant operational outcome. Colloids penetrate the 0.45 µm filtering membrane (Kennedy et al., 1974; Boulton, 1996; Cortecchi et al., 2009). When water samples filtered in that way are analyzed by means of spectrometric methods (AAS or ICP), both phases - solution and

colloidal - will be analyzed together, resulting in a positive deviation of the charges balance.

5. CONCLUSIONS

By directly assessing, through atomic absorption spectrometry (AAS), the heavy metals and the arsenic contents of natural water-flows that cross regions where large-scale mining activities are carried out, there are quite accurately estimated the corresponding amounts of contamination. The reasonably low detection limits of the indicated method, as well as its high accuracy, recommend it for performing detailed analytical investigations, in spite of the fact that it is less fast as compared to ICP methods.

The utilized AAS methods capabilities have been illustrated by the results of a water-chemistry survey that was conducted over an almost 110 km

long section of the stream Arieș, and that addressed both the surface flow and the adjoining hyporheic zone. By analyzing two series of samples, a relatively normal distribution of the contaminants has been identified on the one hand, while on the other, a severe surface-water pollution accident was detected. As a general rule, also the hyporheic zone was contaminated with heavy metals carried by the stream Arieș, yet the corresponding concentration levels were significantly smaller, the latter circumstance outlining the role played by the indicated zone in the self-decontamination processes.

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REFERENCES

- Bencala, K. E.**, 2000. *Hyporheic zone hydrological processes*. Hydrol. Process., 14, 2797–2798.
- Bird, G., Brewer, P. A., Macklin, M. G., Balteanu, D., Driga, B., Serban, M. & Zaharia, S.**, 2003. *The solid state partitioning of contaminant metals and As in river channel sediments of the mining affected Tisa drainage basin, northwestern Romania and eastern Hungary*. Appl. Geochem., 18 (10), 1583–1595.
- Bird, G., Brewer, P. A., Macklin, M. G., Serban, M., Balteanu, D. & Driga, B.**, 2005. *Heavy metal contamination in the Arieș river catchment, western Romania: Implications for development of the Roșia Montană gold deposit*. J. Geochem. Explor., 86 (1), 26–48.
- Bogatov, V. V. & Bogatova, L. V.**, 2009. *Heavy metal accumulation by freshwater hydrobionts in a mining area in the south of the Russian Far East*. Russ. J. Ecol., 40 (3), 187–193.
- Bou, C. & Rouch, R.**, 1967. *Un nouveau champ de recherches sur la faune aquatique souterraine*. C.R. Hebd. Séances Acad. Sci. Ser. III. Sci. Vie, 265, 369–370.
- Boult, S.**, 1996. *Fluvial metal transport near sources of acid mine-drainage: relationships of soluble, suspended and deposited metal*. Mineral. Magazine, 60, 325–335.
- Bridge, J. W.**, 2005. *High resolution in-situ monitoring of hyporheic zone biogeochemistry*. Tech. Rep. SC030155/SR3, Environment Agency, Rio House, Almondsbury, Bristol.
- Brown, B. V., Valett, H. M. & Schreiber, M. E.**, 2007. *Arsenic transport in groundwater, surface water, and the hyporheic zone of a mine-influenced stream-aquifer system*. Water Resour. Res., 43 (11), W11404+.
- Brunke, M. & Gonser, T.**, 1997. *The ecological significance of exchange processes between rivers and groundwater*. Freshwater Biol., 37, 1–33.
- Burkholder, B. K., Grant, G. E., Haggerty, R., Khangaonkar, T. & Wampler, P. J.**, 2008. *Influence of hyporheic flow and geomorphology on temperature of a large, gravel-bed river, Clackamas River, Oregon, USA*. Hydrol. Process., 22, 941–953.
- Casiot, C., Egal, M., Elbaz-Poulichet, F., Bruneel, O., Bancon-Montigny, C., Cordier, M.-A., Gomez, E. & Aliaume, C.**, 2009. *Hydrological and geochemical control of metals and arsenic in a Mediterranean river contaminated by acid mine drainage (the Amous River, France); preliminary assessment of impacts on fish (Leuciscus cephalus)*. Appl. Geochem., 24 (5), 787–799.
- Cortecchi, G., Boschetti, T., Dinelli, E., Cidu, R., Podda, F. & Doveri, M.**, 2009. *Geochemistry of trace elements in surface waters of the Arno River Basin, northern Tuscany, Italy*. Appl. Geochem., 24 (5), 1005–1022.
- Custer, C. M., Yang, C., Crock, J. G., Shearn-Bochsler, V., Smith, K. S. & Hageman, P. L.**, 2009. *Exposure of insects and insectivorous birds to metals and other elements from abandoned mine tailings in three Summit County drainages, Colorado*. Environ. Monit. Assess., 153, 161–177.
- Damian, F. & Damian, G.**, 2006. *Geochemical characterization of some old mine waste dumps from Baia Mare area and their influence on the natural vegetation*. Carpathian Journal of Earth and Environmental Sciences, 1 (2), 63–72.
- Dogwiler, T. & Wicks, C.**, 2006. *Thermal variations in the hyporheic zone of a karst stream*. Int. J. Speleol., 35 (2), 59–66.
- Ellison, S. L. R., Rosslein, M. & Williams, A.**, 2000. *Quantifying uncertainty in analytical measurement*. Tech. rep., EURACHEM/CITAC Guide CG 4.
- Feris, K., Ramsey, P., Frazar, C., Moore, J. N., Gannon, J. E. & Holben, W. E.**, 2003. *Differences in hyporheic-zone microbial community structure along a heavy-metal contamination gradient*. Appl. Environ. Microbiol., 69 (9), 5563–5573.
- Feris, K. P., Ramsey, P. W., Frazar, C., Rillig, M., Moore, J. N., Gannon, J. E. & Holben, W. E.**, 2004. *Seasonal dynamics of shallow-hyporheic-zone microbial community structure along a heavy-metal contamination gradient*. Appl. Environ. Microbiol., 70 (4), 2323–2331.
- Florea, R.-M.**, 2007. *Studiul chimico-analitic al ecosistemului Roșia Montană*. Ph.D. Thesis, Catedra de chimie analitică, Facultatea de Chimie, Universitatea din București.
- Forray, F. L.**, 2001. *Aplicarea analizei factoriale în*

- studiul poluării râului Arieș (Munții Apuseni)*. Studia Univ. Babeș-Bolyai, Geologia, 46, 47–58.
- Forray, F. L.**, 2002. *Geochemistry of the environment in the areas of mining works from Arieș valley (Apuseni Mountains, Romania)* (abridged version). Ph.D. Thesis, Babeș-Bolyai University of Cluj.
- Forray, F. L. & Hallbauer, D. K.**, 2000. *A study of the pollution of the Aries River (Romania) using capillary electrophoresis as analytical technique*. Environ. Geol., 39, 1372–1384.
- Friedel, M. & Linard, J.**, 2008. *Initial sediment transport model of the mining-affected Aries River Basin, Romania*. Tech. Rep. Open-File Report 2008–1171, U.S. Geological Survey.
- Friedel, M. J., Tindall, J. A., Sardan, D., Fey, D. & Poptua, G. L.**, 2008. *Reconnaissance study of water quality in the mining-affected Aries River basin, Romania*. Tech. Rep. Open-File Report 2008–1176, U.S. Geological Survey.
- Fuller, C. C. & Harvey, J. W.**, 2000. *Reactive uptake of trace metals in the hyporheic zone of a mining-contaminated stream, Pinal Creek, Arizona*. Environ. Sci. Technol., 34 (7), 1150–1155.
- Gandy, C. J., Smith, J. W. N. & Jarvis, A. P.**, 2007. *Attenuation of mining-derived pollutants in the hyporheic zone: A review*. Sci. Total Environ., 373 (2–3), 435–446.
- Grosbois, C., Schäfer, J., Bril, H., Blanc, G. & Bossy, A.**, 2009. *Deconvolution of trace element (As, Cr, Mo, Th, U) sources and pathways to surface waters of a gold mining-influenced watershed*. Sci. Total Environ., 407, 2063–2076.
- Guemmouh, R., Essafi, K. & Aouad, N.**, 2005. *Bacteriological study by bacterial counting on the level of the interstitial sediments of Sebou River*. Mex. J. Condensed Matter, 6 (1), 49–53.
- Harvey, J. W. & Fuller, C. C.**, 1998. *Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance*. Water Resour. Res., 34 (4), 623–636.
- Herbert Jr., R. B.**, 2006. *Seasonal variations in the composition of mine drainage-contaminated groundwater in Dalarna, Sweden*. J. Geochem. Explor., 90 (3), 197–214.
- Hinkle, S., Duff, J., Triska, F., Laenen, A., Gates, E., Bencala, K., Wentz, D. & Silva, S.**, 2001. *Linking hyporheic flow and nitrogen cycling near the Willamette River - a large river in Oregon, USA*. J. Hydrol., 244 (3–4), 157–180.
- Jelea, M., Jelea, S.-G., Kovacs, Z.-M. & Gheța, D. E.**, 2007. *Research concerning the oxidation degree of the sulphidic tailings from the Novăț tailings storage facility*. Carpathian Journal of Earth and Environmental Sciences, 2 (2), 45–57.
- Jonsson, K.**, 2003. *Effect of hyporheic exchange on conservative and reactive solute transport in streams. Model assessments based on tracer tests*. Ph.D. Thesis, Acta Universitatis Upsaliensis, Uppsala.
- Kara, D., Fisher, A. & Hill, S.**, 2005. *Preconcentration and determination of trace elements with 2,6-diacetylpyridine functionalized Amberlite XAD-4 by flow injection and atomic spectroscopy*. Analyst, 130 (11), 1518–1523.
- Kara, D., Fisher, A. & Hill, S. J.**, 2006. *Comparison of some newly synthesized chemically modified Amberlite XAD-4 resins for the preconcentration and determination of trace elements by flow injection inductively coupled plasma-mass spectrometry (ICP-MS)*. Analyst, 131, 1232–1240.
- Kennedy, V. C., Zellweger, G. W. & Jones, B. F.**, 1974. *Filter pore-size effects on the analysis of Al, Fe, Mn, and Ti in water*. Water Resour. Res., 10 (4), 785–790.
- Kraft, C., von Tümpling Jr., W. & Zachmann, D. W.**, 2006. *The effects of mining in Northern Romania on the heavy metal distribution in sediments of the rivers Szamos and Tisza (Hungary)*. Acta Hydrochim. Hydrobiol., 34 (3), 257–264.
- Laborda, F., Ruiz-Beguería, S., Bolea, E. & Castillo, J. R.**, 2009. *Functional speciation of metal-dissolved organic matter complexes by size exclusion chromatography coupled to inductively coupled plasma mass spectrometry and deconvolution analysis*. Spectrochim. Acta, Part B, 64 (5), 392–398.
- Liu, Y., Chang, X., Guo, Y., Ding, B. & Meng, S.**, 2005. *Solid phase extraction and preconcentration of trace heavy metal ions in natural water with 2,2'-dithiobis(4-aminophenyl) modified amberlite XAD-2*. Solvent Extr. Ion Exc., 23 (5), 725–740.
- Lizárraga-Mendiola, L., González-Sandoval, M., Durán-Domínguez, M. & Márquez-Herrera, C.**, 2009. *Geochemical behavior of heavy metals in a Zn-Pb-Cu mining area in the State of Mexico (central Mexico)*. Environ. Monit. Assess., 155, 355–372.
- Lăcătușu, R., Cîtu, G., Aston, J., Lungu, L. & Lăcătușu, A. R.**, 2009. *Heavy metals soil pollution state in relation to potential future mining activities in the Roșia Montană area*. Carpathian Journal Earth and Environmental Sciences, 4 (2), 39–50.
- Luca, E., Roman, C., Chintoanu, M., Luca, L., Pușcaș, A. & Hoban, A.**, 2006. *Identificarea principalelor surse de poluare din Bazinul Arieșului*. Agricultura - Știință și practică, 59-60 (3-4), 84–90.
- Luís, A., Teixeira, P., Almeida, S., Ector, L., Matos, J. & Ferreira da Silva, E. A.**, 2009. *Impact of acid mine drainage (AMD) on water quality, stream sediments and Periphytic Diatom communities in the surrounding streams of Aljustrel Mining area (Portugal)*. Water, Air, Soil Pollut., 200 (1-4), 147–167.
- Marshall, M. C. & Hall Jr., R. O.**, 2004. *Hyporheic invertebrates affect N cycling and respiration in stream sediment microcosms*. J. N. Am. Benthol. Soc., 23, 416–428.

- Matache, M., Pătroescu, C. & Pătroescu-Klotz, I.**, 2002. *Evoluția concentrației metalelor grele în sedimente acvifere dunărene pe tronsonul Baziaș-Porțile de Fier I (1996-1999)*. Rev. Chim. (Buc.), 53 (9), 623–626.
- Nagorski, S. A. & Moore, J. N.**, 1999. *Arsenic mobilization in the hyporheic zone of a contaminated stream*. Water Resour. Res., 35 (11), 3441–3450.
- Neacșu, A., Popescu, G. C., Constantinescu, B., Vasilescu, A. & Ceccato, D.**, 2009. *The geochemical signature of native gold from Roșia Montană and Musariu ore deposits Metaliferi Mts. (Romania); preliminary data*. Carpathian Journal of Earth and Environmental Sciences, 4 (1), 49–59.
- Nordstrom, D.**, 2000. *Advances in the hydrogeochemistry and microbiology of acid mine waters*. Int. Geol. Rev., 42 (6), 499–515.
- Orghidan, T.**, 1955. *A newly defined domain of underground aquatic life: "the hyporheic biotope"* (in Romanian). Bul. Șt. Sec. Biol. Științe Agr. și Sec. Geol. Geogr. Acad. R. P. Romîne, 7 (3), 657–676.
- Orghidan, T.**, 1959. *Ein neuer Lebensraum des unterirdischen Wassers: Der hyporheische Biotop*. Arch. f. Hydrobiol., 55 (3), 392–414.
- Rieuwerts, J., Austin, S. & Harris, E.**, 2009. *Contamination from historic metal mines and the need for non-invasive remediation techniques: a case study from Southwest England*. Environ. Monit. Assess., 148 (1-4), 149–158.
- Senila, M., Levei, E., Miclean, M., Tanaselia, C., David, L. & Cordos, E.**, 2007. *Study regarding the water quality in Aries catchment*. Chem. Bull. Politehnica Univ. (Timișoara), 52(66) (1-2), 169–172.
- Serban, M. & Bălțeanu, D.**, 2004. *Mining activities and heavy metal river pollution in the Apuseni Mountains, Romania*. In: BALWOIS Conference on Water Observation and Information System for Decision Support, Ohrid, FY Republic of Macedonia, 25-29 May 2004. p. 11.
- Shabani, A. M., Dadfarnia, S. & Dehghani, Z.**, 2009. *On-line solid phase extraction system using 1,10-phenanthroline immobilized on surfactant coated alumina for the flame atomic absorption spectrometric determination of copper and cadmium*. Talanta, 79 (4), 1066–1070.
- Smith, J. W. N.**, 2005. *Groundwater–surface water interactions in the hyporheic zone*. Tech. Rep. SC030155/SR1, Environment Agency, Rio House, Almondsbury, Bristol.
- Sophocleous, M.**, 2002. *Interactions between groundwater and surface water: the state of the science*. Hydrogeol. J., 10, 52–67.
- Thompson, M., Ellison, S. L. R., Fajgelj, A., Willetts, P. & Wood, R.**, 1999. *Harmonised guidelines for the use of recovery information in analytical measurement*. Pure Appl. Chem., 71 (2), 337–348.
- Thompson, M., Ellison, S. L. R. & Wood, R.**, 2002. *Harmonized guidelines for single-laboratory validation of methods of analysis (IUPAC Technical Report)*. Pure Appl. Chem., 74 (5), 835–855.
- Tokaloğlu, Ş. & Yıldız, S.**, 2009. *A comparative study on the preconcentration of some metal ions in water samples with Cu(II) and Ni(II) salicylaldehyde coprecipitants*. Microchim. Acta, 165 (1-2), 129–133.
- Tokaloğlu, Ş., Yılmaz, V. & Kartal, Ş.**, 2009. *Solid phase extraction of Cu(II), Ni(II), Pb(II), Cd(II) and Mn(II) ions with 1-(2-thiazolylazo)-2-naphthol loaded Amberlite XAD-1180*. Environ. Monit. Assess., 152, 369–377.
- Tuzen, M., Soylak, M. & Elci, L.**, 2005. *Multi-element pre-concentration of heavy metal ions by solid phase extraction on Chromosorb 108*. Anal. Chim. Acta, 548 (1-2), 101–108.
- Wilde, F. D., Busenberg, E. & Radtke, D. B.**, 2006. *pH (ver. 1.3)*. In: National Field Manual for the Collection of Water-Quality Data. Vol. book 9. U.S. Geological Survey Techniques of Water-Resources Investigations, Chap. 6.4, pp. 1–29.
- Zaramella, M., Marion, A. & Packman, A. I.**, 2006. *Applicability of the transient storage model to the hyporheic exchange of metals*. J. Contam. Hydrol., 84, 21–35.

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