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**Geochemistry of the environment in the areas
of mining works from Arieș Valley
(Apuseni Mountains, Romania)**

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1. Introduction

Many efforts have been made in the last decades and especially in the last years to study in detail various aspects concerning industrial pollution of the environment. The necessity appeared in a moment when mankind realized that nature represents the source of life and its resources are limited.

Among industrial branches, mining industry has always been a strong source of environment pollution. The first ever book about mining, written by Georgius Agricola, titled „De re metalica libri XII” and published in 1556, contains the clear description of the negative effect of the mining industry over the environment in Germany (Kelly, 1988).

In Romania, mining industry is a strong source of environment pollution, both visually and chemically. Among the results of mining activities, waste rock embankments and tailings storage facilities produce the most important negative visual impact. They also contribute to the pollution of the environment with heavy metals (Pb, Zn, Cu, Co, Ni, Cd etc.), with powders and dust (metallic and non-metallic) as well as with chemical substances used in the technological processes of metal concentration from ores (foaming agents, cyanides etc.). The discharge of mine waters (untreated or inadequately treated) and effluents from preparation plants in the local hydrographic network lead to serious perturbations of natural geochemical cycles. The perturbations affect the aquatic fauna of the river, ground waters, soil and vegetation.

The famous mineral ores containing precious metals (Au, Ag) from the Apuseni Mountains were systematically extracted since the Roman times, especially for gold. Mining activities have intensified from the end of the XIXth century, extracting, besides gold, important quantities of Cu, Pb, and Zn. Scientific research done in parallel with exploitation led to the discovery, for the first time in the world, of the element tellurium (Te) as well as of a large number of new minerals.

Besides the positive effects of mining, the negative impact has gradually increased, finding its expression in deforestation, building waste rock embankments and tailings storage facilities and finally in various degrees of pollution.

The main extractive industry centres on the Arieş Valley responsible for pollution are the ones from Baia de Arieş and Roşia Poieni. Added to these are other mines located in the hydrographic basin of the Arieş River (Maşca - Băișoara, Roşia Montană and Bucium) contributing to the pollution.

A first step in environment protection is the profound knowledge of natural phenomena. Only after reaching that will we be able to modify actual technologies to reduce the interaction between the *technosphere* and environment to a minimum.

2. Aim and scope

Having in view that Arieş River crosses an important mining district, we considered that the geochemical and geoecological study of the area is of outmost importance.

Our thesis, titled „*The geochemistry of the environment in the areas of mining works from Arieş Valley (Apuseni Mountains)*”, is focused on the geochemical aspects of environment pollution and tries to analyse a part of the phenomena occurring in the hydrographic basin of the Arieş River. The aim is to identify the possible sources of pollution and to establish the degree of this pollution in the area. The complexity of the geochemical phenomena occurring in mining areas unveils a vast field of research of which our work manages to present only a part. Our aim is not and cannot be the exhaustion of all the problems linked to pollution, but may be a basis for future studies in this field. Understanding the complex phenomena that take place in mineral transformation processes may be the only way to solve problems connected to environment pollution in mining areas.

The thesis contains 301 pages, 159 mostly colour graphs and photos, and 56 tables. The references comprise 563 journals, books, reports etc. most of them published in the last ten years.

3. Studied region

The studied region is located in the North-East of Romania, in the Apuseni Mountains (Fig. 1). Altitudes generally between 300 and 1500 m dominate the relief. The temperate climate of the area determines forest vegetation consisting mainly of oak, beech and spruce.

The study was focused on tailings storage facilities (Brezeşti, Valea Sartăş, Valea Ciuşii and Valea Seliştei), ground water (Cheia-Muncel area) and surface water (Roşia Montană – Cheia area). To these is added the south-western part of the Apuseni Mountains, where we studied the concentration of metals in gastropod shells.

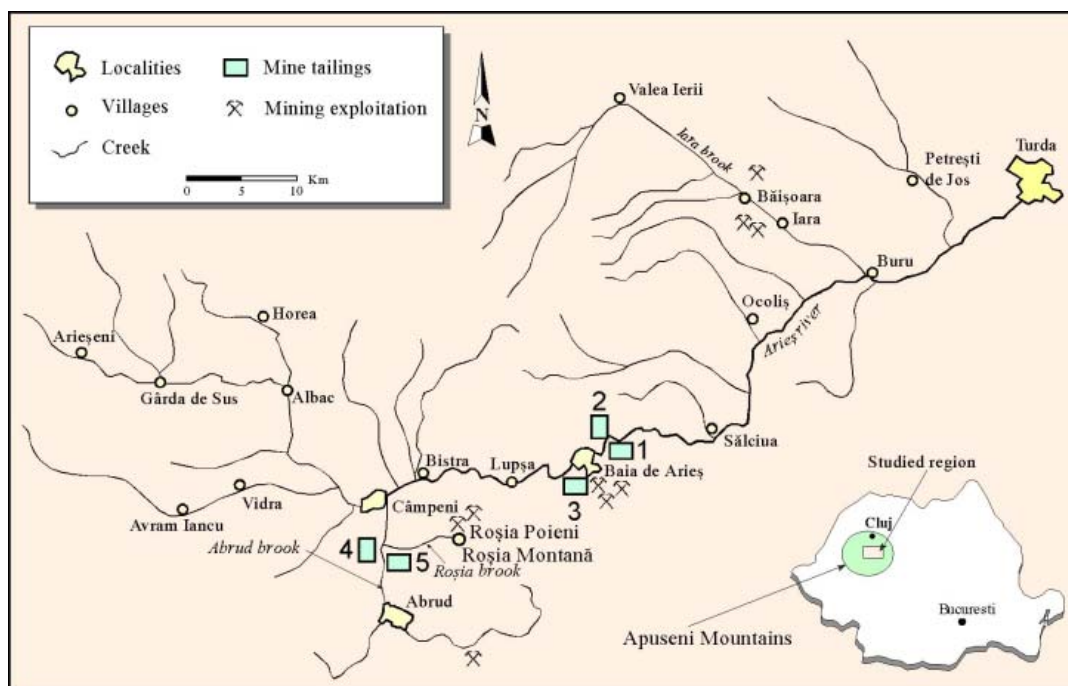


Fig. 1. Map of studied region. 1 –Brezești tailings storage; 2 –Valea Sartășului tailings storage; 3 –Valea Ciuții tailings storage; 4 –Gura Roșiei tailings storage; 5 –Valea Seliștei tailings storage.

The studied area has approximately 7000 km² and a cumulative length of the watercourses of about 170 km.

4. Brief geology

The geologic structure of the area of the hydrographic basin of Arieș river shows a large variety of geological formations. One can notice sedimentary formations (conglomerates, sandstones, clays, limestones etc.), volcanogenic-sedimentary formations (tuffs, volcanic agglomerates etc.), igneous and volcanic rocks with different chemistry from acid to basic, as well as metamorphic formations (with different degrees of metamorphism). The large variety of geological formations determines the complexity of the surface geochemical phenomena occurring in this hydrographic basin.

The metamorphic formations from the Apuseni Mountains have a complex tectonic structure and a varied lithology. A synthesis on the metamorphites from the Apuseni Mountains belongs to Ianovici *et al.* (1976). Later, Balintoni (1985; 1994; 1996; 1997) based on new tectonic and lithostratigraphic concepts, realizes the classification which we use in our study. In the hydrographic basin of the Arieș outcrop the Gârda nappe (consisting of micaschists, gneisses, migmatites, granitic

intrusions, metagabbros), the Arieșeni nappe (sericite fillites and metaconglomerates), the Biharia nappe (dolomites, black quartzites and schists with sericite and chlorite) and the Baia de Arieș nappe (paragneisses, micaschists, amphibolites, carbonatic rocks).

The sedimentary formations from the hydrographic basin of the Arieș river are varied both by lithology and age. They form the cover of crystalline rocks or represent the filling of post-tectonic basins. The detailed description of these formations is done by several researchers (Ivanovici *et al.*, 1976). The eldest pre-Mesozoic sedimentary formations belong to Permian and form the cover of Arieșeni and Gârda nappes. They are represented by sandstones, laminated conglomerates, and shales.

Triassic formations consist of conglomerates, quartzitic sandstones, shales, limestones, and dolomites. Jurassic formations outcrop on small areas and consist of jaspers, shales, massive limestones, and sandstones. Cretaceous formations outcrop on extended areas, as post-tectonic filling of depressionary basins. Lithologically one can notice a predominance of conglomerates-microconglomerates, sandstones, clays and limestones in a flysch facies and Gosau facies (conglomerates, sandstones, limestones with rudists, marls with *Inoceramus*).

Paleogene formations outcrop on the median course of Iara valley, in the Iara – Mașca - Cacova Ierii area, being represented by continental red clays, limy clays, gypsum, limestones and sandstones.

Neogene formations outcrop on the lower course of the Arieș river valley, downstream of Cornești. Petrographically they consist of conglomerates, limestones, gypsum, tuffs, marls, sandstones, sands and clays (Ghergari *et al.*, 1991; Chira, 2000). Due to their high content of highly soluble salts, they exert a strong influence on the chemistry of the Arieș river in the Cornești – Turda sector.

Quaternary formations are deposits on the sides of the Arieș river valley downstream the town of Câmpeni. They are formed by rounded siliciclastic material, more or less rounded rock fragments and some silty and lutitic material.

Magmatic rocks have a lesser distribution compared to metamorphic and sedimentary rocks. Due to their composition and associated metallogeny, they are the main markers in identifying the origin of various metallic elements from soils and water. Magmatic rocks show a large petrographic – petrochemical variety, mainly with an acidic to neutral, and subordinately basic chemistry.

Granites and granitoides of igneous or metamorphic origin occupy large surfaces, playing an important role in defining the chemical character of the left side tributaries of the Arieș River.

The Upper Jurassic-Neocomian magmatic rocks outcrop east from Buru in a large variety – basic, intermediate and acidic rocks (basalts, andesites, trachyandesites, dacites and rhyolites).

The Upper Cretaceous-Paleogene magmatism, also known as the *banatitic magmatism*, has a calc-alkaline character and was generated in the conditions of a contractional geotectonic setting (Balintoni and Vlad, 1996), consisting of granodiorites rhyolites, andesites, dacites.

The Neogene magmatism was generated in an extensional geotectonic setting (Balintoni and Vlad, 1996). In the studied area, it is represented by the igneous bodies from Baia de Arieș, Roșia Montană - Roșia Poieni and the ones from Bucium, consisting of dacites, andesites and to a lesser extent basaltic andesites. The magmatic products (volcanic and subvolcanic) are accompanied by polymetallic, Au-Ag and Cu mineralizations which contribute significantly to the increase of the local or even regional geochemical background, due to the large area of distribution and to the alteration phenomena accompanying them.

5. Analytical methods

For this thesis we studied over 562 samples with 14 analysis methods to a total of 670 analyses both on solid and liquid samples. The analytic methods we used are:

- Potentiometry (Ag/AgCl - ISE-Cu)
- Inductively-coupled plasma emission spectrometry (ICP-OES)
- Atomic absorption spectrometry (AAS)
- Capillary electrophoresis (CE)
- X-ray fluorescence spectrometry (XRF)
- X-ray diffraction (XRD)
- Ultraviolet-visible Spectrophotometry (UV-VIS)
- Transmission electron microscopy (TEM)
- Scanning electron microscopy (SEM)
- Scanning electron microscopy with Energy Dispersed Spectrometry (SEM-EDS)
- Optical microscopy
- PH measurements
- Eh measurements
- Electrical conductivity measurements

The results helped the determination of the main geochemical phenomena that occur in some mining areas from the hydrographic basin of the Arieș river. To

verify the conditions of formation of some minerals we have done some thermodynamic modelling of reactions with the Mintequa2 software.

6. Tailing geochemistry

The tailings storages from Arieş valley (Fig. 1), have very limited facilities to prevent environment pollution; in some cases, these facilities are completely lacking. This situation is quite common, even for other tailings storages. The lack of data on the construction and on their behaviour in time makes the evaluation of the potential impact over the environment very difficult. Our field observations have shown that untreated – or partially chemically treated - waters from ponds are discharged in the rivers. In the case of the functional tailings storages, a summary treatment is performed on the decanted waters, but the effluents from tailings in conservation or closed receive no treatment. Rainwater may mobilize both metals and soluble chemicals left in the waste rock after ore concentration, contaminating rivers, soils and ground water.

At the Valea Sartășului tailings storage, the waste rock consists of feldspars, quartz, muscovite and small amounts of sulphides due to the low yields of ore processing. The TEM analysis of the fine fraction (<0.002 mm – clay fraction) indicates the presence of silica, illite and jarosite (Fig. 2). In what concerns heavy metal concentration, we remarked the presence of Cr (94.6 ppm), Co (30.9 ppm), Cu (171 ppm), Zn (1550 ppm), As (1873 ppm), Cd (8.4 ppm), Ba (1090 ppm), Hg (15 ppm) and Pb (1193 ppm) (table 1). The most toxic of these are arsenic, cadmium and mercury, all present in high concentrations.

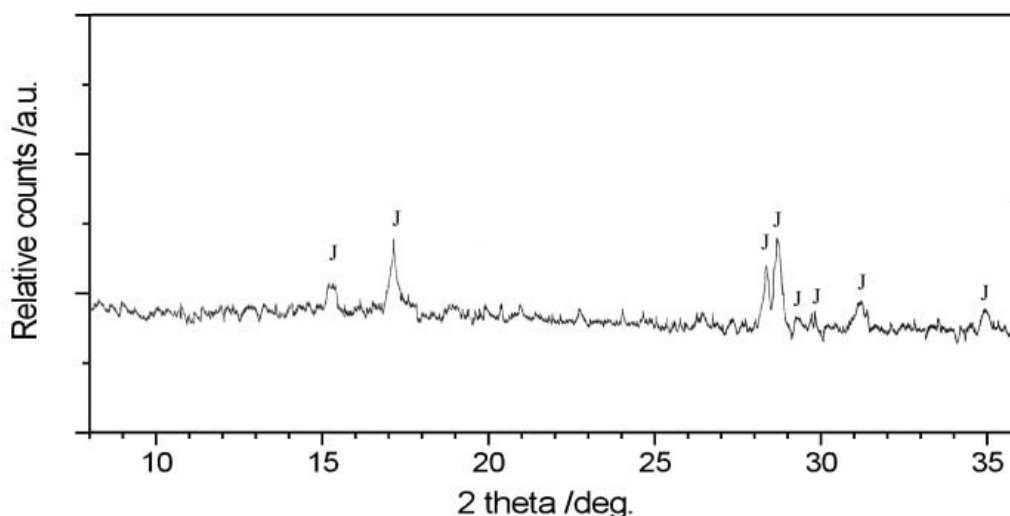


Fig. 2. XRD spectra for sample 49. J – jarosite.

Table 1

Metal contents of tailing samples

	Sample	T47	T49	T72	TS1	TS11
		Brăzeşti	V. Sartăş	V. Ciuţii	Brăzeşti	
V	µg/g	114.8	77.3	102.2	101.3	125.7
Cr	µg/g	24.6	94.6	40.6	21	15.1
Co	µg/g	< 8.9	30.9	< 11	11.2	13.2
Ni	µg/g	5.7	16.9	< 1.7	1.4	1.9
Cu	µg/g	35.6	171.1	113.7	17.5	18.1
Zn	µg/g	281	1550	418.8	129.7	180.8
Ga	µg/g	12.6	6.3	12.4	14.7	13.2
Ge	µg/g	1	1.1	2.1	2	2.1
As	µg/g	1623	1873	2183	400.6	462.1
Se	µg/g	< 0.3	8.7	< 0.4	0.3	< 0.2
Br	µg/g	< 0.6	< 0.8	< 0.8	0.4	0.3
Rb	µg/g	209.9	153.6	200.7	229.5	212.9
Sr	µg/g	77.7	94.6	66.9	144.7	138.4
Y	µg/g	10.2	5.1	9.1	16.9	15.1
Zr	µg/g	119.2	93.9	112.2	105.4	107.3
Nb	µg/g	6.6	5.7	6.8	7.3	7.7
Mo	µg/g	1.6	2.8	2.5	1.1	0.9
Ag	µg/g	< 0.8	0.7	< 0.8	< 0.8	< 0.8
Cd	µg/g	0.8	8.4	1.9	0.9	0.7
In	µg/g	< 0.3	< 0.3	0.5	< 0.3	< 0.3
Sn	µg/g	2.6	2.6	7.7	2	2.2
Sb	µg/g	25.8	30.5	37.7	8.4	22.3
Te	µg/g	1.8	5	1.3	2.7	1.2
I	µg/g	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Cs	µg/g	14.8	5.3	11.8	16.9	15.1
Ba	µg/g	1157	1090	1052	1410	1103
La	µg/g	17.4	12.4	16.7	20.2	21.5
Ce	µg/g	36	25	39.1	41.1	47.9
Pr	µg/g	9.7	5.7	8.7	< 5.0	9.1
Nd	µg/g	18.6	< 5.0	11.2	< 5.0	15.4
Hf	µg/g	3.1	< 4.4	< 3.4	4.4	4
Ta	µg/g	< 3.5	< 8.0	< 6.3	2.8	< 2.5
W	µg/g	5	< 5.0	< 2.8	3.9	3.3
Hg	µg/g	9.4	15	9.7	< 4.0	< 4.2
Tl	µg/g	6.7	6.7	5.4	4.6	4.1
Pb	µg/g	283.3	1193	411.5	54.6	235.4
Bi	µg/g	< 1.7	< 2.6	< 2.3	< 0.8	< 0.9
Th	µg/g	1.7	< 0.5	< 0.5	7.3	3.4
U	µg/g	1.2	< 0.5	< 0.5	4.8	1.3

The ratio between the concentration of the above-mentioned elements in the tailings storage vs the continental crust shows enrichments of over 1800 times for arsenic, 85 times for cadmium and 187 times for mercury.

The tailings from the Valea Ciuţii storage consist of feldspars, quartz, muscovite as well as small amounts of sulphides again due to low yields of ore processing. The TEM analysis of the clay fraction indicates the almost exclusive presence of jarosite (Fig.3 c). The heavy metal content of the tailing is 40.6 ppm (Cr),

113.7 ppm (Cu), 418.8 ppm (Zn), 2183 ppm (As), 1052 ppm (Ba) and 1193 ppm (Pb) (table 1). The most toxic of these is arsenic, present in very high concentrations (enrichments of over 2180 times compared to the continental crust).

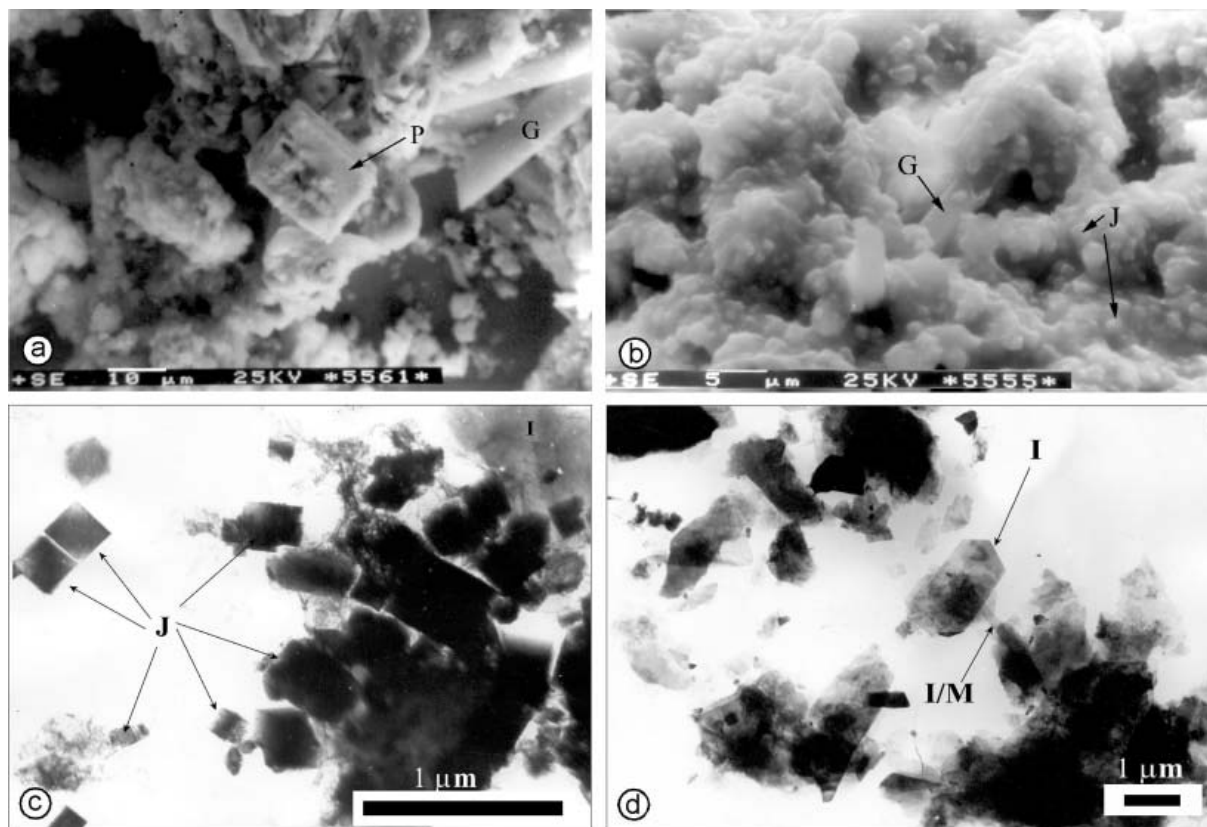


Fig. 3. SEM (a, b) and TEM (c, d) images of tailing samples: a, b sample T47 (Brăzești tailing); c – sample T72 (Valea Ciuții tailing); d – sample TS1 (Brăzești tailing). P – pyrite, G – gypsum, J – jarosite, I – illite, I/M – illite/montmorillonite.

Compositionally, the tailings from Brăzești are similar to the other storages, consisting of feldspars, quartz, muscovite, reduced amounts of sulphides and other various transformation products. The analysis of the material from a local effluence area revealed high amounts of jarosite and less illite, gypsum and quartz (Fig. 3 a,b,d). In the samples from the storage, taken at depths of 0-100 cm, TEM analyses indicate the presence of interstratified clay minerals (illite/montmorillonite), of illite and of sulphides. The arsenic concentration in the waste rock is comprised between 400.6 and 462.1 ppm, while in the effluents it reaches 1623 ppm (4 times higher than in the tailing) (table 1). The situation is similar in the cases of zinc and copper. Zinc has concentrations of 129.7-180.8 ppm in the waste rock and 281 ppm in the waste rock from the effluence area, i.e. ~ 2 times higher. The copper concentration in the tailings is between 17.5 and 18.1 ppm while in the effluence area is 35.6 ppm (up to 2 times higher).

The lead and barium concentration in the tailings and in the effluence area do not show very significant differences. Lead and barium form low-solubility compounds, so their mobilization is difficult.

The presence of arsenic and arsenic minerals within the ores from Baia de Arieş, Roşia Poieni and Roşia Montană is well documented. However there is no report on the potential impact of waste rocks and tailings storages over the environment and population. The samples from waste rock piles, tailings storages and effluents from Baia de Arieş and Roşia Montană indicate high arsenic concentrations (48.4 – 2183 mg/kg).

The villagers from Brăzeşti use the old waste rock piles for grazing, and the effluents– by intentional breaking of the exhaust pipes – for watering cattle. This makes the risks of arsenic intoxication much higher.

The chemical analysis of ochre sample T97 (Seliştei tailing) shows a large iron content (56.58 %), as well as of silica (35.65 %) and SO₃ (1.573 %). The X-ray diffraction only showed the presence of amorphous HFO (iron oxy-hydroxide) (Fig. 4). Due to the high iron concentration of the sample, it shows fluorescence under the incidence of the X rays and determines a high background noise and the decrease in the intensity of the diffracted rays, which makes this kind of analyses very difficult.

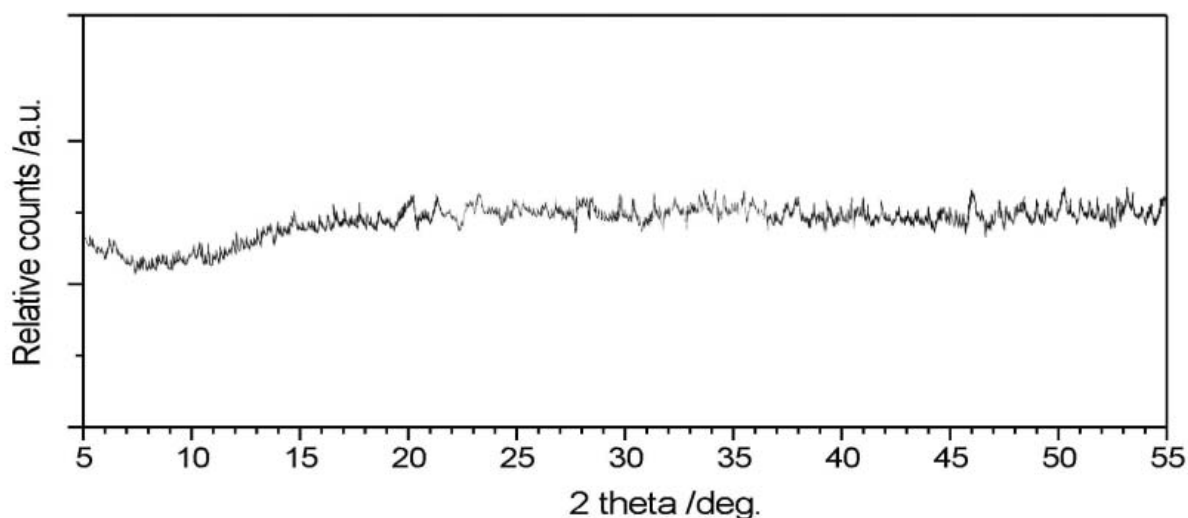


Fig. 4. XRD analysis of sample T97 (Valea Seliştei tailings)

The sample was treated with 0.3 M ammonium oxalate at a pH=3 according to the method used by Schwertmann (Schwertmann, 1964, cf. Lin and Herbert, 1997) in order to remove the weakly crystallized iron oxy-hydroxides. The repeated attempts to use this method gave no results, therefore we assume that the iron is present mainly under the form of amorphous oxy-hydroxides and hydroxy-sulphates. The presence of iron hydroxy-sulphates cannot be accounted with certitude on the basis

of the chemical analyses due to the possibility of adsorption of sulphate at the HFO surface (Webster *et al.*, 1998). As well, a part of SiO₂ appears as a low-ordered gel with no XRD peaks even if it occurs in large quantities.

The amorphous iron hydroxides and hydroxy-sulfates have a large specific surface and may adsorb important amounts of metals. The XRF analysis has shown many metallic elements, of which the high concentration of arsenic is worth noting (1960 ppm).

The main sources for arsenic are arsenopyrite, pyrite and arsenic sulpho-salts. The arsenic concentration in the aqueous phase is controlled by anion exchange reactions, by processes of coprecipitation with iron and manganese oxy-hydroxides, by the redox potential and pH. Arsenic mobility is controlled by the sorption on amorphous iron hydroxides and on carbonate minerals. Iron geochemistry is the basis of the main mechanisms which control arsenic mobility in acid environments, at pH<4 (Williams, 2001). Fe³⁺ precipitation may reduce the amount of arsenic in the water with 99% (Cadena and Kirk, 1995). Several experiments have shown that As³⁺ and As⁵⁺ are normally fast and strongly adsorbed by HFO at a pH of 6-7, in normal conditions (25°C and 1 bar) (Bowell, 1994). The high concentration of arsenic in sample 97 may be explained by this phenomenon. In case that the pH is low (sample 99), arsenic is mobilized in solution and only a small amount is retained by HFO.

The study of Smith *et al.* (1992) on the partition of arsenic between water and suspensions from AMD in various geologic settings from Colorado (USA) indicates a strong sorption of arsenic on SPM (Suspended Particulate Matter) at pH>5. The sorption on iron-rich suspensions seems to control arsenic partition between dissolved phase and suspensions. Webster *et al.* (2000) studied the source of metals and their mode of transport in the hydrographic basin of Hatea river (Whangarei, New Zealand), noting the high concentration of arsenic in SPM (consisting of quartz, feldspars, micas, chlorite-vermiculite and diatoms), even if arsenic is predominantly in the dissolved phase. The study of chemical processes which affect the transport of metals in the Waihou river (New Zealand) and in its estuary was done by Webster (1995), who has shown that arsenic is partly adsorbed over iron hydroxides in suspension and that most of the arsenic is transported under dissolved form.

Goethite and ferrihydrite may transport arsenic (Hudson-Edwards *et al.*, 1999). The mobility of arsenic in natural waters is controlled by its sorption on mineral particles (Mok and Wai, 1994). In the opinion of Hudson-Edwards (1999) arsenic is harder to mobilize from alluvia, tailings storages and waste-rock deposits due to its adsorption on iron oxy-hydroxy-sulphates.

The presence of arsenic in sample AB1 and the presence of goethite in sample SM-8 and SM-7 indicate the possibility of arsenic sorption on iron hydroxides.

More thorough studies are needed in the future to clearly establish the arsenic migration ways and its potential risk for the environment and population.

In numerous points from the perimeter of the Valea Seliștei tailings, we observed iron hydroxides precipitating at a pH for which thermodynamic calculus indicates the impossibility of this phenomenon. The presence of bacteria may be the cause of the change in the pH values to establish thermodynamic equilibrium. To verify this idea we analysed the green “material” found both at the Valea Sartășului tailing storage as well as in the ARD (acid rock drainage) – type effluents from Roșia Montană.

The wet mounts prepared from the material sampled in the summer of 2001 indicate the presence of large populations of *Euglena mutabilis* (Fig. 5). This is the first record of this species from a Romanian mining area.

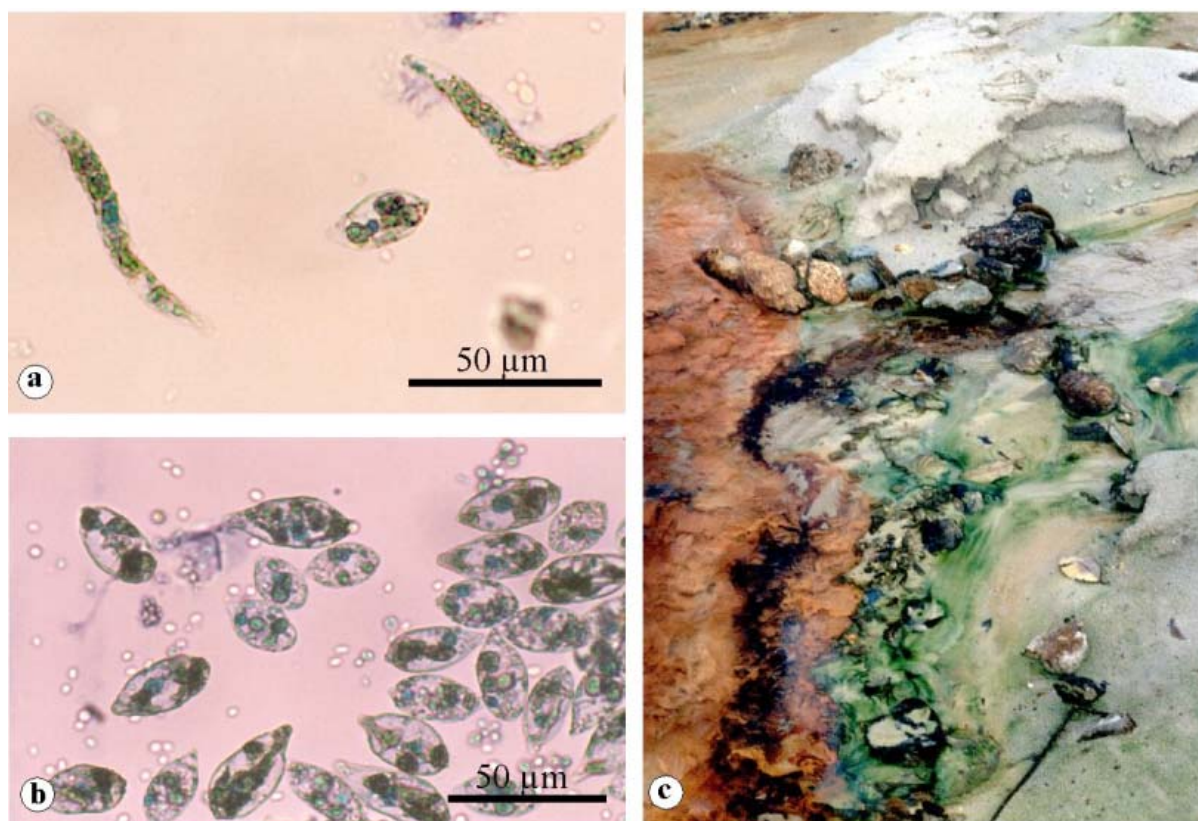


Fig. 5. *Euglena mutabilis* Ehrenberg 1838, image at a transmission optical microscope (sample 3142). a,b – living (fusiform) and dead (roundes) individual; c – green mats in the effluent.

The first mounts prepared from the samples with *Euglena* were done two days after sampling. Most euglenas (with very few exceptions) had an elongated fusiform (anterior rounded and posterior tapered) morphology (with a length of approximately 70 – 100 μm and with of 25-30 μm) and were flagellum-less. The wet mounts

prepared by coloration with methylene blue to show both internal and external structures did not reveal the presence of the flagellum. The lack of flagellum at this species was also observed by Brake *et al.*(2001). We initially considered that the rounded shapes from our samples represent in fact other microorganisms. Later (after 3 months), in the mounts prepared from the same material, most of the shapes were rounded. Our conclusion is that rounded forms were dead individuals, while the fusiform ones were still alive.

This microorganism is an unicellular protozoan found in the ARD of several coal mines from Indiana (SUA) (Brake *et al.*, 2001).

According to Brake *et al.* (2001) these organisms are capable of living in extremely acidic conditions (pH = 1.7) with TDS = 18 g/l. The authors cited established the pH interval where these organisms develop (1.7 – 4.6), with the most prolific development between pH 3 and 3.5. Our studies indicate same behaviour for *E. mutabilis* (Fig. 6).

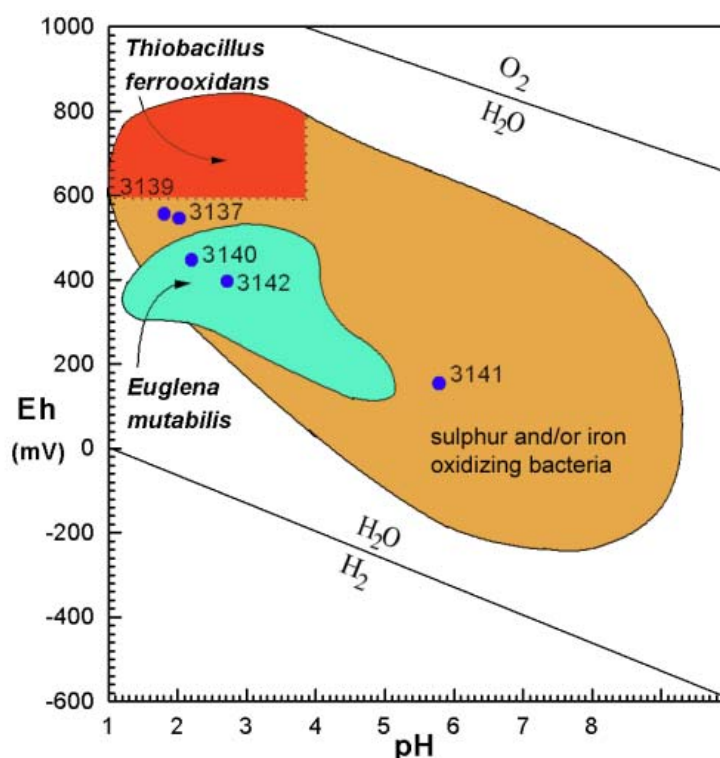


Fig. 6. Eh and pH conditions for samples with *Euglena mutabilis* taken from the effluents from Valea Seliștei and Roşia Montană (Cetate) tailings storages represented in the diagram of optimum fields for the development of some microorganisms (optimum fields diagram is after Brake *et. al.*, 2001).

The role of microorganisms in geochemical processes occurring in Roşia Montană mining district is not fully established. Several studies indicate that such

microorganisms, when developing prolifically, are capable to increase the concentration of dissolved oxygen with up to 200 %. Moreover, the presence of some crystals in the cell of this microorganism points to the possibility that they somehow control metal precipitation from solution (Brake *et al.*, 2001).

Based on the analysis of samples taken from tailings we could elaborate a simplified scheme of the main reactions that occur (Fig. 7).

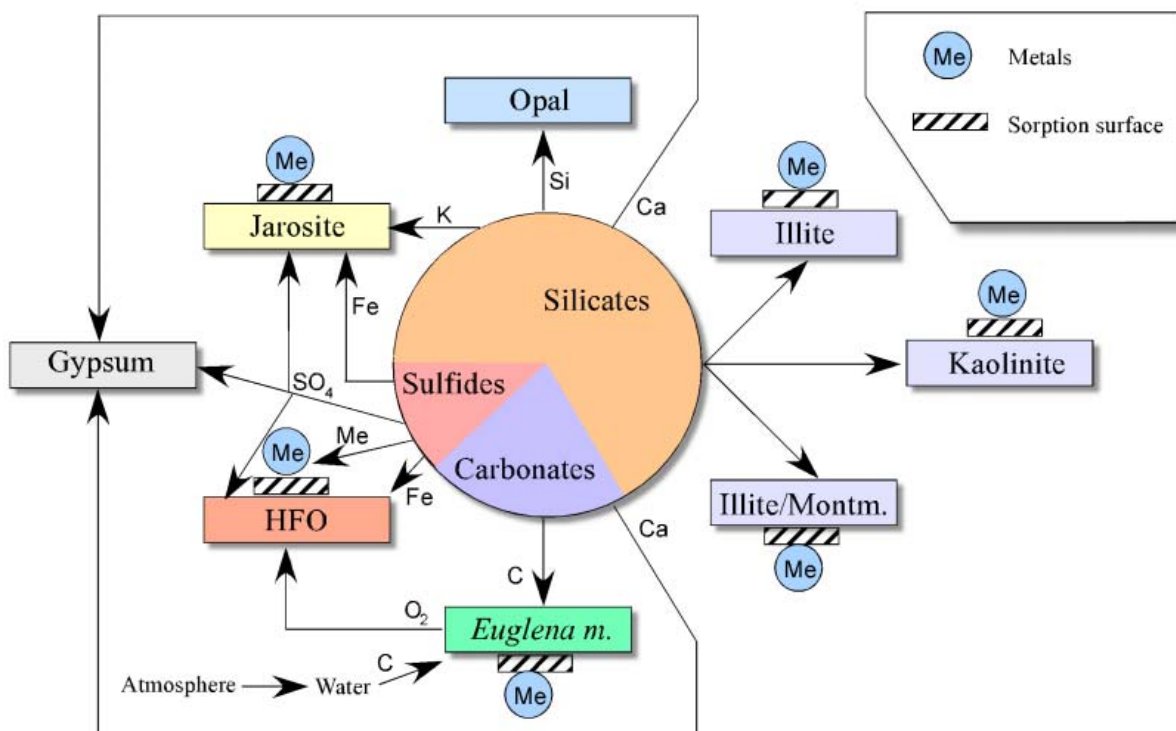


Fig. 7. The main chemical reactions occurring in the studied tailings. HFO – iron oxide or oxy-hydroxide ± sulphate.

The main sources for secondary minerals are silicates, sulphides and carbonates from the tailings. Due to the fact that the tailings are not completely covered with water, sulphides are affected by intense oxidation. The acid environment and the large specific surface of the material from the tailing enhance the alteration of silicates and carbonates. The elements resulted from alteration combine, forming jarosite, gypsum, HFO (iron oxide, iron oxy-hydroxide) ± sulphates, opal, kaolinite, illite, illite/montmorillonite. Some of the secondary minerals may retain metals by sorption. In the case of some minerals with low solubility such as jarosite, sorption is favourable for the environment only if the mineral is stable. Though jarosite is not too soluble, it transforms in time in goethite, therefore it only serves as a temporary host for toxic metals.

Iron oxides, hydroxides oxy-hydroxides and oxy-hydroxy-sulphates, as well as clay minerals with the capacity of metal adsorption form a peculiar group of minerals. These iron minerals, most with poor crystallinity, together with primary or secondary clay minerals (illite, kaolinite, illite/montmorillonite) may contribute to the mobilization/immobilization of some metallic elements. Due to their very small dimensions, the particles may rest in suspension even when the energy of the river is low.

7. Groundwater geochemistry

The water samples taken from wells (Fig. 8) were analysed with the capillary electrophoresis (using a Waters Quanta 4000-type device). The analysis of the waters from wells located on the Arieș valley, in the Cheia – Baia de Arieș area, indicates several geochemical phenomena contributing to defining their characteristics.

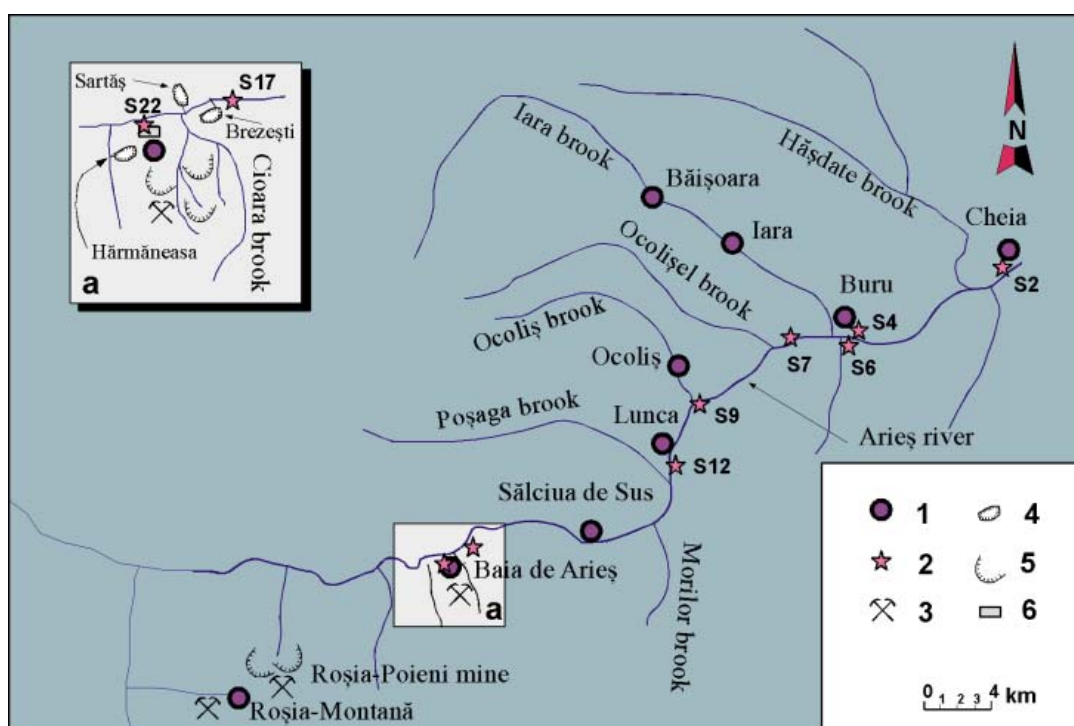


Fig. 8. Sketch of the sampling stations. 1 – villages; 2 – sampling stations with afferent codes; 3 – mines; 4 – tailings storages; 5 – waste rock embankments; 6 – ore preparation plant.

Close to the mining area, the pH of the wells water samples are little lower than in the other samples (Fig. 9 a) due to influence of mining activities (specially the

oxidation of ore deposits and a waste dumps). Sodium concentration in the wells varies between 6 and 141 mg/l (Fig. 9 b).

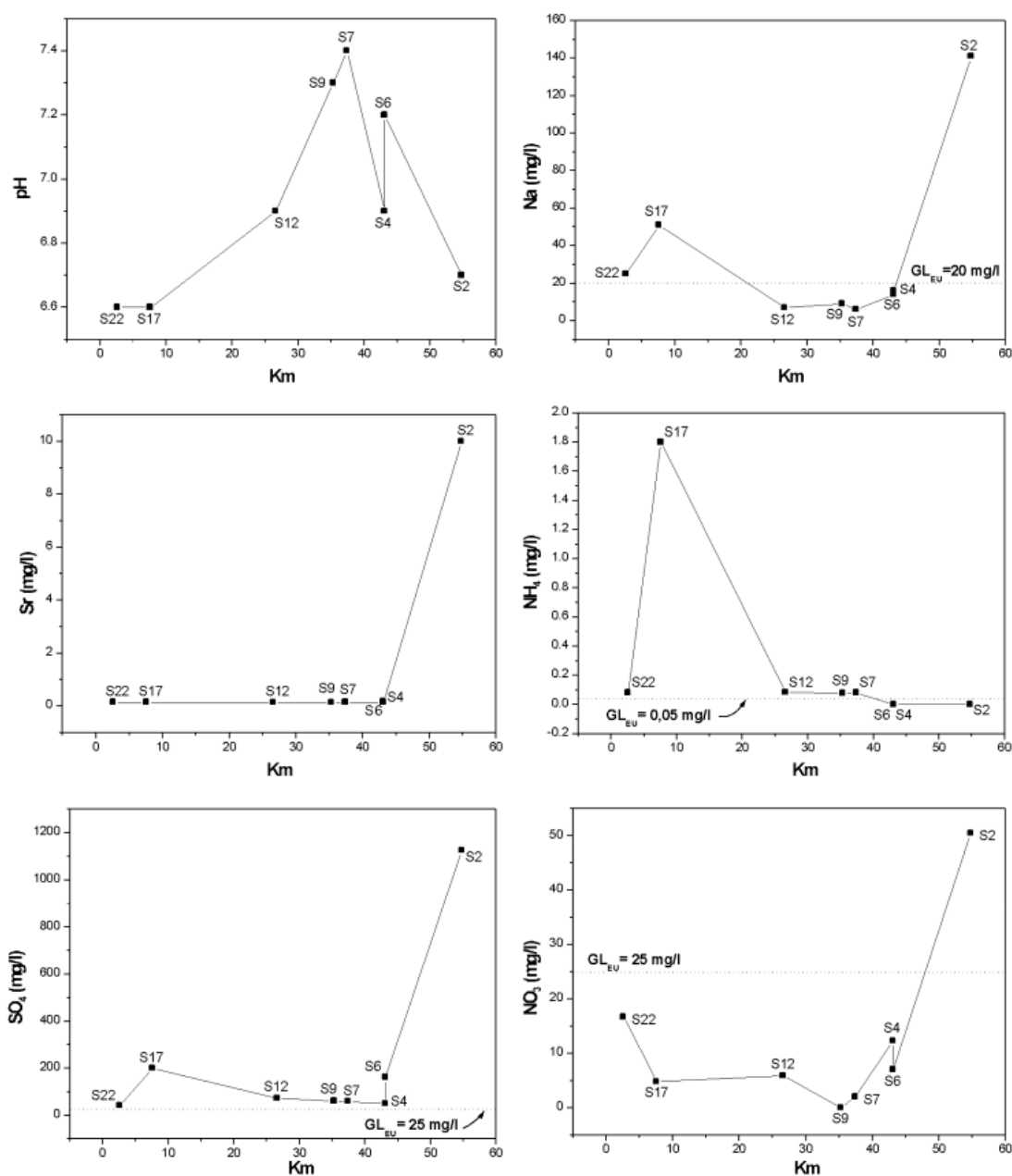


Fig. 9. Graph of pH and Na, Sr, NH₄, SO₄, and NO₃ concentration variations in well water with distance from Baia de Arieş mining area. GL_{EU} – EU guideline for drinking water; GL_{WHO} – WHO (World Health Organisation) guideline for drinking water.

According to E.U. standards for drinking water, sodium concentration must not pass the recommended value of 20mg/l. Three samples (S22, S17 and S2) pass this value. The high Na concentration clearly decreases with the distance from the mining area. High Na values from Baia de Arieş and Brezeşti tailings storage may point to pollution with sodium cyanide, but also to a significant contribution due to the

alteration of plagioclase feldspars from the tailing or from the superficial part of the ore.

Strontium from well water varies between 0.145 and 10 mg/l (Fig. 9 c), but most samples have less than 0.2 mg/l. Sample S2 has the highest Sr concentration (10 mg/l), probably determined by its mobilization from mollusc shells in the limestones. Studies on gastropod shells by X-ray fluorescence have shown the presence of strontium. Its high mobilization capacity explains the higher concentrations from wells dug in the Neogene fossiliferous deposits.

NH_4^+ concentration in well water varies between 0 and 1.8 mg/l (Fig. 9 d). According to E.U. standards for drinking water, it should not pass a recommended value of 0.05 mg/l. Five samples (S22, S17, S12, S9 and S7) pass this value. The main sources for NH_4^+ are fertilizers (both natural and chemical ones), household effluents (i.e. inadequate piping etc.) and especially effluents from stables (i.e. lack of septic pits). NH_4^+ enrichments 36 times higher than recommended values from Brezeşti are due to effluents from stables.

SO_4^{2-} concentration in well waters varies between 53 and 1126 mg/l (Fig. 9 e). According to E.U. standards for drinking water, it should not pass a recommended value of 25 mg/l. In all eight sampling stations SO_4^{2-} concentration passes this value. The main sources for SO_4^{2-} are sulphides from ore, waste rock, and tailings, and sulphates from geological formations (i.e. Neogene gypsum-rich formations). A significant increase (8 times higher than recommended values) has been registered in sample S17, but this increase may be also noticed in surface waters.

The sources of sulphates are mining activities (Baia de Arieş mining area and Sartăş and Brezeşti tailings storages). Downstream Brezeşti, sulphur concentration decreases, but remains more than two times higher than the limit established by the E.U. Further downstream, in Cheia (sample S2), sulphate concentration largely increases (45 times higher than the E.U. recommended value). The latter is due to the high sulphate content from the Neogene formations, which host the ground water.

NO_3^- from well water varies between 0 and 50.5 mg/l (Fig. 9 f). According to E.U. standards for drinking water, NO_3^- concentration should not pass a recommended value of 25 mg/l. This value is exceeded in one of the eight stations sampled (S2). The main sources for NO_3^- are chemical fertilizers, but the bacterial activity from the ground water is also worth mentioning (oxidation of NH_4^- compounds from stables). Concentrations over 44.3 mg/l may provoke the so-called “blue baby” syndrome. Fortunately at Cheia well waters are used only for watering animals, the population using tap water for household and drinking.

8. Surface water geochemistry

The pollution produced by tailings storages was shown by variations in the concentration of selected elements in the Arieş River. Inactive tailings storages like the ones between Baia de Arieş and Brezeşti contribute to the pollution of surface waters. The Brezeşti tailings locally pollute the Arieş River with barium.

The direct discharge of waters from tailings storages in the local hydrographic network, without previous treatment (Valea Hărmăneasa) or with a summary, uncontrolled treatment (Valea Sartăş) leads to a strong pollution of surface waters (see **Appendix I**).

Using the element concentrations determined with the capillary electrophoresis (Forray and Hallbauer, 2000) we performed a factorial analysis to establish the main sources of pollution (Forray, 2001a). Factorial analysis allowed us to determine the percent participation of selected economic branches to the chemical composition of the Arieş River. The pollution induced by tailings storages is somewhat reduced (17%), while the extractive industry participates with 23%, which indicates a strong pollution of the total mining activity. Globally, mining activity is responsible for 40% of the chemical characteristics of the water from the Arieş River. The high value shows that the extractive activity from the mining area determines a high degree of pollution of the Arieş River.

The analyses revealed a series of phenomena (rock-water interface reactions, chemical reactions produced at confluences of rivers with different chemical characteristics and adsorption phenomena) with a significant contribution to the changes in the chemical characteristics of the Arieş river waters, diminishing pollution. Water-rock interaction phenomena were confirmed by statistical analyses, their participation to establishing the chemistry of the Arieş river waters reaching 39%.

Aside from mining activities, other local sources are also responsible for local pollution, such as human activities (determined by factorial analysis), through discharges of effluents from households or stables.

Comparing the results obtained based on the *pollution index* (defined by Forray, 2001b) with the results of the factorial analysis or with the variations in element concentrations (between the villages of Muncel and Cheia) we could confirm the same pollution characteristics. The method of the pollution index proves useful in classifying the pollution by comparing the values of element concentrations from polluted and non-polluted rivers.

In the Roşia Montană – Lupşa area we took 22 water samples from Roşia and Abrud creeks and from the Arieş river to determine the dissolved metal concentration in two different moments. Sampling was done in two stages, one on dry weather and the other one after strong rains. The study of the metal transport in the Roşia Montană – Lupşa area has shown high metal concentrations in the Roşia creek and Abrud river, while during heavy rains the concentration of dissolved metals increases. The 22 samples were analysed by ICP-OES and AAS.

When representing the total concentration of zinc, copper and lead vs. pH in a rainless period (ICP-OES analysis) and after heavy rains (AAS analysis) one can notice high differences between the total concentrations of determined metals (Fig. 10). In the Roşia Montană area these differences are smaller, while downstream they increase substantially. The highest differences were registered for zinc and lead.

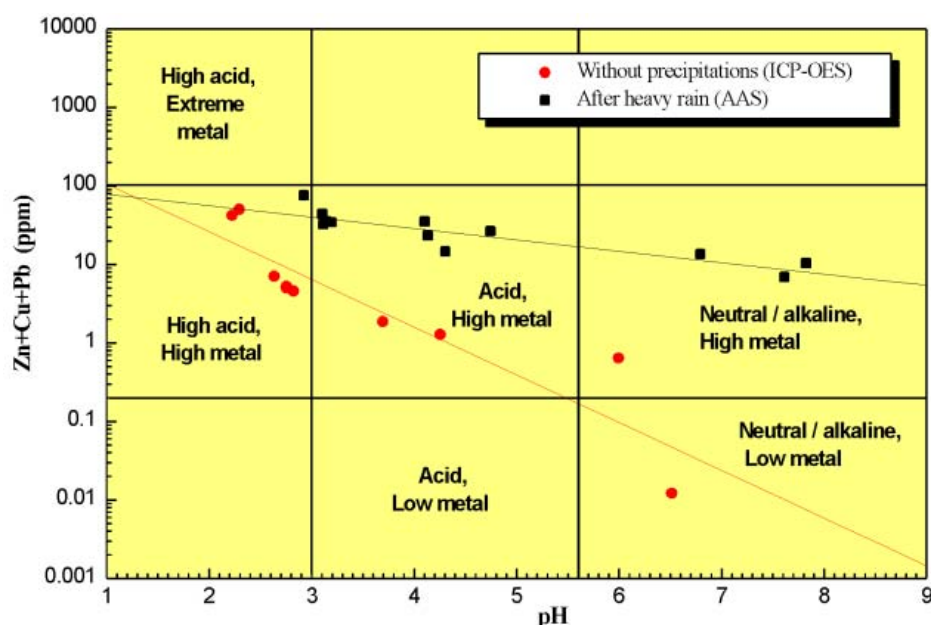


Fig. 10. Representation of total concentration of zinc, copper and lead vs pH in rainless periods (ICP-OES analysis) and after heavy rains (AAS analysis). Diagram type is after Ficklin et al., 1992, with some changes.

During wet periods, the amount of transported zinc increases with up to 1100 times in the Arieş River 200 m downstream from the confluence with Abrud creek. The transport of lead is generally as suspensions but during rainy periods a supplementary transport, as dissolved substances, also occurs.

Iron oxy-hydroxides, both in suspensions and in colloidal form, precipitate in the Roşia creek downstream Roşia Montană. The precipitates generally known as ochre (Fig. 11 a, b), have a yellow, brown or reddish brown colour and cover rock fragments from the riverbed with a crust with thicknesses comprised between several mm and several cm. One could notice alternating lighter and darker bands.

The X-ray diffraction of the crust (Fig. 11 d) indicates the presence of iron oxyhydroxides with very low cristallinity (“amorphous”). Some small peaks of jarosite $KFe_3(SO_4)_2(OH)_6$ (JCPDS 22-827), quenstedtite $Fe_2(SO_4)_3 \cdot 10H_2O$ (JSPDS 17-160), goethite $\alpha-FeO(OH)$ (JCPDS 29-713) and illite could be also noticed. The presence of amorphous HFO in the sample is shown by the high background and by a decrease in the peak intensities.

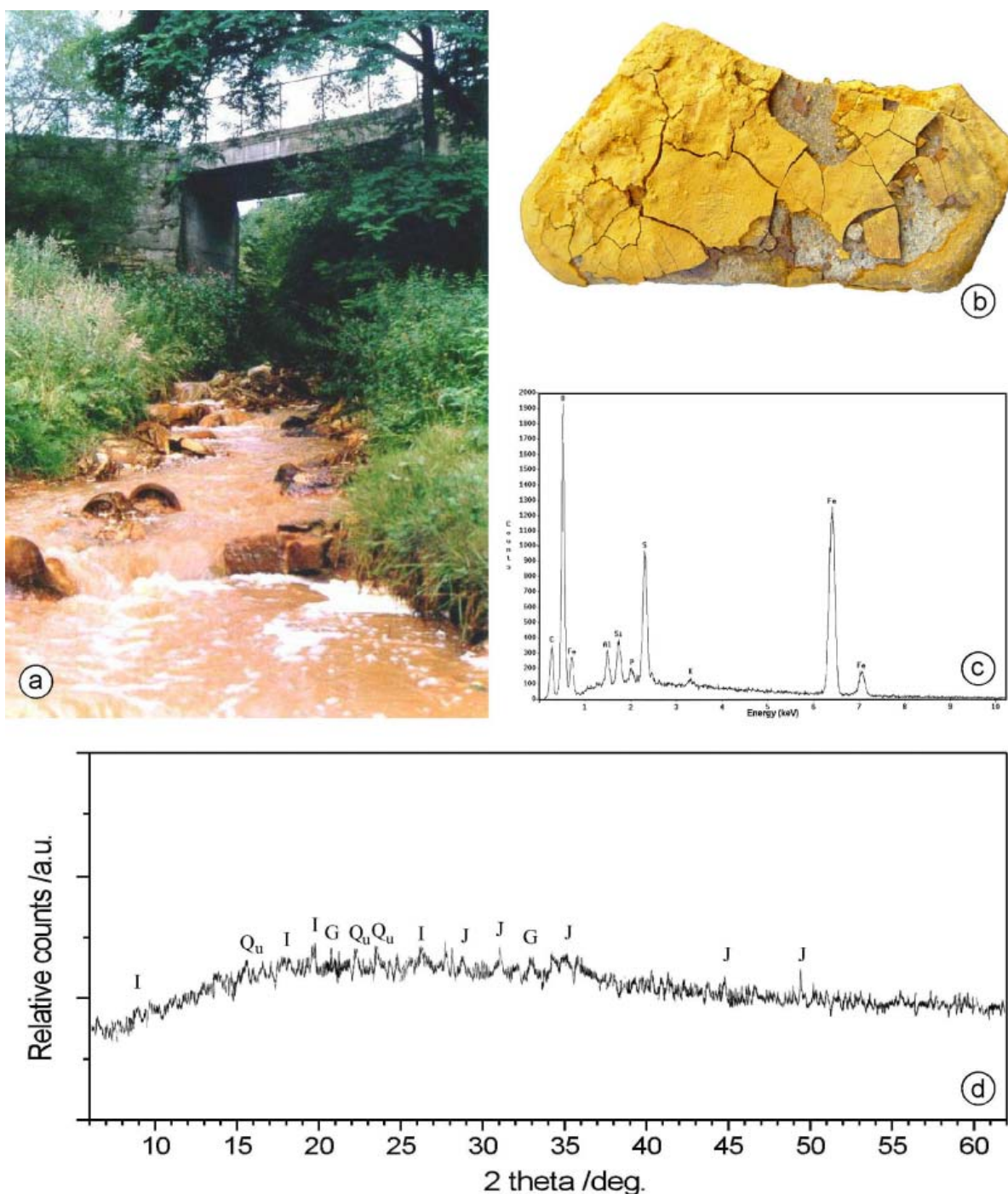


Fig. 11. Ochre precipitates. a – image of Roşia creek downstream the discharge from the main gallery (pH=3.15); b – HFO crust (sample 82); c – SEM-EDS analysis of crust in sample 82; d –XRD analysis of sample 82.

The quantitative analysis of the ochre crust (sample 82) done with a SEM with EDS device (Energy Dispersed Spectrometry) shows amounts of aluminium, silicon, calcium, iron, phosphorous, sulphur, potassium and to a lesser extent copper and arsenic (Fig. 11 c).

Thermodynamic calculus done with Minteqa2 software (Allison et al., 1991; US EPA, 1999), using the chemical composition of water in the sampling point for sample 82 (water sample 44, analysed with ICP-OES), indicates the possibility of formation of several minerals with aluminium and iron (ferrihydrite, goethite, hematite, hydronium-jarosite, jarosite and lepidocrocite). The thermodynamic modelling was done for a case in which element concentrations do not change substantially from dry to wet periods. The change of these conditions is influenced by the durations of rains, their frequency and intensity. The modelling for quenstedtite precipitation could not be realized due to the lack of thermodynamic data. Thus it cannot be stated whether this mineral was formed directly by precipitation or it is a secondary mineral, derived after sampling.

The main sources for phosphate in the water of Roşia creek are household effluents, rich in detergents. The presence of phosphate in the water strongly influences arsenic adsorption on HFO. Arsenic is a mobile element and its concentration in the water of Roşia creek is controlled by the precipitation of iron oxides, oxy-hydroxides, hydroxides and oxy-hydroxy-sulphates. The quantity of arsenic in solution is reduced through sorption/co-precipitation on the iron minerals mentioned. As the phosphate concentration in water increases, a competition appears between phosphate ion and arsenate ion. Phosphate removes the arsenic from iron oxy-hydroxides, remobilising it.

The analysis of ochre crusts (sample 82) indicates large quantities of adsorbed copper, while Zn and Pb are under the detection limit. The greater mobility of zinc may explain its lack in the precipitate. This greater mobility in surface waters was also noticed in Muncel - Cheia area (Forray and Hallbauer, 2000). Lead is an element with very low mobility due to the low-soluble salts formed. This is why it is present mainly as mineral fragments.

The concentration of dissolved metals in Roşia and Abrud creeks and Arieş River is very high compared with unpolluted waters (table 2). Minimum values of metal concentration measured are on average four times higher than unpolluted waters, while maximum values are 3000 times greater than normal values.

Table 2

Concentration of Mn, Cu, Ni, Cd, Co, Fe, Zn, Pb, Al in unpolluted waters (after White, 1998) and in Roșia and Abrud creeks and Arieș river (minimum and maximum values). Values in brackets show how many times the measured metal concentration passes the value of unpolluted rivers.

Element	Unpolluted river ¹ mg/l	Minimum value mg/l	Maximum value mg/l
Mn	0.0082	0.039 (5)	80.4 (9805)
Cu	0.0015	-	1.1 (733)
Ni	0.0005	-	0.29 (580)
Cd	0.00002	-	0.13 (6500)
Co	0.0002	-	0.26 (1300)
Fe	0.05	0.17 (3)	204.2 (4084)
Zn	0.03	0.012 (0.4)	42.6 (1420)
Pb	0.00001	-	0.163 (16300)
Al	0.05	0.15 (3)	260 (5200)

9. Suspended particulate matter

In order to study the transport of metals in suspension, we took 9 water samples from Arieș River, Abrud and Roșia creeks (Fig. 12). On the studied sector, substances in suspension vary between 71 and 282 mg/l.

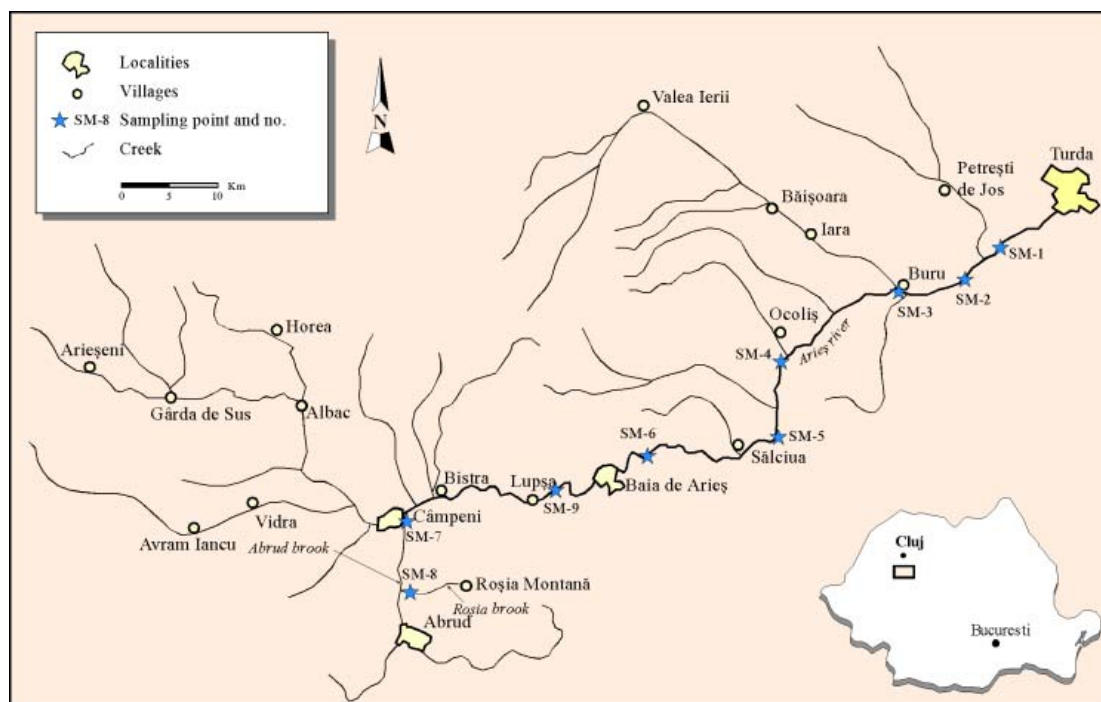


Fig. 12. The map of the upper basin of the Arieș River and the location of sampling stations for SPM.

These values are determined by the formations crossed (Cretaceous and Neogene sedimentary formations), but especially by Roșia Montană, Roșia Poieni and Baia de Arieș mining enterprises. The measurements indicate a larger quantity of dissolved substances than the suspended particulate matter. The average for the three watercourses is 64% (for transport in solution) and 36% (for transport in suspension).

Mineralogically the suspensions consist of quartz, mica, illite, kaolinite, feldspar, gypsum and some other components of various magmatic and metamorphic minerals, and some unidentified biological fragments and diatoms (Fig. 13).

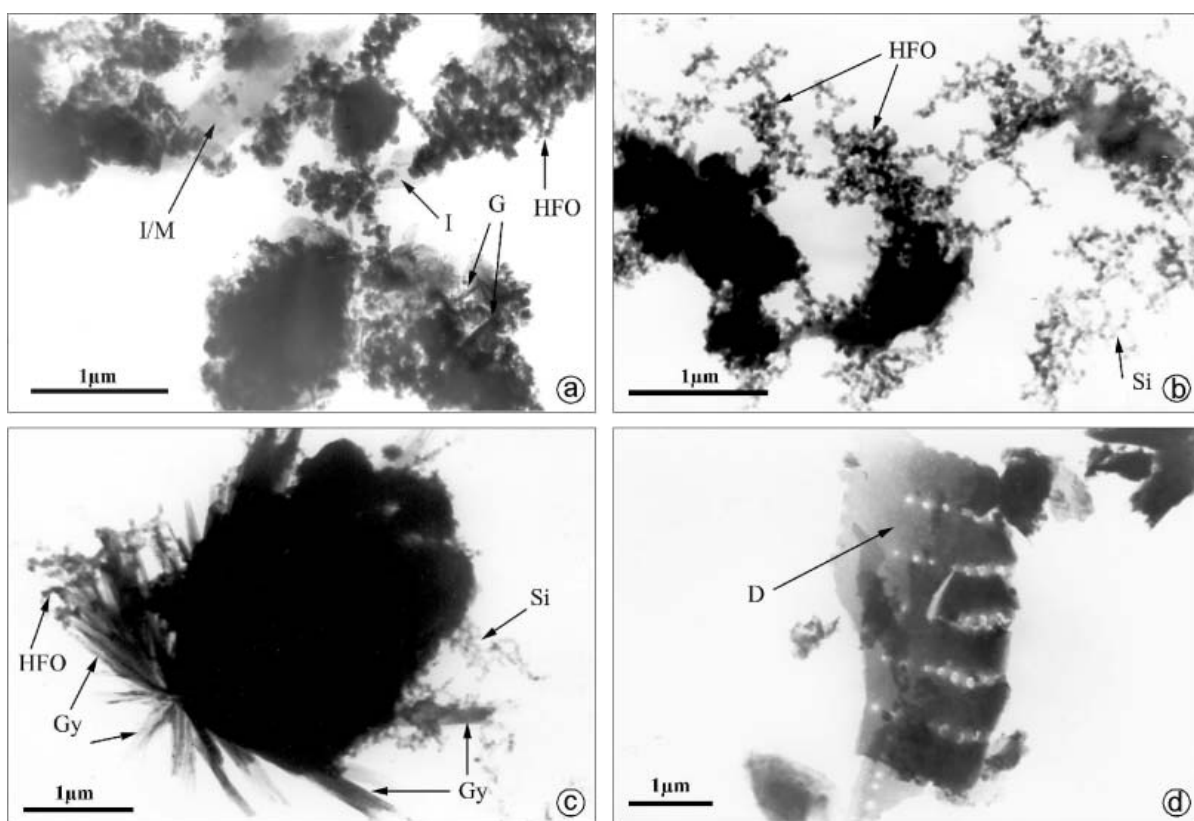


Fig. 13. TEM images of SPM samples. a – sample SM-4; b, c – sample SM-8; d – sample SM-9. I/M – Illite/montmorillonite, I – Illite, G – goethite, HFO – iron oxy-hydroxides, Gy – gypsum, Si – opal, D – diatoms.

The average percent composition of the SPM from the Arieș river shows the predominance of quartz (31%), kaolinite (25%) micas (16%) and feldspar (14%), the rest (gypsum, alunite and others) representing 15%. The composition of Roșia and Abrud creeks differ substantially both by the percent participation of minerals and by the presence of some specific minerals. The average percent composition of the SPM from Roșia and Abrud creeks indicate the predominance of kaolinite (32%),

micas (24%), and gypsum (14%). The presence of goethite is characteristic (8%). Feldspars and other minerals totalise 12%.

The XRF analyses have shown (Fig. 14) large concentrations of iron, and to a lesser extent, copper, zinc, arsenic, lead and manganese.

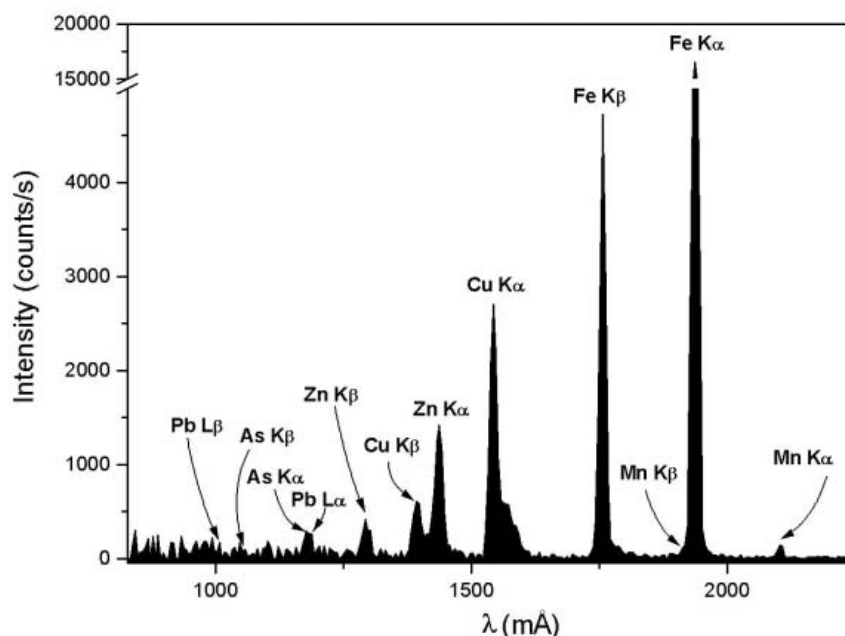


Fig 14. XRF analysis of sample AB1, taken from Abrud River 50m upstream the confluence with the Arieş River.

10. The influence of pollution on fauna

During the activity of organisms, pollutant substances may accumulate in the tissues of plants and animals in concentrations many times larger than the ones of the environment. As the organisms reflect the degree of pollution of a well defined area, it is necessary that the habitat be restricted to an area as small as possible. Gastropods are very useful on this purpose (Yasoshima and Takano, 2001).

Samples were taken from 15 areas from the southeastern Apuseni Mountains (Fig. 15). A part of the samples were taken from areas polluted by the mining industry, i.e. Arieş valley (Duma, 1998, 1999; Forray and Hallbauer, 2000; Forray, 2001b, a) Ampoiului valley (Williamson *et al.*, 1996; Rusu *et al.*, 2000).

In the areas strongly polluted with metals from Ampoiului valley, the vegetation is scarce and we could not sample *Cepaea sp.* gastropods. Samples were taken also from areas considered as not polluted with metals, such as Tureni Gorges (Turda), Paiului Hill (Füstösgödre, Deva) and Făget (Cluj).

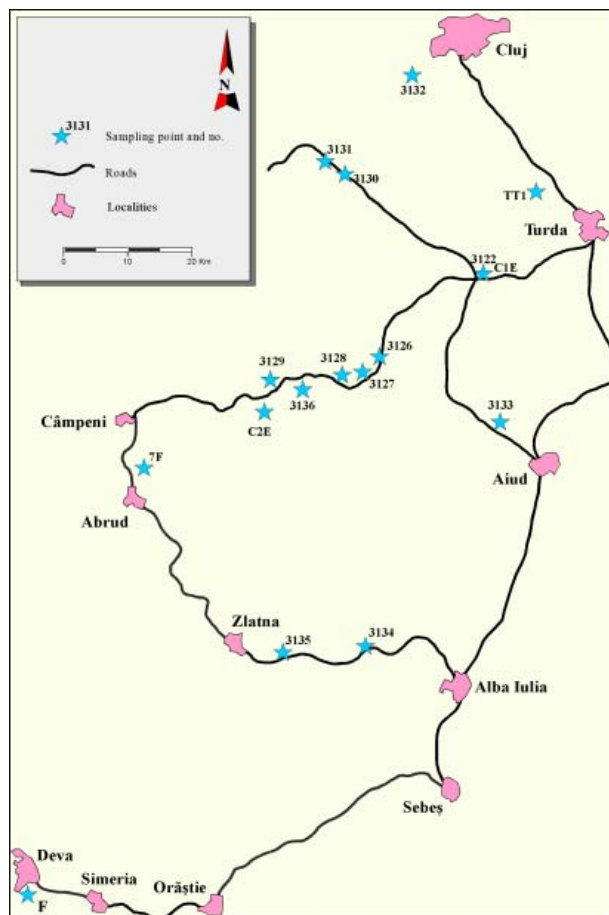


Fig. 15. Sketch of the sampling region.

A total of 242 shells were taken, of which 3 *Helix aspersa*, 229 *Cepaea vindobonensis* (Fig. 16) and 10 *Campylaea faustina*. Our observations, except sample 7F, were done on shells of dead specimens.

As dry rests from tissues could not be removed completely, it is possible that the results do not show in totality the copper concentration of the shell.



Fig. 16. *Cepaea vindobonensis* (Férussca) in the floodplain of the Arieș River (Buru).

The samples were analysed with XRD, XRF and potentiometry (with the ion-selective electrode ISE-Cu). The reference electrode used was RBD type Ag–AgCl. The copper ion-selective electrode is an EMIS-Cu, with a linear response for concentrations between 10^{-1} – 10^{-5} M copper, that is Cu^{2+} concentration between 0.63 and 6354 ppm.

X-ray diffraction for the three samples analysed (3128, 3126 and 3132) shows the presence of aragonite. No other crystallized mineral was evidenced.

X-ray fluorescence analyses of the shells show large amounts of strontium (Fig. 17). Strontium does not form separate minerals in the shells, but it substitutes calcium in the crystalline lattice of aragonite, as it allows substitution with ions with ionic radii > 0.99 (calcium ionic radius; i.e. Sr, Pb, Ba etc.) (Koch and Sztrókay, 1994).

The presence of copper was shown in the shells from an area unpolluted with metals, as the main blood component of gastropods is hemocyanine $\text{Cu}^+/\text{Cu}^{2+}$ (proteine linking a molecule of oxygen between two ions of copper). Thus it is expected that all gastropods have a certain amount of copper.

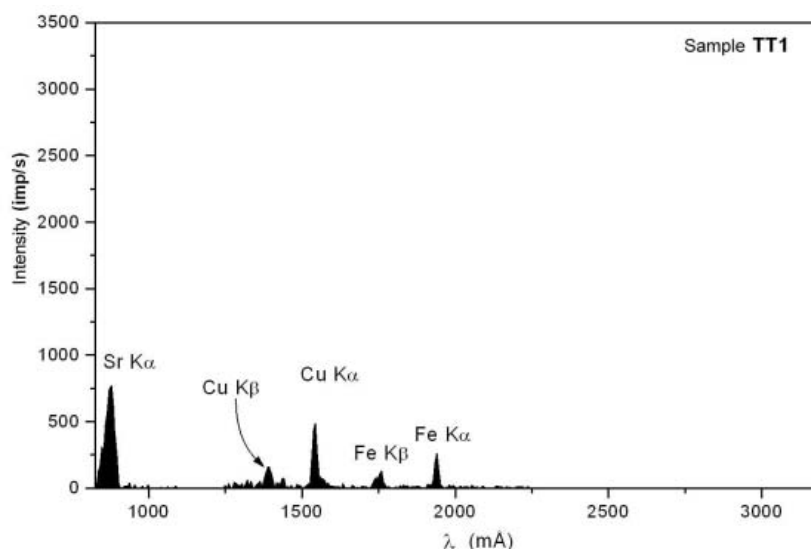


Fig. 17. XRF spectrum of sample TT1 (*C. vindobonensis*). Sampling site: Tureni Gorge.

The XRF analyses of shells taken from the embankment crest of the Seliştei Valley tailings storage reveal, together with large amounts of strontium, the presence of iron, copper, zinc, lead and manganese (Fig. 18), indicating large concentrations of metals in soil. The explanation of the mode of accumulation of metals in snail shells is difficult, because elements with an ionic radius smaller than calcium (Zn^{2+} , Fe^{2+} and Mn^{2+}) can replace it by diadochy only in the calcitic structure. So the accumulation of Zn^{2+} , Fe^{2+} and Mn^{2+} is realized by other mechanisms than diadochy.

The XRF spectrum obtained on shells of *Helix aspersa* point to an interesting phenomenon. Sample 7F (the only one belonging to a live specimen) has a larger quantity of strontium than sample C1E, (where we sampled the shell of a dead individual). This difference may be explained in two ways:

- Strontium concentration in the two environments is different;
- After the death of the animal, the aragonite from the shell becomes unstable and starts changing to calcite, losing some strontium. Aragonite transformation in calcite is a very common phenomenon. In the process of transformation from aragonite (rhombohedral system) to calcite (trigonal system), the structure will not tolerate the presence of strontium with a greater ionic radius and it will be gradually eliminated. The situation is similar for other ions with ionic radii larger than calcium (i.e. Pb^{2+}).

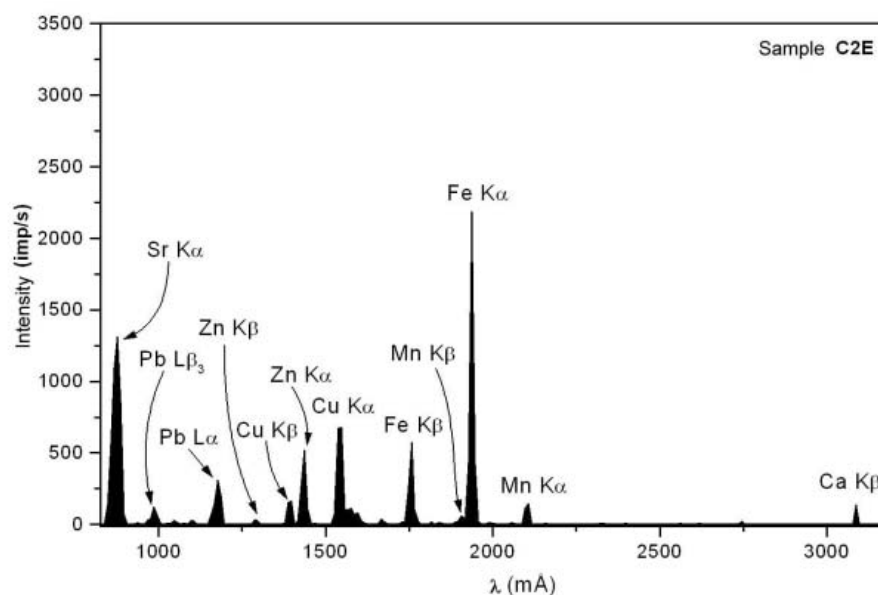


Fig. 18. XRF spectrum of sample C2E (Valea Ciuții).

Watson *et al.* (1995) state that the shells will keep heavy metals accumulated in either aragonitic or calcitic structure, even after the animal dies, in contradiction with the discussion above. Aragonite to calcite transformation takes occurs in a longer or shorter time, depending on the environment, the dimensions of aragonite crystals, aggregate geometry etc. Shells of dead snails mineralogically consist of aragonite, but their strontium concentration is smaller than in live individuals (observation based on the analysis of two shells). This may be explained by the relatively easy removal of strontium before important modifications in the mineral structure of the shell or by its removal by rainwater.

We are sure that future studies will bring much more data on the geochemistry of strontium and on the role of the crystallization process in the mobilization of both

strontium and different metals from the shell structure. We determined the copper concentration on a number of 60 shells, all of them showing values of more than 3 ppm.

The shells included in this study generally had similar dimensions, but we do not exclude the possibility that their ages influenced the results obtained. The presence of copper was confirmed both by XRF analyses and by potentiometric measurements. We consider that is determined by physiologic functions, indifferently if the shells were collected from areas polluted or not with metals.

Copper concentration in areas not polluted with metals (Buru, Iara, Cluj, Livezile, Deva and Tureni Gorge) is low (3-8 ppm); in average polluted areas (Ocoliş, Ampoi, Câmpul Poienii) it is generally under 15 ppm, while in the strongly polluted areas it reaches 28 ppm.

Studying the variations of the copper concentration for a certain sampling site, we could notice a relatively large deviation from the average value. Other researchers also observed this phenomenon. Watson *et al.* (1995) note that the variation of gastropod weights indicates large variations of metal concentration in the shells belonging to the same population.

The difference between the minimum and maximum copper concentrations measured at sampling sites is larger in areas polluted by the mining industry from Arieş valley than in unpolluted areas.

Several processes govern the accumulation of metals in the shells. In the case of carbonate shells, bivalent copper, with an ionic radius of 0.83 Å, can replace calcium (ionic radius 0.99Å) from aragonite only in very small amounts because the difference between the ionic radii is larger than 15%. The main way of copper accumulation probably is adsorption on carbonate surface, described by Schosseler *et al.* (1999).

More thorough studies are needed to clarify the mechanisms of accumulation and removal of strontium and heavy metals from snail shells.

11. Conclusions

The pollution induced by mining industry from the studied area depends largely on the characteristics of the mineralization (quantity of sulphides in the ore), the nature of the host rocks (carbonate rocks, andesites etc.) and on the extraction and preparation technologies. A significant role in mobilizing heavy elements is played by atmospheric precipitations and the suspended particulate matter (SPM). The high metal concentrations from the Arieş River (which may exceed tens,

hundreds or even thousands of times the values from unpolluted waters) are determined by the mining works at Roșia Montană, Roșia Poieni and Baia de Arieș. The influence of pollution may be also noticed on flora and fauna.

The large area and dynamics of the phenomena make impossible the approach of all problems linked to environment pollution from mining areas of Arieș valley. The topic remains opened for future research.

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Appendix I

A study of the pollution of the Aries River (Romania) using capillary electrophoresis as analytical technique

F.L. Forray · D.K. Hallbauer

Abstract This paper examines two issues, the extensive pollution occurring in the Aries River, NW Romania, as a result of unchecked discharge of mining effluents into the river system, and the suitability of capillary electrophoresis (CE) as an analytical method for investigations into water chemistry. The results confirm the first objective by providing details on the pollution of the Aries River and its geochemical system and demonstrate the usefulness of CE. In its upper reaches, the river system is characterized by high contents of SO_4^{2-} as a direct result of acid mine effluents and the oxidation of sulphide minerals on mine dumps as well as inflows from settling ponds. Although continuous dilution by natural branch waters and natural water-rock interaction reduces the pollution to some extent, the total level of SO_4^{2-} remains above European averages. The waters of the Aries River, by comparison, contain contents of Cu^{2+} and Zn^{2+} up to 100 times higher than those of unpolluted river water.

Key words Aries River · Capillary electrophoresis · Mining effluent · Romania

Introduction

The famous treasures of gold and silver from the Apuseni Mountains, NW Romania, have been systematically mined since Roman times. After some pause, the mining activity flourished again at the end of the 19th century.

Large amounts of Au, Ag, Cu, Pb and Zn were extracted. Native Tellurium T was first described from this area, as well as several other new minerals.

Apart from the development of the area in the wake of the mining activity, negative effects, such as forest clearing, waste dumps, settling ponds, and installation of technological equipment, had more and more impact on the environment.

Along Ariesului Valley, the main mining centres are Baia de Aries and Rosia Poieni. Other mines located in the Aries hydrographic basin are Masca-Baisoara, Rosia Montana, Bucium and others. They all contribute to the pollution of the river.

The acid mine drainage (ADM), which feeds directly into the Aries valley, represents the main cause of pollution.

Very rarely, are preliminary chemical treatments with calcium hydroxide or lime carried out. Because of its low pH, mine water can carry large amounts of metals (Wieder and Novák 1995; Durkin and Herrmann 1996; Gräber and Frimmel 1996; Robertson 1996) in solution or in suspension.

Another source of pollution is represented by waste dumps and settling ponds, which are usually placed near the Aries River. Because of their position, the waste dumps are purged by rainwater and the resulting water enters the phreatic water and/or the surface water. During periods of heavy rain, the river level rises sufficiently to reach the base of the waste dumps. Thus, large amounts of barren gangue can also be transported into the river system. Further, the stability of the settling ponds can be affected, endangering the downstream areas.

The technology of metal extraction was, in the past, of low efficiency and large quantities of sulphides were left in the host rocks and gangue. The oxidation of these sulphides then led to removal of soluble metal ions from the waste dumps under the effect of rainfall.

In addition to metals, the Aries River also contains organic pollutants, such as flocculants, surfactants, frothers and others, which originate from ore dressing plants. Further pollutants, not connected to mining, and collected by the Aries River, are the result of domestic and agricultural activities. The most important of such substances are nitrates and ammonium.

To study environmental pollution, several analytical methods can be used, which differ mainly in the pre-treatment of samples, detection limits and in the costs of

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the analyses. This paper presents the results obtained by using capillary electrophoresis (CE) for the analysis of water samples. The method was introduced by Hallbauer and others (1995) for the study of groundwater that was in contact with different types of rocks, or for other geochemical analysis (Hallbauer 1994; Hallbauer and others 1997). This relatively new method of analysis combines the advantages of low costs and high accuracy. Until recently, CE was almost exclusively used in the pharmaceutical industry (Jandik and Bonn 1993), but has developed rapidly into an accepted analytical technique for environmental analysis (Dabek-Zlotorzynska and others 1997).

The studied region and its geology

The area under study covers 54 km along the Aries River, between the municipalities of Cheia (downstream) and Muncel (upstream) (Fig. 1). The average flow rate of the river water in this region is about $24 \text{ m}^3/\text{s}$, ranging from $5 \text{ m}^3/\text{s}$ to $63 \text{ m}^3/\text{s}$. On both sides of the valley, the hills rise to between 1000 and 1200 m in height above sea level and the altitude of the river is $\sim 480 \text{ m}$ in the neighbourhood of Baia de Aries (Fig. 2). In the Muncel-Cheia region the flow velocities of tributary brooks into the Aries River varies between 0.01 and $2 \text{ m}^3/\text{s}$.

The studied region is characterized by a very diverse lithology, consisting mainly of metamorphic and sedimentary rocks, but also of intermediary, magmatic rocks of andesitic composition as well as some basic suites (Fig. 1).

The mining activities in the studied region take place in three major areas (Fig. 3).

1. Baisoara area. The mines in the Baisoara area are located along the Iara Valley, on the left tributary of the Aries River, in the neighbourhood of Buru village. The ore-bearing mineral assemblage is usually hosted by



Fig. 2
Photograph of the Aries Valley in the region of study

magnesium-rich skarns, pyroxene skarns and pyrometasomatic bodies. Detailed description of the ore mineralogy and geology are given by Lazar and others (1972) and Stefan and others (1988). The mining activities take place in underground works and the waste material is deposited in waste dumps or in settling ponds on the surface. The leachate waters, downslope of the dumps, are slightly alkaline (pH 8.02) and the amount of transported metals is very low (F.L. Forray unpublished data). The water of the river Iara, which flows into the Aries River in the neighbourhood of Buru village, thus does not contribute significantly to the pollution of the Aries River.

2. Baia de Aries ore. The Baia de Aries area is the main mining field in the study region. Detailed descriptions of the ore mineralogy and geology are given by Lazar (1966), Radulescu and Dimitrescu (1966), Stefan and others (1988), as well as by Udubasa and others (1992a). The mining is at present confined to underground workings. Because of an intensive oxidation of

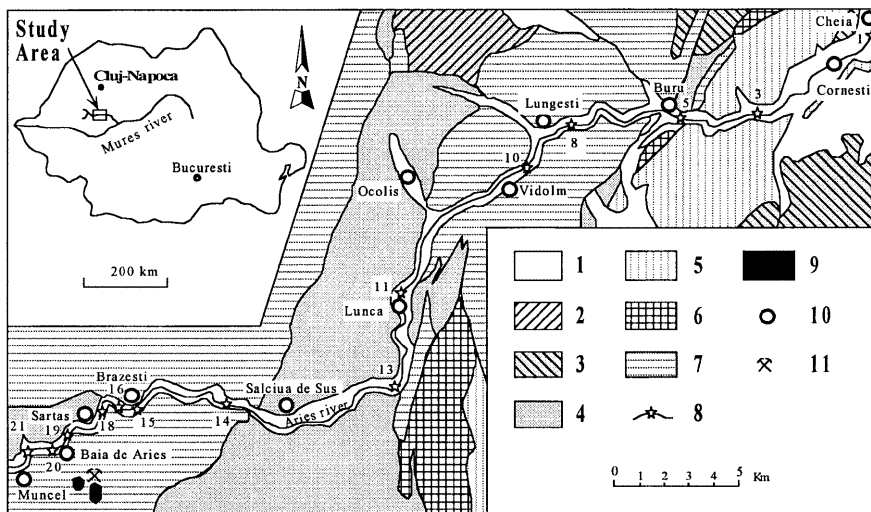


Fig. 1

Simplified geological map of the Aries River valley between the villages of Muncel and Cheia: 1 Quaternary pebbles and sands; 2 Palaeogene continental red clay; 3 Neogene sandstones, clays and sands; 4 Upper Cretaceous sandstone, clays and limestones; 5 Upper Jurassic ophiolites (mainly andesites); 6 Upper Jurassic limestones; 7 Palaeozoic and Precambrian metamorphic rocks (mica-schists with staurolite or garnets); 8 sampling points; 9 andesitic rocks; 10 villages; 11 mines. The flow direction of the Aries River is from west to east (from Muncel to Cheia)

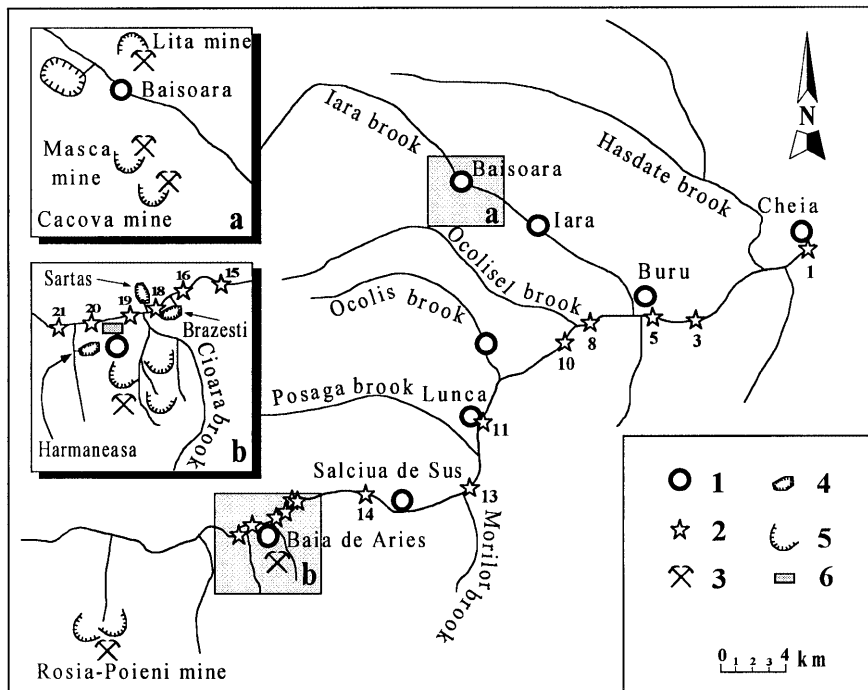


Fig. 3

The main mining regions close to the studied area, which contribute to the pollution of the Aries River: 1 Villages; 2 sampling points; 3 mines; 4 settling ponds; 5 mine waste dumps; 6 crusher/flotation plants

sulphides, both underground and in the waste dumps, the leaching waters are mostly acidic. Their chemistry appears to be directly controlled by the mineralogical characteristics of the ore. In areas where the mineralization is of a hydrothermal-metasomatic type and with limestone as the host-rock, the formation of acidic waters is prevented because of the presence of calcium carbonate. On the other hand, in areas where the veins contain only small amounts of CaCO_3 , and where the host-rocks contain high amounts of pyrite, acidic waters are produced on a large scale. The contents of dissolved metals also increase. The acid mine drainage (ADM) and those components leached from the waste dumps flow directly into the Aries river.

3. Rosia Poieni ore. Rosia Poieni is a porphyry copper-type deposit, with a Cu concentration of 0.4%. Copper ore is being mined in an open pit. Detailed description of the ore mineralogy and geology are given by Ionescu (1974), Ionescu and others (1975), Vlad (1983) and by Udubasa and others (1992b).

Because of the opening of the quarries, considerable amounts of mineralized rock are exposed to rainfall, leaving large amounts of pyrite for intense oxidation and decomposition. This process gives birth to very acidic, leaching waters (pH 2.03) that cannot be buffered because of the very low neutralization capacities of the rocks in the vicinity of Rosia Poieni (F.L. Forray unpublished data). These acidic waters flow into the Aries river lead to a marked increase in pollution.

Methods

Sampling method

The water samples were collected during winter and kept in sterile polyethylene bottles of 100-ml capacity. Each bottle was rinsed several times at the collecting point using river water, in order to reduce the risk of contamination from the manufacture of the bottles. The collecting points were at ~1 m from the riverbank and at a depth of 10 cm. In some areas, especially upstream, it was necessary to break the ice formed at the water surface.

To prevent a subsequent oxidation at the water-air interface, the bottles were completely filled with water and the lid was fixed under water. In the laboratory, in order to preserve the samples, the bottles were kept at 4 °C until measurements were performed. This procedure was recommended by Herr and Gray (1997), and gave good results when the mobility of metals in aqueous solutions was studied. Using these combined techniques of sampling, the preservation of water samples for the study of aqueous species could be assured.

Fourteen water samples were collected between the municipalities of Cheia and Muncel (Fig. 3) along a 54-km stretch of the Aries River. The distance between the collecting points was not constant. When selecting the sampling points, several geological and geomorphological criteria were used. These were changes in geological features within the area and, the water supply from the tributaries or effluents in the mining regions. The causes of specific elemental mobility in aqueous solutions could thus be monitored. The pH values and the conductivity measurements were obtained in the laboratory using a CyberScan CON 20 instrument.

Analytical method (capillary electrophoresis)

High performance liquid chromatography (HPLC) was introduced as an instrumental separation technique in ca. 1970, which was followed by the technique of capillary electrophoresis (CE) about 20 years later. While HPLC is more of an instrumentally controlled analytical technique, CE requires an active input and chemical control by the analyst. From the first marketing of CE instruments, the technique has rapidly developed into a reliable micro-analytical separation technique for a variety of applications (Jandik and Bonn 1993).

The mechanisms responsible for separation in CE are different from those in HPLC. In CE, ionic species are separated based on their charge/size ratios, size being the bulk of the hydrated and/or complexed ionic species. The principle arrangement of a CE separation is shown in Fig. 4. An electrolyte (buffer)-filled fused quartz capillary of $\sim 75 \mu\text{m}$ internal diameter is connected to storage containers of electrolyte. Silanol groups (Si-O-H) are formed on the capillary wall, which have a pK value of ~ 7.7 . H^+ ions form a loose, gliding layer on the wall of the capillary. When an external voltage (5–25 kV) is applied to the electrodes in the containers, a bulk flow or electro-osmotic flow (EOF) of electrolyte (i.e. the electrolyte co-ion) is initiated to the cathode. If a small volume of a sample fluid is injected into the anodic side of the system, the cationic species will move out of the sample plug and separate in the electric field formed, according to their electrophoretic mobilities (μ_c), and also move towards the cathode. Their total migration time, however, is the sum of EOF (or μ_{EOF}) and μ_c . Because only electric forces propel the ionic species, the individual groups form well-defined plugs. Therefore, peaks in CE separations show a lower variance and better resolution in comparison to similar HPLC separations.

At the cathodic side of the capillary the migrating plugs of cations can be detected by their lower absorption in UV light, or indirectly by UV absorption. This requires that the UV absorption of the electrolyte must be about 100 times that of the ionic species in order to arrive at good detection limits.

Sample introduction (Jandik and Bonn 1993) in CE can take two forms: (1) hydrostatic introduction and (2) introduction by electromigration. For hydrostatic introduction or siphoning, the capillary/electrode assemblage is placed in the sample vial, which is then raised for a predetermined time and to a defined level of typically 10 cm above the electrolyte vessel at the receiving end. An introduction time of 30 s then causes a sample volume of $\sim 50 \text{ nl}$ to be injected. For separation, the capillary/electrode assemblage is placed back into the electrolyte vial and a separation voltage (10–25 kV) is applied. In order to achieve a positive flow by hydrostatic introduction a minimum sample volume in the vial of about $300 \mu\text{l}$ is necessary.

Electromigration (EM) is started when the capillary/electrode assemblage is placed into the sample vial and a smaller voltage (1–5 kV) is applied to the electrode. The analyte becomes the terminating electrolyte at the time of introduction. Because of the lower conductivity of the sample only a small amount of fluid is moving into the capillary by EOF. However, the ionic species present in the sample migrate into the capillary under their own electrophoretic mobilities, causing a concentration of ionic species in the sample plug subject to individual mo-

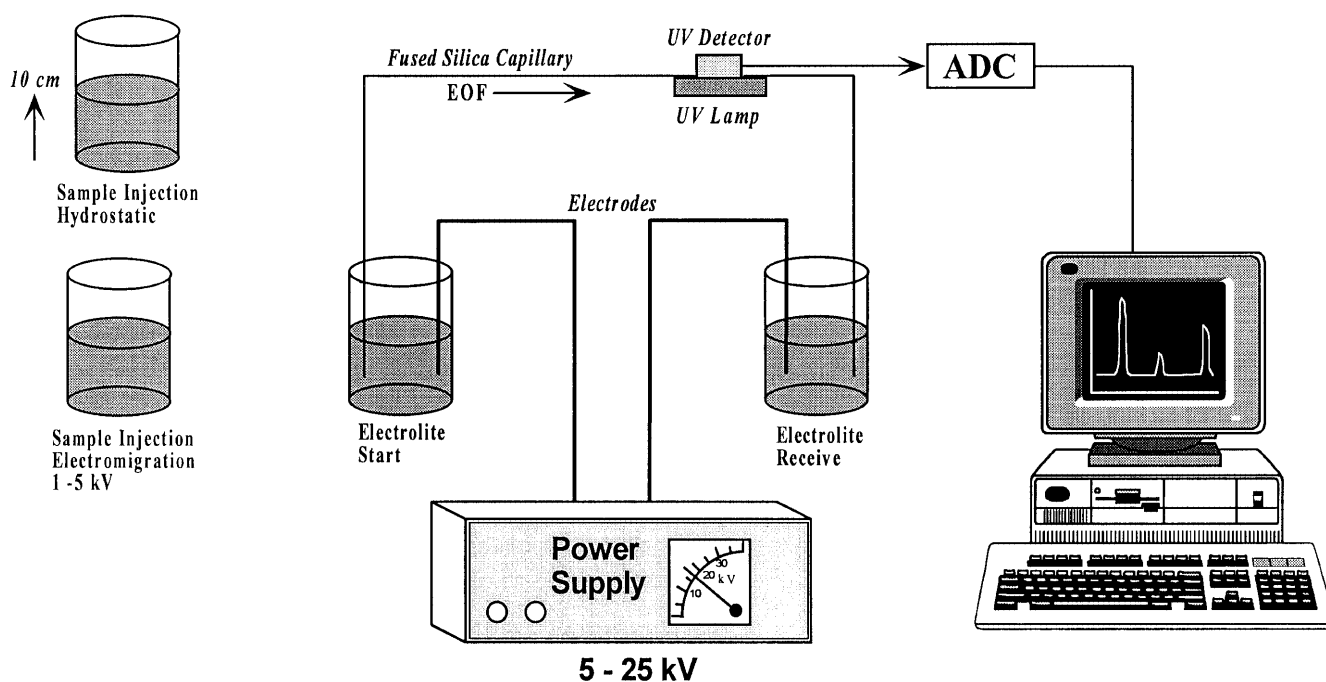


Fig. 4
Principles of CE separation

bilities. The separation is then carried out as described above. Typically, at an electromigration voltage of 4 kV and 10 s introduction time, an enrichment factor of 85 is achieved for potassium. This type of sample introduction is not only different to HPLC techniques, but also allows a lowering of detection limits below the ppb range for some elements such as Li.

One of the requirements for CE is a low conductivity of the sample plug in order to achieve high resolution (Jandik and Bonn 1993). A comfortable detection range for hydrostatic introduction is 0.1–20 ppm for most ionic species. Most cationic species have detection limits for introduction by electromigration introduction of about 0.5–5 ppb. The technique of CE is relatively independent of matrix effects, but a matching of mobilities for the components of the analyte ions and the co-ion is important (Jandik and Bonn 1993; Boden and Bächmann 1996). While the naturally formed silanol groups and the resulting EOF is utilized for the separation of cations, a reversal of the EOF is required for the separation of anions. This can be achieved by adding an osmotic flow modifier (OFM) to the selected co-ion electrolyte (Jandik and Bonn 1993; Dabek-Zlotorzynska and Dlouhy 1994). Such modifiers can be alkyl ammonium compounds or similar,

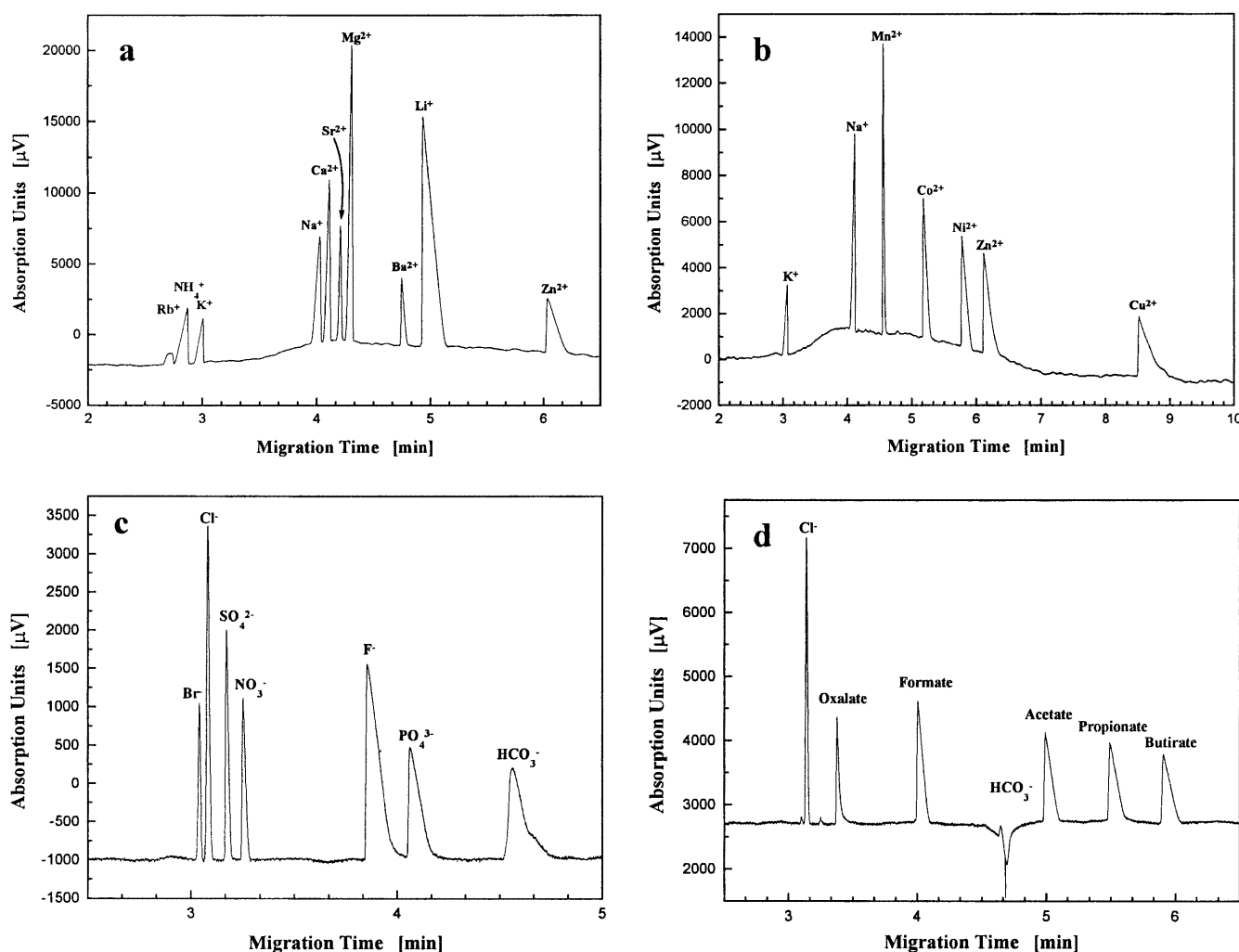
suitable groups, which cover the negatively charged silanol groups by positively charged functional groups. Most are commercially available as preparations for the CE. A reversal of the polarity of the external voltage then allows the migration, separation and detection of anionic species with the same basic instrumentation.

Chemical and instrumental parameters

CE analyses were carried out with a Waters Quanta 4000 instrument. A digital to analogue converter and vendor-provided software assured a smooth sampling of data and their storage on an IBM-compatible PC. Sampling of the UV detector output was set at 50 Hz or 0.02-s intervals.

Fig. 5

Electropherograms of standard solutions: peak concentrations are 5 mg/l for each species. **a, b** Cations. **c, d** Anions. Carrier electrolyte for cations: 10 mM pyridin, 25 mM glycolic acid, 1 mM 18-crown-6 ether. Carrier electrolyte for anions: 5 mM sodium chromate, 4% *n*-butanol, 0.1 mM OFM (Q⁺)-anion-BT, pH=8.0. Capillary: fused silica, 75 μ m \times 60 cm. Separation voltages: Cations: +25 kV; Anions: -20 kV. The samples were introduced by hydrostatic injection for 30 s at 10 cm height



For the preparation of electrolytes, sample dilutions, standards and for cleaning containers and vials only deionized water supplied by a Milli-Q system (Millipore, Bedford, MA) was used. The water blank was routinely checked for contamination and, at present, varies between 0.5 and 1 ppb of K, Na and Ca. Standard solutions were prepared from 1000 ppm stock solutions made from pure chemicals.

A series of tests were carried out to determine the most suitable electrolyte for cation separations. Following the suggestions by (Lee and Lin 1994), pyridine was found to be a universally applicable co-ion. For the conditions of a 60-cm long capillary and average separation voltage of 25 kV, a concentration of 10 mM was found to be optimal for base level separations of Group I and II elements and transition elements. Glycolic acid in a concentration of 25 mM was added as a general complexing agent, resulting in a pH value of ~ 4.5 . In order to separate the co-migrating cations of K^+ and NH_4^+ , a further addition of 1 mM 18 crown 6 ether to complex the K^+ cation (Jandik and Bonn 1993), was found to be sufficient. For the separation of the lanthanide elements to base level the basic pyridine electrolyte was used, but with HIBA (10 mM) as the sole complexing agent. All these electro-

lyte preparations have their maximum UV absorption at 254 nm wavelength.

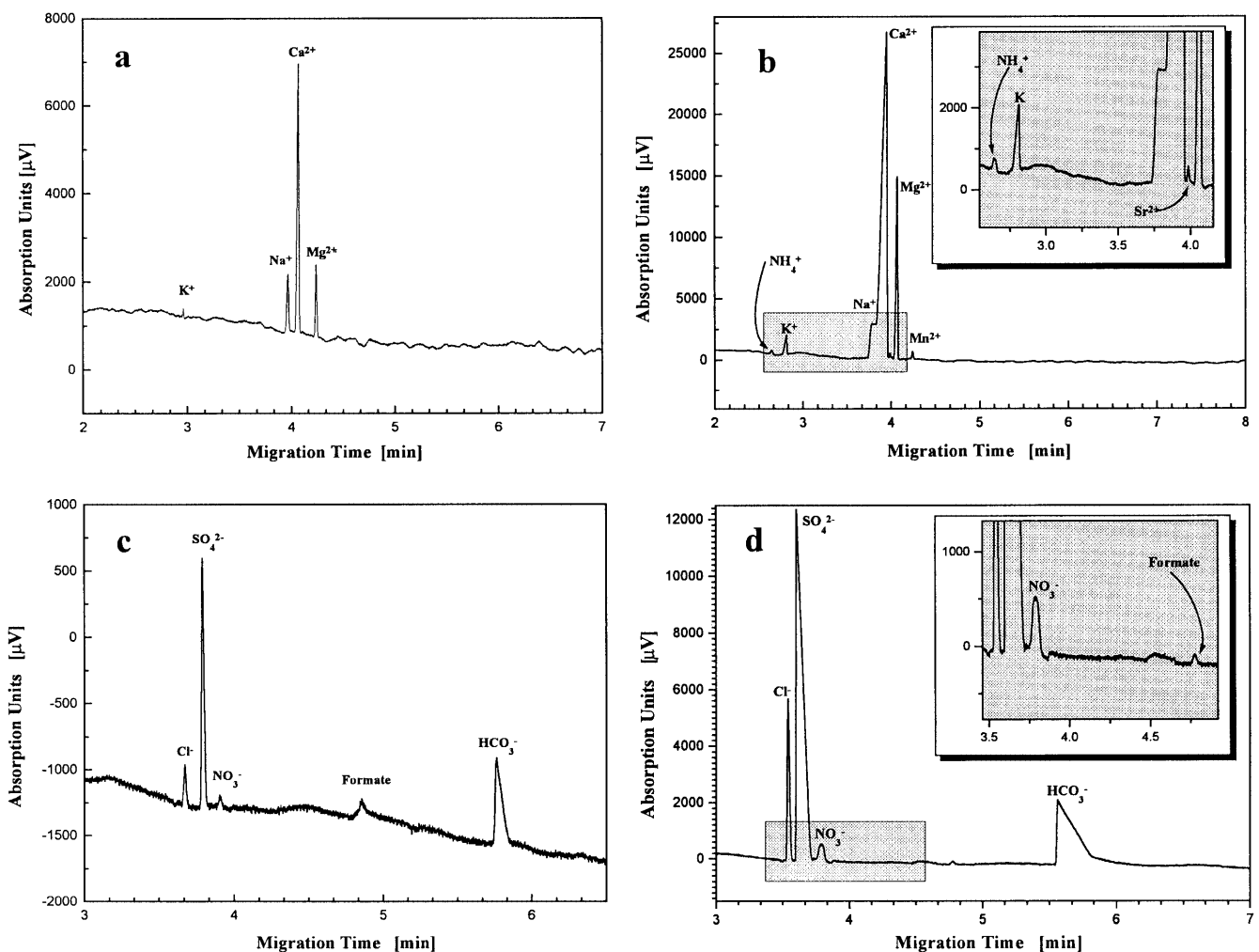
Sample electropherograms for two cation standard solutions of 5 ppm each are shown in Figs. 5a,b and, two anionic standards of 5 ppm each are illustrated in Figs. 5c,d. The sensitivity of CE separation as well as the effect of introduction by electromigration are demonstrated in Figs. 6 and 7 for water samples no. 1 and 19.

In Fig. 6b peaks for NH_4^+ , Sr^{2+} and Mn^{2+} can be discerned, and the peak for K^+ is significantly improved. Similarly, in sample s19 (Fig. 7b), NH_4^+ , Sr^+ , Zn^{2+} and Cu^{2+} could be detected by applying electromigration injection.

A separate capillary was used for the determination of anionic species and this was specially conditioned for use with an osmotic flow modifier (OFM). A convenient co-ion and chromophore is chromate (Jandik and Bonn

Fig. 6

Electropherograms of sample s1. **a, b** Cations. **c, d** Anions. Conditions as in Fig. 5. The samples were introduced by hydrostatic injection as before and, by electromigration for 10 s at 4 kV (**b, d**). Peak concentrations are presented in Table 1



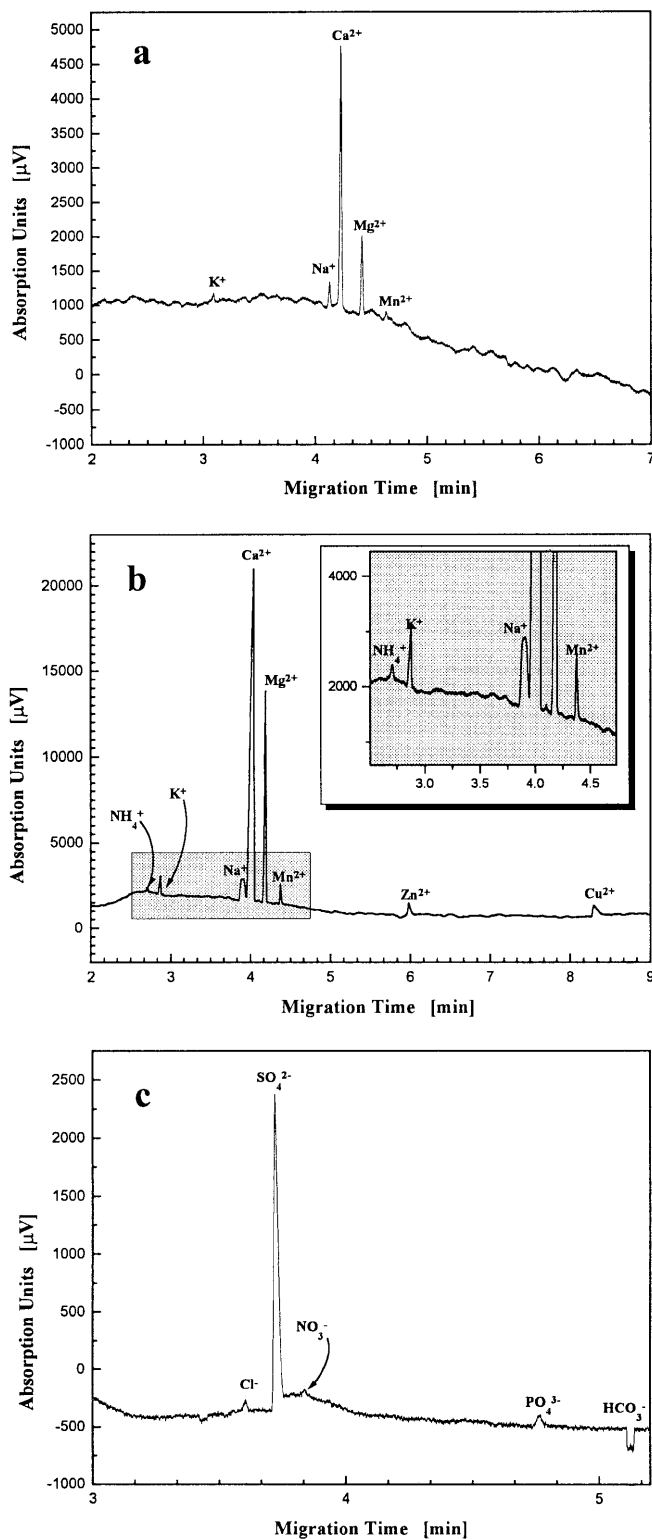


Fig. 7

Electropherograms of sample s19. **a, b** Cations. **c** Anions. Conditions as in Fig. 5. The samples were introduced by hydrostatic injection (**a, c**) and by electromigration for 10 s at 4 kV (**b**). Peak concentrations are presented in Table 1.

1993). It is prepared from sodium chromate tetra hydrate as a 5-mM solution with a pH of ~ 8.0 , adjusted by sulphuric acid. In the original formula the OFM was added at a concentration of 0.5 mM (CIA-Pak OFM anion BT, Waters). Because the OFM is a bromide salt, a small residual Br peak could sometimes be noted. By reducing the OFM concentration to 0.05 mM and adding 4% l-Butanol as stabilizer (Benz and Fritz 1994), an electrolyte without the formation of the residual Br peak was obtained. Best separations were achieved at -20 kV.

All standards were prepared by diluting 1000 ppm stock solutions containing the individual ionic species. Concentrated standards were made up from their salts, which were of analytical grade or better. Three standard levels were used for each introduction type in order to obtain smooth calibration curves.

All quantitative calculations are based on peak area integrations. Very good linear regression fits are normal for standards introduced in the hydrostatic mode. However, it should be noted that the physical nature of electromigrative introduction produces a non-linear fit, usually of the nature $y = a + b \ln(x)$.

Results and discussion

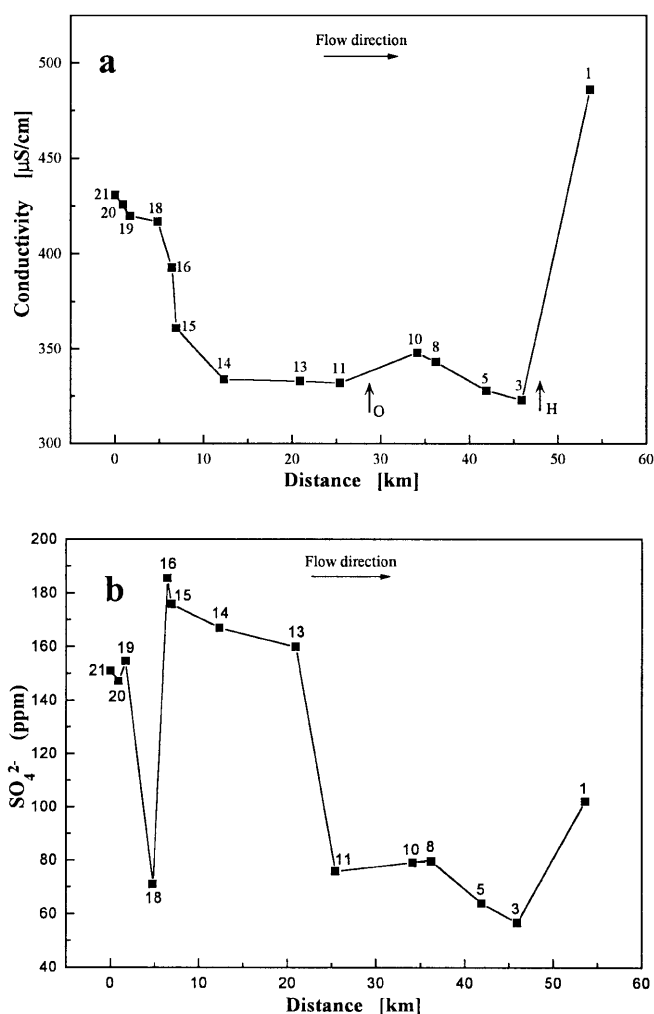
The analytical data obtained on the water samples collected from Ariesului Valley are presented in Table 1. Their chemical composition can be related to some complex processes of regional water-rock interaction and, importantly, the inflow of effluents from mining sources that led to the pollution of the river.

In the Baia de Aries mining area, the electric conductivity (EC) is higher (~ 425 $\mu\text{S}/\text{cm}$), than downstream (Fig. 8a), except for the Cheia locality. Here the influence of the water from Hasdate Brook is apparent. Changes in the composition of river water are often caused by dilution (Stollenwerk 1994). In the studied area, dilution is assumed to be mainly the result of the contribution of the left tributaries in the upper region of the Aries River. Besides dilution, some other processes, such as adsorption, absorption, chemical precipitation and complexing, are likely to occur, which could lead to changes in the composition of the surface waters.

SO_4^{2-} distribution along the Aries River can be connected to the location of mining works (Fig. 8b). The most important inputs are related to the settling ponds from Harmanesei Valley, as well as to those from Brezesti, although the latter is not active anymore. Less significant is the contribution of inflows from Sartesului Valley. The decrease of SO_4^{2-} concentration is mainly caused by the dilution and not to the chemical reactions between SO_4^{2-} and Ca^{2+} , which could lead to the formation of CaSO_4 and precipitation as gypsum. The ion activity product for CaSO_4 , along the river never exceeds a value of 2×10^{-8} , which is well below the saturation level of $10^{-4.5}$ for anhydrite. The SO_4^{2-} concentration in the river waters also directly depends on the lithology of the re-

Table 1Chemical composition of waters from the Aries River. *Acet** Acetate; *Oxal** oxalate; *Form** formate; *Buth** butyrate

Sam- ple	pH	EC μS/cm	Concentration (mg/l)																				
			Ca	Mg	Na	K	Sr	Mn	NH ₄	Ba	Zn	Cu	Cl	SO ₄	NO ₃	HCO ₃	F	Br	PO ₄	Acet*	Oxal*	Form*	Buth*
1	7.5	486	73	8.6	15.6	4.5	0.164	0.207	0.084	-	-	-	12.0	102	3.3	210	-	-	-	-	-	8.3	-
3	7.5	323	47	6.3	7.4	3.2	0.147	0.216	0.088	-	-	-	5.9	57	3.8	177	-	-	-	-	-	-	7.9
5	7.4	328	49	7.1	7.3	1.0	0.147	0.229	0.081	-	-	-	6.3	64	2.7	162	-	-	-	-	-	-	13.7
8	7.4	343	46	6.2	7.0	2.5	0.148	0.251	0.093	-	-	-	5.1	80	2.8	137	0.119	-	-	-	-	-	-
10	7.1	348	49	6.9	8.2	1.5	0.148	0.274	0.096	-	0.175	-	4.0	79	2.5	117	-	-	-	-	-	-	-
11	7.1	332	47	7.2	6.1	1.6	0.148	0.279	0.091	-	0.172	-	5.1	76	4.0	116	-	-	-	-	-	-	-
13	7.4	333	42	6.3	5.6	1.6	0.147	0.278	0.086	-	0.181	-	8.8	160	5.2	163	0.123	-	-	-	-	-	-
14	6.2	334	43	5.5	8.5	1.5	0.145	0.264	0.093	-	0.196	-	7.9	167	6.0	192	-	-	-	-	-	-	-
15	6.0	361	44	5.8	7.3	1.8	0.149	0.261	0.097	-	0.236	0.227	10.6	176	6.6	241	-	-	-	-	-	-	-
16	5.8	393	45	7.4	7.3	2.7	0.147	0.272	0.104	0.174	0.235	0.319	9.8	185	4.9	284	-	-	-	-	-	-	-
18	5.8	417	46	6.6	7.2	2.7	0.145	0.280	0.098	0.190	0.213	0.340	3.4	71	-	108	-	0.210	-	-	10.1	-	-
19	5.5	420	43	6.6	4.4	3.0	0.146	0.284	0.082	-	0.237	0.350	2.3	155	3.0	19.3	-	-	1.4	-	-	6.4	-
20	5.3	426	40	7.0	4.0	1.8	0.147	1.000	0.084	-	0.256	0.406	4.3	147	5.6	35.7	-	-	-	0.697	-	-	-
21	5.3	431	42	7.2	4.3	2.3	0.142	2.000	0.089	-	0.236	0.324	2.4	151	2.1	-	-	-	-	-	-	-	-

**Fig. 8**

Variation of conductivity and SO₄²⁻ concentrations along the Aries River from Muncle to Cheia. O Inflow of Oclis Brook; H Inflow of Hasdate Brook

gion. This is shown by an increase of the SO₄²⁻ concentrations between sample points 3 and 1. The main cause for this rise in concentration is the rock-water interaction between the Aries River water and the Neogene sedimentary rocks, which contain gypsum. In the Cheia area an open pit for gypsum extraction is still operating. In comparison, Stallard (1980) measured 1.7 mg/l SO₄²⁻ in the waters of the Amazon River in unpolluted areas, whereas Zhang and others (1990) found up to 71.7 mg/l in Yellow River waters (China). A comparison of the contents for major anions in the Aries River and three other European rivers is presented in Fig. 9. The high load of SO₄²⁻ for the Aries River is apparent and indicates the negative influences of mining operations along the Ariesului Valley.

The increase of the K⁺ concentration is significant in the Baia de Aries area and downstream (sampling points 8, 3 and 1, Fig. 10a). Water-rock interaction with hydrothermal, and potassic alteration suites of andesitic rocks in the Baia de Aries area is probably the cause of this. The source of K⁺ would then be the weathering of the alteration suite, i.e. the feldspars and micas. In the neighbourhood of sampling point 8, the local increase of K⁺ content is interpreted to be caused by the alteration of metamorphic rocks (mica-schists, sericitic-chloritic schists and amphibolites). A noticeable higher input of K⁺ was also registered in the region where Aries River crosses the complex of ophiolitic rocks.

The concentration of Mn²⁺ is very high (2000 μg/l) upstream next to Baia de Aries, and then decreases extremely fast to 203–284 μg/l over a short distance along the river in a downstream direction (Fig. 10b). Mn²⁺ is present in solution at pH values of ~7.6 (Stumm and Morgan 1981). It is thus very mobile in surface waters. The fast decrease of Mn²⁺ between sampling points 21 and 19 could be explained by adsorption phenomena on iron hydroxides present in the riverbed and, could perhaps be related to the drastic change of the redox system beyond sampling point 20.

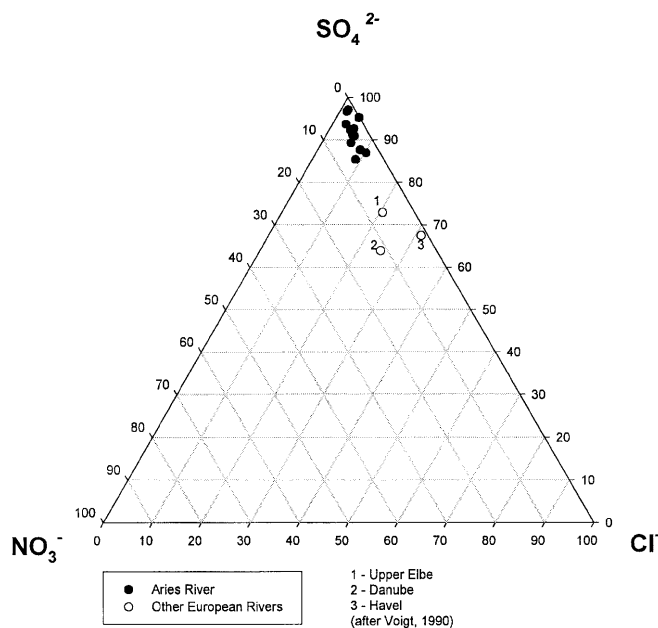


Fig. 9

Ternary diagram showing the relative concentration for Cl^- , SO_4^{2-} and NO_3^- for water from the Arises River and selected European rivers

Reported Mn^{2+} contents in river waters vary considerably. According to Martin and Whitfield (1983), the mean value of Mn^{2+} in unpolluted waters is $\sim 8.2 \mu\text{g/l}$. In Sardinia (Italy), the water of a river located in a mining region contained variable amounts of Mn^{2+} (between 3 and $643 \mu\text{g/l}$, with an average value of $139 \mu\text{g/l}$) (Cabo and others 1992). Konhauser and others (1997) measured the Mn^{2+} content of a river in India and found higher values, between 19.3 and $459.4 \mu\text{g/l}$ (the average value was $144.6 \mu\text{g/l}$). In comparison, the values in Table 1 indicate a significant pollution of Mn^{2+} as a result of the mining activities in Rosia Poieni and Baia de Aries areas. The concentration of Cu^{2+} in the Aries River near Baia de Aries is $\sim 320 \mu\text{g/l}$. A higher concentration of $406 \mu\text{g/l}$ was noticed at sampling point 20 (Fig. 10c). The increase in Cu concentration is related to the presence of a settling pond in Harmaneasa Valley. Downstream from sampling point 19 the amount of Cu decreases rapidly, and downstream of sampling point 14 the concentration is below the detection limit of $\sim 20 \mu\text{g/l}$.

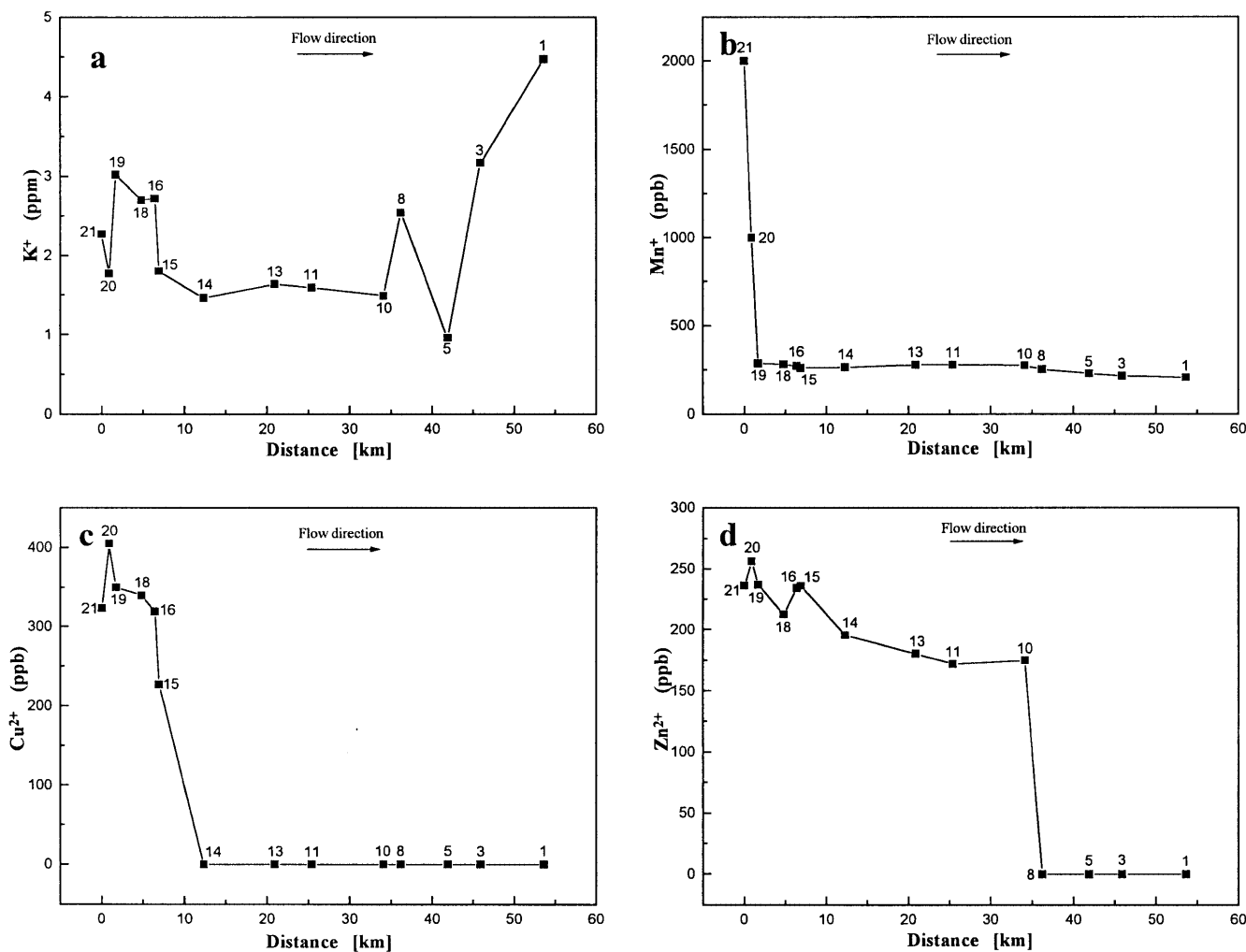
Under normal circumstances, Cu^{2+} is adsorbed onto iron hydroxides, which are present in small quantities in the streambed. Adsorption starts at a pH of ~ 5 (Papp and Kümmel 1992), whereas at neutral pH values, Cu^{2+} concentrations in solution are very low (Kelly and others 1988b). Cu precipitates as hydroxide at a pH of ~ 7.2 (Kelly and others 1988a). Because of the relatively low pH of the Aries River in places, the main process, which is responsible for the decrease of Cu concentration, could be adsorption. The presence of iron hydroxides precipitated from AMD by oxygenation can significantly modify the amount of Cu^{2+} in solution because of adsorption

processes, as mentioned in several papers (Laxen 1984; Johnson 1986; Kooner 1993; Grossi and others 1994). The presence of iron hydroxides in the Aries River in the vicinity of the Baia de Aries mining area is shown by the brownish-reddish crust that covers the surface of pebbles. In unpolluted waters, dissolved Cu^{2+} concentrations in rivers have been reported to be between $0.38\text{--}2.35 \mu\text{g/l}$ (Boyle 1979). The very high concentrations of Cu^{2+} in the Aries River clearly indicate a strong degree of pollution. The main source of Cu^{2+} is the Rosia Poieni quarry, located at $\sim 12 \text{ km}$ upstream from Baia de Aries and, to a lesser degree, the mining works from Baia de Aries. Zn is a very mobile element in many environments (Kelly and others 1988b; Papp and Kümmel 1992). In the studied area, the Zn^{2+} concentration varies from 172 to $256 \mu\text{g/l}$ (Table 1). A comparison between the distributions of Cu^{2+} (Fig. 10c) and Zn^{2+} (Fig. 10d) supports a contention of the high mobility of the latter as mentioned by several authors (Kelly and others 1988b; Papp and Kümmel 1992). Downstream of sampling point 15, at a pH of 6, there is a continuous decrease in Zn^{2+} concentration. When the pH reaches a value of 7.4, the Zn^{2+} concentration decreases below the detection limit. As in the case of Cu^{2+} , an increase in Zn^{2+} content is registered at sampling point 20 because of the input of the metal from the settling pond from Harmaneasei Valley (Fig. 3). At sampling points 16 and 15, the increase of Zn^{2+} is caused by the input of effluents that originate in the settling ponds of Brezesti and Sartesului Valley (Fig. 3).

At pH values between 6 and 8, the main chemical species of Zn is the $2+$ cation in solution (Hem 1972; Vuceta and Morgan 1978). Within these limits, dilution and adsorption processes, more than chemical precipitation, control the Zn^{2+} concentration of the Aries River in the studied area. At pH values of 6, the adsorption of Zn^{2+} onto the surface of iron hydroxides is very low (Florence 1980; Papp and Kümmel 1992), but at higher values the process becomes more significant (Johnson 1986; Papp and Kümmel 1992).

According to Shiller and Boyle (1985) filtered water samples contain between 0.02 and $1.8 \mu\text{g/l}$ Zn^{2+} , while in the polluted areas the mean Zn^{2+} content is between 0.07 and $15.6 \mu\text{g/l}$. Unpolluted waters were reported to contain $\sim 11 \mu\text{g/l}$, whereas Elderfield and others (1971) and Abdullah and Royle (1972) report an average Zn^{2+} concentration in river waters of $24 \mu\text{g/l}$. Comparing these data with the values in Table 1, a significant pollution of the Aries river is demonstrated.

With the analytical technique employed, no traces of Fe^{2+} and Al^{3+} could be recorded, in spite of the fact that these elements are quite common in water polluted by mining activities. In primary sulphide ores, the elements in minerals are present mainly in the reduced form (Wiggering 1993). When minerals get in contact with the atmosphere they become oxidized. Thus Fe^{2+} , which is unstable in solution, is oxidized to Fe^{3+} . It then becomes unstable under higher pH conditions and is precipitated as iron hydroxide. According to Skelly and Loy

**Fig. 10**

Variation of the concentrations for some cations in water along the flow of the Aries River. Numbers indicate the sample locations on the riverbank

(1973), the critical pH values are ~ 4.3 for Fe^{3+} and 5.2 for Al. In the Baia de Aries mining area, the brown crust, which covers the pebbles on the riversides, indicates the presence of iron hydroxides. Because of pH values higher than the critical ones, Fe^{3+} and Al precipitate, thus they are no longer available in solution and not present in the measured data.

Conclusions

In this paper, the authors have tried to demonstrate that, because of its efficiency and resolution and its ease as an analytical procedure, the CE method can be applied successfully for the determination of dissolved anions and cations, as well as for the analysis of organic anions from

river water. The relative low costs and the high reproducibility plead for an acceptance of the CE method in water pollution control as compared with other methods. The results show the evolution of the Aries River water from an SO_4^{2-} contaminated, slightly acidic water to a condition where, by successive leaching of carbonate (Fig. 11a), the composition of the river water changes to a more neutral stage. The changes in the anionic composition along its flow are greater than those in its cationic contents (Fig. 11b).

From the study it is also apparent that the degree of pollution caused by mining activities in the drainage area of the Aries River is correlated to

1. specific features of the ores mined in the region (e.g. sulphides of Cu, Zn and carbonates);
2. the type of the host-rock and country rock (carbonate rocks, andesites and others); and
3. the methods of exploitation used.

The oxidation of sulphides does not generate acidic waters from the mines of Baisoara and Baia de Aries because of the high amount of calcite in the gangue. However, for the ores from Baia de Aries (the vein-type mineralization) and those from Rosia Poieni, because of the low amount of buffer minerals (especially calcite), the

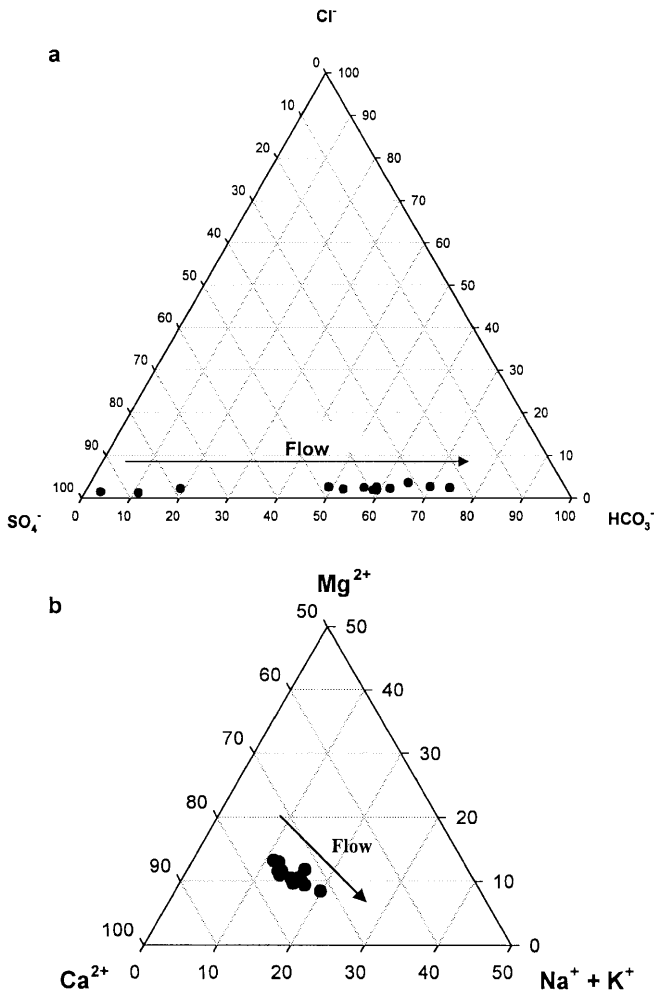


Fig. 11

Ternary diagram of the major a anionic species and b cationic species in the Aries River

same process of oxidation gives rise to acid drainage, waters with low pH values and high amounts of dissolved metals.

Local variations in the concentration of different elements, in addition, point to a source of pollution identified as the settling ponds from Harmanesei Valley, Sartasului Valley and Brezesti. Apart from the pollution caused by mining activities some local sources of pollution were recognized, such as the input of domestic and agricultural effluents in the vicinity of the settlements along the riverbanks.

Several processes: water-rock interaction, and chemical reactions at the junction of Aries river with other tributary systems of different composition and adsorption patterns contribute in a significant way to the modification of the chemical composition of the water of the Aries River.

Zn, because of its high mobility, migrates far from its source. The variation of Zn²⁺ concentrations in the filtered fractions of the water is apparently controlled by

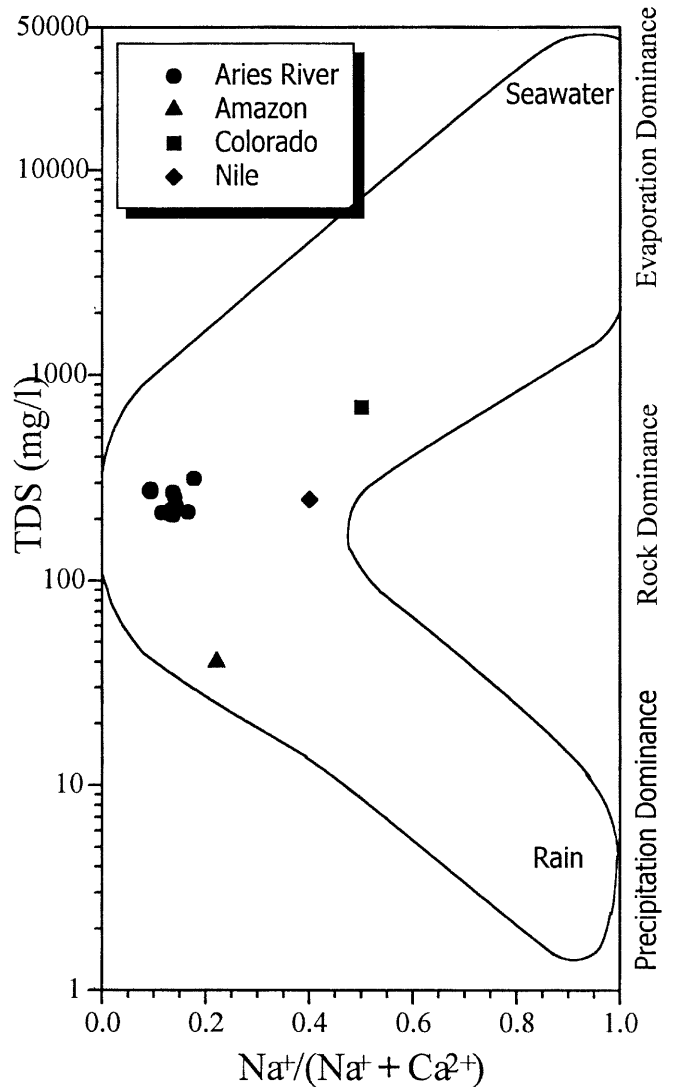


Fig. 12

The classification of surface waters according to Gibbs (1970), showing some major stream systems [concentration data: Amazon from Stallard (1980); Colorado and Nile from Meybeck (1979)] as well as the position of the Aries River

adsorption phenomena, at pH values >6. The active and inactive settling ponds also have a major influence on Zn²⁺ concentration. The waters of the Aries River, by comparison, contain concentrations of Cu²⁺ and Zn²⁺ that are up to 100 times higher than those of unpolluted river water.

Compared with larger river systems worldwide (Fig. 12), the Aries River has a high degree of water-rock interaction and pollution. In this classification (Gibbs 1970) it shows a relatively high amount of TDS, yet a low content of Na⁺.

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