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AN INVESTIGATION INTO THE Cu, Pb AND Zn POLLUTION OF THE SOMES AND LAPUS RIVERS OF BAIA-MARE AREA, ROMANIA

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ABSTRACT. An evaluation of Cu, Pb and Zn in sediment and water collected in the catchment of the Somes river one year and a half after the cyanide spill accident in January 2000 is presented. The sediments show a high content of heavy metals in the range (mg Kg^{-1}): 8.9 – 339 (Cu); 59 – 465 (Pb) and 56 – 2060 (Zn) that demonstrate their potential toxicity for the ecosystem. As compared to data recorded after the accident, the content of heavy metals decreased at the station near the place of cyanide spill and increased downstream. Copper exceeds the admissible level in water near the place of cyanide spill (0.070 mg L^{-1}), while Pb is below the admissible level. The high concentration of Zn up to 1.038 mg L^{-1} in water can not be attributed exclusively to the pollution but is also due to natural background. The situation in the investigated period is better than that after the accident, when Cu and Zn exceeded up to 10 and 68 times, respectively the permissible limits.

INTRODUCTION

Baia-Mare area, situated in the nord-west of Romania, is one of the "environmental hot spot". The town is the site of two major plants and a flotation station for Pb, Cu and Zn ore processing, which caused in time a significant pollution with heavy metals. These phenomena were investigated in previous studies concerning the speciation of Pb, Zn and Cu in sedimented dust and soil [1] and the determination of Cd in sedimented dust [2]. The speciation indicated that in the sedimented dust Pb and Zn occurred mainly as sulfides and sulfates, while Cu as sulfides and oxides. The analysis of soil revealed a residual pollution with sulfides. Besides plants to process Cu, Pb and Zn ores, a company for gold extraction exists in the area of Baia-Mare. The technological process involves extracting gold and silver by cyanide leaching from older tailings in an existing dam situated near the town. Gold

and silver are extracted by carbon-in-pulp technology, since the resulting slurry is transported by pipeline on a distance of 6 km to be deposited in a decantation pond. The resulting slurry contains about 400 mg L^{-1} cyanide, half of which as free cyanide, and the rest as complexed cyanide. After decantation the resulted water containing cyanide is fed back to the plant.

In January 2000 a major cyanide spill took place following a breach in the decantation pond as a result of improper structural elements and operational conditions. It caused the release of a huge volume of liquid mine tailings containing a high quantity of cyanide and heavy metals. The pollution spread across the local fields and entered the river system through the Lapus and Somes rivers. The spill was recognized as having long-term consequences for the ecosystem that has determined periodical evaluation of the river system.

The aim of this paper is to present an evaluation of Cu, Pb and Zn in sediment and water collected from the Somes and Lapus rivers one year and a half after the cyanide spill and to compare data with those recorded after the accident. These elements were selected for the study as they are the main products of the mining and nonferrous metallurgical industry in the area and are more likely to be found in the tailings and in the wastewater in a significant amount.

EXPERIMENTAL

Sample collection and digestion procedure. Sediment and water samples were collected during June 2001 from 10 sites upstream (20 km) and downstream (30 km) from the Somes and Lapus rivers confluence. Sampling stations were divided on equal split number between upstream and downstream. In addition, two more stations were included in the study, namely Bozanta Mare, the first village downstream from the dam and a station further upstream from the dam in the mountainous area of Codru Butesii. The last station was selected to act as a control one since it is high up in the low population area of the mountains, free from any industrial or agricultural activities. The twelve collection sites are shown on the map in Fig. 1. In order to get an overall picture of the distribution of heavy metals in the Somes river in the vicinity of the confluence with the Lapus river, sediments for the deposited particulate phases as well as water samples for the dissolved and suspended phases were collected.

Reagents. Single element stock solutions of 1000 μg mL^{-1} were prepared by dissolution of the high-purity metal (Merck, Darmstadt, Germany) in the minimum volume of HNO_3 (Cu, Pb) or HCl (Zn) and diluting to 1 L. Starting from these, multielement standards were prepared. The reagents used for the digestion of sediment and water samples and for standards preparation were HNO_3 puriss 65%, HCl purris p.a.>36.5% (Flucka, Riedle-de Haen) and H_2O_2 puriss 30% (Merck, Darmstadt, Germany). The blank sample contained only the reagents used for the digestion. All solutions were stored in plastic vials cleaned with acid solution and rinsed with distilled water.

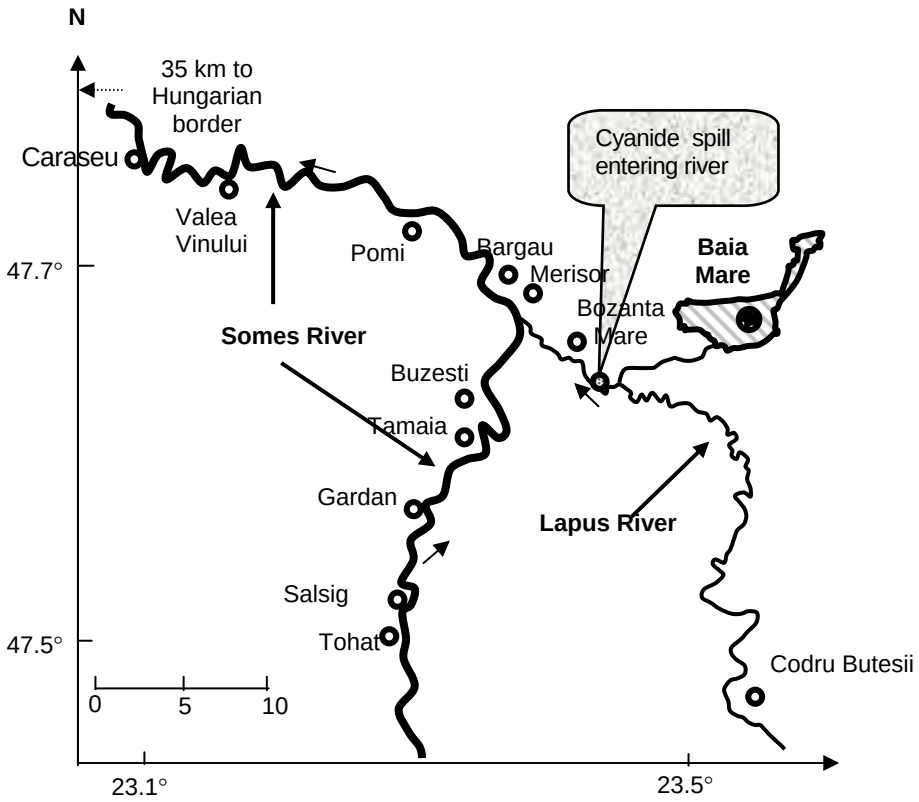

Fig. 1. Sampling sites for sediments and water

Sediment. At each station two sediment samples were collected from the surface of the riverbeds in order to obtain samples from the same surface layer and to ensure the same environmental conditions for all samples. Samples were transferred into polyethylene bags and closed. The samples were first dried at 105 ^{o}C to constant weight, homogenized and sieved through a 2 mm sieve, then through a 125 μm sieve. Five g of precise weight aliquot of dried sample were refluxed with 20 mL concentrated (65%) HNO_3 for 15 min. The mixture was cooled and again refluxed with 10 mL 30% H_2O_2. After cooling the resulting solution was quantitatively filtrated through a precleaned G4 glass filter and diluted to 250 mL.

Water. At each station, three water samples were collected in nitric acid (65%) clean polyethylene bottles, acidified to pH ≤2 and stored at 4^{o}C. Before analysis, a 50 mL sample was digested with HNO_3 (0.5 mL) and HCl (1.5 mL) by heating on a sand bath for 15 min. After cooling, the filtrate was diluted to 50 mL.

Copper, Pb and Zn in sediment and water samples were determined by ICP-AES.

Instrumentation. The determination by ICP-AES was performed using a SPECTROFLAME (SPECTRO, Kleve, Germany). The main characteristics and the operating conditions are presented in Table 1.

Table 1

Instrumental conditions used for measurements by ICP-AES

Plasma frequency	27.12 MHz
RF power / W	1200
Torch Ar flow	cooling 12 L min^{-1}; nebulizer 1 L min^{-1}
Auxiliary Ar flow	1L min^{-1}
Observation height	15 mm
Nebulizer	Concentric, Meinhardt type
Pump rate for analysis	2 mL min^{-1}
Flush time	20 s
Calibration	4 – point linear
Data acquisition	Smart Analyzer Soft, Pentium III CPU 450 MHz

	Cu	Pb	Zn
Wavelength / nm	324.76	283.31	213.86
Standard range / mgL^{-1}	0 - 10	0 - 10	0 - 50

RESULTS AND DISCUSSIONS

Distribution study of Cu, Pb and Zn in sediment and water. The concentration range for Cu, Pb and Zn in sediment and water collected from the stations in Fig.1 are summarized in Table 2, while their distribution in the sampling points along the rivers is presented in Fig. 2. Data corresponding to a site represent the average of 2 independent sediment samples and 3 independent water samples, respectively.

Table 2

Concentration range for Cu, Pb and Zn in sediment and water in the Somes river

	Cu	Pb	Zn
Water / mg L^{-1}	< 0.007 – 0.070	< 0.030 – 0.045	< 0.005 – 1.038
Control sample / mg L^{-1}	< 0.007	< 0.030	0.055
Sediment / mg Kg^{-1}	8.9 - 339	59 - 465	56 - 2060
Control sample/ mg Kg^{-1}	59	120	315
Maximum admissible concentration in water[a] /mg L^{-1}	0.050	0.050	0.030

[a] Romanian Standard 4706/88

For the content of heavy metals in sediment, values in order of hundreds of mg Kg^{-1} were recorded. The maximum level of Cu, Pb and Zn occurred at Bozanta Mare station. From data in Fig. 2, curves 1, it is evident that there is a marked difference between the ranges of heavy metals concentrations in sediments upstream and downstream from the inflow of Lapus in Somes river. Data are related to both natural background of the river and water quality. Other characteristics, like flow, velocity and turbulence are decisive factors for the sediment quality and composition.

A comparison of the mean contents of heavy metals in the Somes river, upstream and downstream from the inflow of the Lapus river, revealed different situations for Cu and Zn on one side and Pb on the other side. Thus, for Cu the means were 17.1 and 109.1 mg Kg^{-1} and their ratio, expressing a concentration factor, was 6.4. The corresponding data for Zn were 104.5 and 854.5 mg Kg^{-1}, respectively and the concentration factor was 8.2. In the case of Pb, the two means were closer, 100.2 and 176 mg Kg^{-1} and the concentration factor was only 1.8. The fact could be explained on the basis of the history of Pb pollution in the area resulting from its industrial past. This generated a widespread dispersal of Pb in the area, reflected in a more uniform Pb content in sediments upstream and downstream from the confluence.

On the other side, a comparison with data recorded after the cyanide spill in 2000 [3] revealed that the Cu content in sediment from Bozanta Mare station decreased in time, since that of Pb and Zn remained almost constant. Downstream from the confluence with the Lapus river the content of all three elements has increased during the period after the accident.

The possible toxic potential of heavy metals in the sediment is difficult to evaluate since there are no Romanian Standards regarding the maximum admissible level of heavy metals in sediment. The toxic potential could be estimated either by assimilating the sediment with soil and the application of the Romanian Standards [4] and /or by using Canadian sediment quality guideline, which gives the Probable Effect Levels (PEL) [3,5]. In fact, there is a relation between these values, as PELs for Cu and Pb are similar with Romanian intervention level for soil in sensitive area (mg Kg^{-1}: Cu-200; Pb-90) and PEL for Zn with Romanian alert level for soil in sensitive area (300 mg Kg^{-1}). These limits are exceeded many times at most of the stations downstream from the inflow of Lapus river, which demonstrates the potential toxicity of the sediments on ecosystem.

In the case of water (Fig. 2, curves 2), the Cu content was below the limit of detection throughout the collection sites excepting Bozanta Mare, where it reached 0.070 mg L^{-1} and exceeded the admissible limit. The situation was better than in 2000 after the accident [3], when the recorded levels were 0.491 and 0.120 mg L^{-1} Cu at Bozanta Mare and in the Somes river immediately after the

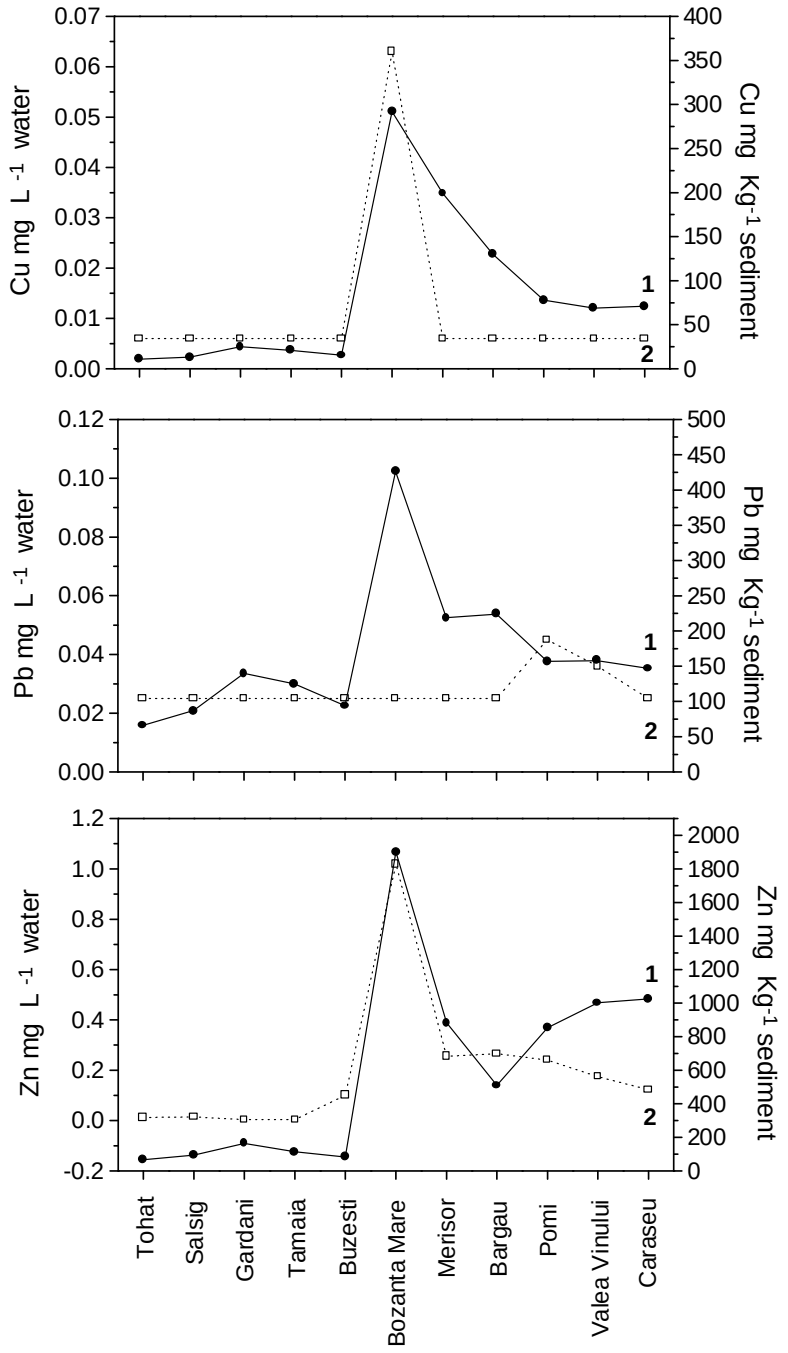

Fig. 2. Graphical sketch of Cu, Pb and Zn concentrations in sediment (1) and water (2)

confluence with Lapus, namely 10 and 2.5 times the permissible limits. For Pb, the present study revealed concentrations that scarcely exceeded the limit of detection in two sites and, unlike Cu and Zn, there was no maximum corresponding to Bozanta Mare station. In fact, Pb did not exceed the admissible level even after the cyanide spill in 2000. The case of Zn is different. The present study indicated that Zn exceeded the admissible level in 10 out of 12 collection sites. However, compared to results recorded in 2000 after the accident, the Zn concentration in Bozanta Mare station decreased to half, but remained almost constant in the Somes river after the confluence with the Lapus river. An interesting case is that of the station taken as control. Codru Butesii is a small village situated in the Lapus Gorges, far from the units with mining profile and close to its springs. However, the found Zn concentration in water exceeded the admissible level. This proves that the high content of Zn in the Lapus river is due to the natural background. The chemistry of rivers is often greatly affected by the physical surroundings that characterize the water [6].

The concentrations of Cu, Pb and Zn were determined also in several filtered water samples and were generally lower than in unfiltered water. Thus, Pb level was throughout below the limit of detection, while Cu content was above the limit of detection only at Bozanta Mare. The concentration of Zn in filtered water was below the limit of detection upstream from the confluence, up to 0.928 mgL^{-1} at Bozanta Mare, and did not decrease below 0.037 mg L^{-1} downstream from the inflow of Lapus in Somes river, exceeding 3-30 times the admissible concentration.

The concentration of heavy metals in surface water depends on sampling date, because the pollution level is strongly influenced by the river flow and temperature. Our samples were collected during summer, period of minimum velocity flow of water. Consequently, it is expected that the majority of the suspended matter most associated with the river transport of pollution [7,8] will be in the deposited side of the equilibrium between re-suspension and deposition.

Summarizing, the water quality does not represent an alarming problem, even though several critical values were recorded. In the case of Zn they can not be attributed exclusively to the pollution. The water quality strongly depends on the discharge of the used waters from the ore processing units in the area.

Analytical merits of chemical analysis

Limit of detection (LD). The limits of detection for Cu, Pb and Zn were calculated as three times the standard deviation of replicate background readings. For sediment they were related to dry mass taking into account the weight of the sample and the dilution (Table 3).

For sediments the use of ICP-AES as analytical method was the best one as its dynamic range cover several orders of magnitude. For Cu and Zn the admissible levels in water are seven and six times respectively, the detection limit and there is no difficulty in establishing them. The limit of detection for Pb was not low enough in comparison with the admissible level, but it raised no problem, as in most of water samples Pb was below the limit of detection.

Internal precision (Relative Standard Deviation, RSD). The internal precision was evaluated on the basis of three subsequent readings taken during the measurements of each of the samples.

Table 3

Analytical merits of Cu, Pb and Zn determination by ICP-AES using SPECTROFLAME (SPECTRO, Kleve, Germany)

Matrix		Units	Cu	Pb	Zn
Sediment	Precision (n=24)	%	0.3 – 2.3	0.4 – 3.3	0.2 – 6.6
	Concentration range	mg Kg^{-1}	8.9 - 339	59 - 465	56 - 2060
	Reproducibility (n=3)	%	1.8 – 3.6	0.5 -2	5 – 6
	Concentration range	mg Kg^{-1}	34 - 130	190 - 219	218 - 1099
	Limit of detection	mg Kg^{-1}	0.35	1.5	0.25
Water	Precision (n=36)	%	-	48.9 – 61.1	0.5 – 3.7
	Reproducibility (n=3)	%	-	-	0.8 – 37.6
	Concentration range	mg L^{-1}	-	0.036 – 0.045	0.038 – 0.240
	Limit of detection	mg L^{-1}	0.007	0.030	0.005

Reproducibility. To evaluate the reproducibility selected sediment samples (3) were chosen and 4 sub-samples were subject to the same chemical sample preparation step and subsequent measurements. The samples chosen were encompassing low and high concentrations. With respect to the water samples, three aliquots were measured from each sample.

As seen in Table 3, the internal precision was good for all the sediment data and in general below 3% except slightly higher errors for Zn in the low concentration ranges (RSD between 3 and 6.6% for concentrations below 200 mg Kg^{-1}). This good internal precision is due to the fact that measured concentrations are relatively high compared to the limit of detection. The lowest concentration was at least 10 times above the limit of detection (for Pb) but in general well above 50 fold. The water samples show good internal precision (RSD<3%) for Zn, where concentrations are well above the limit of detection. In the determinations of Pb just above the detection limit, the RSD was higher than 50%.

The reproducibility of the analysis in sediments indicated similar trends like the internal precision. Different concentration ranges had similar errors (RSD<5%) for all three elements.

Conclusions

In the investigated period the water quality of the Somes river was within the range of Romanian standards in respect of Cu and Pb. Critical values were found in a few sites, but they did not represent a major problem. The situation was found to be better than after the cyanide spill accident when the concentrations of Cu and Zn exceeded many times the admissible values. The high content of Zn in water can not be attributed exclusively to the pollution, but also to natural background.

The sediment situation is different, as the contents of the investigated heavy metals are exceeding manifolds the critical limits for soil in Romania or Canadian Possible Effect Limits (Canada) and demonstrates the potential toxicity of sediments for the ecosystem.

The cyanide spill accident that occurred close to Baia-Mare, Romania, in 2000, was recognized as having long-term consequences for the ecosystem, which impose further periodical evaluation of the river system status.

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