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DISTRIBUTION AND BIOAVAILABILITY OF MOBILE ARSENIC IN SEDIMENTS FROM A MINING CATCHMENT AREA

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Abstract. In the paper is studied the dynamic partition of As among solids and liquid phases in Baiaga River from Certej catchment area, as result of historical pollution caused by mining activities. In order to evaluate the mobility of arsenic from sediments via surface water, were collected and analyzed both sediments and surface water samples from ten points along Baiaga River. As chemical extraction procedure was chosed a method applied on a certified reference material (WQB-1, provided by National Laboratory for Environmental Testing - National Water Research Institute, Ontario, Canada) for comparing the As mobility from sediments and CRM WQB-1. The extraction procedure consist in cold acid treatment using 5% HCl, sediment / extraction solution ratio 1:20, followed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) for determination of As content. Total and mobile As values were situated in the range 46 to 775 mg/kg dry matter, exceeding the MAV for sediment quality, which is 29 mg/kg in Romanian Legislation. The results indicated a relatively high percentage of mobile As reported to the total content (32.1% to 65.5%), percentage correlated with As values founded in surface water samples. The study revealed a significant pollution level in the aquatic system as results of arsenic mobility.

Keywords: sediments, mobility, arsenic, pollution, surface water

AIMS AND BACKGROUND

Mining industry represents a major source for aquatic pollution with heavy metals, an important group of toxic contaminants that accumulates in sediments[1-3]. Environmental pollution generated by heavy metals has been studied extensively because these metals are not biodegradable and could exist in chemical species with high solubility, in some cases exceeds the maximum admissible values for sediment quality[4, 5].

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The heavy metals from sediments are either absorbed on the surface of mineral particles or linked to the organic matter, sulfides, and carbonates fractions, in proportions depending on the physical-chemical conditions existing in the sediment and in the associated pore water. For evaluate the reactivity and bioavailability of heavy metals in soils and sediments, many speciation and leaching tests, often single procedure, have been developed and implemented [6-10].

Arsenic is a toxic metal found in rocks, soil, water, sediment and air. In the terrestrial and aquatic ecosystems, arsenic is found through a combination of natural processes, such as reactions due to atmospheric conditions, biological activities, the volcanic emissions, and as a result of anthropogenic activities[11, 12]. In the aquatic environment, arsenic is distributed in both sediment and surface water. High concentrations of arsenic in natural waters are usually associated with sedimentary rocks of marine origin rich in arsenic, weathered volcanic rocks, fossil fuels, geothermal areas, mineral deposits and mining waste[13]. Mobility, bioavailability and toxicity of heavy metals in aquatic systems depend on the chemical forms in which metals are found in sediments and surface water. Therefore, in addition to the quantification of the total heavy metal amount existing in the considered aquatic environment, it is important to estimate the bioavailability and the distribution, both in water and in the sediment matrixes[14].

In the present paper, were studied the distribution and mobility of arsenic in sediments samples and the total content in surface water in ten sampling points situated in Certej catchment area, Hunedoara County, Romania. In order to determine the arsenic mobility from sediment samples, a cold extraction procedure was performed[15].

EXPERIMENTAL

The investigated sector (Baiaga Stream) is situated in Certej catchment area, Hunedoara County, Romania. The mining activities of non ferrous ore developed in this area for several hundred years has been generated acid wastewaters with high concentration of metals.

Sediment samples and surface water samples in contact with sediments were collected from ten sampling points on the Baiaga Stream in two sampling campaigns performed in 2014 (August and October). The schematic map of sampling point is presented in figure 1 and the GPS coordinates and description of sampling points are in table 1.

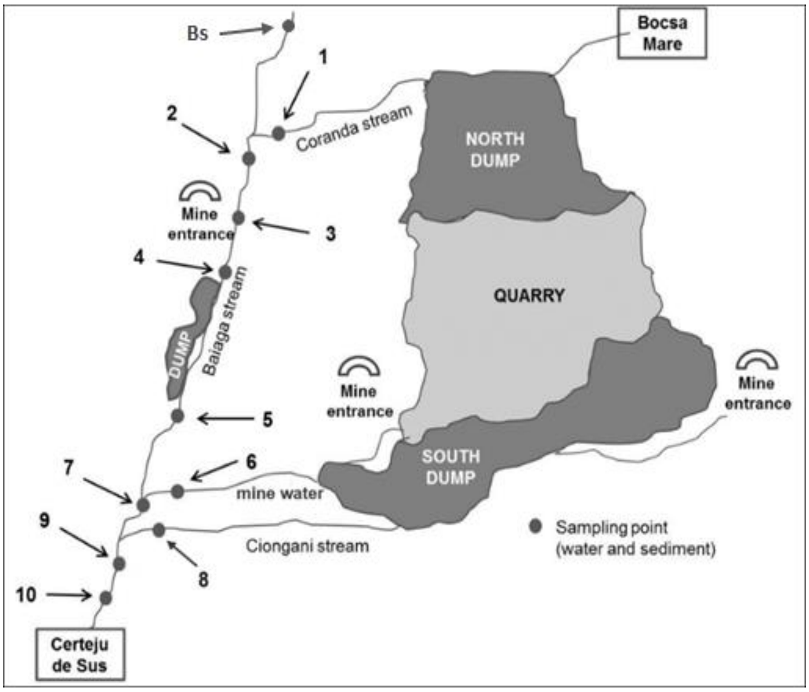

Figure 1. Map of sampling points (Certej area)

Table 1. GPS coordinates and description of sampling points

No.	GPS Coordinates	Sample type / Indicative	Observations
1	45˚59’84.3” N 23˚00’25.9” E	water (W1), sediment (S1)	Sampling point situated on Coranda Stream - upstream
2	45˚59’81.9” N 23˚00’13.1” E	water (W2), sediment (S2)	Sampling point situated on Baiaga Stream, downstream of the confluence with Coranda stream
3	45˚59’80.1” N 23˚00’06.3” E	water (W3), sediment (Sd3)	Sampling point situated at the exit Nicodim gallery
4	45˚59’67.7” N 22˚59’96.6” E	water (W4), sediment (Sd4)	Sampling point situated on Baiaga Stream, downstream of the confluence with career water from Nicodim gallery
5	45˚59’41.8” N 22˚59’74.0” E	water (W5), sediment (S5)	Sampling point situated on Baiaga Stream, upstream of the confluence with career water
6	45˚59’41.7” N 22˚59’73.9” E	water (W6), sediment (S6)	Sampling point from career water, before of the confluence with Baiaga Stream
7	45˚59’39.8” N 22˚59’74.1” E	water (W7), sediment (S7)	Sampling point situated on Baiaga Stream, downstream of the confluence with career water and upstream of the confluence with Baiaga Stream

8	45˚59’41.0” N 22˚59’72.2” E	water (W8), sediment (S8)	Sampling point situated on Ciongani Stream before of the confluence with Baiaga Stream;
9	45˚59’39.8” N 22˚59’68.3” E	water (W9), sediment (S9)	Sampling point situated on Baiaga Stream, downstream of the confluence with Ciongani Stream
10	45˚59’20.7” N 22˚59’06.5” E	water (W10), sediment (S10)	Sampling point situated on Baiaga Stream, in the Hondol Village;
11	46˚00’29.6” N 23˚00’51.3” E	sediment blank sample (Bs)	Sampling point situated on Baiaga Stream - 2 kilometers away from the quarry area.

Materials and Methods

Collection and analysis of water and sediment samples: The sediment samples (around 1 Kg) were collected from sampling points (depth to 0-5 cm). The samples were collected in polypropylene containers and kept at 4ºC during the transport to the laboratory. At the same time, water samples were taken from the same locations as sediments. The water samples were kept in high density polyethylene bottles and preserved by addition of ultrapure nitric acid.

Surface water samples pretreatment: 5 mL surface water samples were digested in microwave oven (Berghof, Germany), at 200 °C with 6 mL of nitric acid (65%) and 2 mL hydrochloric acid (37%), acids of ultrapure quality.

Sediment pretreatment

Total content – A part of each sediment sample was air-dried, homogenized, and fraction less than 63 μm for evaluation of the total content of arsenic was separated by sieving in a Fritsch Analysette 3 Spartan Vibratory Sieve Shaker. 2 g sediment samples were digested in a microwave oven (Berghof, Germany) at 175°C with a 1:3 (*v/v*) nitric acid (65%): hydrochloric acid (37%) mixture.

Mobile fraction - For mobile fraction determinations, the other part of each sediment sample was sieved in wet condition using surface water from same sampling point to maintain same structure as in natural condition. The fraction less than 63 μm was collected. Mobile fraction of arsenic was determined using a cold extraction treatment, applied also on a certified reference material

WQB-1, in order to verified the single chemical extraction procedures (recovery in the range 99.70% to 99.88%)[16].

The cold extraction procedure (figure 2) was performed three times per each sediment sample, the final result was reported as average of the results. To control the quality of the extraction (contamination during procedure), blank extraction (without sediment) was applied for each set of analysis.

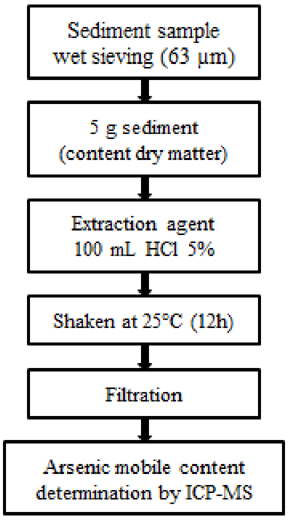

Figure 2. Scheme of cold extraction procedure for mobile content

The total content of arsenic in sediment samples and surface water were analyzed by ICP-MS (Bruker – Aurora M90) in CRI mode (Collision Reaction Interface) using hydrogen gas. All the chemicals and extraction agents were analytical reagents grade provided by Merck. Calibration curve was performed using a Certified Reference Material ICP multi-element standard solution XXI for MS (Merck quality).

RESULTS AND DISCUSSION

The pH of aquatic environment is an important factor in the study of metals mobility. Therefore, the acid pH values in surface water and sediments increase the mobility of arsenic species that will be found in dissolved forms in surface water[3].

The pH values in surface water were within the acid range, around 3-4 pH unit. (figure 3), comparing with the limits imposed by Romanian Order no.161/2006 for surface water quality[17].

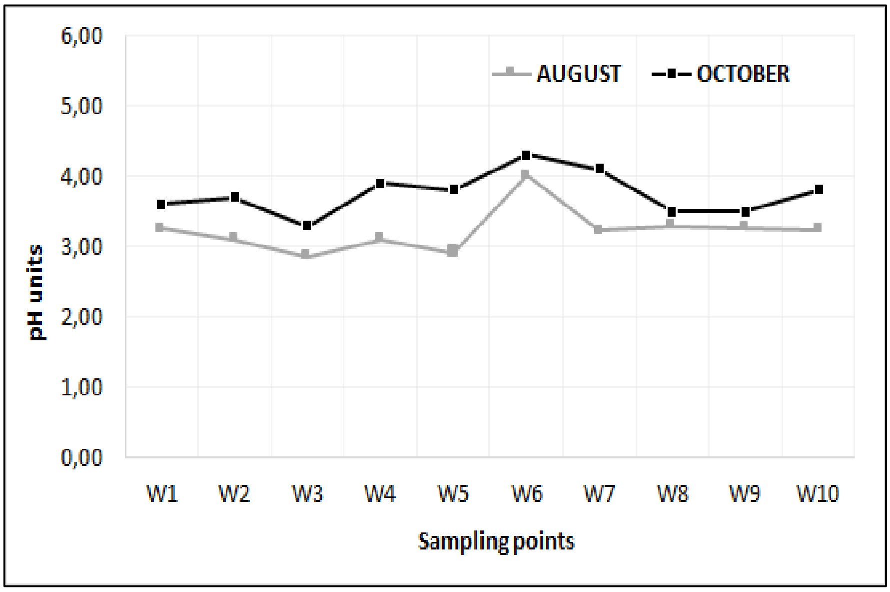

Figure 3. Variation of pH in surface water samples – two sampling campaigns

The obtained results regarding total content of arsenic in surface water, for two sampling campaigns, are presented in figure 4:

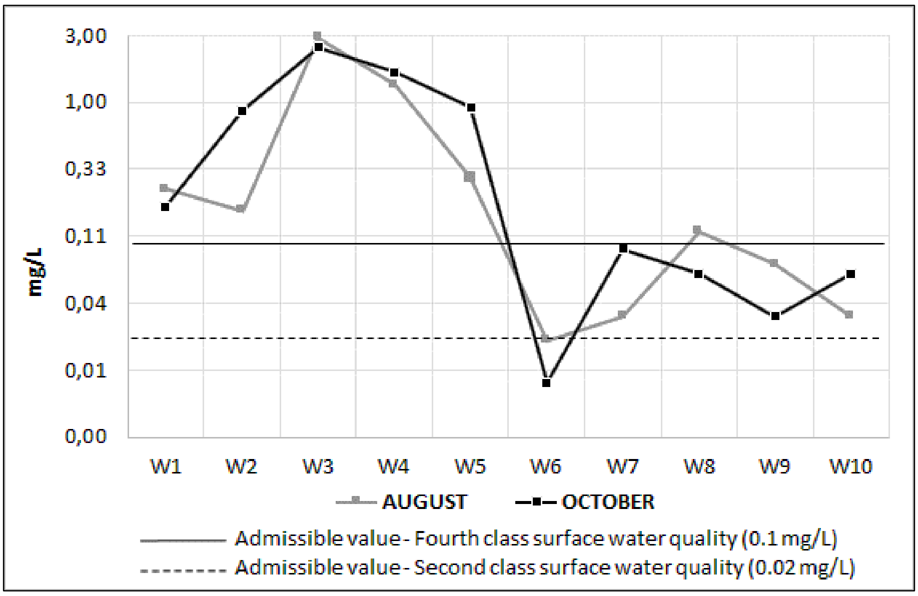

Figure 4. Variation of total arsenic in surface water – two sampling campaigns

The results for total and mobile arsenic contents in sediments, for two sampling campaigns are presented in figure 5 and 6.

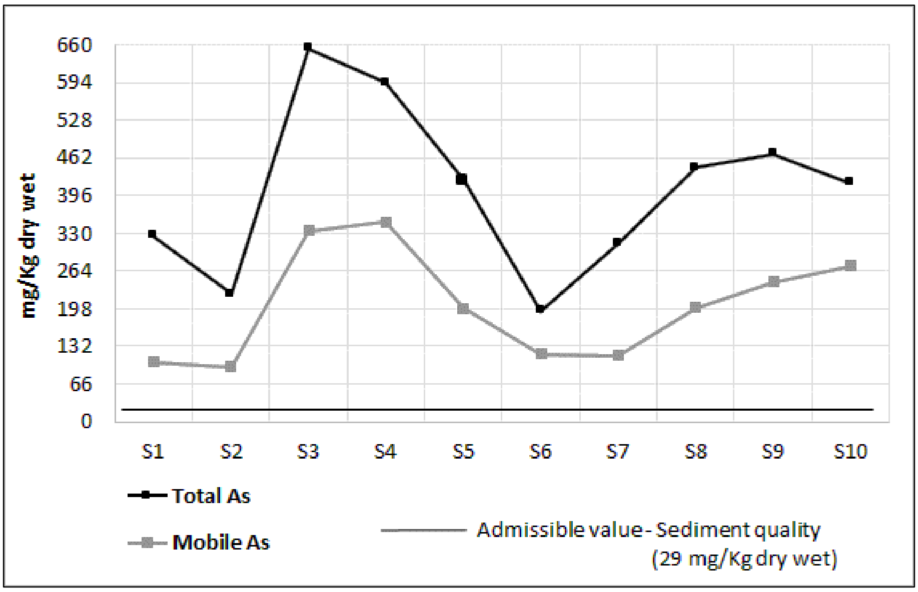

Figure 5. Variation of total and mobile arsenic in August campaign

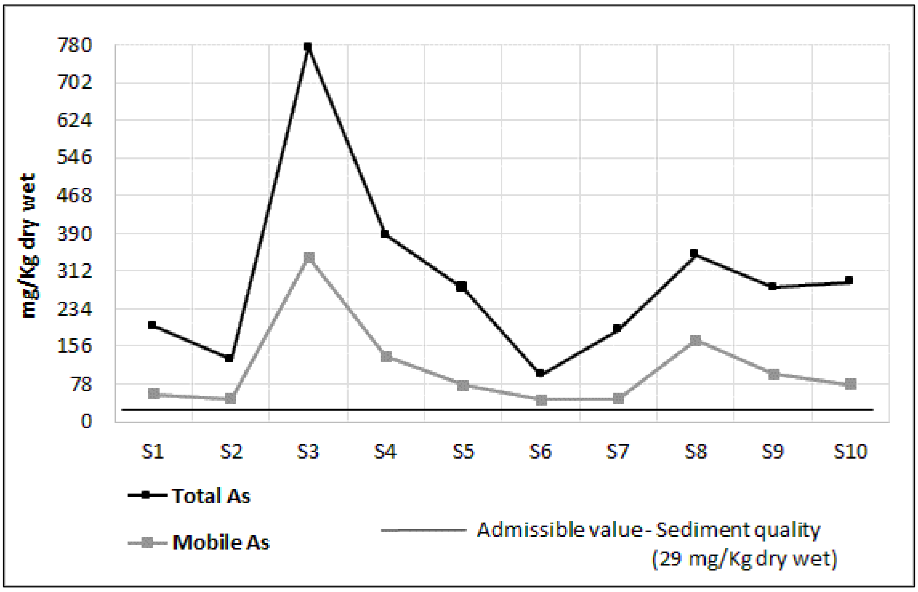

Figure 6. Variation of total and mobile arsenic in October campaign

Total and mobile arsenic concentrations in sediment samples were situated in the range 46 to 775 mg/kg dry wet, exceeding in some points more than 26 times the maximum admissible value according to Romanian Legislation. The total arsenic content determined in natural area background (Bs sampling point) was 9.34 mg/kg dry wet. It was observed that the lowest concentration value founded in S6 sediment sample (97 mg/kg dry wet), exceeds more than 10 times the natural background (figure 5 and 6).

The leachable fraction of arsenic in sediment samples indicate a relatively high percentage of mobile As reported to the total content (32.1% to 65.5%). Therefore, high amount of arsenic is found in surface water samples. Consequently, the water quality is of poor quality and exceed in all cases the second class quality for surface water.

In October, the total and mobile concentrations of As, are lower compared with values obtained in August sampling campaign, excepting the arsenic concentration obtained in S3 sediment sample due to fluctuations of career water flow coming from Nicodim gallery. In downstream, relatively low flows of mine water are diluted with surface water coming from Ciongani Stream.

High content of mobile As, over the maximum admissible value imposed by the Romanian Legislation (29 mg/kg d.m.) for the total content, indicate the presence of bioavailable fraction that can be transported through the aquatic environment either as soluble species or adsorbed on suspended solid particles.

Bioavailability index

For estimation the sediment ability to transfer As in surface water and implicitly in the environment, was calculated the bioavailability index[18, 19] by formula[8]:

$$iBA_m(\%) = (C_{m(l)} * 100)/C_{m(total)})$$

Were: $C_{m(l)}$ – metal content in leachable form, soluble in water

$C_{m(total)}$ – total metal content

Table 2. The bioavailability indexes of arsenic in sediment samples

Bioavailability index (%)										
Sediment sample	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	31.9	43	51.1	58.9	47	60.8	36.9	44.9	52	64.9

October	28.5	36.8	44	34.9	27.5	47.4	25	48.9	35.5	26.4

The high percentages of bioavailability indexes ranging between 25% to 64.9%, shows a permanent risk of pollution both through the area acidic and high concentrations of total arsenic contents. Thus, the precipitations as rain, will wash permanently the sediments and will collected significant amounts of toxic metal.

CONCLUSION

In this paper we studied the arsenic distribution and mobility in river sediments via surface water in an area affected by anthropogenic industrial activities.

Arsenic pollution due to mining activities in the Certej area, although ended many years ago, continue to affect both the quality of sediments and surface water. Arsenic is found in proportion of 40-50% in the mobile form, in this acidic area and thus is permanently leachate to surface water. Depending on the seasonal precipitation amounts, the concentration of arsenic in the surface water may be higher or lower but over the maximum admissible values for second class for surface water quality in accordance with Romanian Legislation.

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