Availability of trace elements in the abandoned Freixeda gold mine area, NE Portugal

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Abstract Selected geochemical results are presented from Freixeda gold mine area. The purpose was to establish the geochemical patterns of trace elements, which are useful for predicting their release ability into the aquatic environment for the assessment of pollution extension on surface waters along the Freixeda stream. Stream sediment and water samples were found to be contaminated for a considerable distance downstream. Based on chemical sequential extraction the distribution of trace elements in sediments, in particular As, is linked to exchangeable and acid-soluble species, upon which desorption and ion-exchange reactions may originate the release of these readily mobile and available phases.

Keywords Abandoned mines, selective chemical extraction, availability, trace metals, arsenic

Introduction

Freixeda mine is located in NE Portugal and was exploited for Au, Ag and Pb until 1955. The mine was closed after 1995, where more than 0.5 Mt of tailings remained exposed to erosion for more than 50 years. Several studies on soils, sediments, surface water and groundwater were carried out in the last 15 years (Montes *et al.* 2007; Pereira *et al.* 2007, 2008) in order to evaluate the environmental impact of Freixeda mine in the surrounding region.

The objective of the present study was (a) to study the geochemical patterns of As, Cu, Fe, Mn, Pb, and Zn; (b) predicting their availability to the aquatic environment and (c) the assessment of pollution extension along the Freixeda stream till the mouth in Tua river, a source of public water supply.

Geological and environmental setting of the study area

Freixeda Mine is part of the Gold-Silver Metalogenetic Province of Iberian Peninsula. These Au-Ag deposits are usually associated with Paleozoic quartzites and black schists and not so often they are intragranite. Gold ocurrences are associated with veins in metamorphic metasediments, affected by Variscan Orogeny (Almeida and Noronha 1988). According to Montes *et al.* (2007) the Freixeda quartz veins are composed by silicate minerals (mainly quartz and chlorite) and sulfide minerals (such as arsenopyrite, pyrite, sphalerite, galena, chalcopyrite and As, Pb, Fe and Sb sulphosalts). Arsenopyrite is the most representative mineral. In this mineral some As was replaced by Sb. Pyrite has some As in its composition reaching 1.74 % (Montes *et al.* 2007). Studies carried out by Cogema (1988) showed that soils presents higher As (6 to 7663 mg kg^{-1}) and Pb concentrations (18 to 1000 mg kg^{-1}). According the same study soils were classified as inappropriate for agriculture. Pereira *et al.* (2008) showed that the AMD impacted stream has $3.5 < pH < 4.2$ and the water samples are classified as Mg-SO_4 type with high concentration

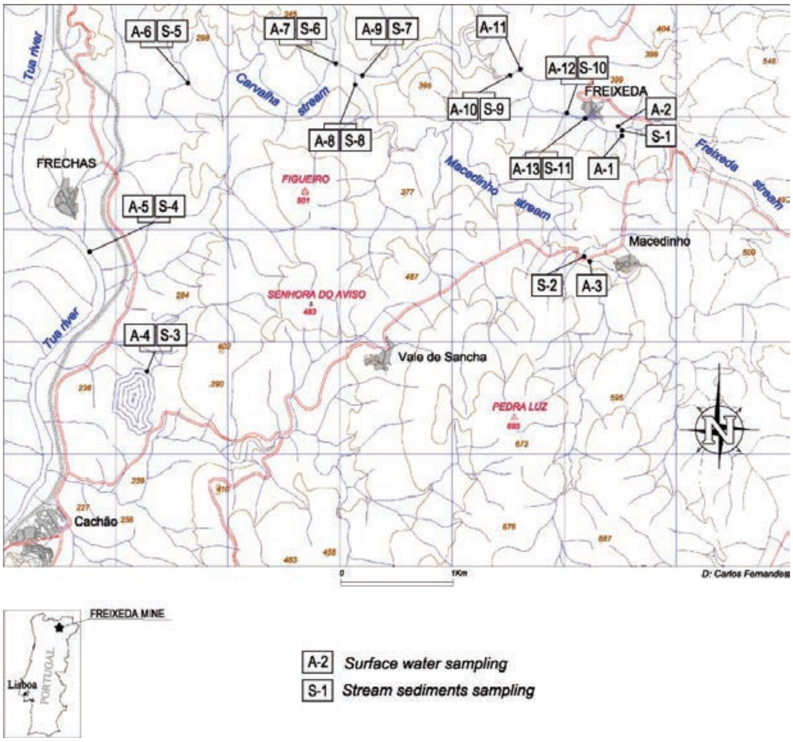

Fig. 1 *Sampling locations of waters and sediment samples in the Freixeda study area.*

of Al (1.01 mg L^{-1}), Fe (5.22 mg L^{-1}), Mn (10.1 mg L^{-1}) and low As concentration (18 µg L^{-1}). Main environmental problems in the region are related to As concentration in groundwater and in surface water.

Materials and Methods

In order to assess the dynamics of leaching, transport, and accumulation of some selected trace elements, stream surface waters (A) and sediments (S) were sampled (Fig. 1).

Sampling and analysis of water samples

Thirteen water samples were collected (Fig. 1). Sample A-1 represents the adit outflow, A-2 from a deep well, A-3: samples collected in Macedinho stream; A-4: sample collected outside the Freixeda mine influence, representing the local geochemical background; A-5 to A-13 samples collected in the Freixeda stream from the adit confluence to the Tua river. Water samples were filtered *in situ* by filling a 60 mL syringe, rinsed three times with the water, and forcing the water passing through a 25 mm disposable disk filter of cellulose acetate membrane with a pore size of 0.20 µm. After filtration into 100 mL polyethylene bottles, samples were immediately acidified at 2 % HCl for the analysis of major cations and trace metals by ICP-OES or AAS. For the analysis of major anions and alkalinity, samples were collected into 1-L polyethylene bottles and filtered through a 0.45 µm acetate cellulose membrane only in the moment of the sample analyze preparation. Field blanks for assessing possible contaminations were prepared with de-ionised water in the field.

Temperature, pH, and electric conductivity (EC) of the waters samples were recorded at each site. The pH was measured using a HI 8424 microcomputer pH meter and EC using a HI 8633 microcomputer electric conductivity meter. All EC measurements are referenced to 25 °C.

Water sample analysis was carried out in the Laboratory of the LNEG an accredited lab by the Portuguese official authority of Quality IPAC. At least, 20 % of the samples were analyzed in duplicate and some tests of recuperation were also performed. Quality control was assessed for accuracy by analysing a reference water sample (AQUACHECK) and also for accuracy and precision by analysing an internal control standard solution. The analyzed elements include major anions (HCO_3^-, Cl^-, NO_3^- and SO_4^{2-}), major cations (Na, K, Mg and Ca), as well a suite of dissolved trace elements (Ag, Al, As, Bi, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, and Zn). Chloride, NO_3^- and SO_4^{2-} on filtered unacidified samples were analyzed using a Dionex 1000i ion chromatography (IC) Work33 station. Bicarbonate was determined by titration on filtered unacidified samples. The concentrations of major cations and trace elements in acidified waters were determined using mass inductive plasma spectrometry (ICP-MS).

Stream Sediments Sampling and Analysis

In order to evaluate the extent of contamination, 11 stream sediments samples (composite samples of 3 sub-samples collected from several places at the sample site) were collected (Fig. 1). Sample S-1 was collected upstream AMD inflow to Freixeda stream; samples S-2 and S-3 were collected in a different watershed. Sample S-3 represents the local geochemical background; samples S-5 to S-11 were collected in Freixeda stream; and sample S-4 was sampled in the Tua river.

Stream sediments for chemical analysis were oven dried at 40 °C before dry sieving, mixed, homogenized, and sieved through a 200 mesh screen for chemical analyses. The homogenized stream sediments were analyzed also in the Laboratory of the LNEG. For trace metal analyses, a 0.5-g split was leached in hot (95 °C) aqua regia ($HCl–HNO_3–H_2O$) for 1 h. After dilution to 10 mL with deionized water, the solutions were analyzed for Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, P, Pb, Sb, V, Y, and Zn by conductive plasma emission spectrometry.

Selective Chemical Extraction Procedure

Aiming to establish the geochemical patterns of selected trace elements (As, Cu, Fe, Mn, Pb, and Zn), which are useful for predicting their release ability into the aquatic environment and into the ecosystem, the elements were analytically partitioned into labile and residual fractions using a selective sequential extraction (SCE) procedure proposed by Cardoso Fonseca and Ferreira da Silva (1998). According to Cardoso Fonseca (1982), the extractable fractions were obtained with different solutions: (a) F1 – ammonium acetate (1M NH_4Ac, pH 4.5) for extraction of water soluble and dissolved exchangeable ions, specifically adsorbed and carbonate-bound; (b) F2 – hydroxylamine hydrochloride (0.1M $NH_4OH.HCl$, pH 2) for elements adsorbed by Mn oxyhydroxides; (c) F3 – ammonium oxalate (dark) (0.175M $(NH_4)_2C_2O_4$–0.1M $H_2C_2O_4$, pH 3.3 in darkness) for elements linked to amorphous Fe oxides; (d) F4 – H_2O_2 35 % to extract elements associated with organic matter (on this step sulfide-bound as primary sulfide minerals could not be totally leached out according to Rapin and Forstner (1983) and Khebonian and Bauer (1987)); (e) F5 – ammonium oxalate (UV) (0.175M $(NH_4)_2C_2O_4$–0.1M $H_2C_2O_4$, pH 3.3 under UV radiation for extract ions associated with crystalline Fe oxides; (f) F6 – mixed acid ($HCl+HNO_3+HF$) where metals strongly associated with crystalline structures of minerals (such as the remaining silicates) will be decomposed (they are therefore unlikely to be released). In this study the SCE was carried out on 1 g of selected samples that were previously air dried at room temperature in order to not disturb the original metal distribution (as suggested by Quevauviller *et al.* 1994). Samples were sieved to obtain the appropriate particle size distribution (Filgueras *et al.* 2002). After each reaction timing the solutions were centrifuged and filtered. Metal analyses were carried out by AAS (for Cu, Pb, Zn, Fe) and by hydride generation combined with AAS (for As). The accuracy of the sequential treatment, considered as a whole, may be estimated by the comparison of the total sum of the amounts obtained after each sequential extraction step with the total amount obtained after hot mixed-acid attack of the same sample. The overall recovery rates ranged from 77 % to 112 %.

Results and Discussion

Results of water chemical analyses are presented in Table 1. Mine gallery outflow (A-1) results classifies this sample as AMD: low pH (4.1) and high Fe, SO_4^{2-}, and Al, Cd, Cu, Mn and Zn concentrations. Groundwater from a deep well (A-2) shows near neutral pH (6.5) and high As (745 µg L^{-1}) and Fe (6.6 mg L^{-1}) concentrations. This well is overflowing during all the year,. During driest years Freixeda stream is dried and it was possible to identify points of discharge from the aquifer into the stream from the left margin (Pereira *et al.* 2008).

Surface water A-3, is from a different watershed (Macedinho stream) shows influence from sulfides mineralization associated with Pedra Luz and Macedinho mining works. Sample A-4 is representative of local geochemical background values (pH 8.0, low SO_4^{2-} (13 mg L^{-1}), As (12 µg L^{-1}) and trace metal concentrations below the detection limits of the method. After the confluence of AMD with Freixeda stream (A-13), SO_4^{2-} reaches 127 mg L^{-1}, and trace element concentrations increase to As = 326, Zn = 515, and Mn = 207 (µg L^{-1}). Composition of surface water downstream sample A-13 is characterized by samples A-12 to A-5 (distance of about 6 km), being A-5 the sample collected at the confluence of Freixeda stream with Tua River. Cadmium, Cu and Pb are bellow detection limit in all samples. Manganese and Zn concentrations decrease below detection limits about 1 and 3 km distance, respectively. Sulfate and As decrease to background values at Tua River (A-5) but As keeps in solution with high concentration for longuer distance that other trace elements (Fig. 2).

Table 2 presents the analytical results from 11 stream sediment samples. Background values are represented by sample S-3 (in mg kg^{-1}): As = 32; Cu = 21; Mn = 558; Pb < 32; Zn < 12 and Fe = 4.53 %. It can be observed that some of the stream sediments are seriously contaminated compared to local geochemical background values, despite some mitigation after the confluence with the Tua River. Comparing the concentrations obtained in the Freixeda stream samples (S-11 to S-5) with background values, it is clear that they are moderately to strongly enriched (As – 3.4 to 35 times;

Sample ID	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10	A-11	A-12	A-13
Temp. (°C)	18.2	17.3	20.4	26.2	25	21.7	26.6	26.7	29.2	23.9	23.0	22.3	23.3
pH	4.1	6.5	6.5	8.1	6.9	6.4	6.6	6.6	6.8	5.9	5.9	6.0	6.6
EC (µS cm^{-1})	624	695	145	110	53	124	146	123	153	266	267	315	350
Al (mg L^{-1})	2.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.13	< 0.1	0.32	0.83
Ca (mg L^{-1})	59.6	57.2	10.5	7.13	4.0	8.6	9.6	8.1	11.1	21.9	21.9	25.5	30.0
Mg (mg L^{-1})	48.6	47.6	5.4	4.47	2.2	4.9	5.5	4.7	6.1	13.2	13.5	16.7	15.9
Na (mg L^{-1})	16.4	69	14.5	11.3	5.4	13.0	13.4	12.9	14.2	20.4	20.5	22.9	21.5
K (mg L^{-1})	5.3	3.90	3.04	1.48	0.75	1.42	1.72	1.62	1.94	7.4	7.3	9.9	20
Sr (mg L^{-1})	0.25	0.94	0.07	0.05	0.02	0.07	0.07	0.06	0.07	0.14	0.14	0.16	0.17
SO_4 (mg L^{-1})	405	345	13.8	13.4	2.9	16.3	17.4	12.6	24.2	73	71	118	127
HCO_3 (mg L^{-1})	1.2	157.8	52.9	38.2	25.7	46.8	51.5	44.3	55.7	65.3	67.9	53.4	55.2
Cl (mg L^{-1})	4.7	8.4	14.3	10.3	4.5	11.1	11.0	12.2	10.1	15.6	15.7	14.4	12.8
NO_3 (mg L^{-1})	4.81	< 1.1	3.88	1.31	0.98	< 0.3	< 0.3	< 0.3	< 0.3	5.07	5.84	< 0.5	5.26
Fe (mg L^{-1})	1.12	6.6	0.66	<0.02	0.06	<0.02	0.05	<0.02	<0.02	<0.02	<0.02	0.03	0.10
Mn (mg L^{-1})	9.36	1.98	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.45	0.21
Cu (µg L^{-1})	47	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25
Zn (µg L^{-1})	4820	20	< 15	< 15	< 15	< 15	< 15	< 15	< 15	35	18	330	515
Cd (µg L^{-1})	37	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8
Pb (µg L^{-1})	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200
As (µg L^{-1})	< 5	745	185	14	12	62	75	96	24	46	50	171	326

A-1: AMD sample outflow from the adit; A-2: deep well, A-3 Macedinho stream; A-4: sample collected outside Freixeda mine influence and representing the local geochemical background; A-5: Tua river near the mouth of Freixeda stream; A-6 to A-13: Freixeda stream.

***Table 1** Chemical composition of water samples from Freixeda study area.*

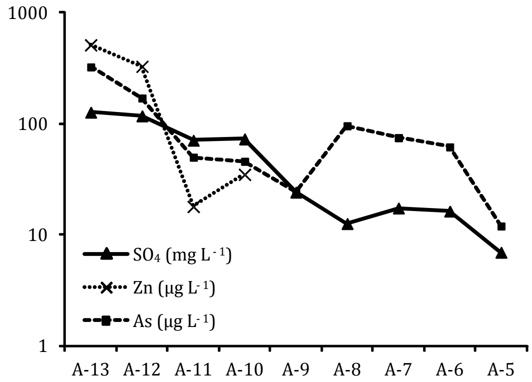

Fig. 2 *Variations in sulfate, As and Zn concentrations from surface water of Freixeda stream downstream Freixeda mine adit until discharge in Tua River (A-5).*

Pb – 2 to 17 times; Zn – 6 to 100 times). Given the toxicity of these elements, this represents a potentially harmful situation.

In areas exposed to AMD, stream sediment samples usually consist of a complex mixture of geochemical bearing phases containing potentially toxic metals. It is well known that the availability of such hazardous metals strongly depends on their specific chemical forms and binding capabilities, rather than on the total element concentrations. Table 3 shows the geochemical partitioning of some selected elements in those metal bearing phases for each selected sample.

According to the SCE results (Table 3) Fe is mostly extracted in the fraction linked to amorphous Fe oxyhydroxides (25 to 52 %). A considerable proportion of Fe (36 to 43 %) appears to be also accumulated in the residual fraction associated to the primary sulfides. It must be pointed out that the easily extractable Fe, in the sediments, still reached around 30 %.

Copper and Pb show high and similar partitioning pattern with ammonium oxalate (dark) (34.3 to 42 % for Cu and 32.9 to 36.3 % for Pb) suggesting that Pb may also be linked, to some extent, to amorphous Fe oxides. Moreover, part of extracted Pb was obtained with ammonium acetate indicating that the exchangeable/carbonate fraction is probably a preferential sink for Pb.

High extraction percentages of As (20.8 to 36.5 %), Zn (9.8 to 53 %), and Mn (8.2 to 61.7 %) were also extracted by ammonium acetate, probably related with secondary minerals and sulphosalts dissolution. Arsenic concentration values extracted in F1 ranges from 13 µg L^{-1} to 441 µg L^{-1}. Nevertheless these elements also show considerable extraction in ammonium oxalate (dark) fraction (As 42.3 to 57.4 %, Zn 17.8 to 19.8 %, and Mn 11 to 18.8 %) suggesting sorption onto amorphous Fe oxi-hydroxides.

Sample ID	**S-1**	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	**S-9**	**S-10**	**S-11**
As (mg kg^{-1})	118	385	32	65	108	139	115	418	140	271	1129
Cu (mg kg^{-1})	35	33	21	19	24	26	21	34	22	45	55
Fe (%)	3.97	3.09	4.53	2.66	3.02	3.45	3.49	3.58	3.49	3.55	2.61
Mn (mg kg^{-1})	862	743	558	496	805	746	734	1051	854	1042	534
Pb (mg kg^{-1})	38	47	<32	<32	<32	<32	<32	55	33	64	273
Zn (mg kg^{-1})	645	37	<12	<12	80	80	104	46	314	880	636

1: Freixeda stream, near AMD outflow; S-2 Macedinho stream; S-3: sample collected outside Freixeda mine influence and representing the local geochemical background; S-4: Tua river, near the confluence with Freixeda stream; S-5 to S-11 Freixeda stream.

Table 2 *Concentrations of As, Cu, Fe, Mn, Pb and Zn in Freixeda stream sediment samples.*

	S-11						**S-6**						**S-4**					
	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F1**	**F2**	**F3**	**F4**	**F5**	**F6**	**F1**	**F2**	**F3**	**F4**	**F5**	**F6**
As	36.5	3.7	42.3	1.4	1.4	0.9	24.9	1.4	47.1	0.4	24.4	2.1	20.8	2.3	57.4	0.5	14.4	5.2
Cu	29.8	0.0	42.0	0.0	0.0	20.9	0.0	0.0	34.3	0.0	23.3	42.1	0.0	0.0	41.0	0.0	21.3	37.7
Fe	18.5	3.7	32.7	0.5	0.5	36.0	8.9	3.0	24.7	0.2	20.4	42.8	33.8	10.9	51.9	0.6	37.6	42.6
Mn	61.7	7.5	18.8	1.6	1.6	4.0	49.3	12.4	18.8	0.6	12.4	6.5	8.2	3.8	11.0	0.0	13.2	63.7
Pb	37.9	0.0	32.9	3.7	3.7	14.3	18.6	0.0	36.3	0.0	24.5	20.4	18.2	0.0	33.9	0.0	22.1	25.7
Zn	53.0	12.3	19.8	1.0	1.0	8.0	15.0	8.3	20.8	0.0	24.3	31.6	9.8	4.5	17.8	0.0	29.1	39.0

Table 3 *Relative extraction ratio (%) of As, Cu, Fe, Mn, Pb and Zn of each step of the SCE procedure.*

The percentage of extraction associated to the 3 initial steps of the sequential extraction reaches values of 34.3 to 71.8 % for Cu, 44.1 to 85.1 % for Zn and 73.4 to 82.5 % for As, revealing that these elements are bioavailable and may be easily mobilized to the ecosystem through the modification of pH and Eh conditions. This interpretation is supported mainly by high As concentrations measured in water samples.

Conclusions

In this study it was intended to investigate and quantify the impact of the former Freixeda mine in the surrounding environment, with a basis on geochemical analysis of stream sediments and waters.

Obtained data allowed a better understanding of the chemical dynamic, between stream sediments and surface water, of As, Cu, Fe, Mn, Pb, and Zn and their environmental relevance. The geochemical results obtained indicate that the Freixeda stream sediments are contaminated in As, Cu and Zn. Iron is mostly extracted in the fraction linked to amorphous Fe oxy-hydroxides, but about 30 % is easily extractable Fe. High percentages of As and Zn were also extracted by ammonium acetate, probably from secondary minerals and sulphosalts dissolution. Nevertheless these elements also show considerable extraction in ammonium oxalate (dark) fraction suggesting sorption onto Fe oxi-hydroxides.

The approach based on chemical sequential extraction demonstrates that the distribution/accumulation of As, is mainly linked to exchangeable and acid-soluble species upon which desorption and ion-exchange reactions may originate the release of this readily mobile and available metalloid into surface waters.

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