Arsenic and trace metals in groundwater of abandoned Au-Ag Freixeda Mine (Portugal NE)

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ABSTRACT
Freixeda mine is located in Portugal NE and was exploited for Au, Ag and Pb. The mine was closed in 1955 but tailings are still present. Samples from parental rock, tailings, soils and sediments were analysed in order to study the mobility of trace elements. The results show that there's an important mass transfer of As, Zn, Cr and Cu from tailings to soils. In soils the recommended maximum value for agricultural use is exceeded in particular for As, Cr and Cu.
Groundwater from a spring outside the influence of the mine has a conductivity about 200μS/cm, pH slightly acid (6.5) and is of Bic-Ca/Na type, with no detectable As and no significant concentration in trace metals. Preliminary field and laboratory data from water samples collected in a mine gallery, show high mineralization (conductivity about 700μS/cm), low pH (3.5-4), SO_4-Mg type with dissolved Mn, Cu, Zn, Fe, Co, Ni and As. Groundwater exploited from a confined aquifer in the region show the influence of rock mineralization. This groundwater is SO_4/Mg type, pH about 7 and conductivity about 1000μS/cm. Trace metals such as Fe, Zn, Mn and As are present and the last one has a concentration above 500ppb.

INTRODUCTION

Geological setting

Freixeda mine is located 10 km SE from Mirandela (Portugal NE) and belongs to the Auriferous Methalogenic Province of NW of Iberian Peninsula. From a geological point of view mineralization is present in quartz veins, located in metasedimentary Paleozoic formations, in the dependency of Hercynian granites.
At Freixeda mineralized quartz veins are intruded in the phyllite-quartzite complex of the Unidade Alóctone Inferior (Figure 1). Calcopyrite, pyrite, arsenopyrite, blend, sulfosalts, galena and native elements, are present in quartz veins (Parra *et al*. 2001).

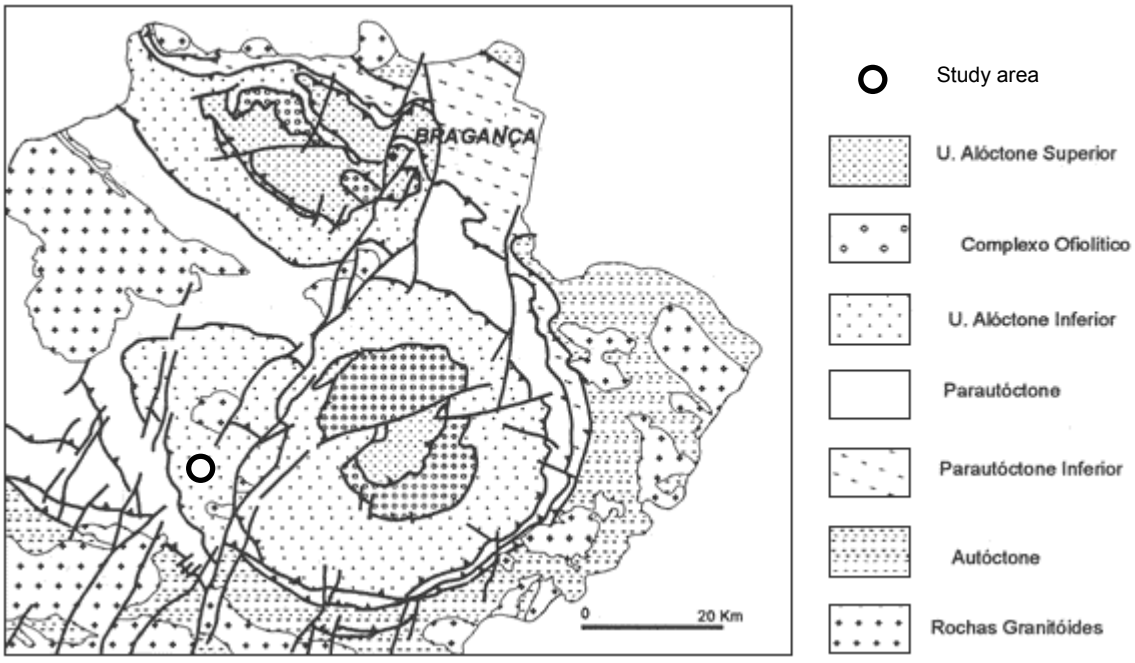

Figure 1 – Geologycal setting of Portugal NE and localization of study area. Adapted from Oliveira J. T. & Pereira E. (coord)1992.

The main veins of Freixeda mine - São Jerónimo e Santo André - were exploited underground, between

Furthermore, there are also present Cu, Zn, Sb, and As rich minerals.
The mine was closed in 1955 but tailings are still present, without any protection or natural vegetation growth.

GEOCHEMISTRY OF PARENTAL ROCK, TAILINGS, SOILS AND SEDIMENTS
Samples from parental rock, tailings, soils and stream sediments were analysed in order to study the mobility of trace elements (Montes *et al.*2004). In Table 1 there's a representation of minimum and maximum values measured in analysed samples.

Material	As	Cr	Cu	Pb	Zn	Ag	Sb
Rock (n=1)	<20	51	40	<16	356	<2	<12
Tailings (n=6)	167-21000	7-45	10-58	35-2700	57-298	6-38	62-911
Soils (n=516)	6-7663	12-118	8-395	18-1000	65-1247	<0.1-95	0.9-640
Sediments (n=5)	24-95	17-35	11-20	15-22	87-317	<2	<12

Table 1 –Minimum and maximum values (in mg/kg), obtained from samples of parental rock, tailings, soils and sediments at Freixeda mine. n - number of samples

Looking at the results we see that values founded in samples from tailings and soils show a very high variation in particular for As and Pb content.
In Figure 2 there's a representation of the average values of analysed elements from the different types of studied samples.

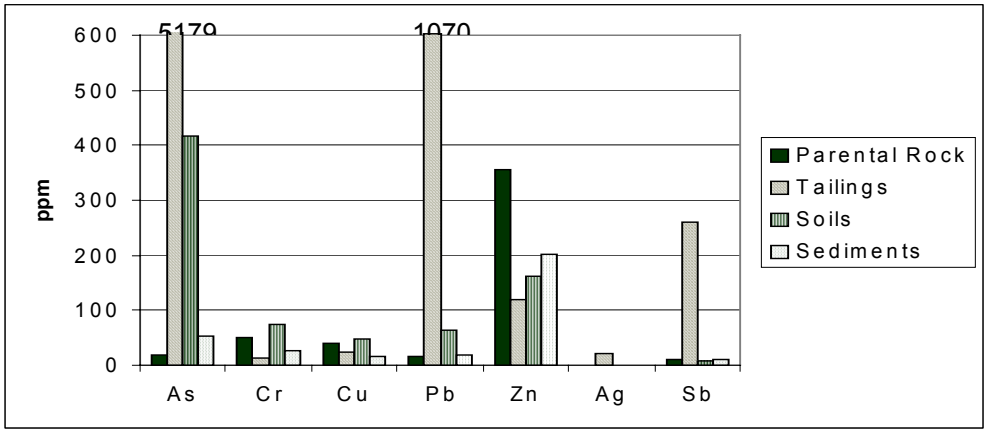

Figure 2 – Average values of elements (As, Cr, Cu, Pb, Zn, Ag e Sb) in ppm, from parental rock, tailings, soils and sediments (in ppm).
The As, Pb, Ag e Sb concentration in tailings, soils and sediments are clearly higher than in parental rock and the values decrease from tailings to soils and from soils to sediments. The results show an important mass transfer of those elements from tailings to soils. This fact can be due to a certain immobility of these elements in the surface of soils because they have a high affinity to be adsorbed in Fe oxides and hydroxides in soils.
Elements such us Cr, Cu and Zn show a similar behaviour between them. They have higher concentration in parental rock than in tailings, but they are accumulated in soils, or in sediments (in the case of Zn). The mobility of these elements is very high in acid to neutral environment. In soils they tend to keep immobile due to interaction between organic compounds and minerals (Montes et al.2004).
Comparing the results of trace elements for soils with the standards for agricultural purpose of Canadian Norm (CEGQ 2002) it's possible to confirm that the recommended maximum value are exceeded in several samples, in particular for As, Cu and Cr.

WATER RESOURCES OF FREIXEDA
Hydrogeochemistry of suface and groundwater
Preliminary field and laboratory data from water samples were collected to characterise physical and chemical properties of acid mine drainage (AMD), surface water of Ribeira de Freixeda and groundwater (Figure 3).
To study AMD samples were collected from a mine gallery (Galeria 2). It shows high mineralization (conductivity about 700μS/cm), low pH (3.5-4.0) and an SO_4-Mg type.
Surface water collected in the creek of the watershed (at Rio Montante) is Bic-Ca, with low mineralization (149μS/cm) and a slightly basic pH (7.5). Near the confluence between the acid mine drainage from Galeria 2 and the stream (at Rio Ponte) water becames SO_4-Ca/Mg type, with higher mineralization (255μS/cm) and a lower pH (6.55). Downstream (at Rio Jusante) water keeps these characteristics, but with slightly higher mineralization.
Groundwater from a spring outside the influence of the mine (Nascente) has a conductivity about 200μS/cm, pH slightly acid (6.5) and is of Bic-Ca/Na type. Groundwater exploited from a well near the mine (Furo), in a confined

aquifer, shows the influence of rock mineralization and is of SO_4-Mg type, pH about 7 and conductivity about 1000μS/cm.
According to the results we could say that water from Nascente and Rio Montante, upstream of Ribeira de Freixeda are not affected by Freixeda Mine. Downstream superficial water becames sulphated due to influence of sulphides oxidation.

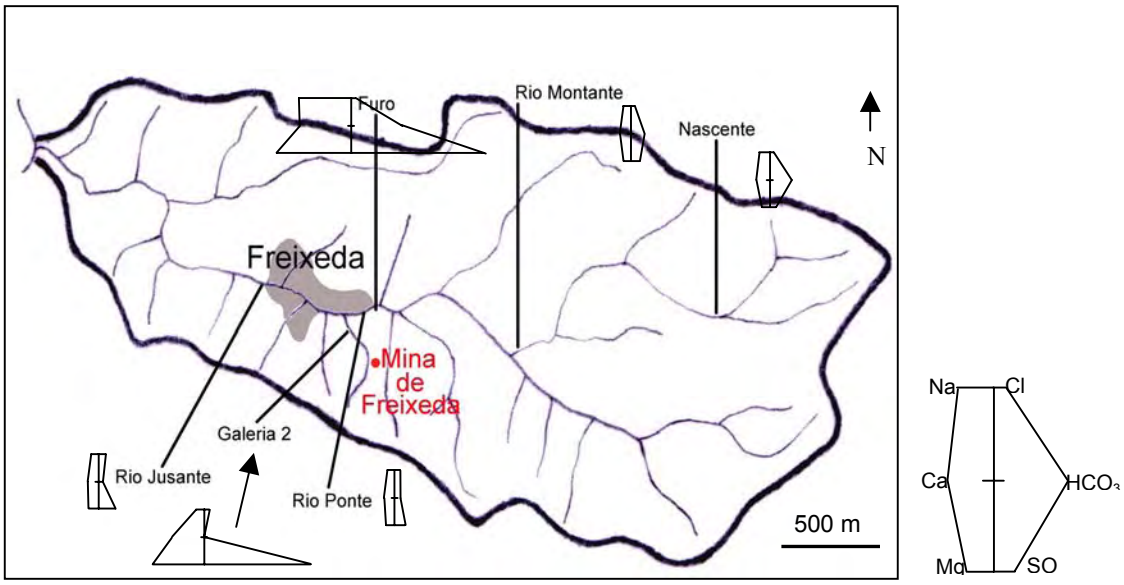

Figure 3: Water samples location and hydrochemical facies. Nascente - Spring; Rio Montante -Rio Ponte-Rio Jusante (superficial water from stream); Galeria 2 - DAM; Furo -well.

The groundwater mineralization is much higher than the one of surface water or AMD with a higher content of sulphate and magnesium. Bicarbonate and sodium are also increased.
The chemical composition of water resources is strongly affected by oxidation of sulphides, which releases cations, SO_4^{2-} and H^+ ions. These free H^+ ions contribute to the dissolution of carbonates (present in cement of metasedimentary rocks) and to the hydrolysis of silicate minerals (plagioclases) and with the consequent alkalinity and pH increase (Pereira *et al*. 2000). All those reactions led to a high mineralization of groundwater.

Arsenic and Trace Metals in water
Some trace elements were measured in water samples by ICP-MS. Obtained values for Zn, Mn, Pb, Fe, As and pH are represented in Figure 4.
In superficial water As, Zn and Mn are the ones that keep longer in solution.
A natural attenuation factor of heavy metals contamination is identified in Ribeira de Freixeda. The heavy metals concentration downstream the confluence between the mine drainage and the creek are lower than the expected values by the mixture rule (Pereira *et al*. 2004).
This can be explained by the precipitation of Mn oxides and Mn, Zn and Pb hydroxides, due to the mixture with higher oxygenated waters with a higher oxidation-reduction potencial. These assumptions are supported by the saturation indices, calculated with PHREEQC program and by the ferrugineous cromatization of drainage path.
In groundwater from spring there´s no significant concentration of heavy metals but groundwater from deeper origin (Furo) show a high concentration specially in Fe, Zn, Mn and As.
Content of As in superficial water is much lower than in groundwater probably do to adsorption of As on oxyhydroxides of Fe that precipitates in stream sediments. This is supported by the absence of dissolved iron in superficial water samples. In groundwater the Eh and pH conditions that allow Fe to be dissolved could be responsible by the higher concentration of As - 850 ppb.
The region has intensive agricultural practices and there are several particular wells in the surroundings used for human consumption and for agricultural purposes.
An analysis of water quality, from a chemical point of view, was made for the samples analysed in this study. For drinking purposes the Decreto-Lei 243/2001 and Decreto-Lei 236/98 of portuguese law were used; for agricultural purposes - irrigation-, the Decreto-Lei 236/98 was followed.

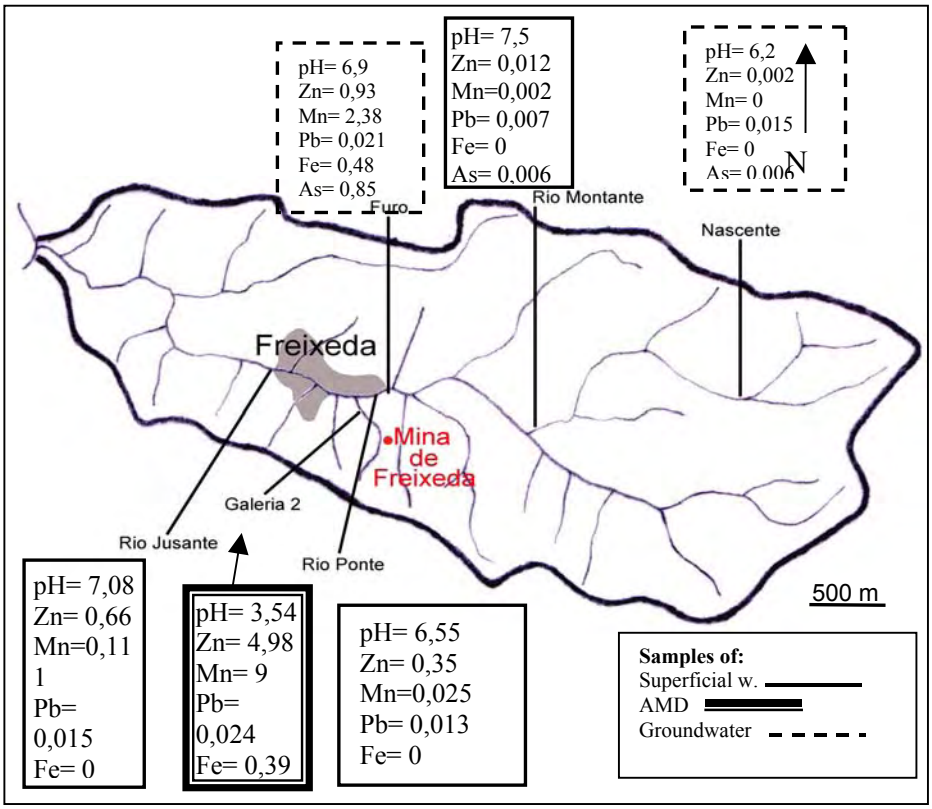

Figure 4: pH and metals concentration (in mg/l) of water samples from Freixeda. Nascente - Spring; Rio Montante -Rio Ponte-Rio Jusante (superficial water from stream); Galeria 2 - AMD; Furo -well. Quality of water resources

In Table 3 are represented only the parameters out of range, in each sample (shadowed), for drinking purposes. From the results presented we could classified the samples of Nascente and Rio Montante as appropriated for drinking (from a chemical point of view).

	SAMPLES						DRINKING WATER LIMITS	
	Nascente	Rmont.	Rponte	RJusante	Furo	Galeria 2	VMR (mg/l)	Parametric value (mg/l)
pH							-	6,5 – 9
Mg							-	56
Mn							-	0,05 I
Fe							-	0,2
Zn							0,1	-
SO_4							-	250
As							-	0,01
Cd							-	0,005
Ni							-	0,02

Table 3 – Parameters out of range (shadow cells) for drinking according to portuguese law (Decreto-Lei 243/2001 and Decreto-Lei 236/98). VMR - Maximum Recomended Value.

The water from Ribeira de Freixeda at Rio Ponte and downstream (Rjusante) is not suitable for drinking due to high concentration of As, Mn and (Zn).
Groundwater from deep circulation (Furo) has to much Mg, Mn, Fe, SO_4, As and (Zn) and is not suitable for drinking.
In Table 4 are represented only the parameters out of range, in each sample (shadowed), for agricultural purposes. From the results presented we could classified the samples of Nascente, Rio Montante and Rio Ponte, suitable for irrigation.
Downstream the confluence with AMD stream water becomes not suitable for irrigation due to the high content in As. Groundwater from the well has a concentration of As higher than the admitted and also Mn is in a concentration above the recommended value.

	SAMPLES						IRRIGATION	
	Nascente	Rmont.	Rponte	RJusante	Furo	Galeria 2	**VMR (mg/l)**	**VMA (mg/l)**
pH							**6,5 – 8,4**	**4,5 – 9**
Mn							**0,2**	**10**
Zn							**2**	**10**
As							**-**	**0,1**
Cd							**0,01**	**0,05**
Co							**0,05**	**10**

Table 4 – Parameters out of range (shadow cells) for irrigation according to portuguese law (Decreto-Lei 236/98). VMR - Maximum Value Recomended; VMA - Maximum Admited Value.

CONCLUSIONS

Geochemistry study at Freixeda abandoned mine show that mine tailings that are present on mine area are the main focus of contamination of soils and stream sediments. Tailings, stream sediments and soils have higher concentrations of As, Pb, Ag and Sb than parental rock, showing mass transfer of metals from tailings to stream sediments and soils. Chemical leaching from tailings is dependent on migration capacity of elements and the pH of the surroundings. In soils heavy metals are strongly adsorbed by clay minerals, organic matter and oxides and hydroxides of Fe.

Comparing the soils content of As, Cu and Cr, with the recommended maximum values for agricultural purpose these are higher, for several samples, than the recommended ones.

The influence of abandoned mines in water resources of Freixeda is reflected in higher mineralization of major ions in particular of SO_4 in superficial and in groundwater. Oxidation of sulphides is responsible by the high content in sulphate and, as a proton donor, promotes the dissolution of silicates (with precipitation of kaolinite and silica) and carbonates. All these reactions leads to a high mineralization that is more intense in groundwater.

In superficial water from Ribeira de Freixeda upstream the Freixeda Mine influence water is of good chemical quality for drinking purposes. After the confluence with mine drainage water becomes more concentrated in particular in Zn, As and Mn. A natural attenuation factor was identified downstream that corresponds to precipitation of Mn oxides and Mn, Zn and Pb hydroxides, due to the mixture with higher oxygenated waters. Even so water is not suitable for drinking or irrigation in particular due to the high concentration in As.

In groundwater heavy metals concentration is higher than in superficial ones, in particular the content of As, Mn, Fe and Zn and the water is not suitable for drinking or irrigation purposes.

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