Environmental Contamination Associated with Some Abandoned Mines in Central Portugal

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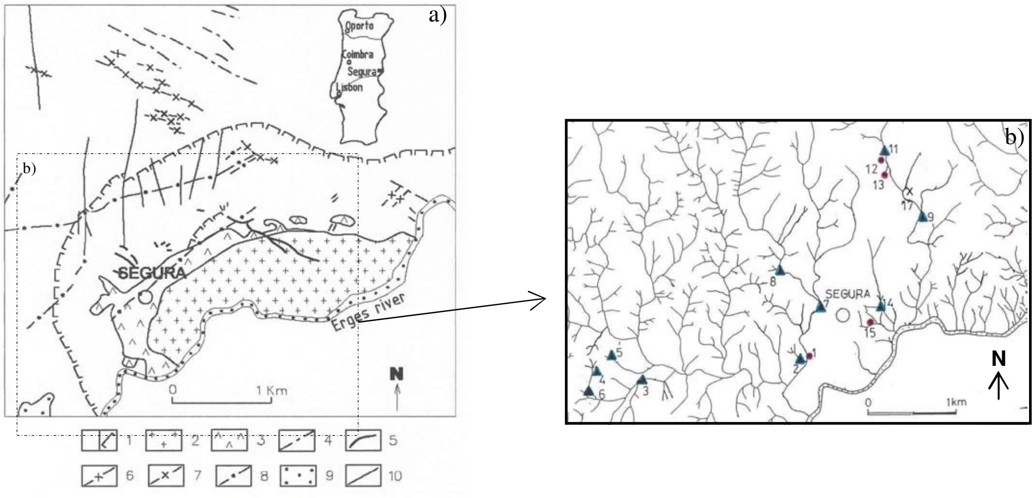
Abstract
At Segura, aplite-pegmatite veins with cassiterite and lepidolite, Sn-W, and Ba-Pb-Zn quartz veins were exploited; mine tailings were left exposed. Sn, W, B, As, and Cu anomalies in stream sediments and soils are related to the Sn-W quartz veins, while Ba, Pb and Zn anomalies are associated with the Ba-Pb-Zn veins. Soils are contaminated in Sn, B, As, and Ba and must not be used for agriculture and human residences or industry. The waters are contaminated in As, Fe, and Mn and should not be used for human and agricultural activities. Sn, B, Cu, and Pb were not detected in waters.

Key words: Sn-W and Ba-Pb-Zn mineralizations; anomalies; soils; stream sediments; water; Segura

Introduction
Mines extract and process valuable materials, and sometimes leave behind waste that is very susceptible to erosion and chemical weathering. Consequently, mining can have a large local impact on the environment. High concentrations of metals have been found in soils, stream sediments, and waters related to polymetallic mineralization in mining areas (Marszalek and Wasik, 2000). Sulphide mineralization produces acid waters bearing high concentration of metals (Rahn et al., 1996). However, acid mine drainage can be neutralized by the occurrence of carbonates, which reduces the intensity of contamination (e.g., Rahn et al., 1996). There are several abandoned mines in Portugal and the environmental impacts of some of them have been published (e.g., Antunes et al., 2002; Pinto et al., 2004; Gomes and Favas, 2006). At Segura, in central Portugal, there are Sn-W and Ba-Pb-Zn mineralized deposits, which were exploited for Sn, W, Ba, and Pb between 1942 and 1953. There has been no remediation/reclamation since the closure of these mines, and the mine tailings and rejected materials remain where they were deposited on the ground, uncovered by vegetation. These materials are exposed to the air and water, and can affect the environmental geochemistry of the area.

Geology and Petrography of Mineralized Veins
The Segura area is located in central Portugal, near the Portuguese-Spanish border (Fig. 1a). A Cambrian schist-metagraywacke complex predominates, consisting of alternating metapelites and metagraywackes with metaconglomerate and marble intercalations. The Variscan Segura pluton intruded this complex; it consists of medium- to coarse-grained two-mica granite and medium- to fine-grained muscovite granite. NW-SE to NNW-SSE granitic aplite veins intersect the schist-metagraywacke complex and granites, whereas sub-horizontal NE-SW Li-bearing granitic aplite-pegmatite veins with cassiterite and lepidolite and NW-SE to WNW-ESE quartz veins containing cassiterite and wolframite intruded the complex. Later, ENE-WSW to NNE-SSW quartz veins with barite, galena, and sphalerite cut the schist-metagraywacke, and a few of them also cut the muscovite granite (Fig. 1a). Sn-W quartz veins and Ba-Pb-Zn quartz veins fill late- to post-tectonic Variscan faults. The Li-bearing aplite-pegmatite veins are up to 15 cm thick and 300 m long, and consist of quartz, microcline, albite, muscovite, apatite, zircon, and rutile. They frequently contain montebrasite, topaz, lepidolite, cassiterite, columbite group minerals, and microlite (Antunes et al., 2007). The Sn-W quartz veins contain sulphides such as pyrrhotite, arsenophyrite, pyrite, sphalerite, chalcophyrite, stannite, and the sulphosalts, matildite and schapbachite. These quartz veins are up to 1300 long and 10 cm thick. Cobaltite, pyrite, sphalerite, chalcopyrite, and galena were found in the Ba-Pb-Zn quartz veins, which also contain a homogeneous barite that represents 20 to 30% of these veins, is up to 3 m thick, and up to 2500 m long.

Figure 1 *Maps of Segura area (Central Portugal)*



a) Geological map of Segura area and the location of Fig. b). 1. Schist-metagraywacke complex, contact metamorphic aureole; 2. medium- to coarse-grained two-mica granite; 3. medium- to fine-grained muscovite granite; 4. granodiorite porphyry veins; 5. granitic aplite veins; 6. Li-bearing granitic aplite-pegmatite veins with cassiterite; 7. Sn-W quartz veins; 8. Ba-Pb-Zn quartz veins; 9. arkoses; 10. faults. b) Streams from Segura area showing sample locations. Water points: ● - springs; ▲ - stream and small retentions; x - well.

Methodology and analytical techniques

Samples collected from mineralized veins and tailings were analyzed for major and trace elements by electron microprobe, using a Cameca Camebax electron microprobe at Instituto Geológico e Mineiro (S. Mamede de Infesta, Portugal), and a Jeol JXA 8600 electron microprobe at Bristol University (United Kingdom). A total of 717 samples of stream sediments (671 schist samples and 46 granite samples) were collected between 50 m upstream and 100 m downstream of the confluence of the streams (Instituto Geológico e Mineiro, 1988). Based on these data, 1008 soil samples were collected, to a depth of 30 cm, north of Segura. Sn and W from stream sediments and soils were analyzed by X-ray fluorescence, while B, As, Cu, Ba, Pb, and Zn were determined by ICP-AES at Instituto Geológico e Mineiro (S. Mamede de Infesta), with a precision of 10%.

Fifteen sampling points located close to the abandoned old mine workings were chosen (Fig. 1b). Four times during the year, a water sample was collected from each point to identify the environmental impact of the old mining and its seasonal variability. Temperature, pH, Eh, dissolved oxygen, specific conductance, and alkalinity were all determined on site. All the waters were acidified and kept at 4ºC. Alkalinity and Cl^- were determined by titration, while nitrates, nitrites, and phosphates were analysed by molecular absorption spectrometry and Na, K, Ca, Mg, As, Fe Mn, Cu, Pb, and Zn were determined using a flame atomic absorption spectrometer. Sulphate was determined gravimetrically. All the analyses were obtained with a precision of ± 5%.

Results and Discussion

Stream sediments and soils from Segura are enriched in metals relatively to the parent granites and schists. The highest metal concentrations are associated with the mineralized veins. In general, the maximum soil concentrations for trace elements are generally higher than those of the stream sediments (Table 1). The highest Sn, W, and B concentrations in the stream sediments are associated with Sn-W mineralization. Ba, Pb, and Zn anomalies in stream sediments are related to the Ba-Pb-Zn quartz veins and As and Cu anomalies are related to both mineralizations. Sn, W, B, As, and Cu anomalies of soils are mainly related to Sn-W quartz veins, which contain arsenopyrite and chalcopyrite. Ba, Pb, and Zn anomalies of soils are associated with quartz veins containing barite, galena, and sphalerite. These anomalies are also related to the old mining activities. Mechanical transport of sediment downstream is an important mechanism for the mobility of heavy metals from mineralized veins and tailings (Boulet and Larocque, 1998), and at Segura, the separation of ore minerals from gangue minerals was carried out by water in the headwaters of the streams. However, the contamination progressively increases downstream. The soils have high concentrations of Sn, B, As, and Ba and must not be used for agriculture and human residences. Due to their high As contents, they must also not be used for industrial activities (Table 1). The As levels are the most problematic due to the high toxicity of As.

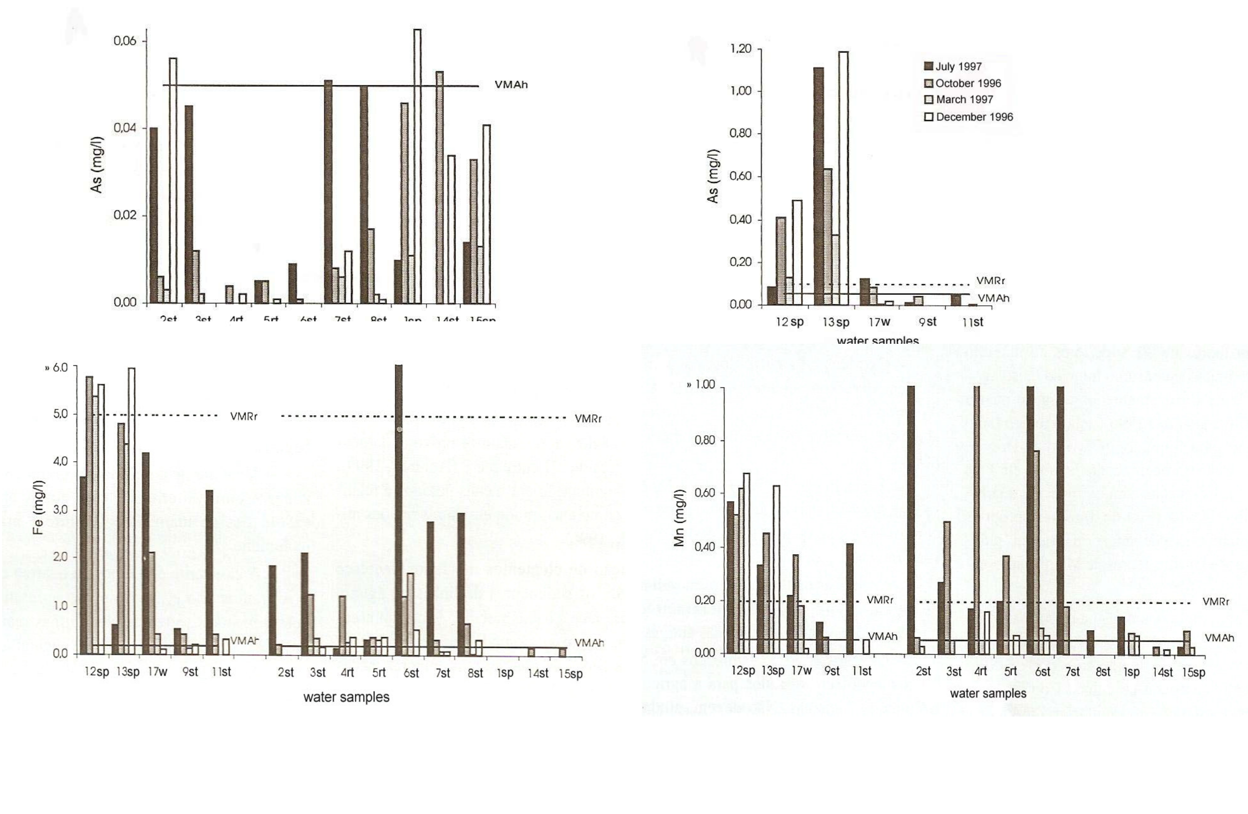
Table 1 *Trace elements contents of stream sediments and soils from Segura compared with recommended maximum concentrations*

	Segura area				Recommend maximum values		
	Stream sediments (ppm)		Soils (ppm)		Soils (ppm)		
	min.	max.	min.	max.	a)	b)	c)
Sn	< 2	> 20	< 4	> 75	5	50	300
W	< 10	> 70	< 10	> 45	-	-	-
B	< 40	> 175	< 55	> 300	2	-	-
As	< 20	> 175	< 20	> 375	20	30	50
Cu	< 24	> 60	< 40	> 100	150	100	500
Ba	< 500	> 1100	< 675	> 1500	750	500	2000
Pb	< 27	> 75	< 20	>120	375	500	1000
Zn	< 125	> 225	< 125	>290	600	500	1500
N	717		1008				

min. – minimum; max. – maximum; - not defined. a) agricultural soil; b) human residence soil;
3 – commerce and industry soil (Canadian Council of Ministers of the Environment, 1991).
N – number of samples.

The waters associated with the Sn-W quartz veins and As anomalies in soils have higher As contents than the waters associated with the Ba-Pb-Zn quartz veins. Arsenic water content tends to decrease from springs to wells and to streams associated with the Sn-W quartz veins (Fig. 2). The waters with the highest As concentration also have high Fe and Mn. However, the highest Fe and Mn contents are related to the Ba-Pb-Zn quartz veins (Fig. 2).

Figure 2 *Seasonal variations for As, Fe and Mn water contents from the Segura area*



Water samples collected on: sp – springs; w – well; st – streams; rt –small retentions. VMAh – human recommended values; VMRr – agricultural recommended values (Portuguese Law, 2001)

As and Fe correlate poorly, as found by others (Nickson et al., 2000). Sn, B, Cu, and Pb were not detected in waters from Segura, but were found in stream sediments and soils (Antunes, 1999), which can be explained by their low solubility in water. The highest Ba content was found in waters located close to a Ba-Pb-Zn quartz vein. These water samples have the lowest pH, specific conductance, and ionic concentration (Antunes, 1999).

At Segura, there is no significant acid mine drainage associated with the old mine workings, which can be attributed to the marble intercalations in the schist-metagraywacke complex. Consequently, the metal concentration is relatively low, as found in other mining areas (Rahn et al., 1996). The waters from wells and streams have lower concentrations of As, Fe, and Mn during winter than during summer, which may be due to dilution. However, the concentrations of these elements in the goundwater springs are higher during winter than in summer (Antunes, 1999). The Segura area waters are contaminated with As, Fe, and Mn and must not be used for human consumption or agricultural activities, according to Portuguese Law, 2001. There is a decrease in trace element content from soils to stream sediments and to waters due to their relatively low mobility,

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