Geochemical signatures and mechanisms of trace elements dispersion in the area of the Vale das Gatas mine (Northern Portugal)

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Abstract

A geochemical survey involving the collection and analysis of 170 stream sediment samples was carried out in Vale das Gatas area in order to delineate geochemical signatures and to detect pollution hazards due to mining.

Factor analysis applied to the data showed that the most important variables accounting for the first factor are Ag, Pb, Bi, As, W, Cd, Zn and Cu. These variables represent the most significant metalliferous elements of the original paragenesis, which still maintain a close relationship in the secondary geological environment. The spatial distribution of the factor scores referred to factor 1 indicates that positive scores occur predominantly in the Vale das Gatas and Sabrosa streams and in the main Pinhão river. The results also show that the Vale das Gatas mine is the most important contamination source in the Vale das Gatas district.

In order to study the dispersion, transfer and uptake mechanisms of trace elements from the Vale das Gatas mine, additional sample media were collected, i.e., stream sediments, tailings, coatings, waters (surficial and mine waters) and specific biological species. Four sample stations were selected, namely two in connection with abandoned adits of the Vale das Gatas mine, one located in the Vale das Gatas stream and one located in the Pinhão River. The results show that chemical reactions of leaching and precipitation took place controlling the heavy metals in areas near the Vale das Gatas mine.

At the same time, positive anomalous patterns are visible along the Pinhão river for about 20 km. The mineralogical composition of the stream sediments suggests that processes of mechanical dispersion also interfere in the secondary distribution of the metalliferous elements in that media.
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1. Introduction

It is nowadays accepted that environmental damages can occur around mine sites where

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management did not follow the rules and policies of sustainable development. Most of these sites are "abandoned mines" where no economical activity takes place since some time. In order to characterize old mines without owner or property rights occurring in Portugal, the Government took the responsibility to carry out the inventory and characterization of the main abandoned mine sites, which are scattered over the country. To achieve this, the Instituto Geológico e Mineiro of Portugal (IGM), assisted by some universities and private companies, developed a comprehensive program of studies aiming: (a) to characterize those main mine sites; (b) to assess the symptoms of risks inherent to former mining operations; (c) to promote measures that best fit to the rehabilitation of the environmentally affected areas (Santos Oliveira, 1997).

The results of this program led to the identification of more than 100 abandoned mines scattered around the country (Santos Oliveira et al., 2002). These old mines were classified and hierarchized according to the following general criteria: type and magnitude of chemical anomalies in soils, stream sediments and waters; actual conditions of mining safety; size and stability of the mine landfills (tailings); visual impact; degree of land and water use; archaeological (museum) relevance of the mine structures.

Previous geochemical exploration surveys carried out around the tin–tungsten Vale das Gatas district showed the existence of significant contents of Sn, W, Zn, Pb and As in stream sediments. Most of the geochemical anomalies were assigned to a number of dispersed mining activities in the area (Santos Oliveira, 1984). Nevertheless, the geochemical dispersion patterns were not fully discussed at the time in terms of the geochemical mechanisms involved in the transport, dilution, deposition and remobilization of metals.

The present study shows selected geochemical results obtained in the Vale das Gatas area on the perspective of a better understanding of the dynamics inherent to leaching, transport and accumulation of some elements with environmental relevance (in particular, Cu, Pb, Zn, Cd and As) in different chemical–mineralogical and biological sampling media.

2. Geology and mining

2.1. Geology and mineralization

According to the palaeogeographic and tectonic zonography established for the Hercynian Chain of the Hesperic massif, the study area is located in the Central Iberian Zone (Lotze, 1945; Julivert et al., 1974; Pereira and Cruz, 1980).

The major lithological units outcropping in the region are flyschoid metasedimentary rocks of Cambrian age (pelitic schists, quartzites, psammites, phyllites, hornfelses and greywackes) which are commonly included in the so-called Schist–Greywacke Complex (Sousa, 1982). These metasediments were intruded by granitoids, mostly two mica granites with porphyroid and non-porphyroid facies (Vilela Matos, 1991). Fig. 1 shows the main geological aspects of the area.

The Vale das Gatas mine is part of an important tin–tungsten province of the Central Iberian Zone (Pereira and Cruz, 1980). The mineralization occurs associated to numerous quartz veins and is located in two shear zones derived from tectonic movements generated during the third Hercynian phase (Noronha et al., 1979).

The mineral paragenesis (Gaspar and Bowles, 1985) comprises mainly cassiterite, wolframite (with chemical composition close to hubnerite) and scheelite (locally replacing wolframite). Sulphides, particularly arsenopyrite, pyrite, pyrrothite, chalcopyrite, sphalerite, galena and stannite, are abundant. Sulphosalts are reported as minor minerals.

The Vale das Gatas ore deposit is strongly affected by hydrothermal alteration with emphasis to greisenization, albitization, tourmalinization, sericitization and silicification.

A maritime temperate climate prevails in the area. The mean annual precipitation value in the area is 900 mm.

2.2. Mining exploitation

Mining activities regarding tin–tungsten exploitation were developed extensively in the Vale das Gatas district for many years starting from 1883 until 1986. The extracted ore was concentrated in the mine's plant, using hydrogravitic procedures followed by
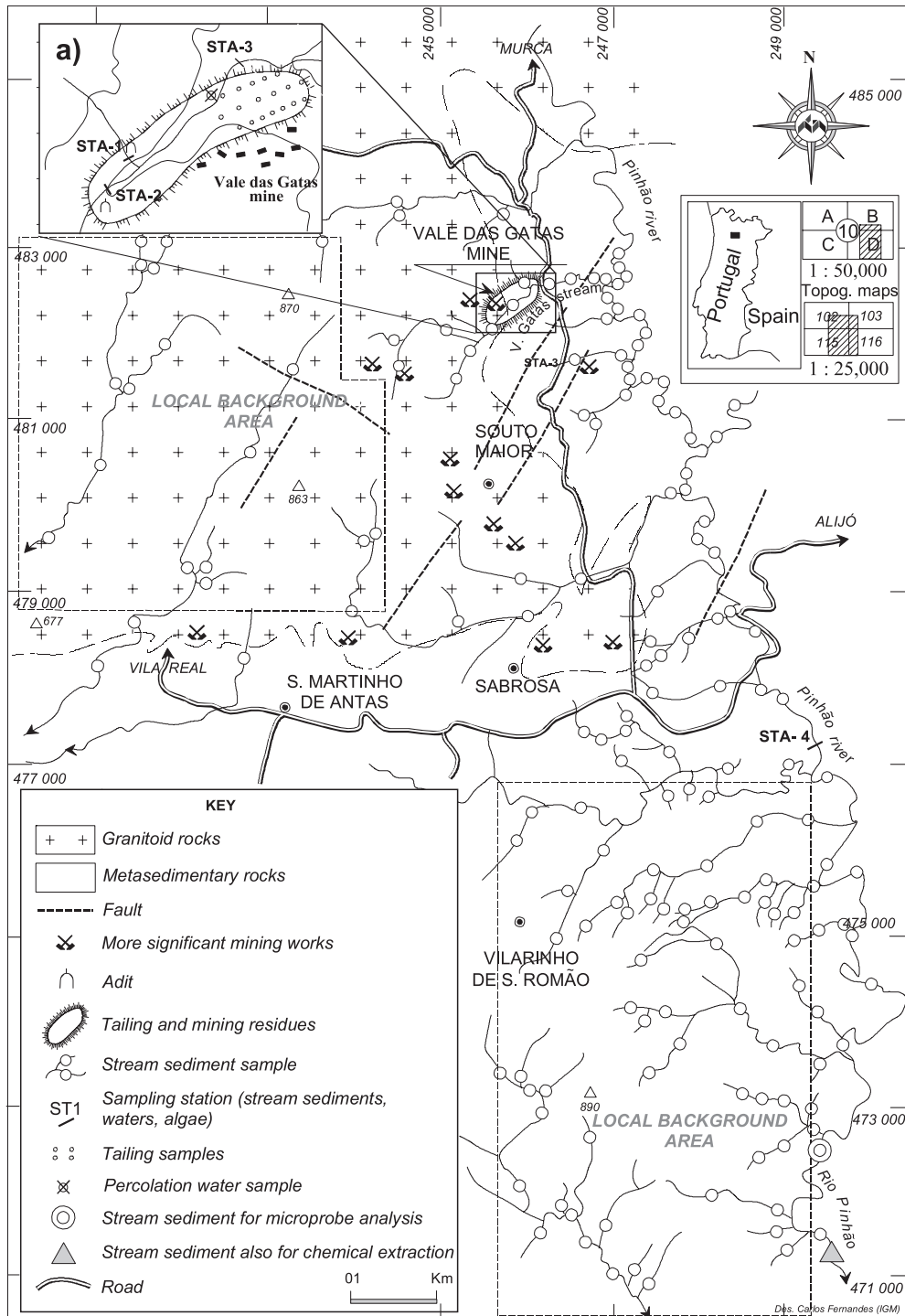
Fig. 1. Generalized geologic map of the Vale das Gatas area, sampling sites and location of local background areas.

froth flotation, magnetic and electrostatic separation in order to obtain a final wolframite–cassiterite–scheelite concentrate (Almeida and Amarante, 1993).

After closure of the mines more than 100 tons of tailings containing high contents of Cu, Zn, Pb, As and Cd remain deposited in a landfill disposal nearby the mine plant.

3. Sampling and experimental procedures

3.1. Collecting and sample preparation

The main sequential steps adopted in this study were: (i) a geochemical stream sediment survey in the Vale das Gatas area to delineate geochemical signatures and detect contaminated areas; (ii) geochemical studies in selected sites (sample stations) to investigate the dynamics of leaching, transport and accumulation of some selected metals and metalloids (Cu, Pb, Zn, Cd, As) in different chemical–mineralogical and biological phases.

In the first stage of the work 170 stream sediment samples (Fig. 1) were collected extensively in the area (sample density of 1 sample/km^2). In the second step four sample stations were selected: two in connection with abandoned adits of the Vale das Gatas mine (STA 1, STA 2), the third situated in the Vale das Gatas stream near the tailings (STA 3) and the fourth located in the Pinhão river (STA 4), about 7 km downstream of the mine site (Fig. 1). In these stations additional sample media were collected: stream sediments, tailings, coatings, waters (surficial and mine waters if present) and specific biological species.

The stream sediment and tailing samples were dried at 40 °C and sieved at 80 mesh. After this, they were crushed, homogenized and sieved, retaining the <200 mesh fraction for chemical analysis. The coating samples were dried at a temperature of 40 °C, disaggregated and sieved through a <200 mesh sieve.

Water samples were collected from each selected site with a cleaned 1 l polyethylene bottle and stored by cooling to 4 °C until further analysis. In order to analyse the dissolved phase, one volume of 250 ml was taken from each sample and filtered on-site (through 0.45 μm Millipore filters) using an all-plastic pressurized filtering system (ASTM, 1984). Samples collected for trace metals analysis were immediately preserved, when necessary, in the field to pH 2.0 using HNO$_3$. Samples were stored under cool and dark conditions prior to analysis.

Some algae which frequently occurring in the vicinity of the mine (a Chlorophyta—*Microspora tumidula Hazen*) were also collected. To avoid risks of contamination due to particulate material and fine sediments adsorbed on the algae surface, samples were strongly washed and carefully rinsed with distilled water, oven-dried at 35 °C and ground.

3.2. Analytical techniques

The fine-grained (<200 mesh) fraction of the stream sediment, tailing and coating samples were submitted to multielement analysis in an accredited Canadian lab (ACME Anal. ISO 9002 Accredited Lab—Canada). A 0.5 g split was leached in hot (95 °C) aqua regia (HCl–HNO$_3$–H$_2$O) for 1 h. After dilution to 10 ml with water, the solutions were analysed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-ES) for a high number of chemical elements, which included Ag, Al, As, Au, Ba, Bi, Ca, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Sr, Th, Ti, U, V and Zn. In spite of the entire dataset is available upon request, emphasis was given to the Cu, Pb, Zn, Ag, As, Ni, Co, Cr, Mn, Fe, Cd, Bi, P, V, Ba and W elements based on their geochemical or/and environmental significance.

The biological samples were digested with a chemical mixture (HCl–HNO$_3$–HF) and analysed by Atomic Absorption Spectrometry for Cu, Pb, Zn, Cd and As.

In order to control the analytical procedure, precision of the analytical results for stream sediments, tailings, coatings and biological samples was estimated by replicate analysis (Garrett, 1973). Analytical precision, defined as the percent relative variation at the 95% confidence level, ranged from 2% to 8%: (i.e., 2% for Cu, Zn, P and Mn; 3% for As, Ni, Cd and V; 4% for Fe, Ba, Cr and W; 6% for Ag and Pb; 8% for Bi and Co).

The sequential scheme used to define the metal-bearing phases of As and Pb in selected sediment samples comprised a series of six chemical extractions, each reagent or mixture being able to dissolve in a selective way a potential carrier of trace elements in the sample. The reagents used in this

procedure, as well as the mineralogical phases extracted in most background soils and sediments, were the following (Cardoso Fonseca and Ferreira da Silva, 1998):

Step 1: Ammonium acetate (1 M NH_4Ac, pH 4.5): corresponds to water soluble and dissolved exchangeable ions, specifically adsorbed and carbonate-bound;

Step 2: Hydroxylamine hydrochloride (0.1 M $NH_4OH \cdot HCl$, pH 2): Mn oxyhydroxides;

Step 3: Ammonium oxalate (dark) (0.175 M $(NH_4)_2C_2O_4$–0.1 M $H_2C_2O_4$, pH 3.2 in darkness): amorphous Fe oxides (see Chao and Zhou, 1983);

Step 4: H_2O_2 35%: organic matter and sulphides (primary sulphide minerals could not be totally leached out in this step; see Rapin and Forstner, 1983 and Khebonian and Bauer, 1987);

Step 5: Ammonium oxalate (U.V.) (0.175 M $(NH_4)_2C_2O_4$–0.1 M $H_2C_2O_4$, pH 3.3 under U.V. radiation): related to crystalline Fe oxides (see Schwertmann, 1964);

Step 6: Three-acid mixture ($HCl_{conc.}$+$HNO_{3\ conc.}$+$HF_{conc.}$) decomposition gently heated until complete dryness: residual fraction (matrix bound in lattice positions). Resistant oxides and sulphides.

The selectivity feature of these reagents taken individually for a given type of soil component has already been discussed (De Endredy 1963; Segalen, 1970; Schwertmann, 1973; Gatehouse et al., 1977). In other studies the complex dissolution mechanisms and their controlling parameters have been fully investigated (Stone, 1987; Suter et al., 1991; Cornell and Schwertmann, 1996; Nesbitt et al., 1998; Dold, 1999, 2003a,b); other authors tried to enhance the selectivity of the dissolution leaches (Schwertmann, 1964; Fischer, 1976; Reyes and Torrent, 1997). The adopted leach sequence has already been tested and proved to be useful in some geochemical studies (examples of Cu, Pb, Zn, As and U) based on soils, sediments and mine tailings (Bolle et al., 1988; Cardoso Fonseca and Martin, 1986; Cardoso Fonseca et al., 1992; Cardoso Fonseca and Ferreira da Silva, 1998; Patinha, 2002).

Sequential extractions determine only operationally defined speciation. This depends on different experimental parameters such as chemicals employed and the selectivity of these reagents to attack a given phase, the time (time of reaction) and nature of contact and the sample to volume ratio. In order to establish the time of reaction for each reagent of the sequence, two well-characterized soil samples from the Vale das Gatas area (one representative from the background area and another from the contaminated area) were analysed in kinetic dissolution mode (Cardoso Fonseca and Martin, 1986). The chemical extraction for a given sample and reagent was considered to be complete when the amount of the extracted Fe and As in the solution reached an asymptotic value.

The ratio of solid to solution (g/ml) used in each step of the sequence is respectively: 1/20 for ammonium acetate, hydroxylamine hydrochloride and hydrogen peroxide; 1/40 for ammonium oxalate; and 1/6 for the mixed acid attack. Each sample was submitted sequentially to the six above-mentioned reagents, with a reaction time of 10 h for ammonium acetate, hydroxylamine hydrochloride, oxalate dark and oxalate U.V., and 48 h for H_2O_2. The selectivity of these reagents has already been emphasised by some authors (Cardoso Fonseca and Martin, 1986; Cardoso Fonseca et al., 1992; Patinha et al., 2001).

The accuracy of the sequential treatment taken as a whole may be estimated by 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 (the sum of 6 fractions/total concentration) ranged from 85% to 110%. These results are of the same magnitude of those obtained by Cardoso Fonseca and Martin (1986).

In order to increase the analytical sensitivity, a sample pre-concentration method (freeze-drying pretreatment on BRAUN CHRIST ALPHA 1-4 equipment) was adopted. The dissolved component in water samples was analysed by Atomic Absorption Spectrometry for some trace elements (Fe, Cu, Pb, Zn and Cd). Arsenic was analysed with a hydride generation apparatus, followed by Atomic Absorption Spectrometry.

Coatings and stream sediment samples were also submitted to mineralogical and microanalytical studies with a Camebax microprobe.

4. Results and discussion

4.1. Geochemical signatures and pollution areas

Table 1 summarizes the analytical results obtained for stream sediments collected around the Vale das Gatas area. These data show that Cu, Pb, Zn, Ag, As, Cd, Bi and W occur with anomalous concentrations in many places. Nearby the mine (in the Vale das Gatas stream) these values increase drastically when compared with average local background values obtained from samples taken in two areas without mines and mineralisation (see Fig. 1). The Vale das Gatas tailings, therefore, appear as the main source of contamination, whereas the rocks outcropping in the area do not contribute significantly with respect to metal inputs. Noteworthy, other elements, i.e., Cr, Ni, Co and Mn, are not influenced by the mining activities (Table 1).

It is commonly accepted that the interpretation of stream sediment data, particularly if supported by multivariate statistical methods, may constitute an effective tool to quantify anthropogenic effects (Birke

and Rauch, 1993). With factor analysis the raw geochemical data are transformed into a new reference system which can be viewed and interpreted more easily in terms of geological and anthropogenic processes. This facilitates data interpretation. R-mode analysis is particularly relevant in working out a process oriented interpretation (Saager and Sinclair, 1974; Closs and Nichol, 1975) while the use of the Q-mode analysis, focusing on individuals rather than variables, is well suited to study sample sets where the individuals may be thought of as mixtures of end members (Hitchon et al., 1971; Nichol, 1973; Saager and Sinclair, 1974). Table 2 shows the results of Principal Component Analysis (PCA) using log data. Following criteria adopted by some authors (for example, Davis, 2002), three significant components with eigenvalues >1 and accounting for about 88% of the total variance were extracted. By taking only values ±0.5, the first component is defined by the association of Pb–Ag–Bi–W–Cd–As–Zn–Cu–P, which groups the most significant metalliferous elements. For the second component, the most important variables are Cr–V–Fe–Ni–Ti–Co. This

Table 1

Average contents for selected chemical elements in stream sediments, tailings and bedrock of Vale das Gatas area

Elements	Stream sediment					Bedrock	
	Vale das Gatas district (n=170)	Background samples (n=85)	Vale das Gatas stream (n=9)	Pinhão river (n=35)	Tailings (n=18)	Granitic rocks[a] (n=32)	Metasedimentary rocks[b] (n=5)
Cu	114	67	451	87	1457	6	28
Pb	312	51	2088	207	5934	2.3	16
Zn	143	94	446	137	2032	67	96
Ag	7.7	0.6	52	7	149	<0.2	<0.2
Ni	19	21	9	19	11	7	21
Co	10	11	5	10	5	6	10
Mn	413	439	435	328	698	180	475
Fe(%)	2.6	2.6	2.6	2.5	4.0	–	4.5
As	504	78	3268	404	8534	~10	80
Cd	1.2	0.4	5.6	1.3	25	~0.5	~0.5
Bi	37	4	260	23	753	–	–
V	25	25	17	30	16	9	–
P	830	800	1609	500	1300	1460	466
Cr	28	29	18	31	23	–	268
Ti(%)	0.05	0.05	0.02	0.07	0.03	–	–
W	120	11	2274	112	1517	4	5

Arithmetic means in μg/g unless stated.

[a] From Santos Oliveira (1993).

[b] From Santos Oliveira and Ávila (1995).

Table 2
Results of Principal Component Analysis on the stream sediment data (n=170)

Variable	Communalities	PCA1	PCA2	PCA3
Cu	0.7877	0.7673	−0.4379	0.0845
Pb	0.966	0.9762	−0.0112	−0.0314
Zn	0.890	0.8854	−0.2598	0.1970
Ag	0.956	0.9500	−0.1686	−0.1589
Ni	0.903	−0.4082	−0.8496	0.1194
Co	0.909	−0.4005	−0.8132	0.2958
Mn	0.839	0.1562	−0.2622	0.8634
Fe	0.845	0.0498	−0.9049	0.1530
As	0.886	0.9124	−0.1751	−0.1512
Cd	0.887	0.9178	−0.1806	0.0480
Bi	0.928	0.9399	−0.1597	−0.1390
V	0.880	−0.1788	−0.9156	−0.0985
P	0.736	0.5121	0.4903	0.4835
Cr	0.939	−0.2793	−0.9228	−0.0958
Ti	0.851	−0.1284	−0.8414	−0.3559
W	0.885	0.9253	−0.0605	−0.1580
Eigenvalues		7.3849	5.3014	1.3917
Total variance (%)		46.16	33.13	8.70
Cumulative variance (%)		46.16	79.29	87.99

association seems to represent a lithological factor without significant relationships with the mineralization. The third component, only represented by Mn, is supposed to be related with secondary Mn oxides and hydroxides commonly present in the stream sediments. The plot on the first factorial plan (PCA1 vs. PCA2 of Fig. 2) shows that the variables explained by first component are separated by second component in

two groups: P and Cu–Zn–Bi–Pb–As–Cd–W–Ag. This association indicates that the elements representative of the original paragenesis still maintain a close relationship in the secondary environment. Otherwise, the association Cr–V–Ni–Ti–Co–Fe (PCA2 of Fig. 2) is explained as a lithological factor imprinted in some particular types of basic metasedimentary rocks occurring in the area.

Fig. 3 shows the spatial distribution of factor scores 1 depicted from PCA analysis. It is important to bear in mind that in the interpretation of maps referred to factors related to mineralization, a high (absolute) score value at one point of the map will not necessarily be high for the same reasons as a score of similar magnitude in another point on the map (Howarth and Sinding-Larsen, 1983). The results indicate that a clear spatial separation occurs between positive and negative values supporting the interpretation given by PCA1. The positive scores occur predominantly in the Vale das Gatas stream (A zone in the figure), Sabrosa stream (B zone in the figure) and in the main Pinhão river. These high positive values are related to anomalous contents of Ag, As, Pb, Bi, W, Cd, Zn and Cu. From the figure it is also clear that Vale das Gatas mine appears to be the principal source of chemical contamination of the area.

In Fig. 3, it is shown that the positive anomalous patterns persist downstream for about 20 km along the main river. The irregular decay of these patterns
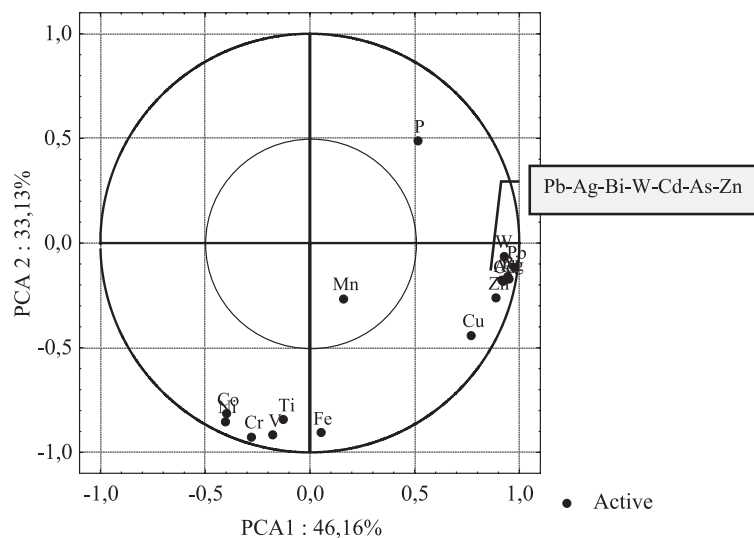

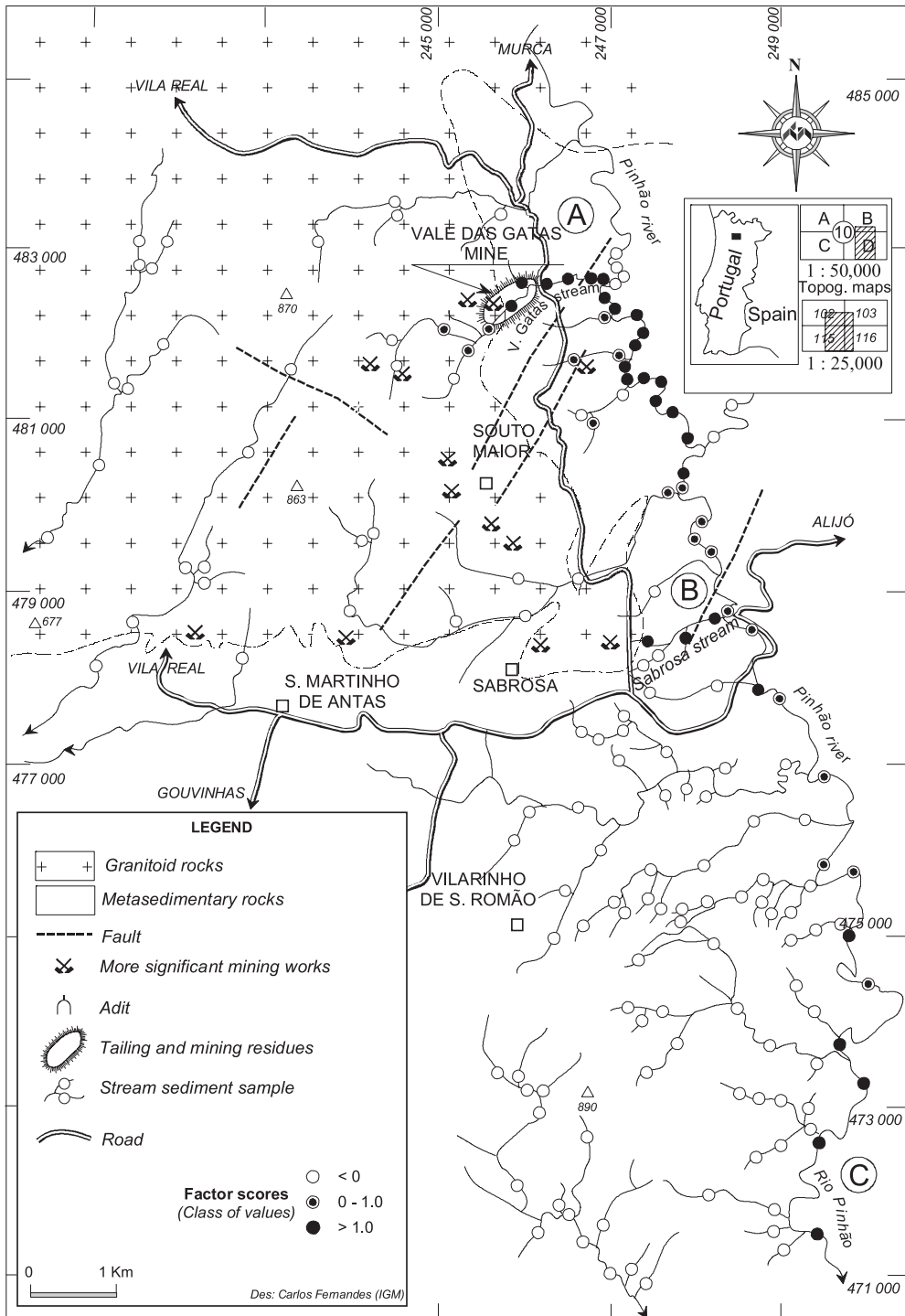Fig. 2. Plot of the first factorial plan.

Fig. 3. First factor scores mapping.

Table 3
Mineralogical composition of the Vale das Gatas sediments

Primary minerals:	arsenopyrite, pyrite, sphalerite, galena and calcopyrite
Secondary minerals:	Fe arsenates (scorodite) hydrated Fe–As oxides, hydrated Fe oxides, Pb–Fe arsenates, Mn hydroxides, Fe sulphates and stannite
Accessory minerals:	cassiterite, wolframite, scheelite, pyrrothite, monazite, sphene, zircon, rutile, ilmenite, tourmaline and apatite

suggests the interference of local hydrological and physiographycal factors (expressed by periods of severe and wet winters affecting a geomorphologically rugged region) which promote mechanisms of fast erosion, transport and accumulation of solid materials, most of which are transported in suspension by the surface waters. An electron microprobe analysis of the heavy mineral fraction (<10 mesh) of one stream sediment collected downstream in the Pinhão river (C zone—Fig. 3) characterized by significant contents of Ag, Pb, Bi, As, W, Cd, Zn and Cu, revealed the presence of sphalerite, galena, chalcopyrite, pyrite, arsenopyrite and wolframite, together with some Fe–Pb sulphates, Pb–Fe arsenates and Fe hydroxides (Table 3). This suggests the persistence of significant primary ore minerals at long distance from the mine sites.

4.2. Dispersion, transfer and uptake mechanisms of trace metals

Taking into account the characteristics of the metal anomalous patterns, a detailed investigation was

undertaken to understand the mechanisms of Cu, Pb, Zn, Cd and As dispersion. The behaviour of these elements in different sampling media (sediments, water, algae—Table 4) was investigated with basis on the comparison of their contents in a area near the Vale das Gatas mine (STA1, STA2 and STA3 stations) and away from the mine (STA4 station in the Pinhão river).

An electron microprobe analysis of the heavy mineral fraction (<10 mesh) of those stream sediments indicates that all the samples contain arsenopyrite, pyrite, sphalerite, galena and chalcopyrite as principal minerals, and cassiterite, wolframite, scheelite, scorodite, hydrated Fe–As oxides, hydrated Fe oxides, Mn and Fe hydroxides, Pb–Fe arsenates, Fe sulphates, stannite, pyrrothite, monazite, sphene, zircon, rutile, ilmenite, tourmaline and apatite as accessory minerals. Most of them are secondary neoformed minerals.

In addition, the recently formed stream sediment coatings collected in STA1, STA2 and STA3 stations also host significant amounts of some metals (90–1370 μg/g Cu, 540–4190 μg/g Pb, 2200–61,600 μg/g As), which is interpreted to be related with the recent formation of Fe–As oxides and Pb–Fe arsenates in those places. This strongly supports that chemical reactions of leaching and chemical precipitation take place in areas near the Vale das Gatas mine.

Table 5 presents the results of total extraction of Pb and As in one selected sample collected downstream in the Pinhão river (C zone in Fig. 3). An electron microprobe analysis showed that this sample contains galena, arsenopyrite, Fe hydroxides and Pb–Fe arsenates. The chemical results show that As and Pb are mainly extracted by ammonium oxalate dark (60%

Table 4
Contents of Cu, Pb, Zn, Cd and As in stream sediment, water and algae samples collected in sampling stations

STA1	Cu	Pb	Zn	Cd	As	pH	Conductivity	STA2	Cu	Pb	Zn	Cd	As	pH	Conductivity
Sediment	549	738	802	58	92,000	–	–	Sediment	1274	3380	733	12	970	–	–
Water	141	7	1370	15	9	4.7	178	Water	14	3	35	0	9	6.0	29
Algae	208	442	370	4	38,560	–	–	Algae	1272	1260	476	4	1519	–	–

STA3	Cu	Pb	Zn	Cd	As	pH	Conductivity	STA4	Cu	Pb	Zn	Cd	As	pH	Conductivity
Sediment	1164	3273	1560	26	1600	–	–	Sediment	80	115	116	11	190	–	–
Water	1030	51	2900	50	36	4.9	180	Water	3	4	41	0	2	6.6	55
Algae	1368	3052	346	1	28180	–	–	Algae	–	–	–	–	–	–	–

Location: STA1—Vale das Gatas mine; STA2—Vale das Gatas mine; STA3—Vale das Gatas stream; STA4—Background Pinhão river.
Water samples: metals in μg/l; Conductivity in μS/cm; sediment and algae samples: metals in μg/g.

Table 5
Total extraction (%μg/g) of As and Pb by each reagent for a selected stream sediment sample collected near downstream of Pinhão river

Reagents	%Extract As	Concentr. As	%Extract Pb	Concentr. Pb
Ammonium acetate	5.4	48	3	50
Hydroxylamine hydrochloride	2.8	38	2	0
Ammonium oxalate (dark)	60	1084	64	115
H_2O_2 35%	1	33	2	33
Ammonium oxalate (U.V.)	16	364	21	253
Mixed acid (HCl+HNO$_3$+HF) attack	11	254	15	223

Pb and 64% As), by ammonium oxalate U.V. (16% Pb and 21% As) and less by hot mixed acid attack (11% Pb and 15% As). The interpretation of the data of Table 5 together with the composition of the heavy mineral fraction in the same sample shows that the distribution of Pb and As in different mineralogical phases of the sample, is as follows:

(1) ammonium oxalate (dark) extractable Pb (60%) and As (64%) are probably related to hydrated Fe–As oxides and hydrated Fe oxyhydroxides;
(2) ammonium oxalate (U.V.) extractable Pb (16%) and As (21%) are probably associated to Pb–Fe arsenates or Fe oxyhydroxides;
(3) Pb and As extracted by the hot mixed acid attack may be assigned to the presence of galena and arsenopyrite in the sample.

Table 6 shows the content of Cu, Pb, Zn, Cd and As in tailing samples and percolation water (sampling referred to May 2000). Comparing the results of Tables 3 and 5, it is noted that tailing percolation water is more contaminated than surface water collected in the STA1, STA2 and STA3 sampling stations, particularly for Cu, Pb, Zn and Cd. However, it must be pointed out that As does not follow this tendency, mostly due to the precipitation of the element with iron at pH higher than 3.0. These results agree with the equilibrium trends established by Eary (1999) for mine pit waters in which Pb and As concentrations are controlled by pH and adsorption phenomena. Agreement is also found with conclusions presented by Azcue et al. (1995) and Moreno et al. (1999), who claim that the limited solubility of As in tailings is due to adsorption and co-precipitation with ferric oxyhydroxides.

The lower values of metals in surficial waters were observed at 7 km from the Vale das Gatas mine (STA4 in Table 4), in opposition to their behaviour in stream sediments (Fig. 3). This fast decay in the water is due to dilution effects and precipitation in relation to Eh–pH conditions. However, it must be emphasized that, even if the water quality improves, the environmental situation may change with time due to the possibilities of metals being trapped in secondary precipitated minerals and later released in response to changes of the local physical–chemical conditions (Benvenuti et al., 1997).

The metal uptake by the biota from sediments and waters is confirmed by the analysis of samples of *M. tumidula Hazen* algae occurring in streams nearby the Vale das Gatas mine (Table 4). Although not confirmed definitely by SEM analysis, these results seem to indicate that this biological species may accumulate significant amounts of Cu, Pb, Zn and As.

The chemical results obtained in the STA1, STA2 and STA3 stations suggest that the sulphide-oxidation

Table 6
Metals in tailing and percolation water samples (Vale das Gatas mine)

	Cu	Pb	Zn	Cd	As	pH	Conductivity
Tailing ($n=18$)	1763	6647	2590	31	9670	–	–
Percolation water ($n=1$)	93,500	101	785,000	5000	5	3.6	3100

Water sample: metals in μg/g; conductivity in μS/cm.
Tailing samples: metals in μg/g.
Sampling referred to May 2000.

reactions and the chemical precipitation of metals in the Vale das Gatas mine are a continuous long-term process which can change the sediment and water composition and characteristics of the neighbourhood areas in long term. The intensity of these processes is obviously dependent on the reactivity of the materials involved (Walder and Chavez, 1995). Nevertheless, these data agree with conclusions obtained by other authors who studied areas affected by mine wastes (Prusty et al., 1994; Fanfani, 1995; Azcue and Nriagu, 1995; Juillot et al., 1999).

On the other hand, the irregular decay of the anomalous patterns, the result from the electron microprobe and the interpretations of sequential extraction data, suggest that mechanical transport seems to be an important factor leading to the secondary dispersion of the metalliferous elements in the stream sediments. Data from other sources where similar geochemical processes have been interpreted to occur (Hudson-Edwards et al., 2001; Lee et al., 2001; Silva et al., 2002) indicate that metals may be remobilised and transported downstream and down-slope from the tailings by clastic movements.

5. Conclusions

This study based on the geochemistry of Cu, Pb, Zn, Cd and As in stream sediments, water and algae collected in the Vale das Gatas mining district led to the better understanding of the dynamics inherent to leaching, transport and accumulation of these elements.

Two types of mechanisms are suggested for Cu, Pb, Zn, Cd and As mobilization, namely mechanical and chemical. The first one is supported by the high concentrations of Cu, Pb, Zn, Cd and As and the mineralogical composition of the stream sediments in the Vale das Gatas stream and in the Pinhão river. The second appears reflected in the chemical composition of water samples collected near the mine site and by the presence of high levels of Cu, Pb and As and neoformed minerals in coatings of the stream sediments.

These geochemical and mineralogical results support the existence of actual chemical leaching–precipitation reactions taking place near the Vale das Gatas mine tailings.

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