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Spatial risk assessment related to abandoned mining activities: an environmental management tool

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Abstract Mining activities and resulting wastes can be considered one of the most important sources of toxic metals and metalloids in the environment. To assess environmental risk in the surrounding areas of old abandoned W-Sn and Pb–Zn mines and resulting tailings and rejected materials, 333 samples were collected in stream sediments under the influence of abandoned mines. Samples were prepared and analyzed for Fe, Ba, P, Cu, Cr, Ag, B, Zn, Be, Y, Nb, Pb, Ni, V, Mn, Mo, As, W, Co, Cd, Sn and U. The inexistence of Portuguese legislation concerning parametric values for stream sediments led to the application of a quantitative index for progressive contamination on stream sediments, the Geoaccumulation Index (Igeo), as variables to create risk maps. A first exploratory multivariate statistical analysis, using the Principal Component Analysis (PCA), applied to the obtained Igeos, shows a first factor (F1) explaining the dependence of P and B (positive correlation with the axis) and the inverse correlation of these two elements with the cluster formed by Cr, Ni and V (negative correlation with the axis); the second factor (F2) explains Ni, Fe, Zn and As; Cd and U Igeos are not explained in the new factorial space and, therefore, are characterized individually. The variographic studies showed the existence of spatial structure for the new synthesis variables (F1, F2) as well as for Cd and U Igeos. The experimental point-support data was then interpolated using ordinary kriging within a narrow search window as shown in the fitted variogram models. The obtained maps show extremely high levels of pollution in Cd and W and strongly high levels of pollution in Cr, B, Ag, Zn and Pb. The accumulation of these elements in the studied stream sediments is higher on the abandoned mining areas and in their vicinity.

Introduction

Mine tailings contain high concentrations of potentially toxic metals whose mobility may pose an environmental hazard (e.g., Allan 1997; Mlayah et al. 2009; Favas et al. 2011; Kusimi and Kusimi 2012; Park and Choi 2013; Larios et al. 2013; Servida et al. 2013). In Portugal, ore extraction and processing has been an important supply of wealth and were actively developed until the early 1970s. However, until recently, a lack of specific regulations for tailings disposal have produced numerous mine wastes dispersed through various mineralized zones of the country, since the waste products remain accumulated in tailings and cause significant impacts on water, stream sediments and soils. They are an important source of potentially toxic metals and metalloids which can be easily dispersed and constitute a significant environmental concern, due to their toxicity, high enrichment factor and slow removal rate (Alloway and Ayres 1997). The chemistry and potential hazard of tailings depend on ore mineralogy, processing methods and thus particle size distribution, climate and time since the mine closure (Lottermoser 2010).

In Portugal, many abandoned mining areas are known for their associated contamination (e.g., Antunes et al.

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2002; Antunes 2008; Godinho et al. 2010; Gomes et al. 2010; Favas et al. 2011; Antunes and Albuquerque 2013). Only a few of them have been object of environmental studies and remediation processes decreases with natural attenuation. The mineralized elements constitute one of the most toxic inorganic pollutants that may occur in soils (Siegel 2002) and their toxicity increases with the accumulation process and decreases with natural attenuation (Bradl 2004).

Geochemical cartography is a goal in geochemical exploration and associated mining prospection since the late 20s of the past century (e.g., Instituto Geológico e Mineiro 1988; Batista et al. 2001; Ávila et al. 2005). More recently with the remarkable development of the analytical methods, the implementation of a geochemical mapping became a strong possibility, working as a tool in natural resources management. Geochemical cartography in environmental applications is mostly oriented to the recognition and quantification of anthropogenic impacts. An accurate characterization of the natural background values is an essential and unavoidable step to evaluate the input of mining activities in the environment.

The aim of this manuscript is the construction of an environmental risk cartography through a geochemical approach in an old abandoned mine region—Lardosa region. A point-support dataset of 333 samples of stream sediments was analyzed for trace elements contamination (Fe, Ba, P, Cu, Cr, Ag, B, Zn, Be, Y, Nb, Pb, Ni, V, Mn, Mo, As, Co, Cd, Sn and W) and the environmental risk mapping computed using adequate Geostatistical and Geographical Information systems' (GIS) tools.

This study, set between 1980 and 1988, has for main purpose the achievement of risk cartography based on a geochemical approach and intended to work as a management tool in mining prospection and environment remediation.

Study area

The study area is located in the district of Castelo Branco (Idanha-a-Nova), about 30 km NE of Castelo Branco, in central Portugal (Fig. 1a) and Central Iberian Zone (CIZ) of the Iberian Massif. The area is mainly composed of schists and greywackes from the Beiras Group—"Schist greywacke Complex" that was intruded by the Castelo Branco and Oledo granitic plutons (Antunes et al. 2009). The intense weathering of the Lardosa granite promoted the mobility and accumulation of cassiterite and ilmenite that represent the "Lardosa Deposits" (Instituto Geológico e Mineiro 1988; Sanches 2012). The area is approximately 130 km^2 large and includes 11 abandoned mine concessions of W, Sn–W and Zn–Pb (Fig. 1b), heavily explored

in the decades 60–80 of the past century (Table 1). The mineralized vein fills late to post-tectonic Variscan faults following the strip of Sn–W mineralization from Góis–Segura. The mineralizations occur in the quartz veins and bundle veins with Fe, Cu and As sulfides that are related to the granite's intrusion.

Agriculture is the primary activity requiring a large amount of superficial and sub superficial water for irrigation (Sanches 2012). The climate of this area is characterized by a temperate climate, with very dry and warm summers. In fact, only a few streams are not dry during the summer. The wet season starts in October and lasts until May with a mean annual temperature of 14.5 °C and annual precipitation ranging from 700 to 1000 mm/year (Agência Portuguesa do Ambiente 2012). The geomorphology of the region is controlled by rocks from Central Iberian Zone. The relief is regular and flattened with altitude reaching between 200 and 400 m (Instituto Geográfico do Exército 1998).

The study area is inserted into the Tagus river catchment and the tributaries Ponsul and Alpreade are the most important rivers (Fig. 2). The definition of the major Rio Ponsul's tributary watersheds allowed considering the specificities of their hydrological dynamics and thus a more accurate characterization and understanding of the processes involved in the metals' dispersion under study. Samples of stream sediments correspond to heterogeneous materials derived from erosion of the surrounding areas (Fig. 2).

Methodologies

Around mine dumps, the mineralogical content of the material exploited consists of inert materials from the gangue constituent's mineralization or mineral constituents of rocks (Maroto et al. 1997). In these areas, the production of anomalous high concentrations of chemical elements, taking into account the background levels, affects not only the soil and water quality but as well all who depend directly or indirectly on them. The presence of anomalies in some chemical elements in the surrounding areas of tailings or mineralized areas indicates the action of dominant wind and transport of fine dust from the superficial layers of the heap (Santos Oliveira et al. 1998). The stream sediments resulting from the alteration of rocks by various physical and chemical processes are mobilized, transported and deposited along the water lines. These materials present variable composition, according to the type of rocks, mineral deposits and soils, presence of natural contamination and anthropogenic activities in the neighborhoods.

A geochemical and spatial characterization were based on a dataset of 333 representative point-support samples
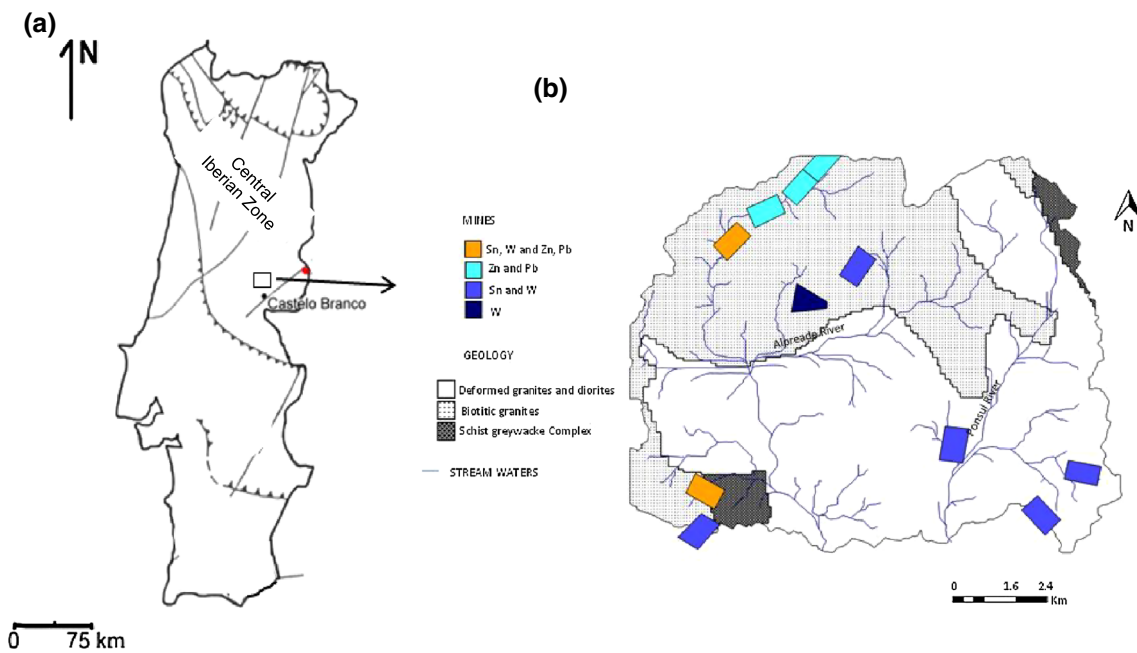
Fig. 1 Study area: a location on the map of Portugal; b geology—study area

Table 1 Identification of the abandoned mine concessions from the study area

Concession designation	Exploitation
Barroca do Marmeleiro	Zn, Pb, Sn and W
Fonte dos Sinos	Zn and Pb
Chão do Tirante	Zn and Pb
Cabeço Onde Mataram os Homens	Zn and Pb
Concessão	W
Concessão	Sn–W
Concessão	Sn–W
Concessão	Sn–W
Tapada de Carvalhos	Sn–W
Concessão	Sn–W
Roncões	W

The first four concessions have been exploited between 1885 and 1964; W and Sn–W have been ceased its exploitation during 1980s (Instituto Geológico e Mineiro 1988)

collected in a narrow region, between 50 m upstream and 100 m downstream the confluence of streams and under mine's influence (Instituto Geológico e Mineiro 1988) (Fig. 2). Geomorphology shows mostly open valleys where stream sediments correspond to incipient and not evolved soils and, therefore, a high contamination hazard.

All samples were prepared with reduction, drying and grinding. The fraction <74 μm was digested with Aqua-Regia and analyzed at Instituto Geológico e Mineiro (S. Mamede de Infesta, Portugal). Total concentration of Fe, Ba, P, Cu, Cr, Ag, B, Zn, Be, Y, Nb, Pb, Ni, V, Mn, Mo, As, Co and Cd was determined by ICP-AES (Jarrel Ash Spectometer), with a precision of 20 ppm for As and 10 ppm for all the other (Instituto Geológico e Mineiro 1988). The detection limits were of 0.10 % for Fe, 20 ppm for Pb and As; 10 ppm for Ba, P, Cu, Cr, B, Zn, Nb, Ni, V, Mn and Co; 5 ppm for Y; 2 ppm for Mo; 1 ppm for Sb, Be and Cd; 0.5 ppm for U and 0.2 ppm for Ag. Sn and W were analyzed by X-ray fluorescence spectrometry and plasma emission with a detection limit and precision of 10 ppm (Instituto Geológico e Mineiro 1988). Internal reference materials, duplicates of samples and reagent blanks were used in the trace element analyses. The spatial geochemical mapping approach was implemented using an algorithm that involves the following steps: (1) Igeo computation (Müller 1979); (2) synthesis variables construction using Principal Components Analysis (PCA) (e.g., Ávila et al. 2005; Salgueiro et al. 2008; Favas et al. 2011) and (3) geostatistical based interpolation (e.g., Verfaillie et al. 2009) was tested (Fig. 3).

Geostatistical methodologies are based on the theory of regionalized variables (Matheron 1971) which states that attributes within an area exhibit both random and spatially structured properties (Journel and Huijbregts 1978). Sample variograms should first be estimated and modeled to quantify the spatial variability of random variables as a function of their separation distance. In practice, an experimental variogram, is computed as

$$\hat{\gamma}(h) = \frac{1}{2N(h)} \left\{ \sum_{i=1}^{N(h)} [z(u_i + h) - z(u_i)]^2 \right\},$$
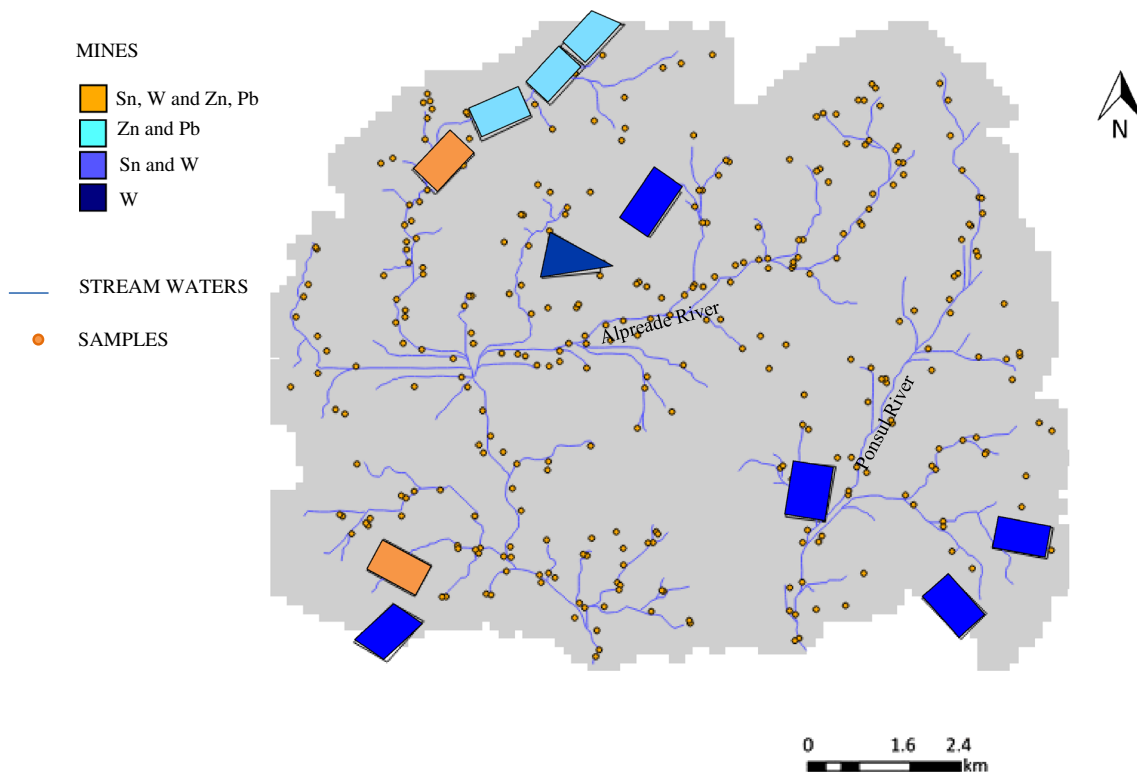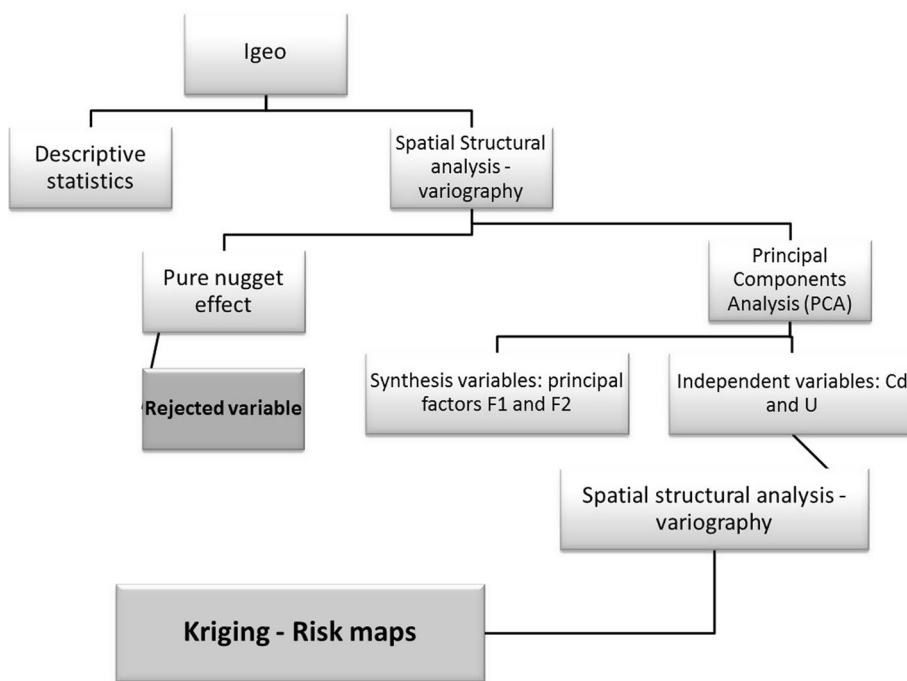
Fig. 2 Location of stream sediment samples collected within the study area

Fig. 3 Spatial geochemical approach algorithm

where $\hat{\gamma}(h)$ denotes the variogram for a distance lag h, $N(h)$ represents the number of data pairs for that lag h, and $z(u_i)$ and $z(u_i + h)$ are the values of the regionalized variable of interest (e.g., As Igeo) at locations u_i and $u_i + h$, respectively. The experimental variogram $\gamma(h)$ is then fitted by a theoretical model, $\hat{\gamma}(h)$ (Isaaks and Srivastava 1989).

Univariate descriptive statistical analysis was performed to characterize Igeos distributions and outliers location,

using the software Xlstat 2013.1.01 (Addinsoft 2013) (Fig. 4). Experimental variograms were computed to characterize the spatial structure using the software ArcGis 9.3 (ESRI 2004). Pure nugget effect variograms mean random spatial behavior and, therefore, the corresponding Igeo was eliminated from the following methodological step to allow noise reduction and more accurate interpolation outputs.

The space of analysis was reduced by a construction of synthesis variables held by PCA (Spearman's rank correlation matrix to reduce outlier's weight) using the software Xlstat 2013.1.01 (Addinsoft 2013). The aim of PCA is to reduce data dimensionality while preserving at the same time the within variability structure (variance–covariance). The analysis starts with p random attributes $X_1, X_2,\ldots, X_p$, where no assumption of multivariate normality is required. The axes of the constant ellipsoids correspond to the new synthesis variables, the principal components (Pereira et al. 2003).

The risk maps were computed using the ordinary kriging (OK) algorithm. It is noteworthy that geostatistics is a

reference approach for characterization of environmental hazards where the information available is typically scarce. The main application of geostatistics has been the estimation and mapping of environmental attributes in un-sampled areas. Kriging is a generic name for a set of generalized least-squares regression algorithms. OK accounts for local fluctuations of the mean by limiting the domain of stationary of the mean to the local neighborhood (Goovaerts 1997).

Results and discussion

Stream sediments have a large capacity to retain toxic and pollutant chemical elements. Their mobility and dispersion are responsible for the amounts of trace elements accumulated in sediments and soils (Table 2). In fact the stream sediments' chemical composition can be a good indicator for environmental contamination, allowing spatial variability assessment and, consequently space-temporal monitoring.

Portugal does not have regulatory thresholds for chemical elements and physicochemical parameters in stream sediments. However, the intensity of heavy metal pollution can be determined by the Index of Geoaccumulation (Igeo) of Müller (1979). The Igeo enables the assessment of contamination and have been applied in the assessment of old mining contamination (e.g., Cesar et al. 2011; Krishna et al. 2013). Igeo is calculated using the following computation:

$$\text{Igeo} = \log_2\left[\frac{C_n}{1.5(B_n)}\right],$$

where C_n = concentration total of the element; B_n = geochemical background and; 1.5 is the multiplication factor due to possible variations in geochemical background's values geologically driven effects.

The Geochemical background values were adopted from literature (Ferreira 2000) (Table 2). Background values for Sn, Be, Y and Nb were not defined. The Igeo is classified into seven pollution's classes, from 0 to 6, in an increasing pollution degree. The higher class (Igeo = 6) stresses a concentration of approximately 100 times the background value (Moreira and Boaventura 2003). The first class (Igeo = 1) corresponds to the lower pollution level, around three times the background concentration (Müller 1979).

High Igeo classes for Cd and W (Igeo = class 6) show extreme pollution in these elements and strong pollution in Cr, B, Ag, Zn and Pb (Igeo = 4). For W, an Igeo above 2 (Igeo = 6) indicates a contents 80 times higher than the background level, while Cd is approximately 55 times
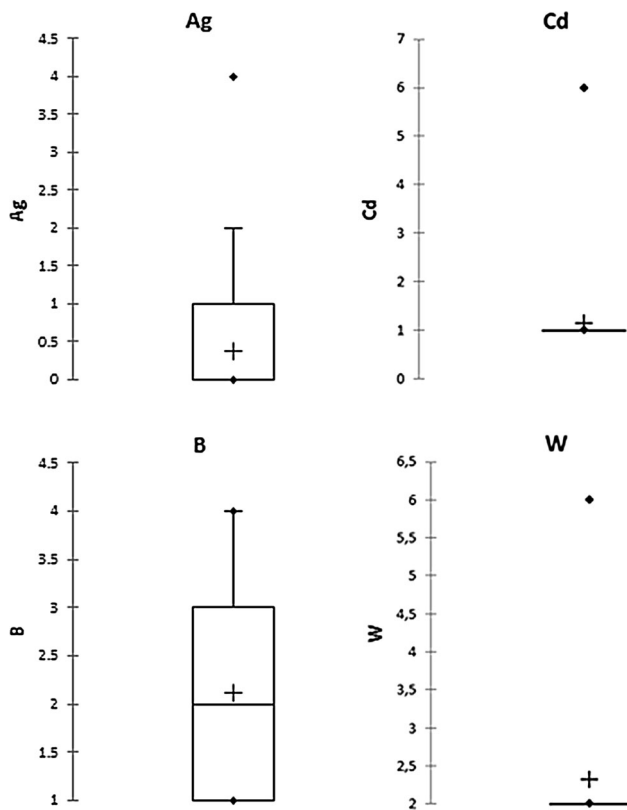
Fig. 4 Box-plot examples: Ag, Cd, B and W's Igeo. Box limits: Inferior = Q1, Superior = Q3; + = Average; — = Median; Outlier limits: Superior = Q3 + 1.5*(Q3 − Q1), Inferior = Q1 −1.5*(Q3 − Q1)

Table 2 Descriptive statistics of trace element contents and background values from stream sediments

Element	DL	Min	Max	Average	Median	Variance	Background values (Ferreira 2000)
Fe	0.10	0.9	5.2	2.5	2.5	0.8	2.0
Ba	10	124.0	655.0	341.4	327.0	87.2	68.0
P	10	299.0	1,865.0	928.5	885.0	318.8	460.0
Cu	10	5.0	49.0	9.3	5.0	7.9	22.0
Cr	10	61.0	431.0	190.4	181.0	74.4	23.0
Ag	0.2	0.1	1.6	0.2	0.1	0.1	0.1
B	10	5.0	33.0	11.4	12.0	5.4	2.0
Zn	10	19.0	1,465.0	82.4	73.0	83.3	74.0
Sb	1	10.0	10.0	10.0	10.0	0.0	2.0
Pb	20	5.0	299.0	25.4	23.0	21.8	19.0
Sn	10	5.0	138.0	8.7	5.0	12.1	nd
Ni	10	5.0	58.0	14.5	12.0	10.0	19.0
V	10	12.0	176.0	46.9	38.0	27.1	26.0
Mn	10	147.0	1,323.0	489.9	470.0	179.1	411.0
Be	1	1.0	16.0	4.8	3.0	3.3	nd
Mo	2	1.0	6.0	1.5	1.0	1.0	1.0
As	20	10.0	105.0	19.7	10.0	14.8	9.0
W	10	5.0	80.0	7.2	5.0	6.5	1.0
Co	10	5.0	16.0	5.5	5.0	1.8	9.0
Y	5	5.0	54.0	14.0	13.0	6.0	nd
Cd	1	0.5	11.0	0.6	0.5	0.6	0.2
Nb	10	5.0	12.0	5.1	5.0	0.8	nd
U	0.5	0.5	21.0	3.5	2.9	2.3	5.0

DL detection limit (Instituto Geológico e Mineiro 1988); *min* minimum; *max* maximum. Fe content in % and other elements in mg/kg

Table 3 Descriptive statistics of Igeo from stream sediments of the study area

Element	Min	Max	Average	Median	Variance
Fe	0.0	1.0	0.1	0.0	0.2
Ba	1.0	3.0	2.1	2.0	0.4
P	0.0	2.0	0.8	1.0	0.6
Cu	0.0	1.0	0.0	0.0	0.1
Cr	1.0	4.0	2.8	3.0	0.6
Ag	0.0	4.0	0.4	0.0	0.6
B	1.0	4.0	2.1	2.0	0.9
Zn	0.0	4.0	0.1	0.0	0.4
Sb	2.0	2.0	2.0	2.0	0.0
Pb	0.0	4.0	0.2	0.0	0.5
Ni	0.0	1.0	0.1	0.0	0.3
V	0.0	3.0	0.6	0.0	0.7
Mn	0.0	2.0	0.2	0.0	0.4
Mo	0.0	2.0	0.3	0.0	0.6
As	0.0	3.0	0.7	0.0	0.9
W	2.0	6.0	2.3	2.0	0.7
Co	0.0	1.0	0.0	0.0	0.1
Cd	1.0	6.0	1.1	1.0	0.5
U	0.0	2.0	0.0	0.0	0.2

Number of samples = 333

min minimum; *max* maximum

Table 4 Variograms' fitted models for the ACP's two first factors—F1, F2—and for Cd and U's Igeo

Variogram parameters	Factorial axes		Cd	U
	F1	F2		
Range (R)	8,751	11,680	11,680	500
Nugget (Co)	1.066	1.067	0.154	0.023
Sill (C1)	3.036	1.676	0.174	0.033
Nugget effect (%)	26	39	47	40

higher than background (Table 3). W and Cd pollution can be associated with the mineralogical paragenesis, while Cr, B, Zn and Pb may be attributed to lithological materials and local mineralizations within the area (Sanches 2012).

The presence of outliers, namely Ag, Cd, B and W distributions (Fig. 4) should not be ignored since they stress values for risk assessment. For all Igeos (Fe, P, Cr, B, Zn, Ni, V, As, Cd and U) omnidirectional experimental variograms were calculated (Table 4; Fig. 5). Ba, Cu, Ag, Pb, Mn, Mo, W, Co, Sn, Be, Y and Nb Igeos showed total nugget effect variograms, meaning a random spatial behavior, and were discarded from the subsequent step. Experimental variograms were computed for the new synthesis variables F1 and F2 and for Cd and U Igeos.
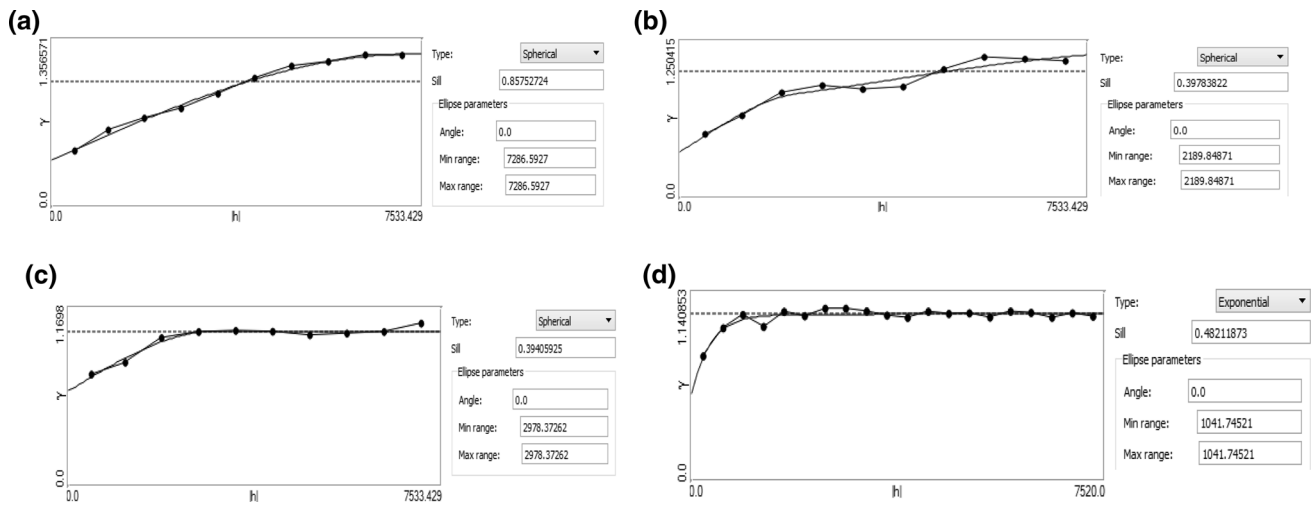
Fig. 5 Experimental variograms and fitted models for the ACP's first factors: **a** F1; **b** F2 and Igeo: **c** Cd; **d** U

Table 5 Results of Principal Component Analysis for Igeo's stream sediments of the study area

	F1	F2	F3	F4
Fe	−0.621	**0.629**	−0.077	−0.082
P	**0.702**	0.315	0.080	−0.143
Cr	**−0.636**	−0.392	0.099	0.062
B	**0.780**	0.278	0.080	−0.145
Zn	−0.251	**0.692**	0.328	0.047
Ni	**−0.654**	0.595	−0.044	−0.053
V	**−0.756**	0.152	−0.097	0.069
As	0.431	**0.698**	−0.018	−0.064
Cd	−0.018	−0.059	**0.915**	0.295
U	0.311	0.250	−0.318	**0.852**
Eingenvalues	3.24	2.14	1.09	0.88
Total	32.41	21.35	10.87	8.80
Cumulative	32.41	53.76	64.63	73.43

The highest contribution for the Igeo to the ACP factors are given in bold

Fig. 6 Igeo's projection on the first ACP factorial plan

Spherical models were fitted and their parameters were used in spatial interpolation process. Ordinary kriging computation was performed using ArcMap 9.3 (ESRI 2004).

With the retained Igeo variables a PCA was performed to reduce the space of analysis and, therefore, the construction of synthesis new variables (Table 5; Fig. 6). The first factor—F1—shows a direct dependence between P and B which on the other hand is negatively correlated with the cluster formed by Cr, Ni and V (Table 5; Fig. 6). These geochemical clusters can be explained by the area's lithology, as mentioned before (e.g., Ávila et al. 2005; Salgueiro et al. 2008). P and B show concentratio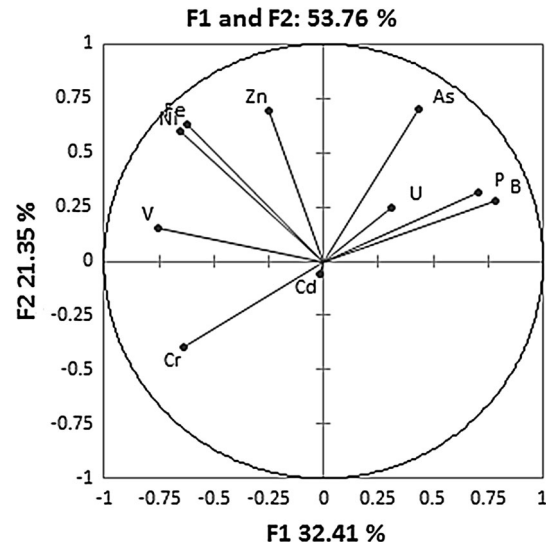n hotspots on the NE and SW corners, while Cr, Ni and V show concentration high-spots predominantly in the NW and SE corners and are under the influence of the old abandoned mines (Fig. 7).

The second factor—F2—explains Fe, Ni, Zn and As with a direct dependence (Table 5; Fig. 5). Zn concentrations can be explained by the exploitation activities in the abandoned mines, while Fe, Ni and As are mostly derived from natural paragenesis' weathering processes (Antunes et al. 2002). The concentration of these elements is higher in the NW and SW corners and related to the influence of the old Zn, Pb, W and W mines (Fig. 8). Cd and U are independent (F3 and F4 factors, respectively) (Table 5). The highest values for Cd and U occur outside the influence of former mining activities (Fig. 9, 10), which can reveal a granitic influence.
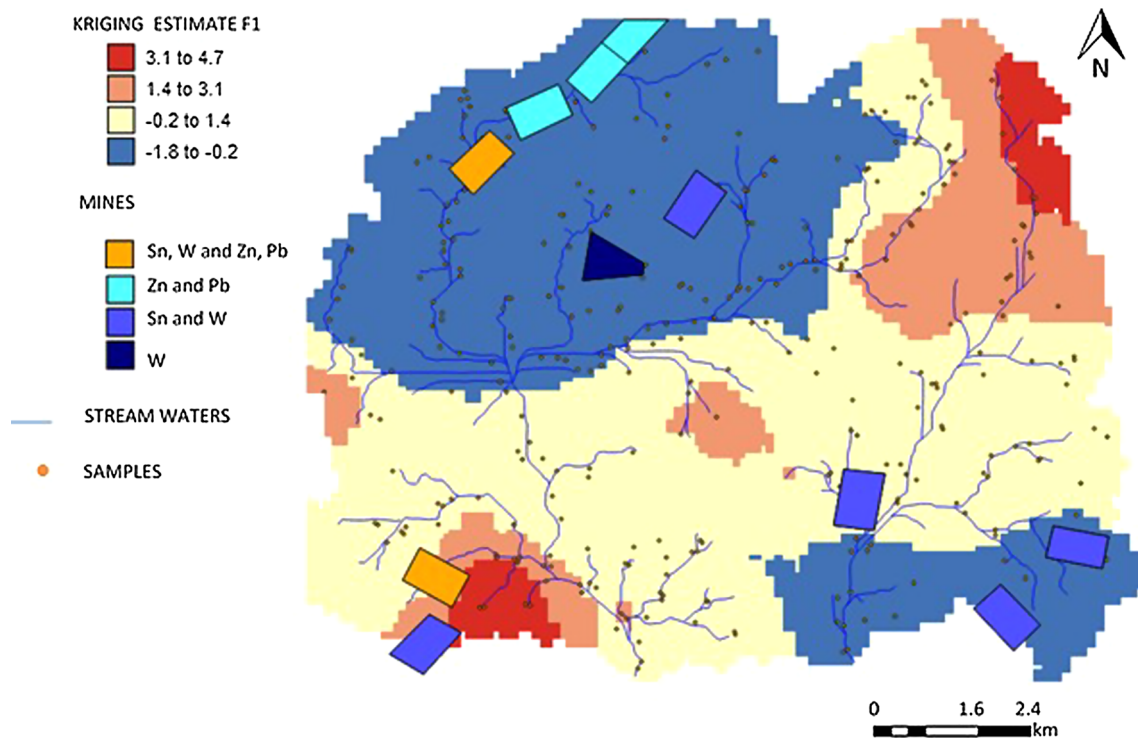
Fig. 7 ACP's first factor mapping (F1): Low (P and B) and high (Cr, Ni, V, Fe), in red; Low to moderate (P and B) and high to moderate (Cr, Ni, V, Fe), in orange; Moderate to high (P and B) and moderate to low (Cr, Ni, V, Fe) in yellow; High (P and B) and low (Cr, Ni, V, Fe) in blue
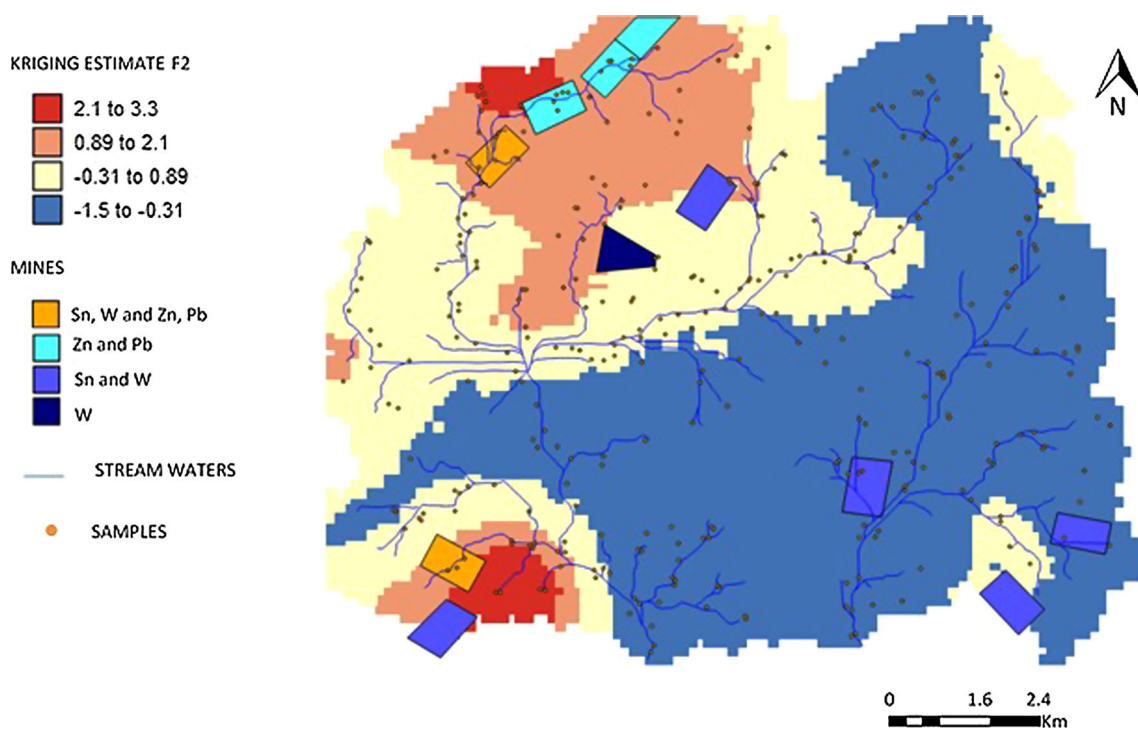

Fig. 8 ACP's second factor mapping (F2): Low (Fe, As and Zn) in red; Low to moderate (Fe, As and Zn) in orange; Moderate to high (Fe, As and Zn) in yellow; High (Fe, As and Zn) in blue
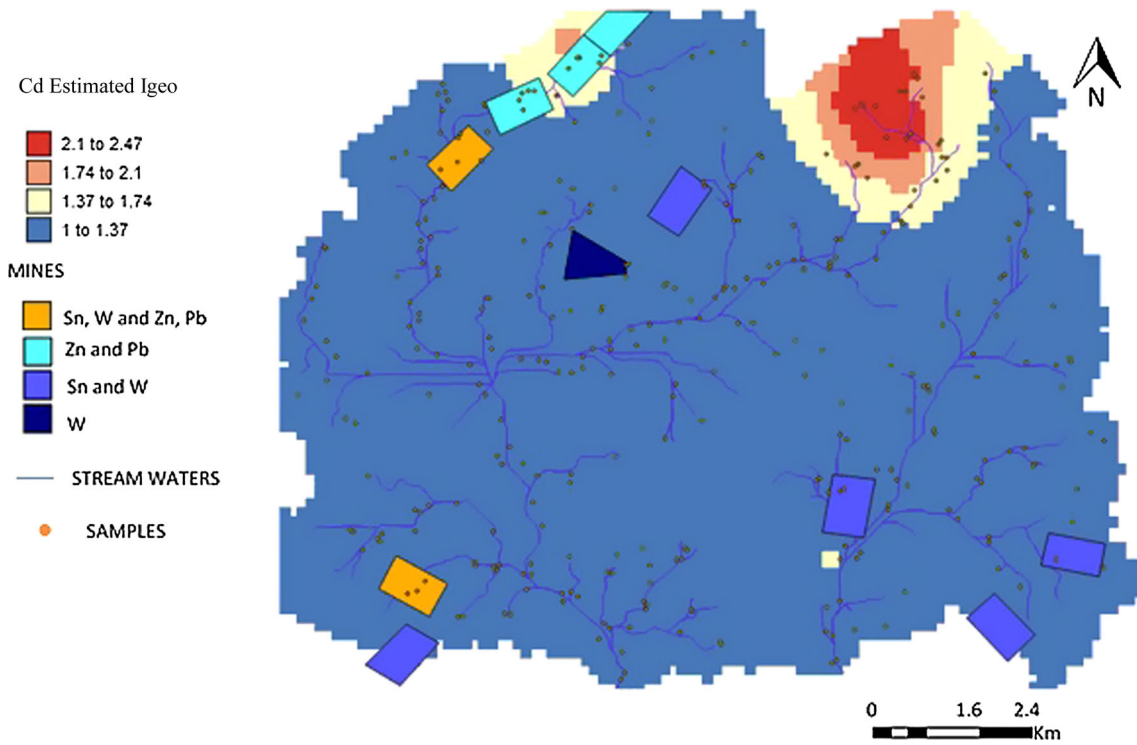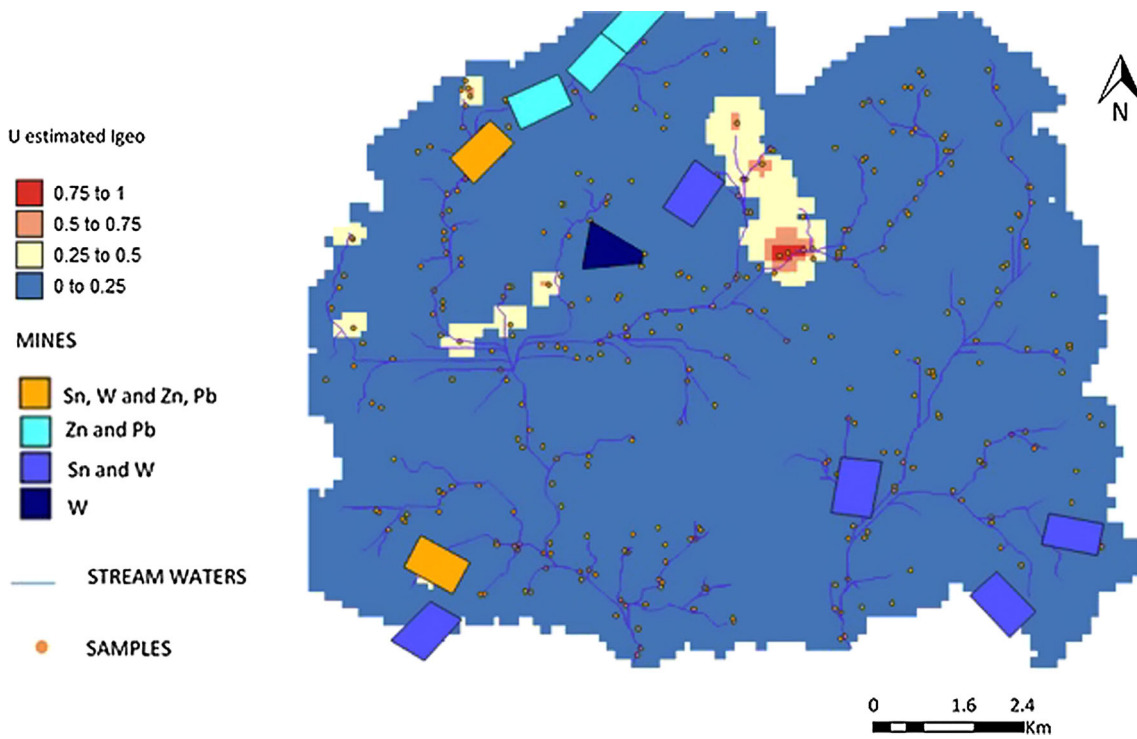
Fig. 9 Igeo mapping for Cd

Fig. 10 Igeo mapping for U

Conclusions

The studied region has many mineral resources highly exploited for decades, with high potential impact on the environment. The highest concentration of trace elements occurs inside mine influence, although some of them could be mobilized to other locals. However, there is no significant dependence between trace element contamination and the exploited paragenetic association.

Overall, the obtained maps show high concentration of the contaminants, with extremely high levels of pollution in Cd and W and strongly high levels of pollution in Cr, B, Ag, Zn and Pb. The accumulation of these elements is higher in the stream sediments located inside the abandoned mining areas and the ones under their influence. An interesting observation is that in the NE corner, high concentration of several elements is observed even though there are no known exploited abandoned mines. It is known that during the Second World War, several unregistered exploitations have been highly spread in the region and may be the cause for these outliers.

The spatial distribution of the Igeos seems to be mainly controlled by the physical, chemical and biological weathering processes within the area. As a result, soils and stream sediment chemical composition is directly derived from the original lithology's weathering. As expected, samples directly collected from within abandoned mines have their trace element contents due to the old mines' paragenesis, although these elements could have been mobilized and dispersed from other areas, even after ceasing of the exploitation period and for an undetermined lag of time.

Geochemical maps became a strong tool in natural resources management. An environmental geochemical approach promotes the recognition and quantification of anthropogenic impacts and consequent adequate monitoring measures. In future work, this cartography could be the starting point to a centered discussion in the human health effects of local communities.

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