

Spatial environmental risk evaluation of potential toxic elements in stream sediments

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Abstract Potential toxic elements (PTE), in stream sediments, were used as contamination indicators for the definition of high-/low-grade spatial clusters in the Monfortinho area (Central Portugal). A set of 271 stream sediment samples was used for spatial modelling and further definition of rings of enrichment—high and low rings. A three-step multivariate statistical and geostatistical approach was used: (1) principal components analysis for PTE's association evaluation and dimensionality reduction; (2) ordinary kriging as an unbiased interpolator for content inference and construction of a continuous representation of the considered attributes, at any arbitrary spatial location; (3) G clustering algorithm for the definition of high and low significance clusters. A moderate contamination in stream sediments is observed for almost all the considered PTE and a very high contamination for Ba, Cr and B. High contamination

clusters are observed for Fe, Ni, Ba, Cu, B, Zn, V—northwest and southeast clusters—and for Cr—north and southwest clusters. The contamination degree index varies from moderate to high, which is mainly associated with the old mineralizations. The high computed rings often overlap the areas of abandoned Ba–Zn mineralization, as well as the sedimentary gold concentrations, along the Erges River banks. Tin and Cd spatial distribution may be related to former cassiterite exploitations in the survey area. Chromium is possibly connected with the schists. The definition of clusters with a PTE spatial enrichment will allow for the identification of contamination activities and therefore, the definition of adequate monitoring and mitigation actions.

Keywords Stream sediments · Contamination factor · Contamination degree · Principal components analysis · Ordinary kriging · G clustering

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Introduction

The occurrence of potential toxic elements (PTE) in a river system is determined by different factors such as geology, mineralogy, hydrology, botany, chemical reactivity, land use pattern and biological productivity (Albanese et al. 2013). These elements entering surface waters from natural or anthropogenic sources become part of the water suspension and the sediment system by absorption, precipitation and ion exchange

processes (e.g. Jain and Sharma 2001; Abreu et al. 2008; Antunes et al. 2016).

Contaminants in river systems can be investigated by analysing either the water and the suspended material or the sediments. However, contaminants in water and suspended material could be influenced by water discharge fluctuations and low residence times (Singh et al. 1997). The geochemistry of stream sediments will be a good tool to evaluate the degree of trace elements contamination, due to their long residence time and the contents being naturally above detection limits (e.g. Bertin and Bourg 1995; Antunes et al. 2016).

The studies of stream sediments have widely become a key of subject interest in research on aquatic systems and environmental assessment, reflecting their quality and providing information on anthropogenic impacts (e.g. urbanization, industrialization, mining activities) (e.g. Baptista Neto et al. 2000; Dauvalter and Rognerud 2001; Santos et al. 2002; Woitke et al. 2003; Alexakis 2011; Romic et al. 2012; Chen et al. 2016; Tzoraki et al. 2015; González-Fernández et al. 2018). Under changing environmental conditions, sediments bounding PTE may be remobilized and added to the water or food chain; surface sediments act both as carriers and traps, catching pollutants and becoming possible sources of contaminants in the system (Chapman and Wang 1999). The fate and transport processes affect the behaviour of PTE in a river system, so it is crucial to outline these processes to better understand the nature—anthropogenic or geogenic—of the contaminating sources and to assess the environmental risk to ecosystems and human health (Zheng et al. 2008; Neiva et al. 2014, 2015).

Stream sediment also remains a common geochemical approach used for regional gold exploration (Fletcher 1997; Darwish and Poellmann 2010; Goovaerts et al. 2014, 2016). The exploration of sedimentary gold (alluvial) has occurred in distinct mineralized areas and is linked up with different genetic deposits (Townley et al. 2003; Chapman and Mortensen 2006; McInnes et al. 2008). PTE associated with gold exploitation—including Cu, Zn, Sn, W, Cr, Cd, As and Pb—can be dispersed downstream due to weathering processes. The extended and degree of PTE contamination associated to mineralization is variable, depending upon chemical characteristics and associated metals, and could influence nearby

residential/agricultural land, stream sediments and streams (Ferreira da Silva et al. 2004; Antunes et al. 2016; Carvalho et al. 2016).

Geochemical mapping, historically used to enhance the interpretation of metal distribution patterns in mineral exploration, has recently become essential in environmental studies (Plant et al. 2001; Antunes and Albuquerque 2013; Antunes et al. 2014; Goovaerts et al. 2016). Understanding the geochemical processes that control precipitation and dissolution of secondary minerals in abandoned or active mines is crucial for the elaboration of models to predict the environmental impact of such sites (Gieré et al. 2003).

The main subject of this paper is the investigation of PTE geochemical distribution in the stream sediments of the Monfortinho area to assess the ecological risk associated with the old gold explorations developed in this area.

Study area

The study area is in the Monfortinho region, about 70 km east of Castelo Branco, Central Portugal. The area belongs to the tin–tungsten sector located in the Central Iberian Zone (CIZ) of the Iberian Massif, in the Portuguese–Spanish border (Fig. 1a). The Monfortinho area is occupied by the Cambrian schist–metagreywacke complex, which consists of alternating metapelites and metagreywackes with metaconglomerate and marble intercalations (Antunes et al. 2009). NW–SE Ordovician quartzites occur in the Cambrian schist–metagreywacke complex and the Tertiary sedimentary materials cover entirely the area (Oliveira et al. 1992).

Gold in Idanha-a-Nova region was widely exploited since the Roman period, especially in the areas of Rosmaninhal, Salvaterra do Extremo and Monfortinho, as demonstrated by the archaeological artifacts found along the region (Batata 2006). The Erges River terraces are divided into six levels, where the four most recent (between 5 and 45 m) were exploited by the Romans for gold (Schwarz 1933). The remains of this old exploitations are still visible in some places, including fronts disassemble, sterile dump mines, supply channels and water tank accumulation. Most traces of operating fronts and other mining structures were changed by urban buildings from the late 1930s (Batata 2006). In the Monfortinho area, a daily exploitation of 2–4 g Au and finding Au

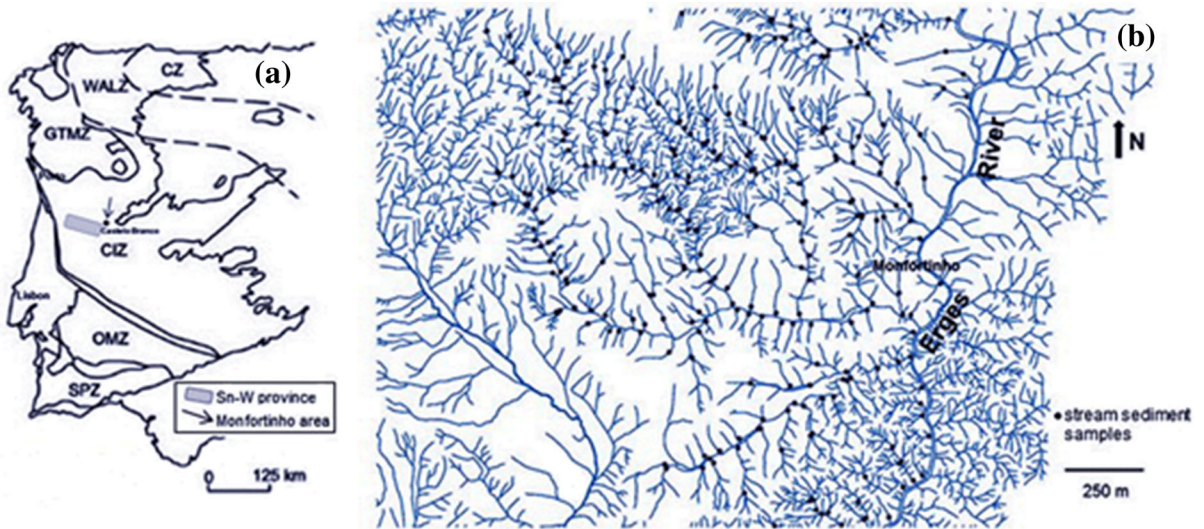


Fig. 1 **a** Location of the Monfortinho area in the Central Iberian Zone (CIZ); **b** Erges River hydrographic network with the location of the collected stream sediment samples

nuggets of 30–40 g have been reported. After 1933, other geological resources overlapped the Au mining activities, such are hot spring waters. In the late 1980s, the ore characteristics of the area were evaluated with prospecting studies, for the extraction of 484 kg of gold (Batata 2006).

The area is included in the basin of Erges River, a tributary of the right bank of the Tagus River. The Erges River has a permanent character waterline, with a flow having strong seasonal fluctuations. The Erges River delimits the transboundary of the Portuguese–Spain border, and is one of the last wild rivers in Portugal with a rare natural value due to its geodiversity and mining landscape features.

The survey area surrounds the old sedimentary gold mining area, in the banks of the Erges River. Around the mine tailings, the mineralogical content is driven from the inert materials present in the gangue. The geochemical anomalies found, near tailings and mineralized areas, indicate the natural process of dominant winds and subsequent transport of fine dust, from the superficial layers of the heap (Santos Oliveira et al. 1998).

The northern area of Monfortinho shows an extremely vigorous geomorphology, with the highest altitudes around 600 m, occurring in the quartzites, and the lowest ones, around 240 m, located in alluvial materials on the Erges River. Agriculture is the main local economic activity with the steep sides mainly

covered by *pinus* and *eucalyptus*. The thermal waters of low enthalpy—Fonte Santa spring—have a noteworthy contribution to the economic system and tourist activities in the area. This area is characterized by a dry climate and intermittent streams drying up in the summer (Antunes et al. 2002).

Materials and methods

Sample collection and preparation

The selected sampling site is included in the Erges river watershed (approximately 140 km²), surrounding the exploited sedimentary gold exploitations. The stream sediments are a result of the bedrock physical and chemical alteration and ulterior mobilization, transport and deposition along the river banks.

A total of 271 representative stream sediment samples (Fig. 1b) were collected in a narrow region, ranging from 50 m upstream to 100 m downstream from the streams' confluences, avoiding, wherever possible, the assemblage of organic matter (Instituto Geológico e Mineiro 1988).

All the samples were collected on the schist–metagreywacke complex, stored in polyethylene bags, and transported to the laboratory of INETI (S. Mamede, Portugal). The samples went through a preparation procedure, including dry sieving at 40 °C,

disaggregation and homogenization. Finally, all the material was sieved through a < 200 mesh screen. The < 250 μm fraction was digested with aqua regia (3:1 HCl–HNO₃) and used for the determination of As, B, Ba, Cd, Cu, Fe, Ni, Pb, V and Zn, by ICP-AES, with a precision of 20% for As and 10% for the other elements (Instituto Geológico e Mineiro 1988). Tin and W were analysed by X-ray fluorescence spectrometry (XRF); the high stability of the XRF system generally allows these analyses with high precision. Tin and W were obtained with a precision of 10% (0.05 ppb) (Antunes et al. 2002; Instituto Geológico e Mineiro 1988).

Spatial modelling

The spatial characterization of PTE distribution was performed through a four-step approach:

- (1) Principal component analysis (PCA) for dimensionality reduction and for variable association evaluation. PCA is one of the most important multivariate statistical methods widely used for data preprocessing and dimension reduction. The space of analysis is reduced by a construction of synthesis variables held by PCA. The aim of PCA is to reduce data dimensionality while preserving, at the same time, the within-variability structure (variance–covariance) (e.g. Zuo et al. 2016). The analysis starts with p random attributes, X_1, X_2, \dots, 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. A Spearman correlation-based method (aiming at the reduction of the outliers' weight) was used to identify features or variations within the datasets by highlighting their similarities and differences. For computation, XLStat 2013.1.01 software was used (<https://www.xlstat.com/en/>).
- (2) Structural analysis—experimental variograms were computed and theoretical models fitted (Matheron 1971; Journel and Huijbregts 1978; Gringarten and Deutsch 2001). For computation, SpaceStat V. 4.0-18. software was used (<https://www.biomedware.com/>).

The variogram is a vector function used to calculate the spatial variability of regionalized variables defined

by the following equation (Matheron 1971; Journel and Huijbregts 1978):

$$\gamma = \frac{1}{2N(h)} \sum_{2N(h)}^{N(h)} [Z(x_i) - Z(x_i + h)]^2. \quad (1)$$

Its argument is h (distance) where $Z(x_i)$ and $Z(x_i + h)$ are the numerical values of the observed variable at points x_i , and $x_i + h$. The number of forming pairs for an h distance is $N(h)$. Thus, it is the median value of the square of the differences between all pairs of points existing in the geometric field spaced at an h distance. The graphic study of the obtained variograms provides an overview of the spatial structure of the variable. One of the parameters that provides such information is the nugget effect (C_0), which shows the behaviour at the origin. The other two parameters are the sill (C_1) and the amplitude (a) which define, correspondingly, the inertia used in the interpolation process and the influence radius of the variable.

- (3) Ordinary kriging (OK) algorithm was used for spatial interpolation aiming to predict the variables' values at any arbitrary spatial location within the study region and, so, compute content maps for the considered attributes (CD_{F1}; CD_{F2}; CD_{F3}; CF_W and CF_{Cr}). It is noteworthy that geostatistics are a reference approach for the characterization of environmental hazards where the data available are typically scarce. The primary application of geostatistics has been the estimation and mapping of environmental attributes in unsampled areas where kriging is a generic name for a set of generalized least-squares regression algorithms. Ordinary kriging (OK) accounts for local fluctuations of the mean by limiting the field of stationarity of the mean to the local neighbourhood (Goovaerts 1997). For the computation, the SpaceStat Software V. 4.0.18, Biomedware, was used (Albuquerque et al. 2014).
- (4) To reinforce the obtained findings of the last section, a Local G clustering was conducted to measure the degree of association resulting from the concentration of weighted points (or region represented by a weighted point) and all other weighted points (Albuquerque et al. 2017), included within a radius of distance

from the original weighted point. Consider a given zone subdivided into n regions, $I = 1, 2, \dots, n$, where each neighbourhood is identified with a point whose cartesian coordinates are known. Each i has associated with it a value x (a weight) taken from a variable X . The variable holds a natural origin and it is positive. The $G(i)$ statistic developed below allows for tests of hypotheses concerning the spatial concentration of the sum of x values associated with the j points within d of the i th point. The following statistic is obtained:

$$G_i(d) = \frac{\sum_{j=1}^n W_{ij}(d)X_j}{\sum_j x_j}, \tag{2}$$

where W_{ij} is a symmetric one/zero spatial weight matrix with ones for all links defined as being within distance d of a given i ; all other links are zero, including the link of point i to itself. The numerator is the sum of all x_j within d of i , but not including x_i . The denominator is the sum of all x_j , excluding x_i (Getis and Ord 1992).

Results and discussion

Descriptive statistics

The range, median and standard deviation of PTE concentrations in the stream sediments of Monfortinho are shown in Table 1. Stream sediments exhibit a large gap in the concentration values, in almost all elements, showing values up to 48,000 mg/kg of Fe, 750 mg/kg of Ba, 464 mg/kg of Cr, 202 mg/kg of Zn and 313 mg/kg of V, indicating a geogenic and mining influence. The higher Fe content probably is due to Fe-oxyhydroxides which retain different metals and metalloids (e.g. Neiva et al. 2014; Antunes et al. 2016; Carvalho et al. 2016).

The variance in the stream sediment PTEs' contents may be viewed in the following box plots (Fig. 2), where the Y axis represents the PTEs' concentration values. The plots bring forward the non-outlier limits, corresponding to the upper and the lower quartiles, within 1.5 times the interquartile amplitude.

Tin, As, W and Cd show severe outliers (Fig. 2). The presence of high amounts of Fe (Table 1) indicates a clear association with Fe-oxy and

Table 1 Fe (%) and PTE contents (mg/kg) in stream sediments

	Minimum	Maximum	Median	SD
Fe	1.1	4.8	2.8	0.81
Ba	95	750	291	103.1
Cu	5	64	18.0	6.25
Cr	125	464	238	64.8
B	5	37	20	6.4
Zn	16	202	57	27.1
Pb	5	90	14	8.2
Sn	–	25	0.5	3.7
V	21	313	65	29.9
Ni	11	42	24	6.8
As	10	44	10	6.1
W	–	8	1.6	1.1
Cd	0.5	1.0	0.5	0.08
N	271			

N number of samples, – below the detection limit

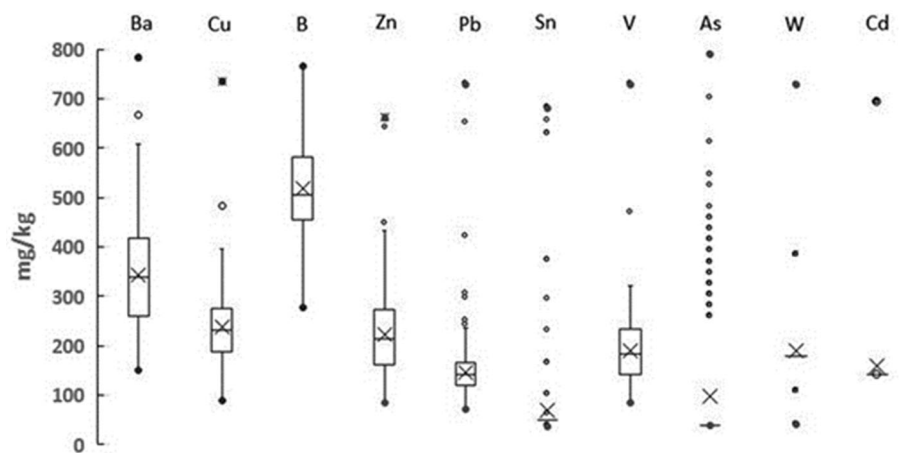
hydroxides which are common in stream sediments (e.g. Holmström and Öhlander 2001; Antunes et al. 2014; 2016; Neiva et al. 2016). Moreover, extreme values observed for Ba, Cu, Zn, Pb, Sn, As, W and Cd point out to the Au, Sn–W and Ba–Zn mineralizations occurring around the study area, as these are responsible for their content in the stream sediments (e.g., Antunes et al. 2002; Jordan et al. 2007; Antunes et al. 2014). Boron and V contents in stream sediments may be associated with a geogenic origin, joined to the predominant lithologies occurring in the region.

Contamination risk evaluation

Several international methods for PTE stream sediment content evaluation are available in the literature, the remarkable ones being the contamination factor (CF), the contamination degree (CD), the enrichment factor (EF), the geoaccumulation index (IGeo), the potential ecological risk index (PERI) and the G2met index (e.g. Håkanson 1980; Wenyl et al. 1997; Verca and Dolenc 2005; Karydas et al. 2015).

The CF was used to assess the enrichment degree of a PTE concentration and the potential toxicity index (RI) of stream sediments from the influence of the mine (Håkanson 1980; Sutherland 2000; Andrew and Sutherland 2004).

Fig. 2 Box plots for the PTE content distribution in the collected stream sediment samples. X—median; 25–75%; • minimum/maximum; o—outlier



The CF spatial distribution for each PTE resulted from the relation between the concentration value of the considered element (C_i) and a reference value of the element (C_b) (Sutherland 2000). The reference values included background concentration for stream sediments of Portugal. The Portuguese background values, from FOREGS Geochemical Atlas of Europe, are as follows: Fe = 2.45%, Ba = 68 ppm, Cu = 22 ppm, Cr = 23 ppm; B = 2 ppm; Zn = 74 ppm, Pb = 19 ppm, V = 26 ppm, Ni = 19 ppm; As = 9.0 ppm, W = 1.0 ppm, Cd = 0.2 ppm (Ferreira 2000) and Sn = 2.25 ppm (Salminen et al. 2005). The minimum, maximum and median stream sediment contamination factors of the selected PTE are presented in Table 2.

Most of the PTE exhibit a moderate contamination degree. However, Ba, Cr and B show high and very high values for the contamination factor index (Table 2). The median CF values, considering the studied attributes, are as follows: Cr > B > Ba > V = Cd > W > Ni > As = Fe > Pb > Cu = Zn > Sn (Table 2), which is explained by the former mining activity in the region. Over 50% of the collected samples show moderate values for the contamination factor index: iron (83%), Cu (76%), Ag (98%), Pb (52%), V (68%), As (82%), W (63%) and Cd (97%), Ba (60%), Cr (100%) and B (94%) (Fig. 3).

The contamination degree (CD) is the result of the total of all the CF and was reclassified accordingly to the number of the considered PTE (13 elements) (Table 2). The CD values in the Monfortinho stream sediments range from 24 up to 61, corresponding to a

moderate (55%) to a high (44%) contamination degree, respectively.

The CF values may suggest a source in PTE in the neighbourhood, but cannot indicate their chemical action or their biological availability (Guo et al. 2010). The potential ecological risk index (E_i^j) is a simple and a relative shortcut index, which not only reflects the single impact of metals on the ecological environment, but also combines the environmental chemistry, biological toxicology and ecology (e.g. Hong et al. 2004; Qinna et al. 2005). This factor is computed using the contamination factor (C_i^j) of the element and the coefficient response of the metal toxicity (T_i^j), suggesting that the hazard for human and aquatic ecosystems is a consequence of its toxicity and its ecological sensitivity (Guo et al. 2010). The applied coefficients (T_i^j) were: Cd = 30; As = 10; Cu = Pb = Ni = 5; Cr = 2 and Zn = 1 (Qinna et al. 2005).

The potential ecological risk (E_i^j) and potential toxicity response index (RI) values are shown in Table 3.

The median values for Fe, Cu, Cr, As and Ni (Table 4) are higher than those recorded in FOREGS—Geochemical Atlas of Europe (Salminen et al. 2005).

Multivariate statistics

In the case study considered, PCA results reveal the existence of three groups (Fig. 4): (a) a first group formed by Fe, Ni, Ba, Cu, B, Zn and V, which is a typical PTE association; (b) a second group composed of Sn and Cd; (c) a third group representing Pb and As.

Table 2 Contamination factor (CF) and contamination degree (CD) of selected PTE in stream sediments

	Minimum	Maximum	Median		Minimum	Maximum	Median
Fe	1.1	4.8	2.3	Sn ^a	–	25	0.5
CF	0.4	2.0	1.1	CF	0	11.1	0.2
Ba	95	750	291	V	21	313	65
CF	1.4	11.0	4.3	CF	0.8	12.0	2.5
Cu	5.0	64	18	Ni	11	42	24
CF	0.2	2.9	0.8	CF	0.6	2.2	1.3
Cr	125	464	238	As	10	44	10
CF	5.4	20.2	10.3	CF	1.1	4.9	1.1
B	5.0	37	20	W	–	8.0	1.6
CF	2.5	18.5	10.0	CF	0.0	8.0	1.6
Zn	16	202	57	Cd	0.5	1.0	0.5
CF	0.2	2.7	0.8	CF	2.5	5	2.5
Pb	5	90	14				
CF	0.4	6.4	1.0				
CD	24.0	61.1	38.6				

CF = C_i/C_b ; C_i —content of the element; C_b —background value (Ferreira 2000; ^aSalminen et al. 2005). CF < 1 low contamination; 1 < CF < 3 moderate contamination; 3 < CF < 6 high contamination; CF > 6 very high contamination. CD = Σ CF; CD < 13 low contamination degree; 13 < CD < 26 moderate contamination degree; 26 < CD < 39 high contamination degree; CD > 39 very high contamination degree

Fig. 3 Percentage of contamination factor (CFs) classes in the area

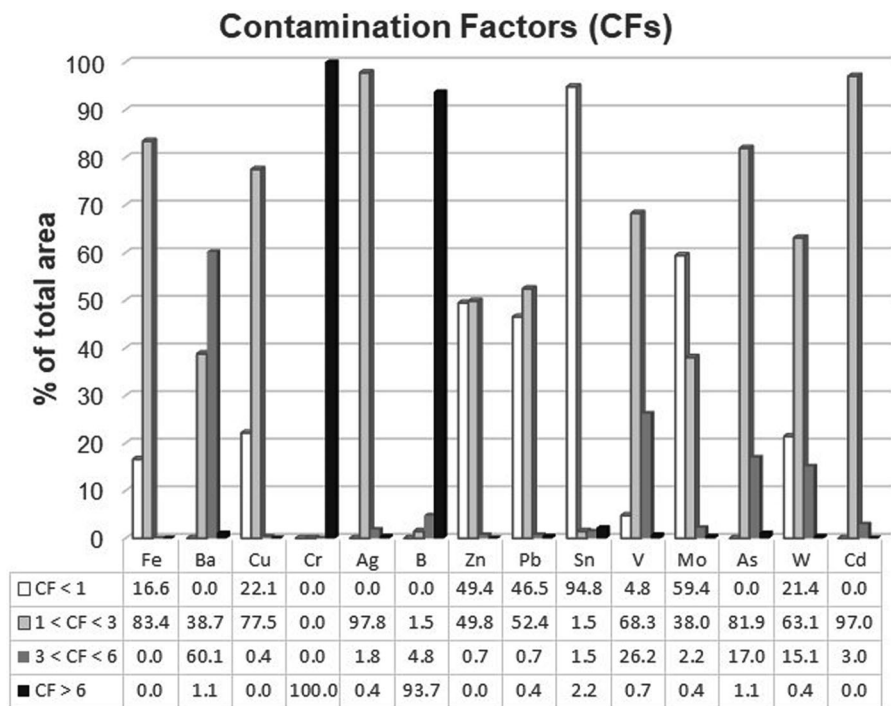


Table 3 Potential ecological risk index (E_j^i) and potential toxicity index (RI) of the selected PTE in stream sediments

	Minimum	Maximum	Median
E_j^i Cu	1.8	22.9	6.4
E_j^i Cr	11.9	44.2	22.7
E_j^i Zn	0.3	3.4	1.0
E_j^i Pb	1.8	32.1	5.0
E_j^i As	16.7	73.3	16.7
E_j^i Cd	53.6	107.1	53.6
RI	92	189	107

Ecological risk index: $E_j^i = C_j^i * T_j^i$; C_j^i = CF coefficient to the element; T_j^i —response coefficient for the toxicity of the element. Ecological risk level: $E_j^i < 40$ —low; $40 \leq E_j^i < 80$ —moderate; $80 \leq E_j^i < 160$ —high; $160 \leq E_j^i < 320$ —very high; $320 \leq E_j^i$ —serious; potential toxicity response index: $RI = \sum E_j^i$. Potential ecological risk level: $RI < 150$ —low grade; $150 \leq RI < 300$ —moderate; $300 \leq RI < 600$ —severe; $600 \leq RI$ —serious

Tungsten and Cr show an independent behaviour indicating a different source of provenance. The performed PCAs allowed to conclude that it is possible to reach a fuller recognition of relevant pollutant associations on setting a dependence on weight between elements: those which increase or decrease proportionally tend to link together.

The contamination degree (CD) was then computed considering the identified associations and classified as follows: (1) CD_{F1} —Fe, Ni, Ba, Cu, B, Zn and V; (2) CD_{F2} —Sn and Cd; (3) CD_{F3} —Pb and As. For W and Cr, the individual contamination factor (CF) was used, as it recorded an independent behaviour (CF_W and

CF_{Cr}). These new attributes were defined as regionalized variables (Matheron 1971) and consequently additive by construction, since the mean value within a given observed support is equal to the arithmetic average of sample values, whatever the statistical distribution of the values. This guarantees that two samples with given profiles in the variable can be replaced by a new individual (Rivoirard 2005; Albuquerque et al. 2014). A subsequent geostatistical approach aiming at spatial hazard definition was employed in the definition of clusters for future monitoring.

Structural evaluation

The experimental variograms $\gamma(h)$ were computed and then fitted by a theoretical model, $\gamma(h)$ (Isaaks and Srivastava 1989). The adjusted parameters for the five attributes (Fig. 5) show that the obtained models are fairly fit. Indeed, all the attributes have nugget effect below 40% of the total variance for all the attributes. The error associated with the interpolation procedure, ordinary kriging (OK), is therefore minimized.

The revealed isotropic structure of CD_{F2} , CD_{F3} and CF_W and the anisotropic structure fitted for CD_{F1} and CF_{Cr} , are noteworthy, showing an important variability along the EW direction for Fe, Ni, Ba, Cu, B, Zn, V and Cr, which may be interpreted as an enrichment (accumulation) due to the lithology, mainly the metapelites and metagreywackes of the Cambrian schist–metagreywacke complex.

Table 4 Stream sediment concentration comparison for Fe (%) and another PTE (mg/kg) between the Monfortinho area and geochemical Atlas of Europe

(mg/kg)	Minimum	Maximum	Median	Minimum	Maximum	Median
Fe	1.1	4.8	2.8	0.06	20	1.97
Cu	5	64	18	1	998	14
Cr	125	464	238	2	1750	21
Zn	16	202	57	7	11	60
Pb	5	90	14	< 3	4880	14
Sn	–	25	0.5	< 1	188	2.25
As	10	44	10	< 5	231	6.0
W	–	8	1.6	< 0.05	82	1.24
Ni	11	42	24	2	1200	16
Mn	63	1301	288	24	18,900	452
Co	5	18	5	< 1	245	8
U	0.2	4	0.8	< 1	98	2

– Below the detection limit

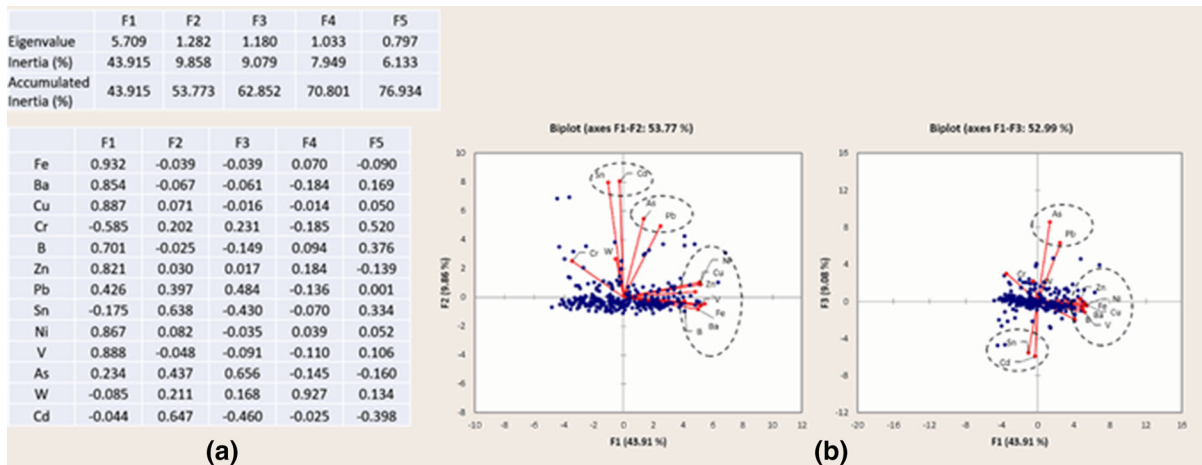


Fig. 4 Principal components analyses and definition of PTE associations. **a** Contributions and correlations between new principal components and the studied PTE; **b** first and second factorial plans with the attributes (red dots) and samples (blue dots) projected

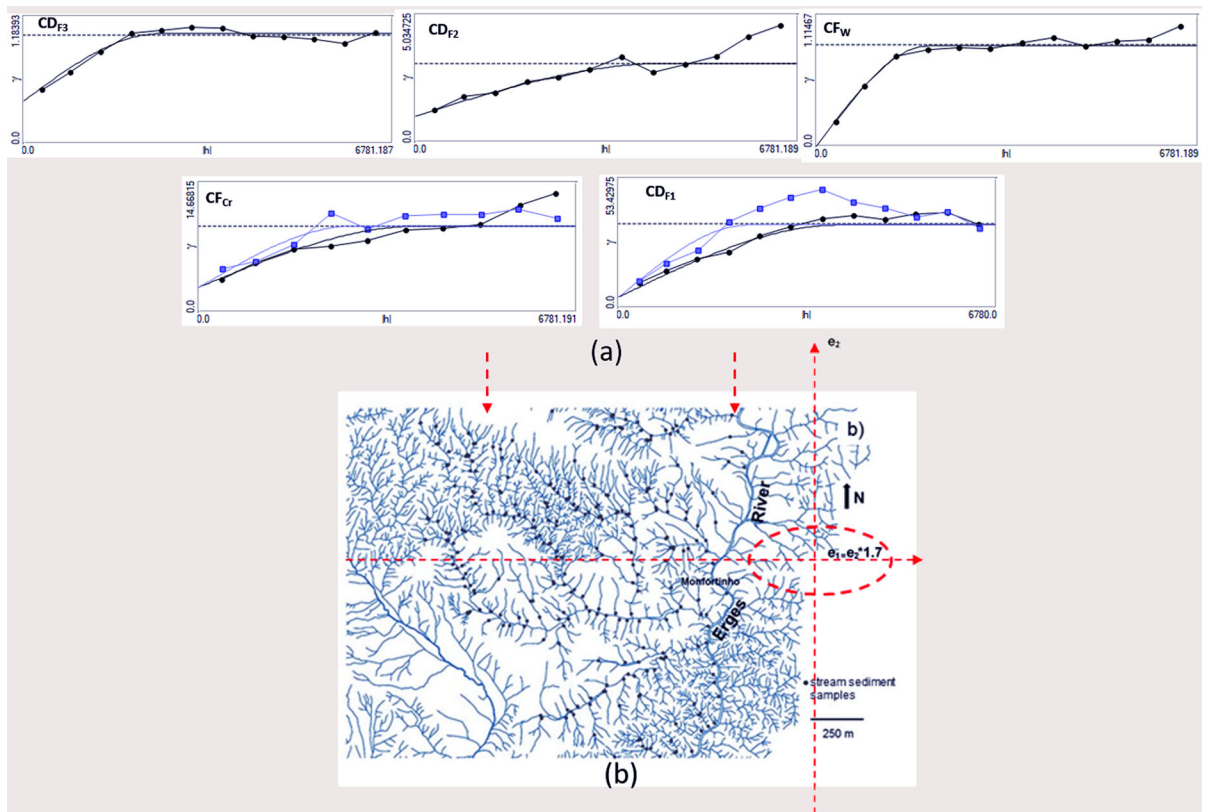


Fig. 5 Experimental variograms and fitted models. **a** Isotropic structure fitted for CDF_2 , CDF_3 and CDF_w and anisotropic ones for CDF_1 and CD_{Cr} ; **b** The anisotropic structures revealed the highest variability along the W–E direction

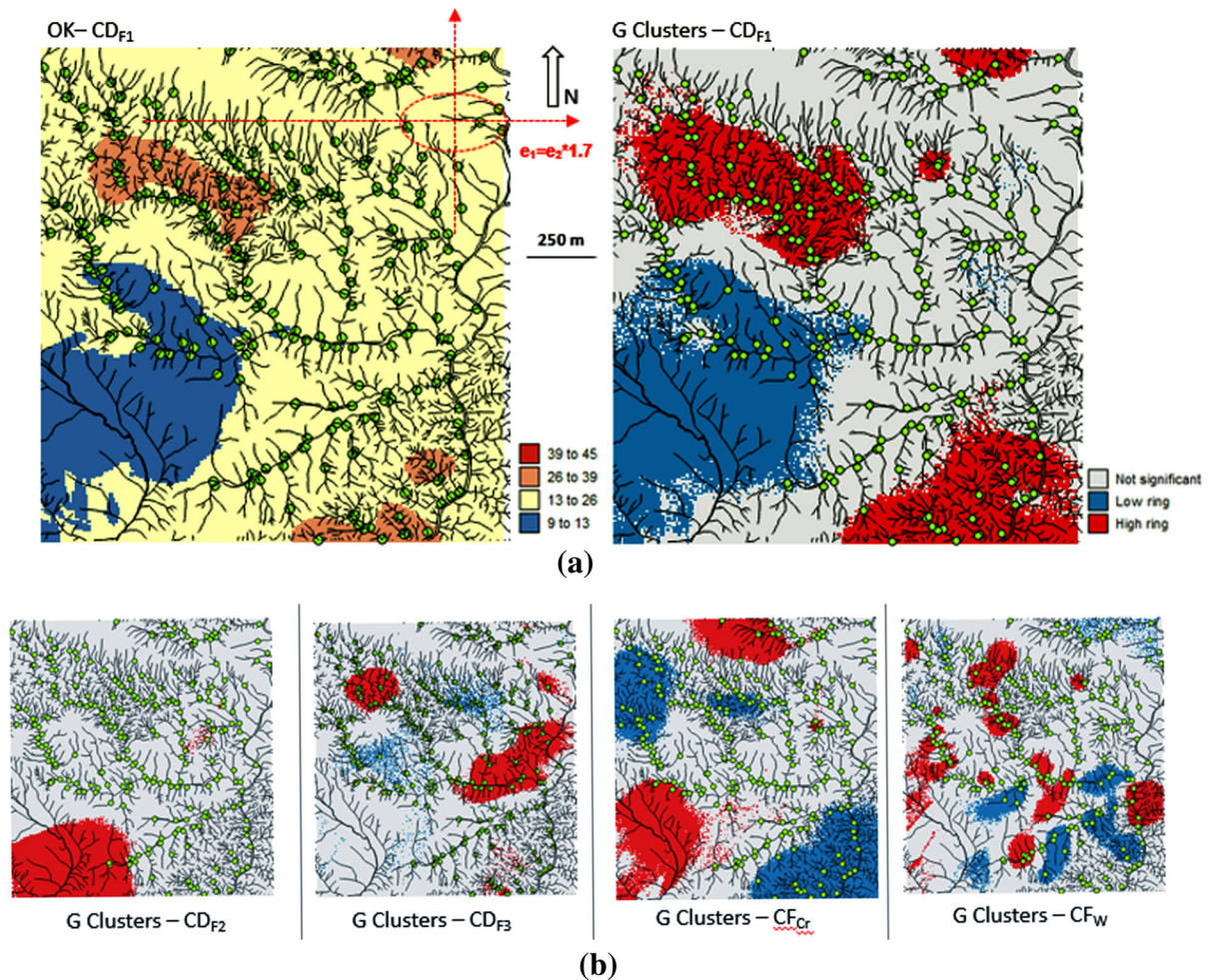


Fig. 6 **a** Distribution and G cluster map for CD_{F1}; **b** G clusters for CD_{F2}, CD_{F3}, CF_{Cr} and CF_W

Spatial analysis and modelling

When analysing the obtained outputs (Fig. 6), it is possible to acknowledge evident contrasts. Therefore, the estimated images obtained by OK and the spatial G clusters allow to determine regions of high significance for PTE enrichment and its potential origin.

Concerning the CDF₁ (Fe, Ni, Ba, Cu, B, Zn and V; Fig. 6), the high content observed, in the upper NW corner, is strongly associated with the local lithologies, as the observed high content in the SE corner may be explained by the Ba-Zn local mineralization as well as with the sedimentary gold along the Erges River banks. In similar geological sites, in the neighbourhood of Monfortinho, high contents in these factors

were also found in stream sediments collected on schists (Antunes et al. 2002).

The observed CDF₂ (Sn and Cd) cluster (Fig. 6) may be related to the cassiterite exploitations in Segura region, which is located less than 20 km south of Monfortinho (Fig. 1a). Tin anomalies were also found in stream sediments from the Segura area, associated with Sn-W mineralizations (Antunes et al. 2002). The CDF₃ (Pb and As) shows two high rings, similar to the ones visible for CDF₁ and overlapping the Ba-Zn mineralization (barite and galena).

Chromium (CF_{Cr}) shows an “inverse” distribution to CD_{F1} and CD_{F3}, which is mainly explained by predominant schist mineralization. Finally, W (CF_W) shows an irregular distribution with higher

concentration near the streams, since this element is easily “retained” in the sediments enriched in clay minerals.

Conclusions

A geochemical spatial distribution of potential toxic elements (PTE) in the stream sediments of the Monfortinho area (Central Portugal) was computed and the level of contamination determined using international evaluation methods, such as contamination factor (CF), contamination degree (CD), potential ecological risk index (E_{rf}^i) and potential toxicity response Index (RI).

A total of 271 representative stream sediment samples were collected from the schist–metagreywacke complex. Stream sediments from the Monfortinho area show a large range of PTE contents, suggesting a geogenic and mine influence. Stream sediments presented a moderate contamination in most PTE, with although a high and very high contamination in Ba, Cr and B. Contamination degree index varies from moderate to high contamination degree, which is primarily linked to the old mineralizations of the Monfortinho area.

Uni- and multivariate statistic methodologies allowed the identification of redundant information and the identification of outliers where the space of subsequent analysis was assessed throughout the building of new synthesis variables—principal component analysis (PCA). Three groups emerged and the contamination degree index was calculated, respectively: 1. CD_{F1} —Fe, Ni, Ba, Cu, B, Zn and V; CD_{F2} —Sn and Cd; CD_{F3} —Pb and As. The contamination factor (CF) was used for W and Cr, as they revealed an independent behaviour.

Spatial modelling due to their significance in contamination forecast was performed and the construction of hazard maps allowed the definition of high significant PTE clusters and to assess their probable provenance and enrichment. The Monfortinho area is greatly affected by the mining legacy and the lithological environment. The NW and SE corners are highly enriched in Fe, Ni, Ba, Cu, B, Zn, V, As and Pb due to local lithologies (NW corner) and the Ba–Zn local mineralization along with the sedimentary gold enrichment in the Erges River banks (SE corner). The Sn and Cd cluster may be referred to the cassiterite

exploitations in the Segura region (20 km south Monfortinho). Finally, Cr shows an “inverse” distribution to the observed for Fe, Ni, Ba, Cu, B, Zn, V, As and Pb, which may be explained by the predominant mineralization in the schist–metagreywacke complex. The irregular distribution of W with higher concentration near the streams could be explained by the low mobility of this element making its retention easy in the sediments enriched in clay minerals.

Future work requires an exhaustive collection of covariates, which will be used to enlighten PTE dynamics and, so, clarifying the main sources for PTE provenance as well as their enrichment through the study area. The multivariate geostatistical methodologies promoted the recognition and quantification of the anthropogenic impacts and consequently allowed the definition of adequate monitoring measures to focus the discussion on the human health effects in local communities.

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