Environ Monit Assess (2013) 185:279–294
DOI 10.1007/s10661-012-2553-9

Major inputs and mobility of potentially toxic elements contamination in urban areas

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Received: 5 May 2011 / Accepted: 25 January 2012 / Published online: 18 February 2012

Abstract Soil quality in urban areas is affected by anthropogenic activities, posing a risk to human health and ecosystems. Since the pseudo-total concentrations of potentially toxic elements may not reflect their potential risks, the study of element mobility is very important on a risk assessment basis. This study aims at characterising the distribution and major sources of 34 elements in two Portuguese urban areas (Lisbon and Viseu), with different geological characteristics, industrial and urban development processes. Furthermore, the potential availability of As, Co, Cr, Cu, Ni, Pb and Zn was assessed, by measuring the fraction easily mobilised. Lisbon is enriched in elements of geogenic and anthropogenic origin, whereas in the smaller city, the high levels observed are mainly related to a geogenic origin. Background values can be more relevant than the dimension of the city, even when anthropogenic components may be present, and this parameter should be considered when comparing results from different cities. Regarding the potential available fraction, a high variability of results was observed for elements and for sampling sites with an influence of the soil's general characteristics. Elements showing very high concentrations due to geological reasons presented, in general, a low mobility and it was not dependent on the degree of contamination. For elements with major anthropogenic origin, only Zn was dependent on the pseudo-total content. Yet, the highest available fractions of some elements, both with major geogenic and anthropogenic origin, were observed in specific contaminated samples. Therefore, a site-specific evaluation in urban soils is important due to the high spatial variability and heterogeneity.

Keywords Potentially toxic elements · Cluster analysis · Urban soils · Mobility · Potential availability · Portugal

Electronic supplementary material The online version of this article (doi:10.1007/s10661-012-2553-9) contains supplementary material, which is available to authorized users.

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Introduction

Urban sprawl is one of the major environmental challenges of our century. In 2006, 75% of European population lived in urban areas, and it is estimated that this will be a dominant human habitat (EEA 2006). As a consequence, urban soils are the only type of soil which most people has contact with. Since soils are a primary sink for contaminants due to their large capacity for retaining potentially toxic elements (PTEs), their accumulation over time not only downgrades soil quality but can also pose a risk to human health and to the ecosystem. In addition, soil contamination can be a useful indicator of the long-term anthropogenic pressures which urban areas are subjected to.

PTEs may be introduced into soil from both natural and anthropogenic sources. The natural inputs include elements present in parent rocks, which may be introduced in the soil-bearing phases, or atmospheric deposition of particles emitted from natural sources such as forest fires, volcanic activity and biogenic emissions. Anthropogenic inputs, especially important in urban areas, include industrial emissions, fossil fuels combustion and industrial and residential wastes. Several contaminants are emitted directly into the atmosphere followed by deposition, being urban areas especially affected by short-range diffuse pollution due to the many nearby sources. This variety of sources makes it difficult to assess urban soil quality due to the high number of possible contaminants. Besides, the high natural spatial variability (due to differences in soil properties and geological background) and the introduction of soils from elsewhere may result in a large range of PTEs levels within an urban area.

The severity of contamination depends not only on the total or pseudo-total PTE concentration but also on the proportion of their available forms. Availability, mobility and solubility of PTEs determine their potential uptake by plants and the migration of contaminants in the environment, as demonstrated by other authors (Madrid et al. 2004; Tokalioğlu et al. 2006). Besides, some studies concluded that PTEs are more mobile in areas under anthropogenic influence (Krasnodębska-Ostręga et al. 2004). Results given by an acetic acid (HOAc) extraction, according to the first step (water soluble, exchangeable and bound to carbonates) of the European Bureau Communitaire de Reference (BCR) protocol for sequential extraction, are an indication of how strongly the elements are retained in soil and how easily they may be released into soil solution under changing conditions, such as soil acidification, for instance (Davidson et al. 2006; Poggio et al. 2009). In addition, the BCR protocol has been successfully applied in several types of soils, including urban soils (Davidson et al. 2006; Poggio et al. 2009).

Little is known about the levels and behaviour of PTEs in Portuguese urban areas, and only two small cities from an industrialised area have been studied: Aveiro and Estarreja (Cachada et al. 2012; Rodrigues et al. 2009). The present study aims at assessing the quality of urban soils in two Portuguese cities (Lisbon and Viseu) with different settings, such as geological and geochemical characteristics, the urban area, industrial growth factor and urban development processes.

The assessment of natural and anthropogenic contributions was made possible by the quantification of a large number of PTEs and application of multivariate statistical methods such as cluster analysis. The main factors controlling the distribution of metals in soils (natural inputs, industry and traffic) were identified, and the easily mobilised fraction, which corresponds to the potentially available fraction, of some selected elements (As, Co, Cr, Cu, Ni, Pb and Zn) and samples was studied. Elements showing a higher risk of mobilisation, and therefore, representing some threat to the environment and human health were identified.

Characterization of the study areas

Lisbon City (Fig. 1) is the largest urban area of Portugal, with a population of 545,245 inhabitants and an area of 85 km^2. Its metropolitan area is highly populated (2.2 million inhabitants) and industrialised (petrochemical, chemical, textile, shipyard and siderurgy industries), with the greatest concentration of industries of the country, and is also the largest corporate merger in the country. Nevertheless, most of these industries are located outside the urban area. Its harbour is located inside the urban area, which is one of the most touristic harbours in Europe and has a very high commercial importance; there is also the international airport, which is the largest in the country (Fig. 1a). In addition, several highways cross the city, with approximately 170,000 cars entering the city every day. Even though the carpool of Lisbon metropolitan area is not very old (36% of cars are more than 10 years old), traffic is one of the most important sources of pollution. The south-western area of the city is occupied by one of the biggest urban parks of the Europe (Monsanto Park), with an area of almost 10 km^2 (Fig. 1a). Geologically, Lisbon area is composed by a great variety of rocks: the Lisbon Vulcanic Complex rocks (such as the lava flows) and limestone at south-west; sandstones with calcic intercalations and terraces are predominant in the rest of the area. Above these rocks, which constitute the substrate of the territory, it is possible to find recent deposits, such as sand dunes and beaches (all with calcic nature), as well as the alluvial plain formed by several water courses including the Tagus River. Soils are mainly chromic vertisols at south-weast, gleyic solonchaks at north-east and calcic cambisols in the rest of the area, according to the FAO classification. The climate in the Lisbon region is temperate, with an average daily temperature of 17.5°C, being the temperature in the town centre normally 2°C higher, especially during summer. The total annual rainfall is 700 mm.

Viseu (Fig. 1) is a small city with 47,250 inhabitants and the urban centre has around 12 km^2 (Fig. 1b). The most important industrial activities, although at a rather small scale, are textile, construction and metallurgy. Other economic activities are mainly related to restoration, wholesale and retail sectors. Regarding traffic, cars are the main transportation and the city is located nearby one of the most important highways of the country. Viseu is in the Iberian Central Zone where the predominant rocks are mainly schists and granites. Soils are classified as humic cambisols (associated to dystric cambisols) from eruptive rocks. The climate in Viseu is characterised by the existence of high temperature extremes, with rigorous and wet winters and hot and dry summers. The mean daily temperature is 15°C, and the total annual rainfall is 1,400 mm.

Materials and methods

Sampling

The sampling criteria were judgmental (ISO10381 2002), in order to cover the entire city area, and designed to select public open spaces. Sampling sites were chosen taking into account different land uses: ornamental gardens (OG), parks and open spaces (PO) and roadsides (RD). Fifty-one composite samples were collected from Lisbon (LIS) and 14 from Viseu (VIS) at depths of 0 to10 cm, after removing the herbaceous cover and discarding plant roots and large debris. Samples were collected by using a plastic spade previously cleaned with distilled water and ethanol and transferred into plastic bags. Once at the laboratory, the samples were dried (oven-dried at 40°C until constant weight) and sieved (<2 mm). Furthermore, a portion of each sample was ground (using an agate mill) and sieved to <0.18 mm. Sampling location maps (Fig. 1) were produced with ArcGis® Software (version 9.3).

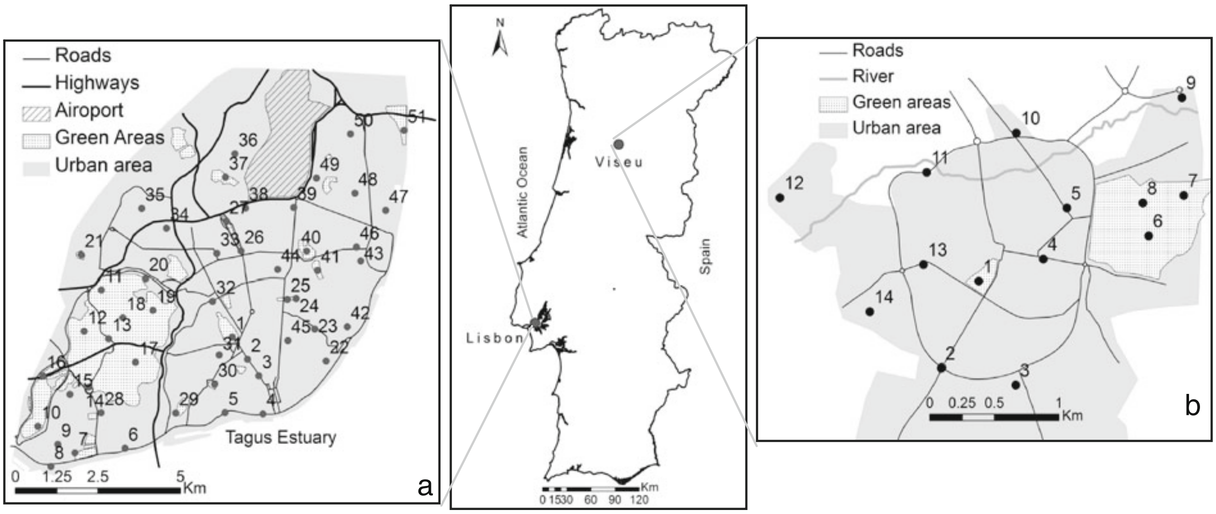

Fig. 1 Location of the studied cities and of the sampling sites in Lisbon (**a**) and Viseu (**b**)

General soil parameters

The following set of parameters was selected in order to obtain a general characterization of soils: pH in water and in $CaCl_2$ (ISO10390 1994); total C and N percentages (microanalyser LECO, CNHS-932); organic matter content (LOI at 430°C); cation exchange capacity (ISO13536 1995); and particle size distribution by quantifying the fractions of sand size particles (<2 mm), silt size (0.05–0.002 mm) and clay size (<0.002 mm) (Micromeritics® Sedigraph 5100).

Potentially toxic elements

The pseudo-total contents of 33 PTEs (Ag, Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Th, Tl, Ti, U, V, W and Zn) were determined by ICP-MS (Perkin Elmer Elan 6000/9000) in an accredited laboratory (AcmeLabs, Canada). Samples (0.5 g of the fraction <0.18 mm) were digested with Aqua Regia at 95°C, for 60 min. Total Hg concentrations were determined by pyrolysis atomic absorption spectrometry with gold amalgamation using AMA-254 (LECO model AMA-254), directly on dried soil samples.

Easily mobilised fraction

A subset of 15 selected samples from Lisbon and five from Viseu was extracted with HOAc, corresponding to the first step of the sequential extraction of the revised BCR procedure (Davidson et al. 2006). The subset was selected to represent: (a) differences in soil properties; (b) different parts of the studied areas (to provide a broad geographical coverage); (c) the most important land use types within each city; and (d) different pseudo-total contents of elements.

The optimised BCR procedure for the first step (water/acid soluble and exchangeable fraction) was followed according to the procedure described by Davidson et al. (2006). To 1 g soil, 40 mL of HOAc was added (0.11 mol L^{-1}). The mixture was shaken for 16 h at room temperature (end-over-end shaking at 30 rpm) and the extract was separated from the solid by centrifugation (3,000 rpm; 20 min). At the end, the supernatants were collected and stored in polyethylene vials at 4°C until analysis by ICP-MS (Thermo X Series). The concentration of seven elements, which are most commonly considered in urban soil studies (Chen et al. 2008; Ljung et al. 2006; Rodrigues et al. 2009; Yesilonis et al. 2008; Zheng et al. 2008), was determined: As, Co, Cr, Cu, Ni, Pb and Zn.

QA/QC methodologies

QA/QC procedures included replicates, procedure blanks and the analysis of certified reference materials. Replicate analysis of the soil samples gave an uncertainty of <10%. The results of method blanks were always below detection limit. The detection limits ranged from 0.1 μg kg^{-1} for trace elements to 100 μg kg^{-1} for major elements.

For the pseudo-total content, recoveries of reference materials (BCR 141R, BCR 142R, Polish soil S-1 and CRM 7002) ranged from 72±3% for Cr to 107±6% for Pb. Recoveries of total Hg were 100±3% (BCR141) and 85±3% (BCR142). Additionally, the reference material BCR CRM 701, which has certified values for extractions of step 1 (water/acid soluble and exchangeable fraction) for Cr, Cu, Ni, Pb and Zn, was used to ensure the quality of the analytical sequential extraction data, and the results of recovery were between 86±4% (Ni) and 95±5% (Zn).

Statistical methodologies

Univariate statistical methods were initially performed to check the variability of data and the presence of anomalies. Normality was tested (Shapiro–Wilk's test for normality, skewness and kurtosis values) and boxplots were obtained. Since some parameters did not follow a normal distribution, Spearman correlations were used to test relationships between variables.

Values below detection limit were considered in statistical analysis as equal to one half the detection limit. Nevertheless, Ag, Bi, Cd, S, Se, Tl and W were omitted in the statistical analysis since they showed more than 5% of samples bellow the detection limit. Furthermore, Na was also omitted due to a low variability of results observed in soils from Viseu.

Cluster analysis (CA) was performed, in order to classify similar observations into groups following an agglomerative hierarchical clustering method (Ward method with Euclidean distances), which maximise the variance between groups and minimises the variance between members of the same group. CA included data regarding general parameters [pH, total carbon (TC), organic matter (OM) and particle size], since the parent material is a very important factor that will influence the natural concentrations and the soil properties itself. Furthermore, data were standardised due to differences in units of measure. Since these methods are severely affected by data distribution and by the presence of outliers, two transformations were tested in order to normalise data: log transformation and Box-Cox transformation. Two different software packages were used for statistical analysis: SPSS® for descriptive and multivariate statistics (Spearman correlations, CA) and Statistica® for Box-Cox transformation.

Results and discussion

Major inputs and controlling factors of PTEs in the studied urban areas

Table 1 shows the results obtained for the general parameters in the cities of Lisbon and Viseu. The high median values of pH and TC observed in Lisbon are in line with the calcareous nature of these soils. The highest OM, cation exchange capacity (CEC) and clay particle size contents were found in samples located at south-west (mainly samples 7, 9–14 and 17–21; Fig. 1a), reflecting the presence of chromic vertisols (heavy texture), which dominate this area. On the other hand, highest percentages of sand size particles observed in the rest of the area point toward the sandy nature of these soils. Hence, the high variability of results observed for general parameters seems to be primarily related to the type of soils found. Even so, the introduction of soils from elsewhere can be a contributing factor to the variability of results observed.

The results of general parameters in Viseu soils are also in agreement with the nature of the parent material and the type of soil of the region. Soils from Viseu City are moderately acidic, with medium pH values, low TC content, low OM and low CEC (Table 1). The particle size results showed lower variability when compared with the Lisbon results, showing also higher median percentages of sand and silt size particles.

The results of PTEs concentrations in Lisbon and Viseu are presented in Table 2, with exception of the ones excluded from statistical analysis [(Table S1, electronic supplementary material (ESM)]. A high number of elements did not present a normal distribution, being this behaviour most evident in Lisbon soils (all elements except K and U) than in Viseu (As, La, Mo, Ni, Pb, Sb, Sr, Zn and Hg) (Table S2, ESM). The Box-Cox transformation was the most effective for data normalisation (Table S2, ESM) for the following reasons: skewness and kurtosis closer to 0; the significance of the Shapiro–Wilk's test ($p>0.05$); and outlier elimination. Even though in some cases it still failed to pass the normality test ($p<0.05$) and outliers remained, the skewness and kurtosis were effectively reduced. Nevertheless, outlier values were retained, as samples with highest PTEs concentrations are of extreme importance in environmental investigations.

Table 1 Results of the general parameters determined in Lisbon and Viseu: pH, total carbon, total nitrogen, organic matter, cation exchange capacity and particle size (sand, silt and clay)

Parameter	LIS					VIS				
	Mean	Median	Std. dev.	Min.	Max.	Mean	Median	Std. dev.	Min.	Max.
pH (water)	7.9	7.9	0.31	7.1	8.5	6.0	5.9	0.82	4.3	7.7
pH ($CaCl_2$)	7.2	7.3	0.22	6.5	7.6	5.3	5.3	0.74	3.9	6.9
TC (%)	4.1	4.1	1.9	0.94	8.6	2.2	1.5	1.7	0.67	7.4
TN (%)	0.45	0.39	0.29	0.04	1.2	0.46	0.38	0.16	0.30	0.83
OM (%)	7.2	6.4	4.4	1.6	19	5.4	4.2	3.5	2.9	17
CEC (cmol kg^{-1})	29	19	13	3.9	52	11	9.5	5.1	5.1	26
Sand (%)	56	57	18	11	96	64	62	11	42	86
Silt (%)	29	29	11	2.9	47	30	31	9.2	11	44
Clay (%)	15	13	9.6	1.0	44	6.2	5.0	3.2	2.8	14

TC total carbon, *TN* total nitrogen, *OM* organic matter, *CEC* cation exchange

Table 2 Descriptive statistics of PTEs concentrations in Lisbon and Viseu urban soils

Element	City	Mean	Median	Min.	Max.	CV (%)
Al (%)	LIS	1.2	0.83	0.21	3.1	70
	VIS	2.5	2.6	1.7	3.3	20
As (mg kg^{-1})	LIS	5.3	4.4	0.50	29	87
	VIS	30	24	17	58	50
Ba (mg kg^{-1})	LIS	107	72	14	429	82
	VIS	79	80	43	130	29
Ca (%)	LIS	3.8	3.1	0.17	13	74
	VIS	0.42	0.44	0.20	0.61	33
Co (mg kg^{-1})	LIS	13	6.8	0.6	49	100
	VIS	5.9	5.9	3.1	7.9	22
Cr (mg kg^{-1})	LIS	38	16	1.0	172	116
	VIS	11	10	6.0	17	25
Cu (mg kg^{-1})	LIS	37	29	3.5	143	70
	VIS	33	27	6.1	78	61
Fe (%)	LIS	2.1	1.6	0.18	5.9	71
	VIS	2.4	2.5	1.5	3.3	20
Ga (mg kg^{-1})	LIS	4.0	3.0	1.0	10	68
	VIS	11	11	6.0	14	20
K (%)	LIS	0.17	0.17	0.03	0.42	47
	VIS	0.51	0.51	0.25	0.82	25
La (mg kg^{-1})	LIS	16	11	2.0	41	62
	VIS	24	22	15	47	37
Mg (%)	LIS	0.53	0.34	0.02	2.0	98
	VIS	0.51	0.51	0.25	0.82	20
Mn (mg kg^{-1})	LIS	337	218	11	1193	88
	VIS	360	368	186	500	26
Mo (mg kg^{-1})	LIS	0.67	0.6	0.1	1.9	51
	VIS	0.61	0.6	0.4	0.8	25
Ni (mg kg^{-1})	LIS	43	20	2.0	209	121
	VIS	5.0	4.5	3.3	9.7	42
P (%)	LIS	0.11	0.10	0.02	0.26	55
	VIS	0.08	0.07	0.03	0.15	50
Pb (mg kg^{-1})	LIS	89	62	4.8	561	110
	VIS	106	46	13	817	195
Sb (mg kg^{-1})	LIS	0.84	0.70	0.10	3.5	76
	VIS	0.78	0.4	0.1	5.6	179
Sc (mg kg^{-1})	LIS	2.4	1.3	0.3	9.8	100
	VIS	6.1	6.4	2.8	8.7	25
Sr (mg kg^{-1})	LIS	76	56	4.0	226	80
	VIS	12	11	5.0	25	49
Th (mg kg^{-1})	LIS	1.8	1.6	0.60	4.9	54
	VIS	9.8	9.4	5.4	16	35
Ti (%)	LIS	0.08	0.03	0.003	0.35	125
	VIS	0.18	0.19	0.08	0.26	28

Table 2 (continued)

Element	City	Mean	Median	Min.	Max.	CV (%)
U (mg kg^{-1})	LIS	0.7	0.70	0.20	1.3	33
	VIS	8.3	8.9	5.9	11	18
V (mg kg^{-1})	LIS	48	27	2.0	178	102
	VIS	37	37	19	48	23
Zn (mg kg^{-1})	LIS	97	88	7.0	269	55
	VIS	88	80	47	190	43
Hg (mg kg^{-1})	LIS	0.36	0.18	0.01	3.8	169
	VIS	0.26	0.11	0.02	1.6	158

CV coefficient of variation

As for general parameters, the pseudo-total concentrations of PTEs seem to reflect the geological background of each city. Lisbon soils show very high concentrations of elements that occur in basaltic or calcareous rocks such as Ca, Co, Cr, Ni and Sr (Table 2), whereas Viseu soils are enriched in elements which are typical of schist and granitic rocks such as Al, Ga, K, La, Sc, Th, Ti and U (Ferreira et al. 2001). In order to better understand these results and group elements according to a possible common origin, a cluster analysis was performed and results will be discussed individually for each city.

Lisbon urban area

In the dendrogram of Lisbon (Fig. 2a), it is possible to distinguish three clusters. The first group of cluster 1 (C1) is formed by the association of typical geogenic elements (Al, Ga, Fe, La, Mg, Cr, Ni, Co, Mn, Sc, V and Ti) which are strongly correlated ($p<0.01$, Table S3, ESM). Aluminium and Ga, in particular, show a very strong association, since they tend to occur in constant ratio due to their geochemical behaviour, regardless the mineral phase. In addition to the high concentrations of Fe and Mg (Table 2), the high concentrations of Co, Cr and Ni indicate that the most probable origin of these elements are the basalts from the Lisbon Vulcanic Complex located at southwest, since these are typical mafic elements with similar geochemical behaviours in natural environment (Ferreira et al. 2001; Yesilonis et al. 2008). The inclusion of soil properties (OM and clay) in this cluster is related to the highest values of these parameters found in this area (chromic vertisols). It is interesting to note that the outliers observed for Co, Cr and Ni (Fig. 3) correspond to samples identified previously as richer in OM, clay size particles and CEC. This area is mainly occupied by the Monsanto Park (the most important green area of Lisbon), being possible to assume that these soils were not introduced, maintaining its local geochemical signature.

Another association observed in C1 is formed by Ba, P and Sr. Barium and Sr tend to substitute Ca in minerals, and they are significantly correlated with the former ($p<0.05$, Table S3, ESM). The high concentration of Ba and Sr found (Table 2) and the correlations observed with the other elements of C1 (Table S3, ESM) could indicate the basalts as their major source. Nevertheless, these elements may have other inputs in addition to the geogenic ones, as observed by the correlations of these three elements with the ones from the second cluster (Table S3, ESM). For example, Ba has been found in high concentrations in urban areas (e.g. Tijhuis et al. 2002) due to traffic, buildings or the proximity of harbours, and P can be present in fertilisers.

Cluster 2 (C2) includes a common group of elements which normally accumulates in urban soils as a result of anthropogenic activities (Biasioli et al. 2007; Ljung et al. 2006; Rodrigues et al. 2009; Wilcke et al. 1998; Yesilonis et al. 2008; Zheng et al. 2008): Cu, Zn, Pb, Sb and Hg. In addition, the behaviour of elements such has Pb, Sb and Hg (coefficients of variation as high as 160% for Hg, kurtosis higher than 5 and positive skewness; Table 2 and Table S2, ESM), suggests an anthropogenic origin of these elements. However, the significant positive correlations ($p<0.05$; Table S4, ESM) observed between the elements of this cluster with OM and CEC content indicate that soil

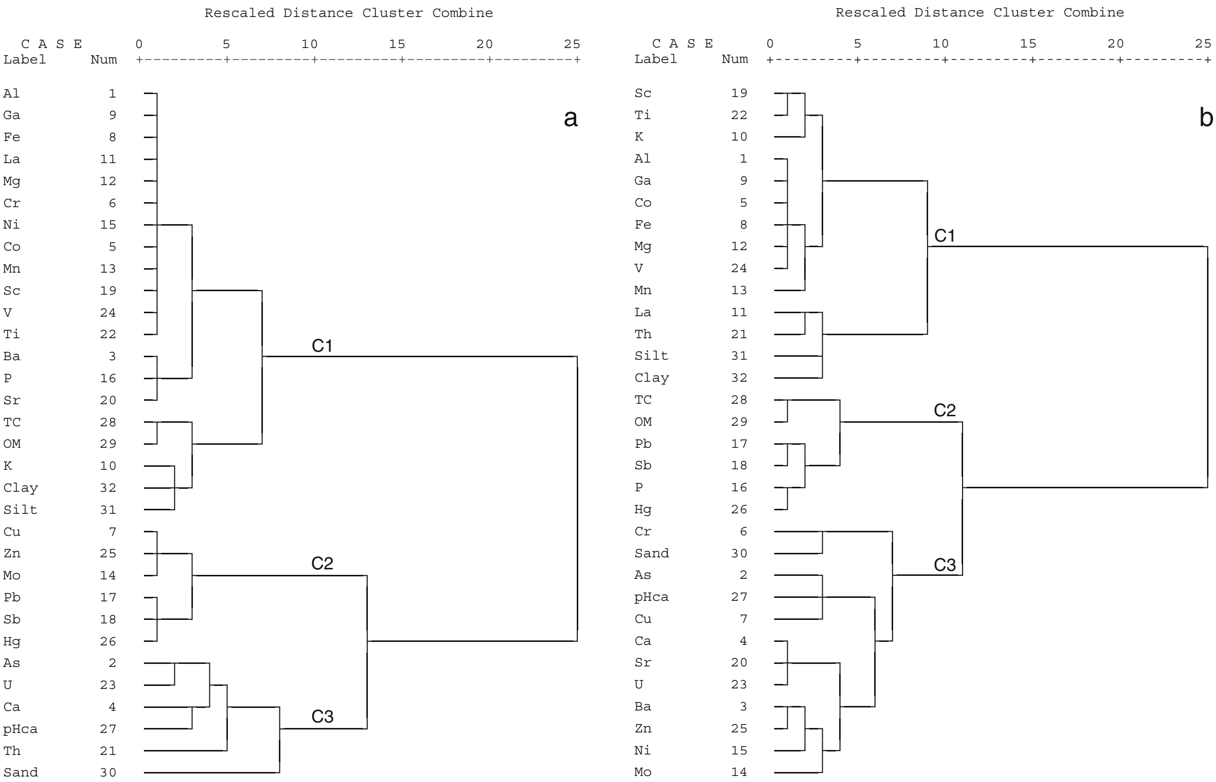

Fig. 2 Dendrogram of the cluster analysis of potentially toxic elements and general parameters for Lisbon (**a**) and Viseu (**b**) soils

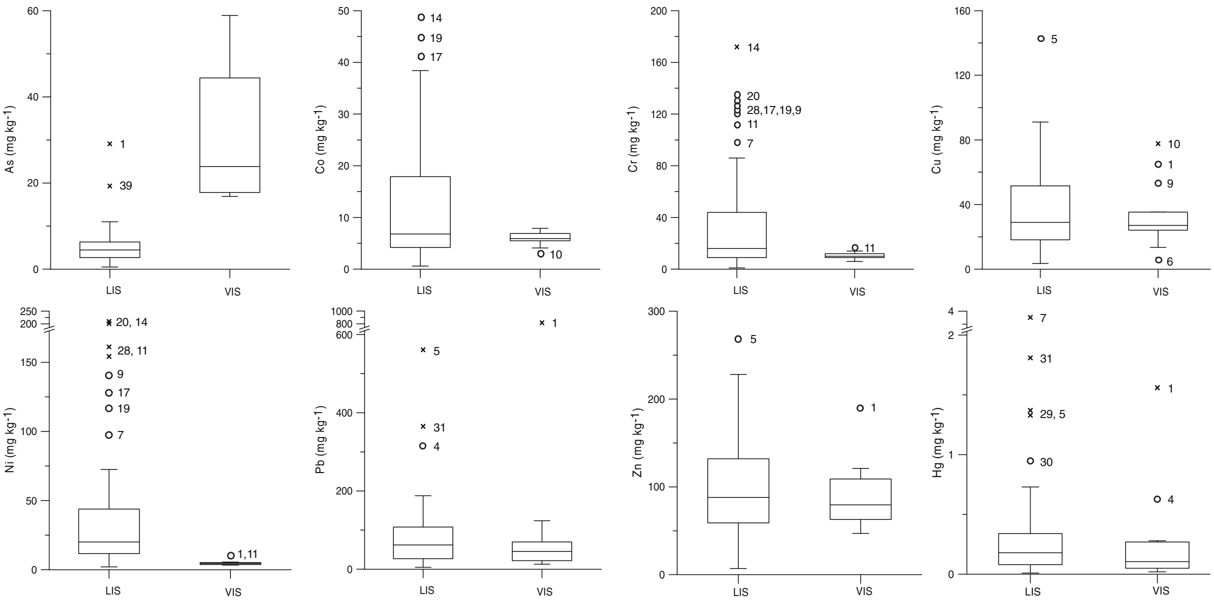

Fig. 3 Box-plots showing the variation of selected elements concentrations. *Boxes* define the interquartile range and the *line* is the median. Outliers are defined as values between 1.5–3 box lengths (O) and extreme values as more than three box lengths (*multiplication sign*)

properties may contribute to spatial distribution of these PTEs.

Copper, Zn and Pb are known as ‘urban elements’ and they are extremely related with traffic. Wear and tear of tyres contributes to Zn emissions, whereas wearable parts on brakes (e.g. disc pads) contain Cu and Zn. Lead is especially related with leaded petrol, and although its use has been banned in Portugal, it may persist in soils due to its long residence time (Tijhuis et al. 2002; Zheng et al. 2008). In addition, Pb and Sb can also be related with metal industry such as shipyard and, together with Zn, they are also used in paints (Peltola and Åström 2003; Tijhuis et al. 2002). Molybdenum, which appears in this cluster, can also be related with traffic emissions (Peltola and Åström 2003). Mercury sources include application of fertilisers, smelting and combustion of fossil fuels (Chen et al. 2008; Tijhuis et al. 2002). Even so, industry, heat and energy plants, incineration and crematoria can be sources of all the referred elements (Ljung et al. 2006; Zheng et al. 2008). Some of the highest concentration of Cu, Pb and Zn were observed nearby, in old sites with very high traffic intensity (samples 4.OG/RD and 5.OG/RD, Figs. 1a and 3). In addition, outlier values for Hg (5.OG/RD, 7.OG, 29.OG, 30.PO and 31.OG, Figs. 1a and 3) were observed in the same area of the city. This area is where the harbour (with shipyards, metallurgy and dismantling of old ships) is located and, historically, it was very industrialised (e.g. tanning and dyeing).

The last cluster (C3) is formed by As, U, Ca and Th, and its position is mainly because these elements show a correlation with pH (even that with low correlation coefficients) and they are not correlated, or show few correlations, with other general parameters and PTEs (with the exception of Ca) (Tables S3 and S4, ESM). The significant positive correlation ($p<0.01$; Table S4, ESM) between Ca and TC, but not with OM, could be related to its carbonated origin (calcic cambisols). Moreover, As, U and Ca are correlated between them ($p<0.05$; Table S3, ESM) and the higher concentrations of the first two elements were observed in areas were sandstones dominate (e.g. 23.OG, 24.OG, 43.OG and 47.OG). The significant positive correlations observed between As, Ca and elements from C2, such as Pb and Sb ($p<0.01$; Table S3, ESM), may suggest an additional anthropogenic origin of these elements. Calcium, for instance, is known to be an important constituent of atmospheric particulates in urban areas due to coal combustion, cement production and incineration (Pouyat et al. 2008). Arsenic has origin in pesticides application, coal combustion, smelters and waste incineration (Chen et al. 2008; Tijhuis et al. 2002). In addition, this element shows a very high coefficient of variation (200%), with an extremely high kurtosis and positive skewness (Table 2 and Table S1, ESM), indicating the presence of specific point sources (sample from the city centre, LIS.01.PO, and a sample nearby the airport, LIS.39.RD; Figs. 1a and 3).

Viseu urban area

In the dendrogram of Viseu (Fig. 2b), C1 also included major rock forming elements (e.g. Al, Fe and Mg) and other typical geogenic elements. The clustering of these elements, in addition to the high concentrations of Al, Ga, La, K, Th and Ti (Table 2), indicates a natural input from metamorphic (schists) and granitic rocks. Titanium and K, in particular, are present in feldspar and Th and La have a tendency to associate with minerals with high content of these elements. As in Lisbon soils, Al and Ga show a very strong correlation ($p<0.01$, Table S3, ESM). General parameters are not correlated or show low correlations with most PTEs (Table S5, ESM). Therefore, the presence of clay in C1 is primarily due to its negative correlations with elements from C2 and C3 (e.g. P and Zn, $p<0.01$; Table S5, ESM),

Cluster 2 included elements from typically anthropogenic origin (e.g. Pb, Sb and Hg) in an urban context. The high coefficients of variation, extremely high kurtosis and positive skewness (Table 2 and Table S2, ESM) observed for Pb, Sb and Hg, which indicates the presence of anthropogenic point sources, is mainly due to one sample (Fig. 3). This sample (VIS.01.PO) was collected in a very old park located in the city centre (Fig.1c) and it was also identified as an outlier for other two typical urban elements: Cu and Zn. For Cu, other two samples from nearby roads (09.OG/RD and 10.OG/RD) were identified as outliers. Nevertheless, the presence of Cu and Zn in C3 and the fact that no significant correlations between Cu, Pb and Zn were observed (Table S3, ESM) indicate another major source of these elements besides the typical urban contamination.

Cluster 3 includes some elements typical of granites and, in addition, the levels of As and U (Table 2) are characteristic from the Central Iberian Zone where Viseu is located (Ferreira et al. 2001; Salminen 2005).

Arsenic and Cu may be associated with sulphide ores occurring in the granites (As–Cu–Pb–Sb) or to pyrite–chalcopyrite deposits (Sb–Hg–As–Cu–Ni), which explains the significant positive correlations ($p<0.05$, Table S3, ESM) observed between As and Hg and the proximity to C2 (Tijhuis et al. 2002). The separation of C2 from C3 can be due to the association of Pb, Sb, P and Hg with OM and TC (Table S5, ESM) reflecting the affinity of these elements to bind with organic fraction of soils and meaning that this soil characteristic may control their distribution. Therefore, clusters 2 and 3 are formed by elements that, in spite of some anthropogenic influence, result from the enriched background.

Levels and sources of PTEs in urban areas: comparison between cities and background values

Since only a few elements are normally considered in urban soil studies, a further detailed comparison between cities and with background values was based in the following elements (Fig. 3): As, Co, Cr, Cu, Pb, Ni, Zn and Hg (Chen et al. 2008; Ljung et al. 2006; Rodrigues et al. 2009; Yesilonis et al. 2008; Zheng et al. 2008). The cities selected for comparison of PTEs levels (two Portuguese and other five European cities, Table 3) were chosen based on the similarity of sampling and analytical protocols used, since there are differences in methodological approaches and difficulty in the comparison between different studies. Results were also compared with the reference value for each region (Table 3), based on the Foregs Geochemical Baseline Maps for topsoils of all Europe (Salminen 2005).

The remarkable differences of As median concentrations observed between Lisbon and Viseu soils (Fig. 3) are in agreement with the background values of each region (Table 3). The major geogenic input was addressed for this element in Viseu, and it explains the very high levels found in this city. For example, in Estarreja, a very small but industrialised Portuguese urban area, high concentrations were found (Table 3) due to the industrial activities; the median value, however, is lower than in Viseu (Cachada et al. 2012). In Lisbon, the low concentrations found (with exception of the few hot spots) were similar to the ones observed in Uppsala, where the probability of natural origin was addressed (Ljung et al. 2006). In other studies over the world, a variety of major inputs was observed: in Oslo, both geological and anthropogenic (Tijhuis et al. 2002); in Beijing, geogenic (Zheng et al. 2008); and in Hangzhou, anthropogenic (Chen et al. 2008).

Median concentrations of Co, Cr and Ni in Viseu soils were in line with the background value, reflecting the major geogenic origin addressed. In Lisbon, where a major geogenic origin was also identified, the median concentrations of Co and Cr were in agreement with the background value, but the median concentration of Ni is much higher. This enrichment in Ni concentrations regarding the local background value is likely to be due to the influence of basalts. Differences observed between cities for these elements (Table 3) are mainly due to parent material, since in all other cities, a major geogenic origin of Cr and Ni was identified (Biasioli et al. 2007; Cachada et al. 2012; Ljung et al. 2006; Rodrigues et al. 2009). Similar conclusions about the origin of these contaminants were addressed in other studies all over the world (Chen et al. 2008; Tijhuis et al. 2002; Yesilonis et al. 2008; Zheng et al. 2008).

As in the present study, other studies on urban soils quality have identified anthropogenic signatures for Cu, Pb and Zn (Biasioli et al. 2007; Cachada et al. 2012; Chen et al. 2008; Ljung et al. 2006; Rodrigues et al. 2009; Tijhuis et al. 2002; Yesilonis et al. 2008; Zheng et al. 2008). Lisbon soils are enriched in these elements regarding the background, as expected due to the presence of many anthropogenic sources. An anomaly of Pb in Lisbon area was identified in a low-density geochemical mapping of Portugal and was attributed to anthropogenic activities (Ferreira et al. 2001). On the other hand, Viseu median concentrations of this element are also higher than the background values for the region which may be explained by old Pb-mining areas (galena) that occur in the area. In addition, the background values in Viseu are higher than the ones from Lisbon, especially for Pb and Zn, reflecting their enrichment and highlighting the importance of background levels in such a small town.

Viseu median concentrations of Pb and Zn are also especially high when compared with other Portuguese cities, where an anthropogenic origin of these elements was addressed: Aveiro, due to urban activities, and Estarreja, due to the chemical industry. Levels of Pb and Zn are much higher in Lisbon than any other Portuguese city, as expected by the great pressure inherent to the higher size of the city. Comparing the results of these PTEs with other European cities, Lisbon has some similarities with Ljubljana, Uppsala or

Table 3 Range and median concentration of As, Cr, Cu, Pb, Ni, Zn and Hg (in milligrams per kilogram) in soils from Lisbon, Viseu and other cities and the local background value (BV)

	Inhabitants	As	Co	Cr	Cu	Pb	Ni	Zn	Hg
Lisbon	564,567	0.5–29 (4.4)	0.6–49 (6.8)	1.0–172 (16)	3.5–143 (29)	4.8–561 (62)	2.0–209 (20)	7–269 (88)	0.01–3.8 (0.18)[h]
Viseu	47,250	17–58 (24)	3.1-–7.9 (5.9)	6–17 (10)	6.1–78 (27)	13–817 (46)	3.3–9.7 (4.5)	47–190 (80)	0.02–1.6 (0.11)[h]
Estarreja[a,b]	7,000	<5–2,190 (10)[h]	–	5.3–55 (15)	9.0–111 (28)	12–66 (35)	2.1–23 (9)	21–284 (59)	0.05–4.5 (0.20)[h]
Aveiro[c,d]	73,500	–	–	2–37 (9)	3–69 (14)	8–180 (22)	2–12 (6)	13–6,213 (37)	0.02–0.5 (0.09)[h]
Glasgow[d]	600,000	–	–	20–230 (37)	18–444 (52)	12–1,330 (161)	18–130 (33)	54–1,340 (179)	–
Torino[e]	900,000	–	–	64–800 (129)	15–430 (71)	14–1,440 (94)	80–830 (153)	56–880 (147)	–
Sevilla[e]	706,000	–	–	11–89 (33)	10–365 (39)	15–977 (76)	16–53 (29)	21–325 (87)	–
Ljubljana[e]	300,000	–	–	12–165 (29)	15–123 (32)	11–387 (68)	14–38 (26)	63–446 (122)	–
Uppsala[f]	136,500	1.4–15 (3.5)	–	14–62 (32)	11–110 (25)	8.5–358 (26)	7.2–39 (19)	45–149 (84)	Bdl-3.7 (0.14)
Lisbon BV[g]	–	<5	–	8–12	6–12	3–7	3–5	21–27	0.01–0.02[h]
Viseu BV[g]	–	15–31	–	12–15	6–8	11–21	5–7	48–61	0.04–0.05[h]

[a] Cachada et al. (2012)

[b] Cachada et al. (2009)

[c] Rodrigues et al. (2006)

[d] Rodrigues et al. (2009)

[e] Biasioli et al. (2007)

[f] Ljung et al. (2006)

[g] Salminen (2005)

[h] Total content

Sevilla. On the other hand, it shows much lower concentrations of most elements when comparing with Glasgow or Torino. The size of the city can therefore be considered as a main factor influencing the levels of anthropogenic elements.

The Viseu Region seems to be slightly enriched in Hg, as shown by the background value (Table 3). Yet, levels observed in both cities are higher than the background. Again, granite mineralization in Viseu and presence of anthropogenic sources in Lisbon should be the reason for this evidence. The levels of Hg in Lisbon are similar to the ones found in Estarreja, which were related to a chlor-alkali plant, and to the ones from Uppsalla, where Hg is also from major anthropogenic sources (Cachada et al. 2012; Ljung et al. 2006). Viseu shows Hg levels higher than Aveiro, where an anthropogenic origin was addressed (Rodrigues et al. 2006), highlighting the influence of background concentrations in the former. In fact, anthropogenic sources of Hg in urban areas were usually identified in other studies around the world (Chen et al. 2008; Tijhuis et al. 2002), which makes the findings related to sources of Hg in Viseu urban soils unusual.

In conclusion, the comparison of PTEs concentration between cities without considering the local geology and the origin of the elements may result in misinterpretation of data. The size of the city is usually (but not always) the most important factor, being the proximity to sources and the geologic background also very important.

The potential availability of PTEs in urban soils

The results of the PTEs pseudo-total content and the HOAc-extracted content on selected samples and elements are presented in Table S6 (ESM). The percentage of potentially available fraction, corresponding to the fraction easily mobilised in each site, was calculated as the ratio between the HOAc concentrations and the pseudo-total content. A high variability of results was observed for both—sampling sites and elements—especially in Lisbon soils (Table 4 and Fig. 4). In Viseu, the variability of results between sites is not as clear, despite the existence of some differences between elements' behaviour.

The high variability observed may be attributed to differences on soil properties and sources of PTEs (geogenic vs. anthropogenic). Some authors (Krasnodębska-Ostręga et al. 2004; Wilcke et al. 1998) suggest that elements in contaminated sites tended to be more soluble than those in noncontaminated ones. On the other hand, it is known that soil characteristics such as clay and OM content influence the sorption strength of the elements to soils (Madrid et al. 2004; Wilcke et al. 1998). From Fig. 4, it is perceptible that samples showing a high percentage of available elements are the ones with low contents of OM and clay, being these, together with CEC (Table S7, ESM), the general parameters with more influence on the potential availability. In Viseu, this relationship is not so evident due to the low variability of the general parameters of soils (Table S8, ESM). Figure 4 also reveals that Lisbon samples with low percentages of available elements (01.PO, 14.PO, 17.PO and 20.PO) are the ones located at south-west (Fig. 1a) where the local geochemical signature seems to be maintained.

The mobility of elements in Lisbon soil samples increased according to the following order: Cr<Pb<Cu<Ni<As<Co<Zn, while in Viseu, it was As<Cr<Ni<Cu<Pb<Zn<Co. Elements showing the

Table 4 Summary results of the potential available fraction (% Av) of selected elements in Lisbon and Viseu soils

% Av	LIS					VIS				
	Mean	Median	Std. dev.	Min.	Max.	Mean	Median	Std. dev.	Min.	Max.
As	6.00	4.80	3.31	0.60	11.7	0.97	0.98	0.36	0.40	1.4
Co	7.79	6.10	4.50	2.40	15.7	6.68	7.05	1.40	4.36	7.80
Cr	0.76	0.85	0.48	0.04	1.70	1.64	-	1.89	0.30	2.97
Cu	1.78	1.60	0.98	0.40	3.40	4.02	4.10	1.05	2.53	5.20
Ni	4.91	4.90	2.84	1.40	10.0	4.93	3.80	3.67	2.80	11.4
Pb	1.22	1.00	0.97	0.30	3.90	3.8	4.34	1.29	1.70	4.90
Zn	11.3	10.5	7.19	2.20	27.4	5.83	6.34	2.27	3.31	8.00

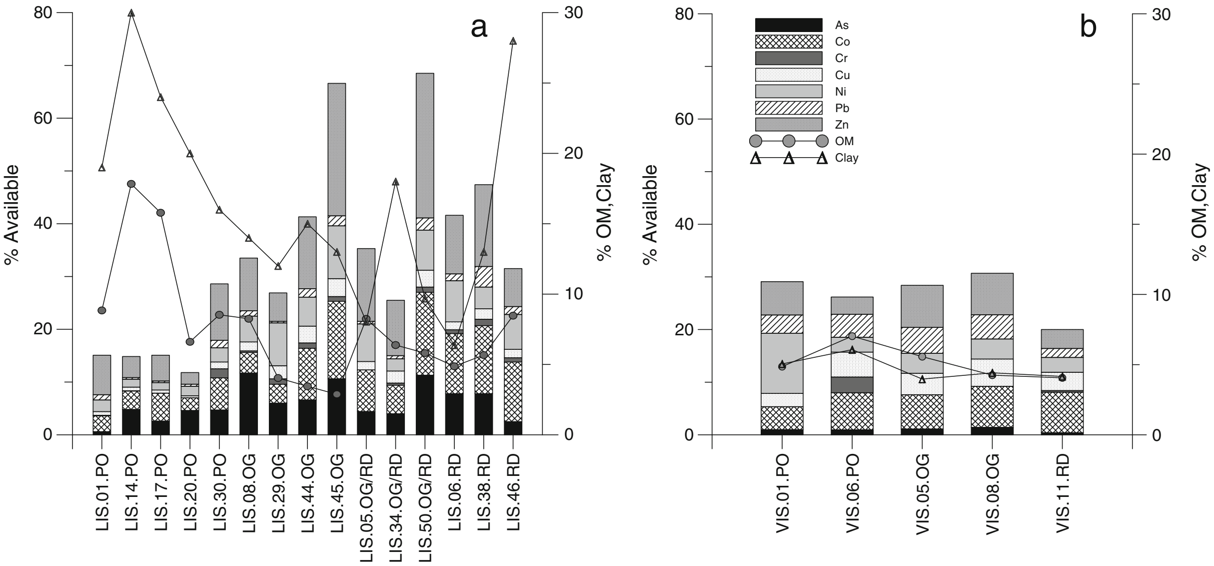

Fig. 4 Percentage of available elements, organic matter (*OM*) and clay content for Lisbon (**a**) and Viseu (**b**) selected samples

greatest variability between sites were Zn, Co and As in Lisbon and Ni and Zn in Viseu (Table 4).

Arsenic had a different behaviour in the two cities, as shown in Fig. 4 and Table 4. In spite of higher pseudo-total concentrations found in the Viseu samples, Lisbon soils showed higher available fractions, reflecting the findings regarding the origin of this element in both cities: natural inputs associated to granites in Viseu; whereas in Lisbon, in addition to the association with sandstones, an anthropogenic origin could explain the results. The significant correlations ($p<0.05$; Table S7, ESM) of the available fraction of this element with soil properties observed in Lisbon reflect their influence on mobility of As. Sample LIS.01.PO was identified as an outlier (Fig. 3), but the percentage of available fraction was the lowest one (Fig. 4, Table S6, ESM), indicating that in this particular case, As is not easily mobilised. On the other hand, sample LIS.08.OG is the one showing a greater As available fraction (12%); however, as it is possible to observe in Fig. 4, it shows high contents of OM and clay, indicating a probable anthropogenic origin.

Regarding other elements with a major geogenic origin (Co, Cr and Ni), the significant negative correlations observed between the pseudo-total content and the available fractions of these three elements ($p<0.01$, Table S9, ESM) in Lisbon soils, indicates that the most contaminated sites (14.PO, 17.PO and 20.PO, Fig. 3) are not necessarily the ones with greater mobility (Fig. 4), therefore confirming that the main origin of these elements is geogenic (basaltic rocks). Previous studies on urban soils concluded that Ni and Cr were mainly associated with the residual phase of the soil matrix (Davidson et al. 2006).

Chromium was the element showing the lowest potential available fraction in Lisbon soils, with some samples showing values below the detection limit and a maximum percentage of 1.7% (LIS.30.PO). In addition to the low mobility of Cr, a low variability between sampling sites was observed (Table 4). In Viseu, a similar behaviour was observed, with only two samples showing HOAc concentrations above the detection limit. Nickel showed a greater mobility in both cities as well as higher variability of results (Table 4). Among the elements with major geogenic origin, Co showed the greatest potential available fraction, with a similar behaviour in both cities. Cobalt and Ni showed a high potential available fraction in some Lisbon sites, being some of these highest values observed in samples located in the city centre where outliers for anthropogenic elements were also identified (LIS.5.OG/RD, LIS.6.RD and LIS.29.OG), and corresponding to high pseudo-total contents (Table S6, ESM). Both elements can be related with anthropogenic activities (e.g. traffic and industry), which may be the reason for the results observed in these samples. Nevertheless, it was also found that soils' properties may have some influence on the mobility of these elements, as observed by the significant correlations ($p<0.05$; Table S7, ESM). In Viseu, only sample 01.PO presented a high available fraction of Ni, and since this park is a very old site located in the city centre (Fig. 1c), it could be affected by anthropogenic emissions, such as traffic.

Copper showed a low variability of results in both cities, with the highest median percentages observed in Viseu (Table 4). This result, along with significant negative correlations ($p<0.01$; Table S7, ESM) between Cu available fraction and OM and CEC observed in Lisbon, could indicate that Cu can be associated with the more resistant phases (reducible, oxidizable and residual fractions), as observed in other studies (Davidson et al. 2006; Poggio et al. 2009; Wilcke et al. 1998).

Lead showed a similar behaviour to Cu, also with the highest median available fractions observed in Viseu samples (Table 4), although, unlike Cu, the available fraction of Pb in Lisbon soils is only negatively correlated with CEC (Table S7, ESM). However, it is known that Pb is a very immobile element in soils and it forms stable chelates with organic matter and stable complexes with Fe–Mn oxides (Wilcke et al. 1998). On the other hand, Poggio et al. (2009) found that Pb and Cu mobility was higher than for other elements in contaminated urban areas, reflecting the heterogeneity of urban soils. Some heterogeneity was also observed in this study. Lead in sample VIS.01.PO and sample LIS.05.OG/RD shows very low available fractions, in spite of the very high pseudo-total concentration found (Fig.3), meaning that Pb is not easily mobilised in these samples. On the other hand, the roadside samples LIS.38.RD and LIS.50.OG/RD from Lisbon and sample VIS.05.OG are the ones with higher available fractions (between 2.3% and 4.9%) and, in addition to the relatively high pseudo-total contents (98, 68 and 124 mg kg^{-1}, respectively), they may represent some concerns.

Zinc was the element showing the highest percentages of available fraction and the greatest variability of results (Table 4), especially in Lisbon (range of 2.2% to 27%), suggesting that this element has high mobility through soil. In addition, Zn is the only element showing a significant positive correlation between the pseudo-total content and the available fraction ($p<0.05$, Table S9, ESM), but this behaviour was observed only in Lisbon soils. These results reinforce the supposition of its anthropogenic origin. Nevertheless, an influence of soils' properties was also observed for this element, especially for clay and CEC contents (Table S7, ESM). Previous studies have also observed a similar behaviour for Zn, i.e. an association with the relatively soluble phases, in urban soils (Poggio et al. 2009).

The evaluation of the available fraction of potential toxic elements in soils is a much more important information than the total or pseudo-total concentration in a risk assessment basis. The levels of PTEs frequently exceed the desired levels indicated in the guidelines due to geological reasons. It is important to understand if these levels represent some concern to human health and to the environment. Some elements may have a major geogenic origin, but anthropogenic sources may also be important in some areas (e.g. Co and Ni), or they might be associated with more labile phases. On the other hand, anthropogenic elements can be associated with phases with low mobility (e.g. Cu and Pb).

The mobility of PTEs indicates how easily they may be released into soil solution, hence becoming available for plant uptake and subsequent entry in the food chain. Even more, it can also be an indication of the risk to human health (e.g. through oral ingestion), since some studies show that bioaccessible fraction will be higher than the easily mobilised (Poggio et al. 2009). Even in a small city like Viseu, where PTEs levels are mainly of geogenic origin, their available fractions can be higher than in other bigger cites like Lisbon (e.g. Cu and Pb), being a potential health hazard. In addition, due to the heterogeneity of results in urban soils, a site-specific evaluation is required in order to reduce remediation costs.

Conclusions

A high variability of results was observed on general parameters of soil, primarily due to the type of soils. Differences between levels of PTEs in urban soils may be attributed to geological origin and anthropogenic sources. Lisbon is enriched in elements coming mainly from basaltic rocks (Cr, Ni and Co), carbonates (Ca) and in typical anthropogenic elements (Cu, Pb, Zn and Hg). These findings are in agreement with other studies conducted in other urban areas: Co, Cr and Ni are controlled by geogenic factors, whereas Cu, Pb, Zn and Hg are controlled by anthropogenic factors.

Viseu soils are enriched in elements typical of granitic and metamorphic rocks such as Al, Ga, K, La, Sc, Th, Ti and U. This region also shows high levels of As, Pb, Zn and Hg, especially when compared with bigger or more industrialised cities, due to geological reasons. In both cities, Lisbon and Viseu, it was observed that soil properties may affect the distribution of both geogenic and anthropogenic elements; nevertheless, a great spatial variability was observed, which made the interpretation of results difficult.

This study shows that the background values of PTEs can be more important than the dimension of the city, and for some elements, there is a predominance of underlying geologic influence although important anthropogenic components can be present. Lisbon, for instance, still preserves its geochemical signature in less disturbed areas, in spite of all pressures that is subjected to. Hence, care should be taken when comparing the cities without considering the background levels and the origin of contamination. Differences in size and history, among other factors are important, but mainly for anthropogenic elements.

The high variability of available fraction of PTEs across samples can be attributed to the variability of sources (geogenic and anthropogenic) and soil properties. In Lisbon, the elements which had the highest available fraction were As, Co, Ni and Zn, both of geogenic or anthropogenic origin. Yet, the highest available percentages were found in some roadside samples. On the other hand, Cu and Pb, even though a major anthropogenic origin was identified, showed lower availability than geogenic elements (except Cr). For Co, Cr and Ni, it was found that availability was not dependent on the degree of contamination. Therefore, the high levels of Co, Cr and Ni observed in the south-western area should not represent a potential hazard. The same was observed for As in Viseu soils: in spite of the very high concentrations, this should not pose a problem since it is not very mobile. However, this city showed available fractions of PTEs (e.g. Cu and Pb) higher than the ones found in Lisbon soils, indicating that the risk of exposition to Viseu soils can be higher than in a bigger city.

In risk assessment, consideration of total amounts of PTEs may be overestimating the risks, since the availability of elements is not always related to the degree of contamination. Therefore, site-specific evaluation in urban soils is necessary due to the high spatial variability and heterogeneity.

Acknowledgements This work was supported by CESAM and by the Fundação para a Ciência e Tecnologia through the research project POCTI/CTA/44851/2002:SOLURB ('Towards a methodology for the assessment of environmental quality in urban soils') and individual research grants attributed to A. Cachada (SFRH/BD/38418/2007), P. Pato (SFRH/BPD/35068/2007), C. Mieiro (SFRH/BD/28733/2006) and T. Rocha-Santos (SFRH/BPD/65410/2009). The authors wish to thank Pedro Faria for the English revisions.

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