

# Assessing the control exerted by soil mineralogy in the fixation of potentially harmful elements in the urban soils of Lisbon, Portugal

C. Costa · A. P. Reis · E. Ferreira da Silva ·  
F. Rocha · C. Patinha · A. C. Dias ·  
C. Sequeira · D. Terroso

Received: 27 June 2011 / Accepted: 17 September 2011 / Published online: 8 October 2011  
© Springer-Verlag 2011

**Abstract** The main purposes of this study are the textural, chemical and mineralogical characterization of the urban soils of Lisbon and the identification of probable relations between the several soil properties. The results are used to infer which soil properties control the superficial dispersion of potential harmful elements to human health. Soil sampling was carried out in 51 selected sites all through the city, under the criterion that such sites should be spaces usually frequented by children. The concentrations of 42 elements in the >2 mm soil size fraction were determined at a commercial laboratory in Canada (ActLabs, LTD), by ICP-MS/ICP-OES after an acid digestion with aqua regia. The soil mineralogy was determined by X-ray diffraction in the <2 and <62 µm size fractions. The results indicate that the urban soils have mainly a sandy texture and a main mineralogical assemblage of quartz, K-feldspar, plagioclase and calcite. In terms of clay minerals, smectite, illite and kaolinite are the main clays in the soil. Smectite and illite show a dichotomy in their distribution, with the smectites prevailing in the soils of the volcanic complex of Lisbon, which are classified as being residual, and illite prevailing in the remaining soils, which are considered mainly as man-made soils. Smectite seems to exert an important role in the fixation of Ni and Cr. The results of the geochemical study show that Ni and Cr have concentrations above the soil guideline value established to the UK and pose a probable risk to human health.

**Keywords** Urban soil · Soil geochemistry · Soil mineralogy · Clay minerals

## Abbreviations

|     |                            |
|-----|----------------------------|
| PHE | Potential harmful elements |
| OM  | Organic matter content     |
| CEC | Cation exchange capacity   |
| CI  | Crystallinity index        |
| Sm  | Smectite                   |
| Kao | Kaolinite                  |
| I   | Illite                     |
| Qtz | Quartz                     |
| Phy | Phyllosilicates            |
| Fk  | Potassium feldspar         |
| Pl  | Plagioclase                |
| C   | Calcite                    |
| Anh | Anhydrite                  |
| D   | Dolomite                   |
| Hem | Hematite                   |
| Sid | Siderite                   |
| Py  | Pyrite                     |
| Mag | Magnetite/maghemite        |

## Introduction

The urban soils are characterized by a very heterogeneous composition due to strong human influence, and often contain more contaminants (metals, hydrocarbons, organochlorines, among others) than rural areas due to high anthropogenic activity (Biasioli et al. 2006). In urban areas, the daily activities among which stand out, such as industrial emissions and traffic, are the main sources of soil pollutants.

C. Costa (✉) · A. P. Reis · E. Ferreira da Silva · F. Rocha ·  
C. Patinha · A. C. Dias · C. Sequeira · D. Terroso  
GEOBIOTEC, Geosciences Department, University of Aveiro,  
Campus de Santiago, 3810-193 Aveiro, Portugal  
e-mail: a37042@ua.pt

Urban land function as “recipient” where they accumulate metals derived from various sources like industrial, vehicle emissions, among others.

Despite pollution, it has been shown that urban surface soils can still reflect the chemical composition of the underlying geological units (Norra et al. 2006). In the solid phase of soils, chemical elements are components of specific minerals and of organic matter. However, specific mineral phases are not usually included in environmental studies on urban soils. Yet, some recent studies (Bianchini et al. 2002; Norra et al. 2006) indicate that the characterization of soil mineralogy may allow to discriminate the nature of the urban soil (geogenic or man-made) and give an useful contribution to risk assessment in the sense that soil minerals can in fact control the fixation of potentially harmful elements (PHE) in the solid phase.

Potentially harmful elements are defined as inorganic elements (mainly metals and metalloids) that are toxic and may be harmful to human health if exposure occurs. Such PHE include elements such as As, Hg, Pb, Cd, Cr, V and Tl, among others. Reduced cognitive development and impaired intellectual performance of children have been linked to Pb exposure (Ljung et al. 2007). Other elements, such as Cu, Cd, Zn, As and Hg are also well-known toxic elements. Populations exposed to these elements develop altered functions in their nervous system, with neurophysiological consequences (Han et al. 2008).

Metals occur in soil as a complex mixture of solid phase/chemical compounds with different particle sizes and morphologies. These compounds include resistant mineral phases, coprecipitate species, adsorb on soil minerals, especially in clay minerals, or organic material and dissolved species that can be complexed by a variety of ligands, both organic and inorganic. Clay minerals are increasingly recognized as an important fraction in soils influencing the retention capacity and bioavailability of heavy metals and their mobility in specific environments. Smectite clays are versatile and strong cationic exchangers and their presence can greatly influence the mobility of PHE (Sultan 2010). The occurrence and relative distribution of metal between these various stages, and the physical relationship between these phases and the ground controls the dissolution of the element and of course their mobility (Cachada et al. 2009; Madrid et al. 2008).

The metals present in urban soils can be transferred to humans through ingestion, inhalation or dermal contact. In risk assessment of potentially toxic elements (PHE) in the soil, oral exposure to contaminants is the main pathway of exposure, particularly in children younger than 6 years, which may ingest considerable amounts of soil through hand-to-mouth (accidental ingestion) or through pica behavior (deliberate ingestion). Pica behavior is the most common in children aged 1–2 years and usually decreases

with age. Studies on soil ingestion reported that the average amount of soil ingested by children varies between 39 and 271 mg/day (Moya et al. 2004).

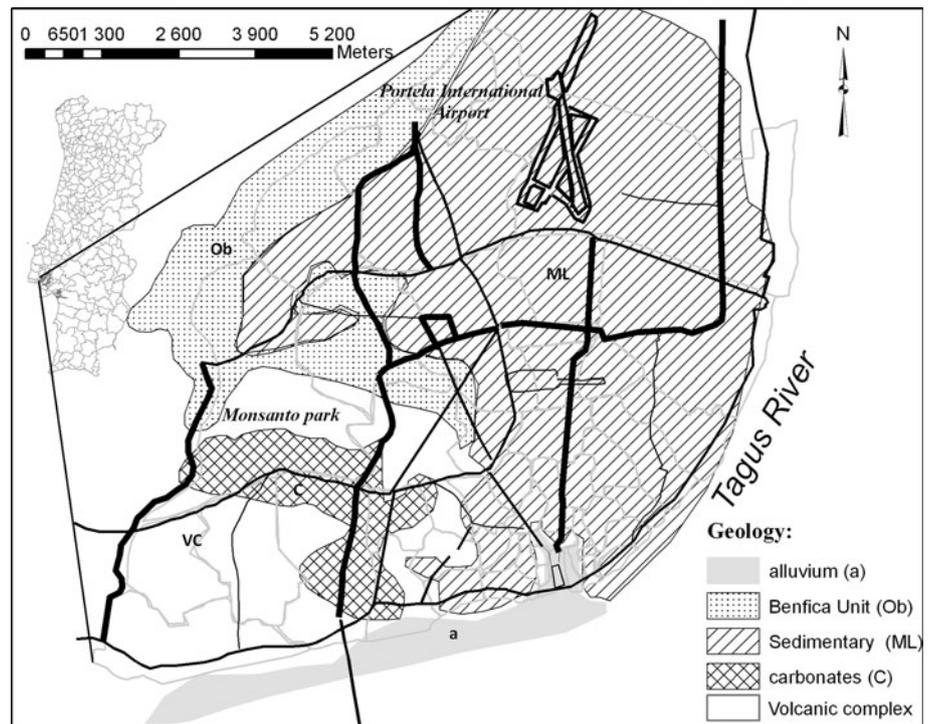
Studies on the effect of particle size on metal concentrations in the solid phase are essential in studies of risk assessment because: (1) metals are preferentially adsorbed by fine particles and to the shaping and implementation of directives is important to know which grain sizes are dominant the immobilization of pollutants, (2) fine particles in PTE's carry an increased risk to health because they are more soluble than the coarse particles that have higher specific surface, (3) fine particles are more likely to cross the gastric mucosa and be adsorbed (Wang et al. 2006), (4) the 0–50  $\mu$  fraction has the greatest likelihood of being accidentally ingested by children (Sheppard 1995), (5) fraction <2 mm is the one that is more likely to be voluntarily ingested by children (Ljung et al. 2007).

This study is part of an R&D project, untitled “URB-SOIL-LISBON: Geochemical survey of Lisbon urban soils: a baseline for future human health studies, PTDC/CTE-GEX/68523/2006”. This project primarily aims the systematic characterization and assessment of the environmental quality of urban soils of Lisbon, daily affected by introductions of various organic and inorganic compounds. The geochemical characterization of the soil, the identification of hot spots of contamination and determination of effective indicators of pollution, constitute an important baseline for the future studies of environmental risk assessment and it is an important source of information for those who want an environmentally conscious management and development sustainable city.

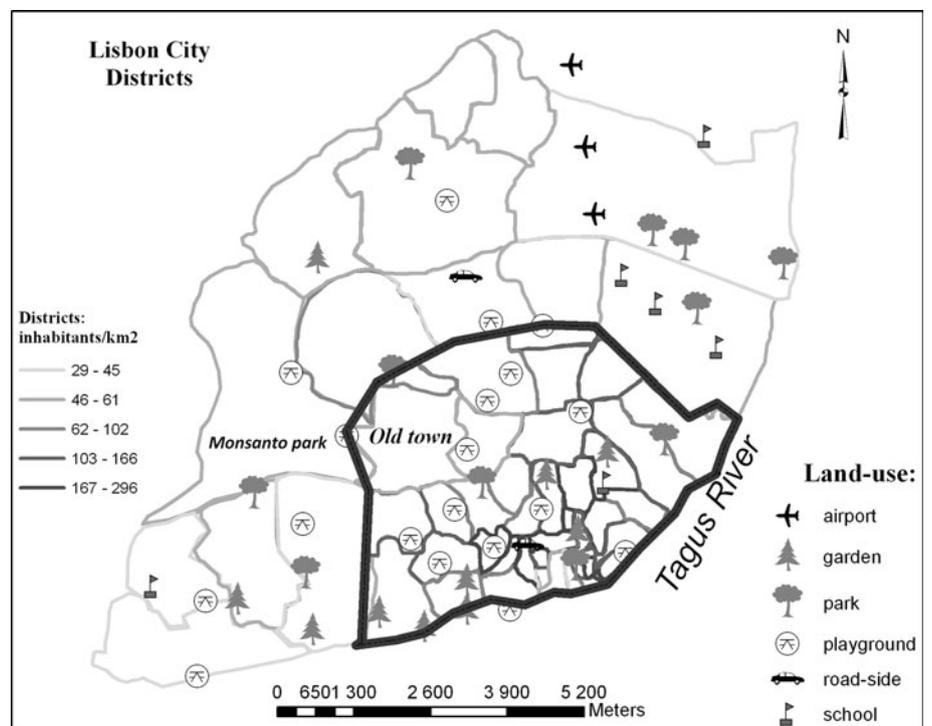
## Study area

The city of Lisbon is located in the western edge of Portugal and is limited at south by the Tagus River (Fig. 1). The capital of Portugal having 556,797 inhabitants (Prazeres et al. 2009) is the largest city of the country. The municipality of Lisbon has an area of about 84 km<sup>2</sup>, an irregular topography and an average population density of about 6,282.1 inhabitants/km<sup>2</sup>. The city is divided into 53 districts (Fig. 2). The Lisbon area has a varied geology, composed primarily of marine and continental sands, clays and carbonates with high fossil content of Miocene age, a volcanic complex neo-Cretaceous which is based on a disagreement over a complex carbonated Cenomanian (Almeida 1986). The map presented in Fig. 1 represents the main geological units of the study area. Thus, the geology of Lisbon is essentially composed of: Alluvium (a); detrital sedimentary rocks with interbedded limestone of Miocene age (ML); Benfca Complex (Ob) composed by conglomerates and mudstones interbedded with limestone;

**Fig. 1** Location of the study area and a simplified geological map of Lisbon (adapted from Serviços Geológicos de Portugal, 1992). The linework shown in the map corresponds to some of the major streets of Lisbon



**Fig. 2** Map with the 53 districts of Lisbon, the respective population density and the land use of the 51 sites of soil sampling; different symbols identify different land uses. The black line outlines the old part of the city



Volcanic Complex of Lisbon (Vc) that is characterized mainly by a band of lava flows with levels of tufts, which are small in number, and some major stacks; Limestone (C).

Lisbon has a temperate Mediterranean climate characterized by having the four seasons. Spring is mild with temperatures varying between 8 and 26°C and low

precipitation. Summer is usually hot and dry, with temperatures ranging from 16 to 36°C. Autumn is characterized by being unstable, with temperatures between 12 and 27°C. Winter is typically rainy and cold, with temperatures between 3 and 17°C. The wind direction is predominantly in Lisbon N20° NW (Reis et al. 2010).

The land use is mostly artificial land (95% of housing, pavements, commercial land, etc.) with minor uses as green-land (3%) and agricultural land (1%, mostly private backyards).

### Possible sources of contamination in the city

The main probable sources of contamination of urban soils in Lisbon are (Fig. 3):

*Lisnave Shipyard* the inks used in the paintings are potential sources of contaminants, as well as steel works, the repair and replacement of pipes and valves.

*Lisbon Por* the activities undertaken at the port of Lisbon involve emissions of compounds such as SO<sub>2</sub> and NO<sub>2</sub>, and potentially toxic elements such as Zn, Pb, Ni and V.

*Lisbon International Airport* the aircraft tire wear, pavement and brake wear, may release potentially toxic elements such as Pb, Tl, Zn, Ni, Sb, Cu, V, HREE, among others.

*Car Traffic* the tire wear, exhaust fumes from cars and pavement wear, are also possible sources of contamination of urban soils in Lisbon by the release of PHE such as S, Be, Cd, Co, Mo, Sb, Cu, Ni, V, Zn, Pb, Sn, Tl, among others.

*Santa Apolonia Station* the wear of the railways promotes the release of PHE such as Pb, Zn, among others, thus being a probable source of contamination to the soils nearby.

*Incinerators* toxic emissions, released by even the most modern incinerators, are formed by three types of hazardous pollutants to the environment and human health: heavy metals, products of incomplete combustion and the new chemicals formed during the incineration process.

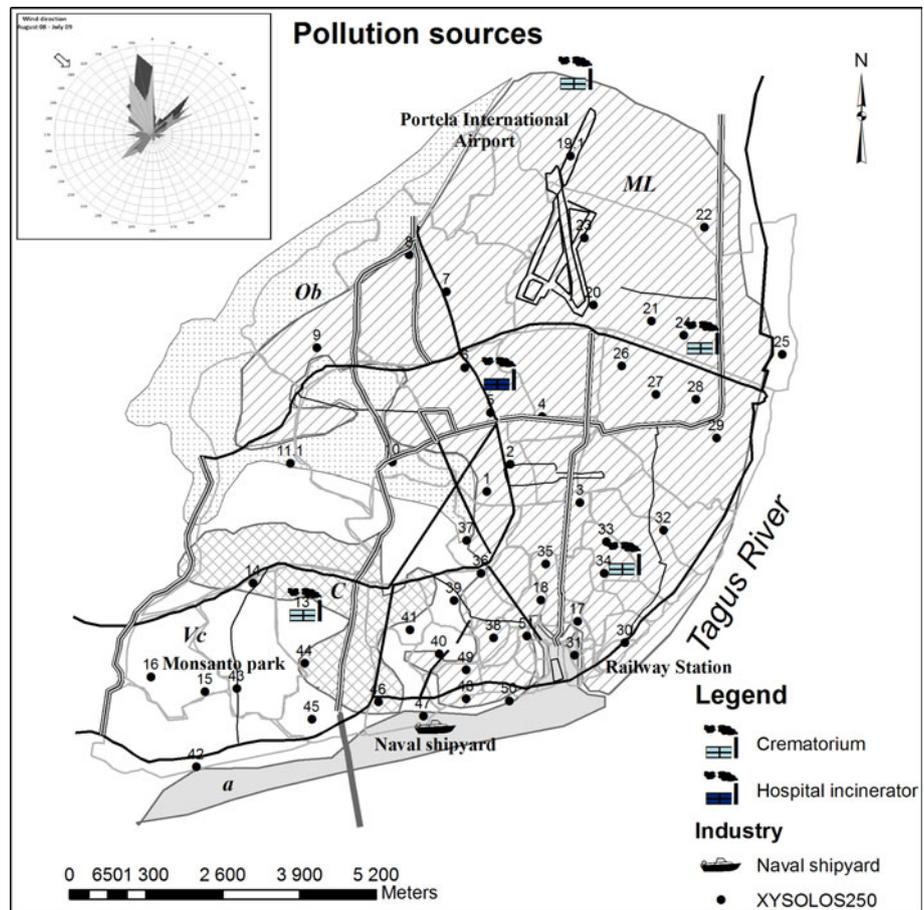
Heavy metals such as Pb, Cd, As, Hg and Cr, are not destroyed during incineration and are often released into the environment in ways even more concentrated and dangerous than the original waste.

### Materials and methods

#### Sampling and sample preparation

In this study, the soil samples were selected as a probable pathway of exposure of young children to PHE. Studies on soil ingestion reported that the average amount of soil ingested by children varies between 39 and 271 mg/day (Moya et al. 2004). Therefore, 51 sites (Fig. 2) were

**Fig. 3** Location of probable anthropogenic PHE sources; the figure also displays the major wind directions



selected using the land use as the main criterion. Those sites include public parks and garden, schoolyards and playgrounds.

Soil samples for chemical analysis of inorganic elements were collected with a steel shovel and stored in plastic bags properly identified. To ensure the representativeness of sampling and to estimate sampling errors, each sample as a composite sample of three sub-samples and several duplicates were also collected.

The first 5 cm of soil were collected as it is the soil layer most likely to be ingested and it is the one that is disturbed by atmospheric deposition of PHE emitted from anthropogenic sources.

The different urban land uses selected for sampling were: 19 playgrounds (PG), 10 gardens (GD), 10 public gardens (PA), 6 schools (SC), 2 road sides (RS) and 3 points sampling at the airport (AE). To assess the contribution of the structures of playgrounds in the contamination of soils, we tried to sample the closest to swings and slides. Figure 2 illustrates the six types of land use sampled in the city of Lisbon.

The samples were dried in a fan assisted oven at <40°C and sieved to provide the <2 mm soil fraction that was preserved for the determination of physical, mineralogical and chemical properties of the soil.

The <2 mm soil fraction is most often used in environmental studies and is recommended by the FOREGS Geochemical Baseline Programme (Salminen et al. 2005). Additionally, the fraction <2 mm is the one that is more likely to be ingested by children who exhibit pica behavior (deliberate ingestion of soil), common up to 2 years (Ljung et al. 2007).

**Methods**

Soil pH was determined as pH<sub>CaCl2</sub> according to the ISO 10390:1994 protocol. Organic matter content (OM) of the soil was determined by weight loss after combustion, at 430°C for about 16 h (Schumacher 2002). The percentages of C, N, H and S in the soil were determined by elemental analysis (LECO, CNHS-932). The cation exchange capacity (CEC) and the exchangeable cations were measured according to the method ISO 13536-1995.

Forty-two chemical elements were analyzed in the soil samples in a certified laboratory (AtcLabs Ltd) The analysis was carried out by ICP-MS/ICP-OES (Finnegan Mat ELLEMENT 2) after a digestion of 0.5 g of sample (fraction <2 mm) in aqua regia.

The texture was determined in all samples as percentages of sand, silt and clay. The percentage of sand fraction between 2 and 0.075 mm was obtained by wet sieving using ASTM 75 micron sieve. The sand fraction between

0.075 and 0.050 mm, silt and clay fractions were quantified by sedigraph, (Lima and Luz 2001).

The determination of the mineralogical composition was carried out on a subset of 26 samples, previously selected to ensure the representativeness of the bulk samples.

Mineralogical studies were carried out on the <2 mm and <2 μm (clay) fractions of the sediments through X-ray diffraction (XRD). The mineral composition was determined both on unoriented powder mounts for <2 mm fraction analyses and on oriented aggregates for the clay fraction ones. The clay fractions were separated by sedimentation according to Stokes law using 1% sodium hexametaphosphate solution to avoid flocculation. For the preparation of preferentially oriented clay mounts, the suspension was placed on a thin glass plate and air-dried. XRD measurements were performed using Philips PW 3050 and X' Pert PW 3040/60 equipment using Cu Kα radiation. Scans were run between 2° and 60° 2θ (unoriented powder mounts) or between 2° and 20° 2θ (oriented clay mounts) in the air-dry state after a previous glycerol saturation and heat treatment (300 and 500°C). Qualitative and semiquantitative mineralogical analyses followed the criteria recommended by Schultz (1964), Thorez (1976) and Mellinger (1979). For the semiquantification of the identified principal minerals, peak areas of the specific reflections were calculated and weighted by empirically

**Table 1** Diagnostic peaks and weighting factors (adapted from Martins et al. 2007)

|                                  | Peak (Å)                    | The area was divided by |
|----------------------------------|-----------------------------|-------------------------|
| <i>Minerals of fine fraction</i> |                             |                         |
| Quartz                           | 3.34                        | 2                       |
| Phyllosilicates                  | 4.45                        | 0.1                     |
| K-feldspars                      | 3.21                        | 1                       |
| Plagioclases                     | 3.18                        | 1                       |
| Calcite                          | 3.03                        | 1                       |
| Anatase                          | 3.52                        | 1                       |
| Anhydrite                        | 3.49                        | 1.5                     |
| Dolomite                         | 2.88                        | 1                       |
| Hematite                         | 2.68                        | 1.3                     |
| Pyrite                           | 2.71                        | 1                       |
| Opal                             | 4.03                        | 0.5                     |
| Zeolite                          | 3.97–3.93                   | 0.8                     |
| Magnetite/maghemite              | 2.53–2.51                   | 1.3                     |
| Siderite                         | 2.79                        | 1                       |
| <i>Clay minerals</i>             |                             |                         |
| Illite                           | 10 (in natural specimen)    | 0.5                     |
| Kaolinite                        | 7 (in natural specimen)     | 1                       |
| Smectite                         | 17 (in glycolated specimen) | 4                       |

estimated factors (Table 1), according to Galhano et al. (1999) and Oliveira et al. (2002).

Crystallinity is a measure of the lattice ordering, and the crystallite size of clay minerals is often used to assess the degree of maturation of a residual soil. The level of crystallinity (crystallinity index—CI) for clay minerals (v/p) was evaluated according to the method of Thorez (1976). According to the method, high values of CI indicate poor crystallinity.

In order to assess the probable risk posed by PHE in the urban soil, the total concentrations are compared with the Soil Guideline Value (SGV) established for the United Kingdom. The selected SGV is the value for residential land without plant uptake, the most appropriate for the land use of the soil in this study. The SGV provide a coherent and consistent way to assess the probable risk to human health from soil contamination as they are intended to provide a means of assessing the impact of a long-term exposure to contamination on human health (DEFRA 2002).

## Results

The results of several soil properties are presented and discussed in detail seeking for relationships between such properties and the behavior and fate of PHE in the urban soils of Lisbon.

### Grain-size distribution and physical–chemical parameters of the soil

The results of grain-size analysis are shown in Fig. 4. Through the analysis of the map, it can be seen that the soils represented by the set of 51 samples tend to be sandy. The grain-size distribution does not have a spatial correlation with the land use or with the geology of the study area.

Table 2 displays the summary statistics of several physical–chemical parameters of the urban soils. The results indicate that some soil parameters, such as OM, exchangeable bases and CEC, are site-specific as they are highly variable between samples. The soil pH is slightly acid to neutral.

### Clay mineralogy

The clay content of the Lisbon urban soils is characterized by variable amounts of smectite (Sm), kaolinite (Kao) and illite (I), (Fig. 5).

The samples were divided into two series, A and B, taking the percentage of smectite into account. Series B soils have predominant amounts of Sm while series B soils have either predominant I or Kao.

On analyzing the map of Fig. 5, it is clear that the soils with higher percentages of Sm (Series B) are those of the Volcanic Complex of Lisbon. In the other samples (Series A) the proportion of clay minerals is quite variable.

To better characterize the clay minerals, it was also calculated the CI of each clay mineral in all samples. The spatial distribution of the CI of smectite (Fig. 6c) is remarkably coincident with the volcanic complex of Lisbon. Smectite in these soils is more crystalline, which implies a longer residence time in the soil and allows us to infer that these urban soils are residual (formed from the local parent material). Moreover, the CIs of Kao and I are somewhat random and conclusions cannot be drawn from them (Fig. 6a, b).

In order to assess the nature of the Lisbon urban soils (natural or man-made) the following ratios were calculated:

1. Sm/Kao
2. (Sm + Kao)/I

On analyzing the ratio of smectite/kaolinite (Fig. 7a), it is clear that the samples from the volcanic complex of Lisbon are extremely enriched in Sm. Being an authigenic, neoformed mineral, smectite, reflects the changing chemistry and the degree of maturation of the soil (Benta 2007), which indicates that these soils are more mature than the soils impoverished in Sm.

Illite is an inherited mineral, so the soils with higher amounts of this mineral are more recent since the weathering process of I is still incipient. The spatial distribution of the second ratio (Fig. 7b) indicates that the soils with higher amounts of illite are those of sites 20, 31, 33, 39 and 48. At these sites, the soil was collected in flower beds inside small public gardens, where the soil is periodically renewed.

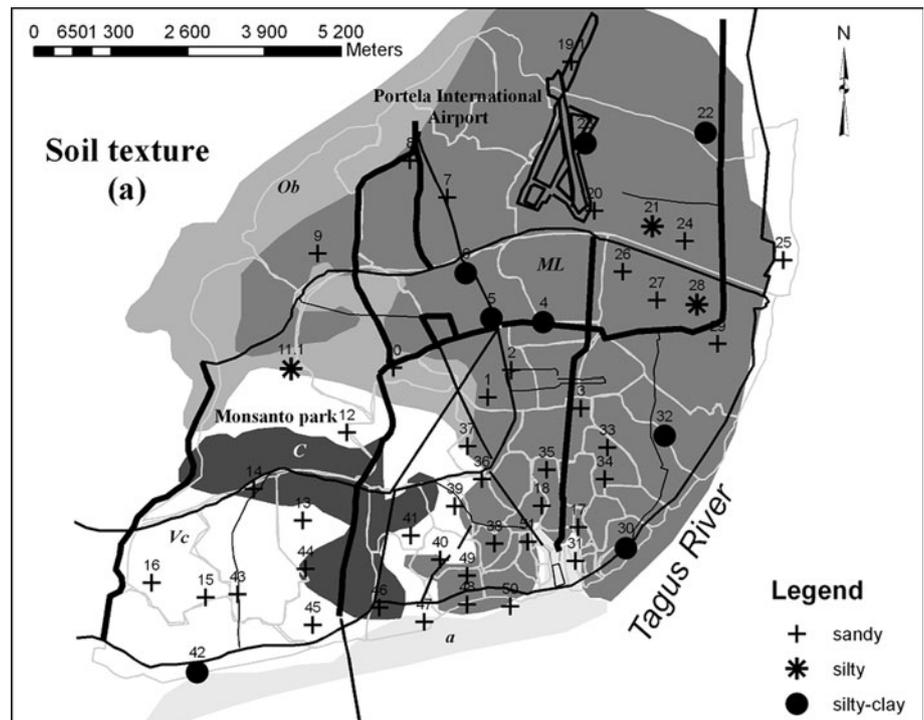
The joint interpretation of the ratios shows two important results: (1) the significant dominance of smectite over other clay minerals in soils on the volcanic complex suggests that these soils are residual, (2) man-made soils of flower beds in small urban recreational areas seem to be enriched in I.

### Soil mineralogy

The mineralogical composition of the soils is mainly siliceous, with quartz (Qtz), phyllosilicates (Phy), potassium feldspar (Fk), plagioclase (Pl) and, in some samples, calcite (C). Mineral like anhydrite (Anh), dolomite (D), hematite (Hem), siderite (Sid), pyrite (Py), opal, zeolite and magnetite/maghemite (Mag) are accessory minerals.

Figure 8 shows the spatial distribution of the soil minerals, grouped according to the chemical composition. Map 8a shows the relative proportions of silicates (Phy, Qtz, Fk and Pl); map 8b shows relative proportions of

**Fig. 4** Map with the soil textural classification



**Table 2** Summary statistics for several soil properties: pH, organic matter content (OM), elemental C–S–N–H, CEC and exchangeable bases (Na, K, Mg and Ca)

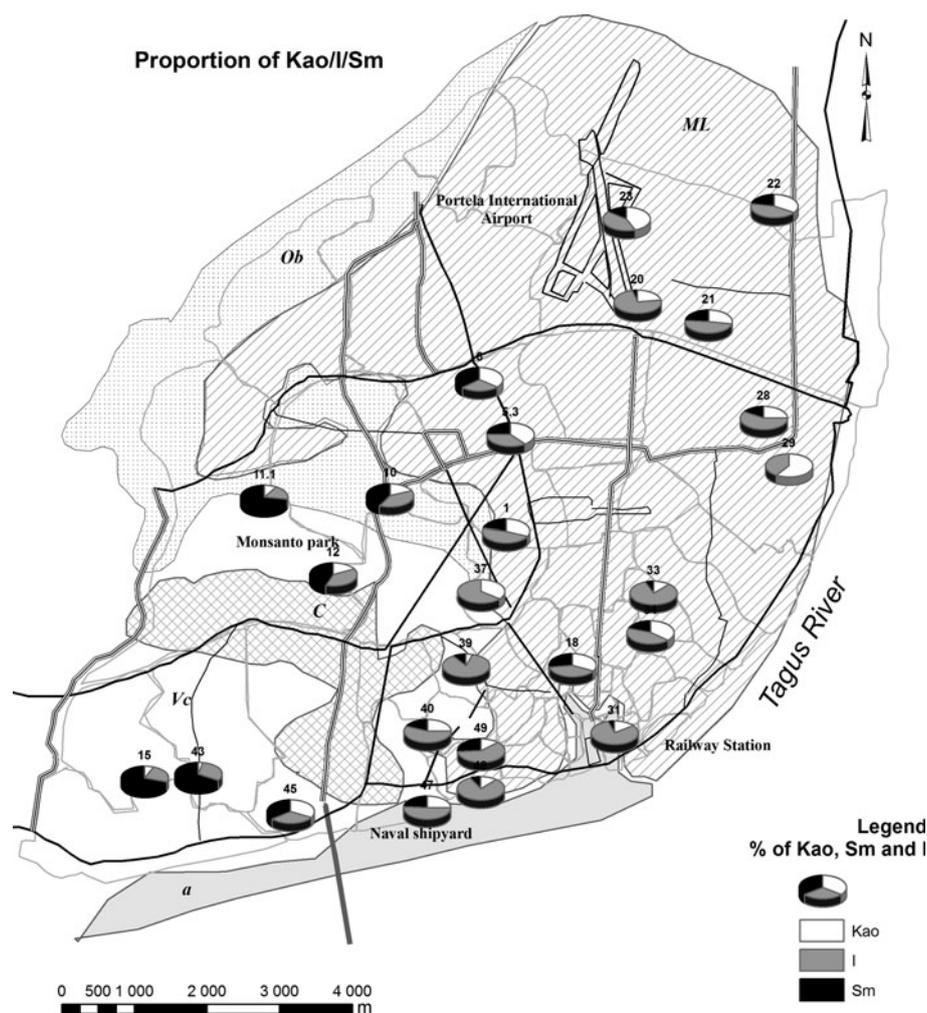
| Soil properties  | N  | Min.  | Q <sub>0.25</sub> | Mean | Median | Q <sub>0.75</sub> | Max.  | Standard deviation | Range | Skew  |
|------------------|----|-------|-------------------|------|--------|-------------------|-------|--------------------|-------|-------|
| pH <sub>Ca</sub> | 51 | 5.46  | 6.61              | –    | 6.74   | 6.93              | 7.19  | 0.282              | 1.73  | –1.74 |
| OM               | 51 | 0.91  | 4.24              | 7.09 | 5.89   | 8.03              | 40.8  | 6.069              | 39.85 | 3.72  |
| TC               | 51 | 0.436 | 2.433             | 4.95 | 4.114  | 6.707             | 24.47 | 3.923              | 24.03 | 2.68  |
| TN               | 51 | 0.003 | 0.168             | 0.31 | 0.297  | 0.392             | 1.067 | 0.215              | 1.07  | 1.23  |
| TH               | 51 | 0.022 | 0.583             | 0.89 | 0.757  | 1.054             | 2.808 | 0.548              | 2.79  | 1.42  |
| TS               | 51 | 0.004 | 0.012             | 0.05 | 0.041  | 0.074             | 0.224 | 0.047              | 0.22  | 1.54  |
| CEC              | 51 | 1.95  | 12.59             | 18.0 | 17.5   | 22.8              | 48.3  | 9.389              | 46.31 | 0.77  |
| ExchNa           | 51 | 0.117 | 0.32              | 0.64 | 0.57   | 0.86              | 2.64  | 0.463              | 2.53  | 1.86  |
| ExchK            | 51 | 0.061 | 0.49              | 1.12 | 0.73   | 0.97              | 20.55 | 2.802              | 20.49 | 6.93  |
| ExchMg           | 51 | 0.001 | 0.69              | 1.75 | 1.13   | 2.00              | 11.05 | 2.099              | 11.05 | 3.27  |
| ExchCa           | 51 | 0.190 | 1.30              | 1.86 | 1.75   | 2.32              | 5.77  | 0.973              | 5.58  | 1.12  |
| Silt             | 51 | 2.80  | 19.1              | 24.1 | 23.9   | 31.3              | 48.4  | 9.946              | 45.63 | –0.08 |
| Clay             | 51 | 0.91  | 6.8               | 12.1 | 11.0   | 18.3              | 26.0  | 6.654              | 25.07 | 0.25  |
| Sand             | 51 | 29.13 | 54.7              | 63.8 | 63.5   | 72.3              | 96.3  | 15.19              | 67.15 | 0.10  |

OM, TC, TH, TS, silt, clay and sand are expressed in percentage; CEC are expressed in cmol/kg, ExchNa, ExchK, ExchMg and ExchCa are expressed in mg/kg

Ca-minerals (C, D and Anh); map 8c shows the relative proportions of Fe-minerals (Hem, Sid, Py and Mag); map 8d shows relative proportions of opal and zeolite. Looking at the distribution of the silicate minerals [map 8a], it can be observed that most of the soils in the volcanic complex are enriched in Phy (probably due to the high amounts of smectite) while the other soils have mainly variable amounts of quartz and K-feldspar. Silicates are the most abundant

minerals in these urban soils. The spatial distribution of Ca-minerals [map 8b] shows that, except at site 15, the soils have mainly calcite, especially at sites 10, 28, 39 and 47, corresponding to different land uses. The common feature to these sites is that the soils are man-made and the pavement of the recreational area is of limestone. So, weathering of the local pavement seems to be introducing calcite in the soil. Ca-minerals are the second most abundant group of minerals

**Fig. 5** Spatial distribution of clay minerals in the studied soils and, the relative proportions of kaolinite (Kao), illite (I), and smectite (Sm) in each sample. The geological map underlay the map; *a* alluvium, *Ob* benfica unit, *ML* sedimentary, *C* carbonates, *Vc* volcanic complex of Lisbon. The *linework* shown in the map corresponds to some of the major streets of Lisbon



in the urban soils of Lisbon, while Fe-minerals are normally minor in these urban soils [map 8c]. Sites 15 and 47 have considerable amounts of hematite but the most common Fe-mineral is normally siderite, although in smaller amounts. It is interesting to notice that site 15 has also some opal and zeolite [map 8d], which do not exist in most soil samples. Both opal and hematite may occur in the fissures of basalts and natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Therefore, this mineral association confirms the volcanic origin of the soil at site 15. In what concerns sample 47, the fact that it is the nearest site from the naval shipyard suggests that hematite may have an anthropogenic origin, related with rusting processes at the shipyard.

#### Potentially harmful elements in the urban soils

The analysis of the data began with an exploratory statistical analysis in which a number of statistical parameters were calculated (Table 3).

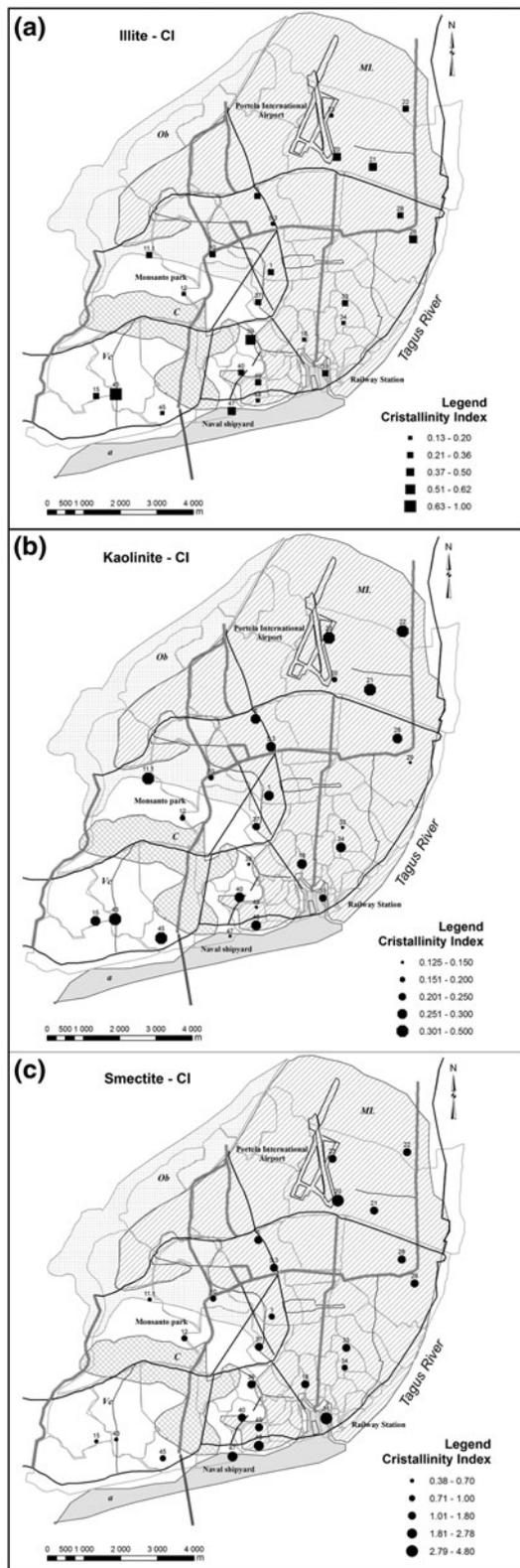
Considering the United Kingdom (UK) guidelines (SGV) for residential areas (Table 3), it appears that only the elements Cr and Ni are present in concentrations potentially harmful to human health. These PHE are present in abnormal concentrations only in samples of the volcanic complex.

Chromium is in abnormal levels in the samples 11.1, 15 and 43, and Ni appears in abnormal levels for the sample 43. The main spatial features of these samples are described in Table 4.

#### Correlations between geochemical and mineralogical properties of soils in Lisbon

In order to recognize if soil mineralogy has some control in the fixation of PHE in the urban soil, correlations (Pearson correlation coefficient) between both soil properties were investigated.

The correlations presented between the PHE's and clay minerals for the series B are presented in Table 5. There



**Fig. 6** Crystallinity index of illite (map a), kaolinite (b) and smectite (c) and their spatial distribution. The geological map underlay the map; *a* alluvium, *Ob* benfica unit, *MI* sedimentary, *C* carbonates, *Vc* volcanic complex of Lisbon. The *linework* shown in the map corresponds to some of the major streets of Lisbon

are not significant correlations between chemical elements and clay minerals for the series A.

The negative correlations with the minerals illite and kaolinite were expected since the soils of the volcanic complex are enriched in smectite. The negative correlation between Sm and As means that these soils have low As concentrations, possibly because most of the volcanic complex is occupied by a wide-forested area (the Monsanto park) without major anthropogenic sources of contaminants.

The positive correlations between smectite and some PHE (Ni, V and Cr) may suggest that the smectite has the ability to control the fixation of these PHE in the soil, which is quite probable since Sm has a high cation exchange capacity. Yet, Cr and Ni in the soils of the volcanic complex are in concentrations that may be potentially harmful to human health. It is therefore important to carry out a future study to estimate the bioaccessibility of Cr and Ni in these soils in order to assess the actual risk to human health.

Quartz shows negative correlations with Ba, Ni, V and Cr for the samples of series B (volcanic complex). Such negative correlation is expectable since the local geology is composed mainly of basalts.

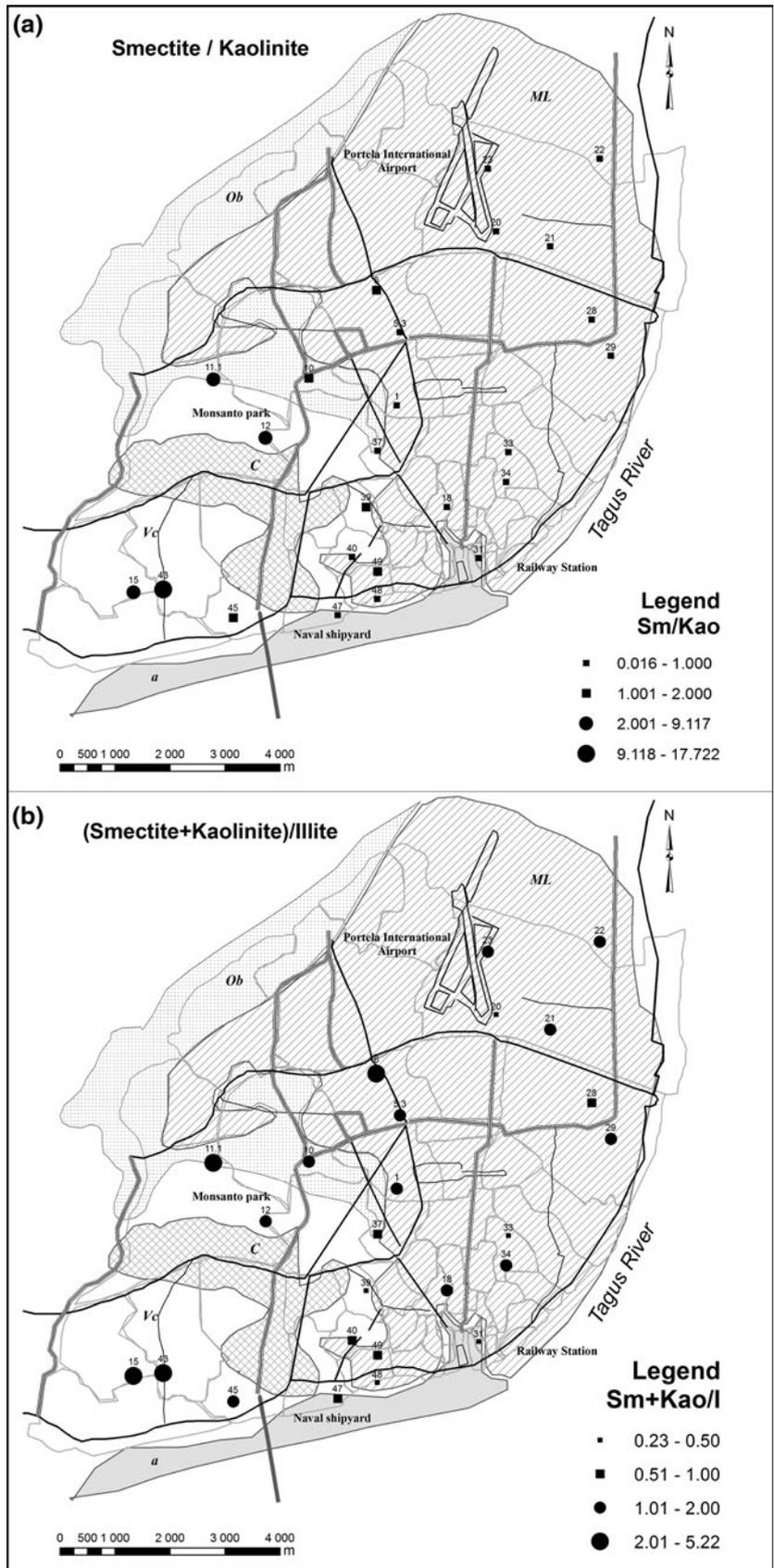
**Conclusion**

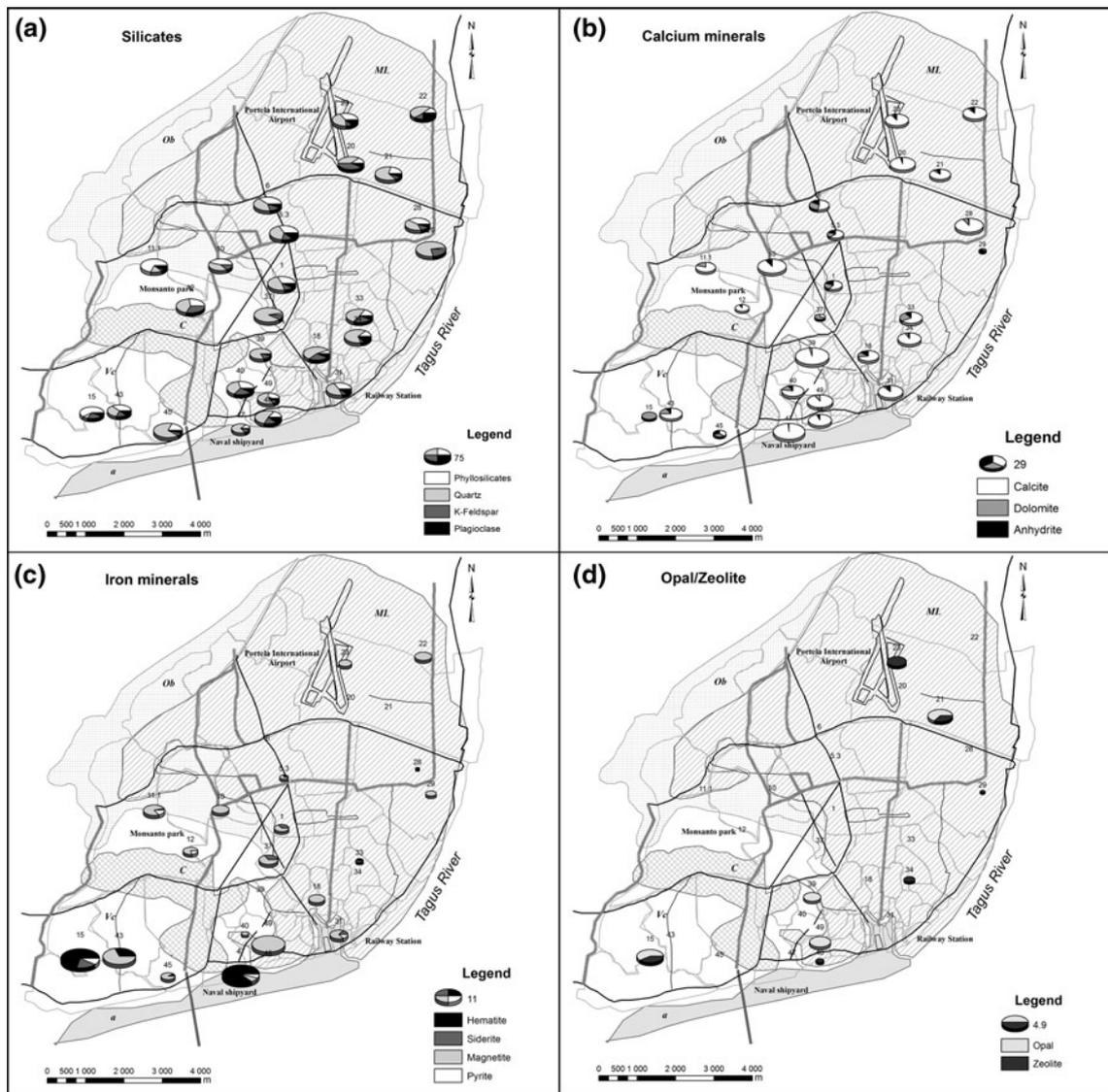
The results show that the Lisbon urban soils are composed mainly of illite, smectite and kaolinite in variable proportions. These different proportions allowed the discrimination of two sets of samples (series A and B): series B samples are richer in smectite, while the series A samples are generally richer in illite. In spatial terms, all samples of series B are located in the volcanic complex of Lisbon.

The crystallinity index of the clay minerals shows that smectite is the clearest in the soils of the volcanic complex, while illite is more ordered in the remaining soil samples. The high crystallinity of smectite in soils of the volcanic complex of Lisbon suggests a greater residence time in the soil and allows us to infer that these urban soils are residual (formed from the underlying bedrock).

The joint interpretation of the ratios shows three important results: (1) the significant dominance of smectite over other clay minerals in soils on the volcanic complex suggests that these soils are residual, (2) man-made soils of flower beds in small urban recreational areas seem enriched in illite; (3) the consistency of results obtained for all samples collected in the area of the volcanic complex indicates that the soils have the same origin, which implies a similar geochemical composition. Thus, marked differences in geochemical composition of these soils can be assumed anthropogenic contributions characteristics of an urban environment.

**Fig. 7** Spatial distribution of ratios **a** Smectite/Kaolinite and **b** (Sm + Kao)/Illite





**Fig. 8** Spatial distribution of the major minerals in the urban soil: **a** silicate minerals, **b** calcium minerals, **c** iron minerals and **d** opal and zeolite

Following the characterization of clay minerals, the samples were analyzed by XRD to identify the mineralogy of the urban soil. The results show that all the tested soils are siliceous, having a major composition of quartz, phyllosilicates (includes micas and clay minerals), potassium feldspar, plagioclase and, in some samples, calcite. The minerals anhydrite, dolomite, hematite, siderite, pyrite, opal, zeolite and magnetite and maghemite are accessory minerals.

Some of the PHE show high correlations with the clay minerals, especially in the samples of series B. The smectite displays positive correlations with V, Cr and Ni for soil series B. This result suggests that smectite has the ability to control the fixation of these PHE in the soil, probably due to its high cation exchange capacity. Yet, Cr

and Ni in the soils of the volcanic complex are in concentrations that may be potentially harmful to human health. The chemical nature of the relation between smectite and the PHE requires further studies, namely through SEM.

The Sm/Kao ratio is positively correlated with Cr and Ni for series B samples where smectite is abundant.

The quartz appears negatively correlated with V, Cr, Ba and Ni in the samples of series B (rich in smectite, and located the Volcanic Complex of Lisbon). These elements are common in mafic rocks, which explain the negative relationship with the quartz.

The use of the soil quality guidelines for human health (SGV) shows that only Cr and Ni in the soil pose a

**Table 3** Statistical summary of the geochemical analysis

|    | Mean   | Median | Standard deviation | Skew  | Var    | Min  | Max   | SGV |
|----|--------|--------|--------------------|-------|--------|------|-------|-----|
| Li | 10.38  | 11     | 3.25               | -0.23 | 13.2   | 3.6  | 16.8  | -   |
| Na | 0.08   | 0.06   | 0.06               | 2.84  | 0.27   | 0.04 | 0.31  | -   |
| Mg | 0.53   | 0.31   | 0.62               | 2.39  | 2.49   | 0.04 | 2.53  | -   |
| Al | 1.32   | 1.03   | 0.96               | 2.03  | 4.02   | 0.25 | 4.27  | -   |
| S  | 0.08   | 0.07   | 0.04               | 0.62  | 0.18   | 0.01 | 0.19  | -   |
| K  | 0.2    | 0.21   | 0.07               | -0.37 | 0.26   | 0.05 | 0.31  | -   |
| Ca | 4.23   | 3.91   | 2.51               | 0.42  | 9.25   | 0.26 | 9.51  | -   |
| V  | 43.68  | 31     | 37.71              | 1.8   | 151    | 5    | 156   | -   |
| Cr | 48.35  | 30.5   | 49.96              | 2.49  | 194.2  | 6.8  | 201   | 200 |
| Mn | 294.96 | 219    | 256.55             | 1.78  | 991    | 49   | 1,040 | -   |
| Fe | 2.3    | 1.84   | 1.61               | 2.03  | 6.79   | 0.52 | 7.31  | -   |
| Cu | 67.82  | 50.5   | 57.51              | 1.91  | 248.49 | 9.51 | 258   | -   |
| Zn | 156.84 | 132    | 112.29             | 2.02  | 527.4  | 12.6 | 540   | -   |
| As | 4.39   | 4.5    | 2.83               | -0.1  | 9.2    | 0.1  | 9.3   | 20  |
| Se | 0.4    | 0.4    | 0.17               | 0.7   | 0.8    | 0.1  | 0.9   | 350 |
| Sr | 90.32  | 70.4   | 75.36              | 2.35  | 360.4  | 6.6  | 367   | -   |
| Ba | 158.18 | 135    | 85.84              | 0.21  | 279.6  | 23.4 | 303   | -   |
| Tl | 0.11   | 0.11   | 0.06               | 0.84  | 0.22   | 0.03 | 0.25  | -   |
| Pb | 114.12 | 124    | 91.88              | 0.58  | 300.3  | 4.7  | 305   | 450 |
| P  | 0.14   | 0.13   | 0.09               | 1.05  | 0.34   | 0.02 | 0.36  | -   |
| Ti | 0.09   | 0.04   | 0.13               | 2.13  | 0.51   | 0.01 | 0.52  | -   |
| Ni | 41.84  | 21.9   | 53.27              | 2.34  | 189.7  | 4.3  | 194   | 50  |
| Rb | 24.27  | 24.3   | 8.13               | -0.19 | 34.6   | 6.1  | 40.7  | -   |
| Zr | 4.06   | 1.7    | 6.38               | 3.09  | 29.5   | 0.1  | 29.6  | -   |
| Mo | 1.67   | 1.35   | 1.35               | 2.76  | 6.44   | 0.52 | 6.96  | -   |
| Cd | 0.23   | 0.17   | 0.25               | 3.27  | 1.27   | 0.01 | 1.28  | 30  |
| Sn | 7.28   | 4.8    | 8.06               | 2.17  | 35.04  | 0.76 | 35.8  | -   |
| Sb | 1.38   | 0.87   | 1.25               | 1.94  | 5.62   | 0.15 | 5.77  | -   |
| Bi | 0.19   | 0.18   | 0.14               | 2.82  | 0.74   | 0.03 | 0.77  | -   |
| Th | 1.82   | 1.9    | 0.84               | 0.08  | 2.8    | 0.5  | 3.3   | -   |
| U  | 1.1    | 1.2    | 0.34               | -0.22 | 1.2    | 0.5  | 1.7   | -   |

*Skew* skewness, *Var* variance, *Min* minimum, *Max* maximum, *SGV* residential without plant uptake

**Table 4** Spatial characteristics of some “anomalous” soil samples

| Samples | Series | Land use | Origin   | Geology                    | “outliers” | Possible sources of contamination     |
|---------|--------|----------|----------|----------------------------|------------|---------------------------------------|
| 11.1    | B      | PG       | Residual | Volcanic complex of Lisbon | Cr         | Car traffic (100 m from a highway)    |
| 15      | B      | PG       | Residual | Volcanic complex of Lisbon | Ni and Cr  | Car traffic (230 m from a major road) |
| 43      | B      | GD       | Residual | Volcanic complex of Lisbon | Ni         | Car traffic (10 m from a main road)   |

**Table 5** Correlations between minerals and PHE

|              | V     | Cr    | As    | Ba    | Ni    |
|--------------|-------|-------|-------|-------|-------|
| I (%)        | -0.53 | -0.5  | 0.41  | 0.05  | -0.54 |
| Sm (%)       | 0.86  | 0.82  | -0.51 | 0.4   | 0.86  |
| Kao (%)      | -0.62 | -0.59 | 0.23  | -0.72 | -0.59 |
| Sm/Kao       | 0.79  | 0.92  | -0.54 | 0.47  | 0.92  |
| (Sm + Kao)/I | 0.75  | 0.67  | -0.53 | 0.19  | 0.77  |
| Quartz       | -0.58 | -0.57 | 0.04  | -0.59 | -0.57 |

probable risk to human health, mainly to children due to their daily activities and particular behavior. Chromium and Ni are above the SGV in soils of the volcanic complex (geogenic source) and in a public garden near de railway station (anthropogenic source, probably the railway).

**Acknowledgments** The authors acknowledge the Foundation for Science and the Technology (FCT) for their support to the project “URBSOIL—Geochemical survey of Lisbon urban soils”.

## References

- Almeida FM (1986) Geological Map of the Municipality of Lisbon, scale 1/10000. Geological Survey of Portugal, Lisbon
- Benta AARCA (2007) Aspectos do Comportamento Geomecânico da Formação “Argilas de Aveiro”. PhD Thesis, University of Aveiro, Aveiro (in portuguese)
- Bianchini G, Laviano R, Lovo S, Vaccaro C (2002) Chemical–mineralogical characterisation of clay sediments around Ferrara (Italy): a tool for an environmental analysis. *Appl Clay Sci* 2:165–176
- Biasioli M, Barberis R, Ajmone-Marsan F (2006) The influence of a large city on some soil properties and metals content. *Sci Total Environ* 356:154–164
- Cachada A, Rodrigues SM, Mieiro C, Ferreira da Silva E, Pereira E, Duarte AC (2009) Controlling factors and environmental implications of mercury contamination in urban and agricultural soils under a long term influence of a chlor-alkali plant in the North-West Portugal. *Environ Geol* 57:91–98
- Galhano C, Rocha F, Gomes C (1999) Geostatistical analysis of the Influence of textural, mineralogical and geochemical parameters on the geotechnical behavior of the “Clays Aveiro” formation (Portugal). *Clay Miner.* 34:109–116
- Han Y, Cao J, Posmentier ES, Fung K, Tian H, An Z (2008) Particulate-associated potentially harmful elements in urban road dusts in Xi’an, China. *Appl Geochem* 23:835–845
- Lima RMF, Luz JAM (2001) Análise Granulométrica por técnicas que se baseiam na sedimentação gravitacional: Lei de Stokes. *Ver Esc Minas* 54(2):7
- Ljung K, Agnes O, Menno D, Olle S, Marika B (2007) Bioaccessibility of metals in urban playground soils. *J Environ Sci Health A* 42:1241–1250
- Madrid F, Biasioli M, Ajmone-Marsan F (2008) Availability and bioaccessibility of metals in fine particles of some urban soils. *Arch Environ Contam Toxicol* 55:21–32
- Martins V, Dubert J, Jouanneau J M, Weber O, Silva EF, Patinha C (2007) A multiproxy approach of the Holocene evolution of self-slope circulation on the NW Iberian Continental Shelf. *Marine Geology*, pp 1–18
- Mellinger RM (1979) Quantitative X-ray diffraction analysis of clay minerals An evaluation. Saskatchewan Res. Council, Canada, SRC Report G-79:1–46
- Moya J, Bearer CF, Etzel RA (2004) Children’s behavior and physiology and how it affects exposure to environmental contaminants. *Pediatrics* 113(4):996–1006
- Norra S, Lanka-Panditha M, Kramar U, Stüben D (2006) Mineralogical and geochemical patterns of urban surface soils, the example of Pforzheim, Germany. *Appl Geochem* 21:2064–2081
- Oliveira A, Rocha F, Rodrigues A, Jouanneau J, Dias A, Weber O, Gomes C (2002) Clay minerals from the sedimentary cover from the Northwest Iberian shelf. *Prog Oceanogr* 52:233–247
- Prazeres C, Batista MJ, Patinha C, Reis AP, Cachada A, Silva ES, Duarte A, Sousa AJ, Figueira R, Sérgio C (2009) Urban Geochemistry: a support to future health studies in Lisbon, Portugal
- RA DEF (2002) Soil guideline values for chromium, lead, arsenic, nickel cadmium and selenium. Environ Agency, Bristol
- Reis AP, Patinha C, Sousa AJ, Bartolomeu S, Silva EA, Cachada A, Batista MJ, Prazeres C (2010) Environmental urban geochemistry at Lisbon City: dispersion patterns of metal-laden ground-level dusts. Book of abstracts of the SEGh-2010, June 27–July 2, Galway, pp 77–78
- Salminen R, Batista MJ, Demetriades A, Lis J, Tarvainen T (2005) Sampling. In: Salminen R (ed) *Geochemical atlas of Europe. Part 1: background information, methodology and maps*, Espoo, Finland, Geological Survey of Finland
- Schultz LG (1964) Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. US Geological Survey Professional Paper, vol 391C, pp 1–31
- Schumacher BA (2002) Methods for determination of total organic carbon (TOC) in soil and sediments. Ecological Risk Assessment Support Centre, USEPA
- Sheppard SC (1995) A model to predict concentration enrichment of contaminants on soil adhering to plants and skin. *Environ Geochem Health* 17:13–20
- Sultan K (2010) Clay mineralogy of central Victorian (creswick) soils: clay mineral contents as a possible tool of environmental indicator. *Soil Sediment Contam* 15:339–356
- Thorez J (1976) Practical identification of clay minerals a handbook for teachers and students. In: Lelotte G (ed) *Clay mineralogy*. Dison, Belgique
- Wang XS, Qin Y, Chen YK (2006) Heavy metals in urban roadside soils, part 1: effect of particle size fractions on heavy metals partitioning. *Environ Geol* 50:1061–1066. doi:10.1007/s00254-006-0278-1