Source and pathway analysis of lead and polycyclic aromatic hydrocarbons in Lisbon urban soils

Amélia Paula Reis [a*], Thomas Shepherd [b], Geoff Nowell [b], Anabela Cachada [c], Armando Costa Duarte [c], Mark Cave [d], Joanna Wragg [d], Carla Patinha [a], Ana Dias [a], Fernando Rocha [a], Eduardo Ferreira da Silva [a], António Jorge Sousa [f], Cátia Prazeres [g], Maria João Batista [g]

[a] *GEOBIOTEC, Departmento de Geociências, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*
[b] *Department of Earth Sciences, Durham University, Durham DH1 3LE, United Kingdom CESAM,*
[c] *Departmento de Química, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193, Aveiro, Portugal*
[d] *British Geological Survey, Keyworth, Nottingham, NG12 5GG, United Kingdom*
[e] *CERENA, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001, Lisboa, Portugal*
[g] *LNEG, Estrada da Portela, Zambujal, 2720-866 Amadora, Portugal*
* corresponding author; email: pmarinho@ua.pt

Abstract

One hundred soil samples were collected from urban spaces, in Lisbon, Portugal, in two surveys that were carried out in consecutive years, to assess the potential adverse human health effects following exposure to potentially toxic elements and organic compounds in the urban soils. The study hereby described follows on from the earlier work of the authors and aims at performing a source-pathway-fate analysis of lead (Pb) and polycyclic aromatic hydrocarbons (PAHs) in the urban soils in order to increase current knowledge on factors influencing exposure of the population. Various techniques were combined to achieve the proposed goal. Geogenic and anthropogenic sources were apportioned by means of Pb isotope mixing models. Isotope data was further coupled with geographic information system mapping to assess local mixed sources of Pb and PAHs. Unleaded vehicle exhaust and cement production show the largest relative contribution to the total soil-Pb, but their respective importance depends on factors such as location and urban landscape. The primary sources of PAHs to the urban soils are probably air and land traffic. Multivariate analysis was used to investigate which soil properties could influence mobility and fate of the contaminants. Whilst principal components analysis indicates carbonates and other calcium phases as probable factors controlling the dispersion of Pb in the urban soils, the linear models obtained from stepwise multiple regression analysis show that soil phosphorous (P) and manganese (Mn) are good predictors of the total soil Pb content. No robust model was obtained for the PAHs, impeding identifying environmental factors most likely to influence their dispersion in the urban soils. The solid-phase distribution study provided critical information to untangle the, at a first glance, contradictory results obtained by the multivariate analysis. Carbonates and other calcium phases, having these a probable anthropogenic origin, are soil components containing major fractions of Pb, P, and Mn.

Keywords: lead isotope ratios, source apportionment, statistical techniques, geographical information system, spatial modelling, solid-phase fractionation study

1. Introduction

Recent studies have focused on identifying the distribution of environmental contaminants in cities and on untangling the factors that cause exposure of human populations (Cave et al., 2013; Fillipeli et al., 2012; Norra et al., 2006). Urban soils have been in the spotlight as they play an important role in maintaining the environmental quality by acting both as source and sink for pollutants that can easily affect human health (Biasioli et al., 2006). The polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants that have been found to have toxic, mutagenic, and carcinogenic properties. Consequently, due to their frequency and/or risk, 16 PAHs are selected as the priority pollutants by the U.S. Environmental Protection Agency (Ma et al., 2009; Siciliano et al., 2010; Thavamani et al., 2011). As PAHs, lead (Pb) is a ubiquitous environmental pollutant and its adverse health effects are well documented. Exposure to Pb is linked to severe cognitive and behavioural deficits, especially in young children (Chiodo et al., 2007). Thus, the identification of hotspots (areas of high accumulation of potentially toxic substances) is important both to protect residents as for informed effective policy. Notably, although such environmental burdens are long known as human health threats in cities, and particularly among vulnerable age groups such as young children, they are still poorly understood from an exposure standpoint. Such knowledge gap is likely related to the fact that, in urban environments geochemical processes do not operate alone, and the combination of complex source factors, concentrated populations, and highly variable landscape features, greatly influence transport and fate of the contaminants (Fillipeli et al., 2012; Schwarz et al., 2012). Thereupon, a comprehensive source-pathway-fate analysis is required if further knowledge on factors likely to control human exposure is the endpoint.

The three main exposure pathways to humans are via ingestion, inhalation and dermal absorption (Environment Agency, 2009a). Whilst various studies available from literature indicate the ingestion of playground soil as key pathway of childhood exposure to Pb (De Miguel et al., 2007; Khan et al., 2016; Reis et al., 2014a), new lines of evidence suggest that for PAHs, such as benzo[a]pyrene (BaP), the three pathways may be of concern (Beriro et al., 2016; Wang et al., 2011; Yang et al., 2014).

Unlike soils in rural areas, the urban soils are usually a heterogeneous mixture of earth and man-made materials where environmental contaminants tend to accumulate following emission from a variety of anthropogenic sources. Environmental Pb and PAHS originate from both anthropogenic sources and natural sources. While PAHs are formed as by-products of incomplete combustion of organic materials, Pb is a natural constituent of the Earth's crust commonly found in soils, plants, and water at trace levels (Cheng et al., 2010; Nam et al., 2003). Major anthropogenic PAHs sources include vehicle emissions, coal and fossil fuel powered generation, petroleum refining, straw and firewood burning, industrial processing, chemical manufacturing, oil spills and coal tars (Nam et al., 2003; Peng et al., 2011). Anthropogenic Pb inputs come from different activities such as lead ore mining and smelting, ferrous and non-ferrous metal manufacturing plants, coal and alkyl-lead petrol burning, waste incineration, leaded glass, lead oxide pigments and ferroalloys, metal fabricating industries, and cement manufacture (Álvarez-Iglesias et al,. 2012; Chen et al,. 2005a; Chiaradia and Cupelin 2000; Diaz-Somoano et al., 2009; Monna et al., 1997). Thereupon, various anthropogenic processes, such as industrial and motor vehicle emissions, waste incineration, smelting, and coal combustion have been adding to the environment potentially toxic elements (PTEs) such as Pb,

zinc (Zn) and cadmium (Cd) along with PAHs. Consequently, PAHs have often been found to co-exist with PTEs due to similar pollution sources (Morillo et al. 2008; Thavamani et al. 2012).

Given the multiplicity of probable anthropogenic sources that are characteristic of urban environments, Pb isotopic studies provide a convenient approach for tracing and quantifying mixed sources of Pb in soils, which can contribute to understanding factors influencing exposure. Although Pb sources have been largely studied in many cities (Chiaradia and Cupelin 2000; Li et al., 2015; Rodríguez-Seijo et al., 2015), to the best of our knowledge this has not been characterised for the urban soils of Lisbon. A few recent studies suggest however coal combustion, vehicular traffic, cements production, waste incineration and industrial emissions as probable sources of a variety of PTEs, including Pb, and/or PAHs, in the city of Lisbon (Cachada et al., 2012; Vieira et al., 2006).

It is now widely recognised that the mobility, bioavailability and toxicity of pollutants in soils strongly depend on the combined action of various factors, including the nature of the hazardous substance and its concentration in the soil, the physicochemical properties of the soil, as well as on the specific chemical forms and binding state (e.g. precipitated with primary or secondary minerals, complexed by organic ligands) of the contaminant in the soil (Gleyzes et al., 2002; Reis et al., 2014a). A widely-used technique for understanding element distribution in the solid phase (known as fractionation) is based on the application of sequential selective chemical extractions (Denys et al., 2007; Patinha et al., 2015a; Reis et al., 2012). However, several limitations are often associated with selective chemical extractions and the great variety of protocols that have been developed reflects the complexity of the problems involved (Cave et al., 2004; Gleyzes et al., 2002). A large proportion of extraction schemes is based on the method of Tessier et al. (1979), which involves the selective extraction of elements through the use of a specific reagent for each phase association. Cave et al. (2004) proposed a non-selective methodology called the Chemometric Identification of Substrates and Element Distributions (CISED). The procedure no longer requires the chemistry of the reagents to be specific as this is now carried out mathematically by the chemometric analysis. Recent studies have shown the CISED to be a useful methodology for understanding the solid-phase fractionation of PTEs and its influence on their bioavailability (Cox et al., 2013; Palumbo-Roe et al., 2013; Reis et al., 2014b).

Risk assessment studies encompassing the three pathways of exposure (ingestion, inhalation and dermal absorption) to PTEs and organic compounds carried out by the authors in the city of Lisbon have suggested that there is some health risk associated with the ingestion of Pb and PAHs in the urban soils (Cachada et al. 2013; Reis et al. 2014a). Thus, understanding factors that cause exposure of human population, and children in particular as the most vulnerable receptor, seemed of paramount importance. The present paper follows on from the earlier work of Cachada et al. (2013) and Reis et al. (2014b), utilising soil samples resulting from two similar environmental surveys carried out in the city of Lisbon. The main aim of the study herein described was performing a source-pathway-fate analysis of Pb and PAHs in urban soils that in their majority were collected from outdoor recreational areas, to increase current knowledge on their potential impacts on the health of the population. Statistical techniques, spatial modelling, GIS, Pb stable isotopes and solid-phase fractionation studies were combined to achieve the proposed goal.

2. Material and methods

2.1 The study area

Lisbon is the largest Portuguese city, has an area of 284 km^2 and roughly half a million inhabitants. The urban area encompasses an old centre, in the southern part of the city, which was developed in proximity and facing the Tagus estuary. Smaller districts and higher population densities, narrow streets and higher housing density, characterise the old city centre. The majority of small public gardens and playgrounds are located in this area (Fig. 1).

Irrespective of some exceptions, the soil collected from different urban areas comprise a mixture of materials such as soil minerals, organic materials, pavement debris, building materials (bricks, paint, concrete, metal, cement), urban waste and ash, and can be classified as technosols (IUSS 2015). Yet, in soils collected from playgrounds inside Monsanto, which has an approximate area of 10 km^2 and is the largest green park of the city, the geochemistry and mineralogy have similar signatures to the underlying bedrock, the volcanic complex of Lisbon (Costa et al., 2012).

The climate is of the Mediterranean type and is characterised by its mild temperatures and two well-marked seasons: a hot, dry summer and a rainy winter with lower temperatures (Costa et al., 2012). Average annual rainfall is usually less than 800mm, unevenly distributed throughout an approximate number of 90 days per year (Alcoforado, 1992). In Lisbon the dominant wind directions are in the range N – N40ºW although during the second sampling campaign the wind was blowing mainly from the northeast.

2.2. Sampling sites, sampling collection and preparation

The sampling surveys were carried out in July of 2007 and November of 2008. The 100 soil samples used in this study were collected from urban playgrounds, gardens and parks, school playgrounds and the international airport of Lisbon. A few road-side samples were also collected adjacent to some of the main streets of the city (Fig. 1).

Samples were collected and processed as previously described in Cachada et al. (2012, 2013) and Reis et al. (2014a). In the laboratory, a representative amount of the <2 mm soil size fraction was ground to a fine powder in an agate mill and used to determine total concentrations of the contaminants and other physicochemical properties of the soil.

2.3. Physicochemical analyses

Textural features of the urban soils were determined in all samples as percentages of sand, silt and clay, as previously described in Costa et al. (2012).

Elemental analysis of carbon, nitrogen, hydrogen and sulphur (C, N, H, and S), total soil organic carbon (TOC), cation exchange capacity (CEC) and the exchangeable cations, and soil pH were measured using standard protocols (Reis et al., 2014a,b).

Soil samples were digested using *Aqua Regia* at 95ºC and the analysis of the 29 chemical elements used in this study, including Pb, was carried out by ICP-MS (Cachada et al., 2013; Reis et al., 2014a, b). The contents of 16 priority PAHs (acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, BaP, chrysene, dibenzo[ah]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene and pyrene) were quantified by GC-MS

following an extraction with hexane and acetone and a solid phase extraction clean-up, as described by Cachada et al (2012).

Quality assurance and quality control procedures included the analysis of laboratory replicates, sample duplicates, blanks and certified soil reference materials, such as Soil S1 (Laboratory of Radiometric Analysis, Krakow, Poland), 7002 (Analytika Co. Ltd, Czech Republic) and NCSZC73004 (China National Analysis Centre for Iron and Steel, China) for Pb, and RTC-CRM124-100 for PAHs (Cachada et al., 2012, 2013; Reis et al., 2014a, b).

Pb isotopes were measured at Durham University where a subset of eight soil samples, from the total under study, were prepared for Pb isotope analysis using conventional nitric acid dissolution techniques followed by bromination of the Pb and standard separation on anion exchange columns. In each case, representative sub-samples were taken based on pre-determined Pb concentrations to yield approximately 50–100 ng Pb for analysis. Routine laboratory blanks using comparable resin columns were better than 0.1 ng Pb. Thus blank corrections for the soil and dust samples were considered to be very small. Isotope compositions were measured using a Thermo Neptune ICP-multi-collector mass spectrometer and reported as $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}/Pb$, $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$ ratios. For each analytical session, multiple analyses of the international Standard Reference Material NBS981 gave average 2σ errors <0.01% for all five ratios. Data were corrected for mass discrimination using thallium $^{205}Tl/^{203}Tl$ as an internal standard (Ketterer et al., 1991). In addition to total soil Pb contents, other criteria such as location and land-use were also decisive to select the sub-set of eight samples.

The solid-phase fractionation of Pb and other elements considered to be relevant for interpretation purposes was carried out in a subset of seven samples by means of a non-selective sequential chemical extraction called CISED, as described by Reis et al. (2014b). The CISED procedure uses Aqua Regia at increasing concentrations to dissolve out the different soil phases. Following analysis of each acid extract for both its major and trace element content, the self-modelling mixture resolution (SMMR) algorithm is used to determine how many phases are dissolved and how much of each phase is dissolved by a particular acid strength (Wragg and Cave 2012). The land-use, the total PTEs concentrations, and their bioaccessible fraction were the criteria used to select the seven samples, which mainly correspond to playgrounds in urban gardens and schools as children were the receptor of concern (Reis et al. 2014b).

2.4 Lead source identification

Previous studies have shown that stable isotopes of Pb allow the discrimination of Pb from anthropogenic or geogenic origin. This is based on the premise that Pb emitted into the atmosphere maintains a characteristic isotopic composition that does not change during the physical or physicochemical processes associated with anthropogenic activities (Ettler et al., 2004; Li et al., 2011). Based on the abundances of ^{206}Pb, ^{207}Pb, and ^{208}Pb measured in the samples, contributions from major Pb sources (natural or anthropogenic) can be apportioned. Different systems of equations have been used to estimate the relative contribution of potential Pb sources. While the well-known simple binary model (Monna et al., 1997) allows the approximate contribution of two end-members (e.g. natural vs anthropogenic) to be calculated, more elaborated approaches such as the three-end-member model (Cheng et al., 2010; Li et al., 2011) have the potential to rank relevant anthropogenic Pb sources that further supports the development of strategies to reduce human health risks. However, it is well established that

these models work satisfactorily only if the isotopic signatures of the end-members are significantly different (Etler et al., 2004; Monna et al., 1997).

In this study, the Pb isotopic signatures in the soils (^{206}Pb/^{207}Pb vs. ^{208}Pb/^{206}Pb) do not follow a linear trend, which indicates that different mixing lines are necessary to model the Pb mix in the urban soils of Lisbon. Thereupon, for a subset of five samples from the eight under investigation, a binary mixing model between unleaded vehicle exhaust and natural Pb was used to estimate relative contributions of natural vs anthropogenic sources. The apportionment of Pb originating from the two sources was carried out with the following conventional mixing equation (Etler et al,. 2004; Monna et al., 1997):

$$X_A = \frac{\left(^{206}Pb/^{207}Pb\right)_{soil} - \left(^{206}Pb/^{207}Pb\right)_B}{\left(^{206}Pb/^{207}Pb\right)_A \left(^{206}Pb/^{207}Pb\right)_B} \tag{1}$$

where X_A is the relative contribution of unleaded vehicle exhaust, $(^{206}$Pb/^{207}Pb$)_{soil}$, $(^{206}$Pb/^{207}Pb$)_A$ and $(^{206}$Pb/^{207}Pb$)_B$ are isotopic ratios in the sample, end-member A (unleaded vehicle exhaust) and end-member B (natural Pb), respectively.

Hereupon, for three of the eight soil samples under study, a ternary model was developed from the three-end-member mixing line shown by the three-isotope plot (^{206}Pb/^{207}Pb vs. ^{208}Pb/^{206}Pb) to calculate the approximate contribution of three potential sources (Cao et al., 2014; Cheng et al,. 2010), which can be written as follows:

$$(^{206}Pb/^{207}Pb)_{Soil} = (^{206}Pb/^{207}Pb)_1 \times f_1 + (^{206}Pb/^{207}Pb)_2 \times f_2 + (^{206}Pb/^{207}Pb)_3 \times f_3 \tag{2}$$

$$(^{208}Pb/^{206}Pb)_S = (^{208}Pb/^{206}Pb)_1 \times f_1 + (^{208}Pb/^{206}Pb)_2 \times f_2 + (^{208}Pb/^{206}Pb)_3 \times f_3 \tag{3}$$

$$f_1 + f_2 + f_3 = 1 \tag{4}$$

where the subscript soil represents the soil sample, the subscripts 1, 2, and 3 represent the potential sources (European leaded petrol, cement and natural Pb, respectively), and $f1$, $f2$ and $f3$ are their relative contribution to the total soil Pb content.

2.3. Statistical analysis and spatial modelling

Relationships between the different quantitative variables measured in the topsoil samples were investigated using multivariate analysis. Principal Components Analysis (PCA) is a mathematical technique adapted to quantitative variables that, in its essence, transforms n possibly correlated variables into a (smaller) number of uncorrelated variables referred to as principal components (Jolliffe 2002). Analysing the relationship between each original variable with the first (and more important) PCA components it is possible to visualise the relationships between the n variables in simple bi-plots. The analysis was performed using the AnDad (v. 7.12) free software package. The data matrix used in the PCA analysis has comprised several physicochemical properties of the soil, the soil Σ16PAHs contents, as well as major, minor and trace elements concentrations.

Ordinary kriging was used to interpolate the concentrations of Pb and Σ16PAHs at point locations that were not sampled, to ascertain spatial distribution patterns of these environmental contaminants in the urban soils of Lisbon. The principle behind kriging is that samples distributed close together in space are more likely to be similar, compared with those that are further apart. The interpolation method uses a semivariogram to describe the spatial relationship between samples with regard to the distance between them (Goovaerts 1999; Reis et al., 2007).

The spherical models fitted to the experimental semivariograms produced the minimum prediction errors (based on measures of root-mean-square and average standard error of cross-validation) in comparison with other models. Although the spherical model is used for all studied variables, the parameters of the semivariograms differ between variables. Theoretical models of spatial continuity, interpolation by ordinary kriging and geochemical maps were obtained using the ESRI®ArcGis for Desktop (v.10.2) software package.

Multiple linear regression analysis (MLR) aimed at investigating environmental factors likely to influence the mobility and fate of Pb and PAHs. Hence, the analysis in IBM SPSS (v. 21) was used to model the relationship between Pb and PAHs concentrations, and the physicochemical properties of the soil, in the set of 100 soil samples. The independent variables under investigation have included manganese (Mn) and major elements (iron [Fe], aluminium [Al], magnesium [Mg], phosphorous [P], potassium [K], titanium [Ti], calcium [Ca] and sodium [Na]), TOC, C_{inorg}, TC, TN, TH, TS, CEC and exchangeable cations. The criteria for stepwise MLR were: probability of F to enter ≤ 0.05 and probability of F to remove ≥ 0.1. The Durbin-Watson test assures the absence of first-order linear autocorrelation in our multiple linear regression data. In the MLR analysis, models having an ANOVA p-value for an independent variable above 0.05 ($p > 0.05$) were discarded and the MLR analysis was repeated after removing the independent variable. Residuals plots were used to assess whether residuals were approximately normally distributed.

3. Results and discussion

3.1. Textural and physicochemical characteristics of the urban soils

Summary statistics for selected physicochemical properties determined in the soil samples (n=100) are provided in the form of supplementary material (Table S1).

Soil pH values range from slightly acidic to neutral or nearly neutral and show a small variability. The CEC of the soil is usually elevated (median value of 17.52%) and Ca is clearly the predominant exchangeable cation (median value of 17.71%). Elemental concentrations of C are higher than those of N, H and S. Abundances of inorganic and organic forms of carbon (C_{inorg} and TOC) range from low to median values. The textural classes of soils, as defined by the USDA system, vary from fine sand to silty-clay, whereas the most frequent size fraction is sandy-loam.

Table 1 shows summary statistics for total concentrations of Pb and PAHs in the 100 soil samples under study. Additional information on individual PAHs that were analysed in this study are provided in the form of supplementary material (Table S2). Although the concentrations measured in the urban soils of Lisbon are not elevated (Pb: median= 61 mg kg^{-1}; Σ16PAHs: median= 563 μg kg^{-1}), they are above the values reported in a few studies for different urban areas. However, median values for concentrations of PAHs in Beijing (Peng et al., 2011) and Pb in Newcastle (Okorie et al., 2011), are well above the ones obtained for the urban soils of Lisbon.

3.2. Relationships between Pb, PAHs, soil chemistry and other measured soil properties

Information on total concentrations is useful to identify potential metal sources. Understanding significant relationships between variables (physicochemical properties, PTEs and PAHs

concentrations), between individuals (soil samples), and between variables and individuals of a given dataset, may provide further knowledge on potential sources (Yongming et al., 2006; Reis et al., 2009, 2015). In this study, such associations were investigated using PCA.

The first three components produced by the PCA analysis account for ca. 62% of the total variance, and were therefore investigated. Figure 2 displays the projections of variables (Fig. 2A) and samples (Fig. 2B) in the first principal components plane (PC1/PC2). Loadings of the variables in the three PCA components under investigation are provided in the form of supplementary material (Table S3).

CEC, TH, exchangeable Ca (ExchCa), exchangeable Mg (ExchMg), P, barium (Ba), strontium (Sr), Na and a cluster comprising several chemical elements (cluster I in Fig. 2A) that are clearly associated, are negatively correlated with PC1 (Fig. 2A). Soil samples with higher negative PC1 scores, which are highlighted by the dashed line in Fig. 2B, were collected from the Monsanto natural park. Thus, more elevated values for variables correlated with PC1 probably occur in these soils. Furthermore, less elevated values of the same variables occur in urban soils with a fine sand texture (grey squares in the positive semi-axis of PC1). The chemical composition of cluster I that includes elements such as chromium (Cr), nickel (Ni), vanadium (V), Fe and Mg, suggests ferromagnesian compositions, which is coherent with the geology of Monsanto (the volcanic complex of Lisbon). Hence, PC1 probably discriminates soils that are less disturbed by anthropogenic activities and still preserve a natural geochemical signature (the bedrock of Monsanto), and is therefore interpreted as a geogenic component.

TC, TOC and C_{inorg}, $\Sigma16$PAHs, sulphur (S), Ca, zinc (Zn), copper (Cu), cadmium (Cd), Pb, antimony (Sb) and bismuth (Bi) are negatively correlated with PC2 (Fig. 2A). Samples with higher negative PC2 scores correspond to soils collected from the international airport (US20), from four small urban playgrounds in the city centre (US38, US47, US48 and US49), and from the Monsanto park (US14). The joint analysis of both bi-plots (2A and 2B) allows associating more elevated values of the aforementioned variables to these samples. Although sample US14 was collected from Monsanto, the site is often used for barbeques and at the time of soil collection significant amounts of burned biomass were observed in the topsoil, which can explain the association of this soil sample to PC2 (and to TC and TOC). The association between Ca and C_{inorg} suggests the presence of carbonates in the soil mineralogy. The group of chemical elements correlated with PC2, which mainly comprises PTEs, allows interpreting this component as having an anthropogenic character. Hence, samples and variables associated with PC2 are likely to be related to polluting activities. Projections in the second principal components plane (PC1/PC3) that accounts for ca. 46% of the total variance (Table S3) further associate TH, CEC and ExchCa to cluster I (not shown), indicating that the soils of Monsanto have more elevated cation exchange capacity.

A previous study carried out in the area focusing on soil mineralogy, utilised soil chemistry and clay mineralogy to trace the origin of the urban soils (Costa et al., 2012). Although it was not possible to achieve a conclusive result for the majority of the soil samples under study, coupling soil geochemistry and clay mineralogy were decisive to conclude that current soils from playgrounds inside Monsanto were formed by weathering of the underlying geologic units, the basalts of the volcanic complex. Furthermore, the amount of smectite in the Monsanto soils seem to be directly correlated with more elevated CEC. Hence, the results obtained by PCA in the present study are in agreement with the ones of Costa et al. (2012), and PC1 can be interpreted as a geogenic component, discriminating less disturbed soils. Other authors have

come to the conclusion that, despite pollution, urban surface soils can still reflect the chemical composition of the underlying geological units (Norra et al., 2006).

Carbonates such as calcite and dolomite are often important mineral phases in the soil samples of Lisbon (Costa et al., 2012), which explains the association between Ca and Cinorg that is observed in Fig. 2A. The association of Pb, TC, TOC and Cinorg with PC2 indicates that organic and inorganic forms of carbon are the most likely controls on the mobility of Pb (less evident for PAHs in Fig. 2A), and therefore of its bioavailability, in the surface environment. This result is in agreement with that of a previous study by Reis et al. (2014a), which has indicated a correlation between the bioaccessibility of Pb and the relative proportion of carbonates in the soil samples. Furthermore, the correlation of Ca with a component (PC2) that is interpreted as anthropogenic suggests that Ca-phases of anthropogenic origin (e.g. cement, limestone pavement debris, and concrete) may exist in these soils. Indeed, the relatively high pH values (Table S1) measured in soil samples that in their majority have a silicate composition (Costa et al., 2012) may be explained by the presence of extraneous materials, such as cement and construction debris(Biasioli et al., 2006), which highlights the importance of these anthropogenic soil-phases in the biogeochemistry of PTEs such as Pb.

3.3. Potential Pb sources and tentative source apportionment

Previous studies have been suggesting that probable sources of Pb in the city of Lisbon include geogenic as well as anthropogenic sources such as vehicular traffic, urban waste incineration, coal combustion, industrial emissions and cement production (Cachada et al., 2013; Vieira et al. 2006). For PAHs, the most likely anthropogenic sources are vehicular traffic, urban waste incineration and industrial emissions (Cachada et al., 2012). Hence, according to information available from the literature, potential sources of mixed Pb and PAHS pollution in Lisbon are Whilst data for Pb isotope ratios of industrial sources is subject to large variation (different industrial sources show variable isotopic compositions) resulting in a number of wide-ranging investigations in many countries (Chiaradia and Cupelin 2000; Etler et al., 2004, Monna et al., 1997; Rodríguez-Seijo et al., 2015), Pb isotopes data on industrial sources in Portugal available from literature is limited. Furthermore, local heavy pollutant industries have been displaced to neighbouring areas and, currently, major sources of Pb to the soils of the city may not include industrial emissions. Nonetheless, anthropogenic Ca in atmospheric aerosol samples from Lisbon has been attributed to cement production in Alhandra (Vieira et al., 2006), a city located 17 km northeast from Lisbon, which is in agreement with the results obtained by PCA (section 3.2) that suggest an anthropogenic origin for Ca-phases in the urban soils under investigation. Given that a variety of studies indicate cement as a probable source of Pb in different environmental media (Li et al., 2011; Tan et al., 2006), cement production was taken into consideration as a probable source in the tentative source apportionment used in this study.

Although coal combustion is referred to as an important source of Pb in certain areas, (Diaz-Somoano et al., 2009; Li et al., 2011) it does not seem to be predominant in Lisbon, even though some industries located north from Lisbon use coal combustion (Vieira et al., 2006). Hereupon, Pb isotope ratios of Spanish and Portuguese coals (Diaz-Somoano et al., 2009) are included in this study (Table 2).

The progressive phasing-out of leaded petrol has resulted in a significant decrease in the global atmospheric Pb burden over the last few decades. In Lisbon, however, current perception on environmental Pb contamination still associates this PTE to vehicular traffic. Given the absence

of information regarding the origin of Pb ores used in the Portuguese alkyl Pb additives, their isotopic signature is assumed to be similar to those from other European countries, which show rather small ranges for measured 206Pb/207Pb ratios that point to a relatively homogeneous source (Monna et al., 1997). In addition to leaded petrol, unleaded vehicle exhaust is often indicated as another potential source of anthropogenic Pb (Chen et al., 2005a; Rodríguez-Seijo et al., 2015). Hence, Pb isotope ratios for European leaded petrol (Monna et al. 1997) and vehicle exhaust (Chen et al., 2005a) are used for traffic derived Pb fingerprinting (Table 2).

With the exception of medical waste incineration, which is carried out in an incinerator situated close to the airport (Fig. 1), urban wastes are currently transported to specific industrial facilities outside the city, whereupon they are either recycled or incinerated. Nevertheless, the Pb isotopic composition of incinerated wastes from a Portuguese industrial facility is also included in the study.

The natural Pb component in the soil that derives from weathering of the underlying rock gives the actual geogenic contribution to the total soil Pb content. Yet, to the best of our knowledge, this has not been characterised in the Lisbon area. In order to assess the relative contribution of natural sources, the Pb isotope ratios of sediments from the Portuguese Setúbal–Lisbon canyon and adjacent open shelf and slope areas (Richter et al., 2009), and those of an agricultural soil located approximately 20 km northeast from Lisbon, which was collected for the GEMAS project (Reimann et al., 2014), are used to assess the natural Pb component of the soil. According to Reimann and co-authors (2012), at the European scale, a close relationship of the Pb concentrations and isotopic ratios with geology is preserved in the agricultural soils, suggesting that the majority of Pb in European agricultural soils is at present still of natural origin. Although the selected soil, among the 35 collected in Portugal for the GEMAS project, is not the closest to the city of Lisbon, it is the closest soil with a predominant geogenic contribution to the soil Pb content (Reimann et al., 2012). Its location is provided in the form of supplementary material (Fig. S1).

Soil-Pb isotope compositions are plotted in Fig. 3 that also shows data for the least and the most radiogenic isotopic signatures considered in this study, which are the ones of European leaded petrol and agricultural soil, respectively (Table 2). The Pb isotope ratios of the eight soils range between 1.1546 - 1.1761 (^{206}Pb/^{207}Pb) and 2.0808 - 2.1029 (^{208}Pb/^{206}Pb). The varied isotopic compositions obtained suggest that the Pb content in the soil derives from the combination of different sources, either natural or anthropogenic. Whereas the soils do not plot along a linear mixing line showing instead a polynomial model (Fig.3), different mixing lines are necessary to model the Pb mix in the soils (Haack et al., 2003).

The Pb isotopes ratios of samples US12, US27, US35, US47 and US48 are plotted in Fig. 4A that also shows data for unleaded vehicle exhaust (Chen et al. 2005a), Spanish and Portuguese coal (Diaz-Somoano et al. 2009), Portuguese sediments (Richter et al. 2009) and the GEMAS agricultural soil (Reimann et al. 2014).

For this subset, the soil samples plot along a well-defined correlation line (y= -1.0866x + 3.3638, R^2= 0.98) between the isotopic signature of unleaded vehicle exhaust and the agricultural soil (Fig. 4A). The displacement of the soil-Pb away from natural Pb (represented by the agricultural soil) towards vehicle exhaust-derived Pb indicates the predominance of this as the primary source in these particular samples. According to the two-end-member linear mixing model shown in plot 4A, coal combustion is not a major anthropogenic source of Pb for these soil samples. Given that the isotopic compositions of leaded petrol, cement and waste incineration do not fit well into the two-end-member mixing model, and are therefore irrelevant

to model the Pb mix in these soil samples, such isotopic compositions were not projected in Fig.4A. Using the two potential sources of Pb as end-members (Fig. 4A) and the Pb isotopes ratios of the samples, a binary mixing model was applied (Eq. 1) to calculate the relative contribution of the natural and anthropogenic sources. The isotopic composition of the agricultural soil (Table 2) is assumed to be the end-member B of the binary mixing model (Eq. 1) used to estimate the relative contribution of unleaded vehicle exhaust to the total soil Pb content (Table 3). From the binary mixing model, source apportionment calculations indicate average contributions of 67.7 and 32.3% for unleaded vehicle exhaust and natural Pb, respectively. The anthropogenic source is the main contributor to the total soil Pb content in the subset of five soils under study (Table 3), with values ranging from 52,7 % (soil US12) to 76,4 % (soil US48). In general, higher contributions from vehicle exhaust correspond to soils with smaller distances to the nearest high traffic density road (Table 3).

Fig. 4B shows the Pb isotopes ratios of samples US11, US20 and US23, European leaded petrol (Monna et al. 1997), cement (Chen et al. 2005b), waste incineration, sediments from the Setúbal–Lisbon canyon and adjacent open shelf and slope areas (Richter et al. 2009), and the agricultural soil (Reimann et al. 2014). The Pb isotopic composition of the urban soils forms a linear trend situated along a mixing line between the isotopic composition of cement-derived Pb and offshore Portuguese sediments-Pb. However, from the plot, it is clear that the isotopic composition of the agricultural soil is the one most likely to represent the contribution from natural Pb to the total soil-Pb content. The Portuguese sediments possess less radiogenic isotopic signatures than the agricultural soil, which confirms anthropogenic Pb contributions that have been referred in the literature for the Tagus and Sado estuaries (Mil-Homens et al. 2013; Richter et al. 2009). Thus, it is assumed that the isotopic signature of the agricultural soil is the one actually representing natural Pb sources. But the contribution of petrol derived Pb cannot be excluded from the system because the observed signatures can be reconstructed by three-end-member as well as two-end-member mixing. With regard to other potential anthropogenic sources, the overlapping Pb isotopic signatures obtained for urban waste incineration and soil samples (Fig. 4B) does not allow the contribution of this anthropogenic source to the Pb burden of the urban soils to be calculated. Whilst the contribution of each component cannot be precisely calculated, relative contributions of leaded petrol, cement, and geogenic sources can be estimated, provided that site-specific characteristics are taken into account while performing a critical evaluation of the results. A ternary mixing model (Eqs. 2, 3 and 4) was used to calculate the relative contribution of the natural and anthropogenic sources (Table 3).

The calculations show that the hazardous legacy left by the use of leaded petrol is currently almost negligible, with the exception of soil US11 that has a relative contribution of 26% from leaded petrol to the total Pb content. While cement is the main Pb source in soil US20, the natural Pb component is predominant in soil US23. However, the possibility of overestimated contributions must be acknowledged since a potential contribution from waste incineration could not be assessed.

Given the variability in the relative contributions obtained, the interpretation of the results in their particular context may reveal probable pathways of exposure to environmental Pb while increasing understanding about potential sources. Recent studies have coupled isotopic data with geographic information system (GIS) mapping in source differentiation of Pb pollution in urban environments, to identify hot-spot areas and to assess local pollution sources (Duzgoren-Aydin and Weiss, 2008).

Figure 5 shows the spatial dispersion pattern of Pb (Fig. 5a) and the relative contributions of potential sources to the total Pb content of the eight soils under investigation. The spatial distribution of Pb in soil shows a hot-spot located in the city centre where car traffic is intense. By coupling the interpolated map with the source apportionment data, it becomes clear that samples having higher contribution from unleaded vehicle exhaust (orange coloured in Fig. 5a) are located in areas with more elevated total Pb contents in the soil (samples US35, US47 and US48). The exceptions are the ones of soils US27 and US12 that have less elevated Pb concentrations although vehicle exhaust is the predominant source of Pb. This dissimilar relationship between the contribution from vehicle exhaust and the soil Pb levels can be explained by the characteristic urban landscape of the city centre (high housing and traffic density, narrow and steep roads), where samples US35, US47 and US48 are located, that impedes normal air movements and the consequent dispersion of Pb particles emitted by vehicular traffic. Thereupon, one may assume that, in the city centre, vehicle exhaust emitted Pb probably tends to settle and accumulate in the topsoil close to its source.

Whilst the important contribution of geogenic sources (in green) to the total Pb content of soils US11 and US12 (located inside the Monsanto park) is not an unexpected result, in the airport soils, the significant natural Pb component (Table 3) must be attributed to the particular settings of the airport, which can be characterised as an urban wide-open space, without natural or artificial barriers preventing air movements that promote the dispersion of airborne particle matter.

The important contribution of cement to the Pb burden of the airport soils can either be explained by pavement wear or by the construction works underway during the soil collection survey.

With regard to soil US11, a playground inside the park of Monsanto but only 100 meters away from a major road, the relative contribution of probable anthropogenic sources has to be interpreted with caution. The proximity of high traffic roads combined with the particular characteristics of the Monsanto soils, which are in situ and relatively undisturbed compared to other collected urban soils, largely justify a 26% contribution from leaded petrol to the total soil Pb (Table 3) that stays accumulated in the soil. If the soil geochemistry of the site is influenced by vehicular traffic, a contribution from unleaded vehicle exhaust is to be expected, although it cannot be assessed. Likewise, a potential contribution from urban waste incineration to the total soil Pb content could not be assessed.

An interesting outcome of the source apportionment study is the NE-SW trend observable (Fig. 5) in samples containing an important contribution from cement to the total soil-Pb (US23, US20 and US11). Considering the location of the cement plant in Alhambra, approximately 20 km northeast from Lisbon, and the N - N40ºE wind directions dominant at the time of soil collection (Fig. S1) is likely that cement production is an actual source of anthropogenic Pb to the urban soils of Lisbon. This is in agreement with the findings of Vieira et al. (2006) and further supports the interpretation of the multivariate analysis. PCA shows an association between Ca and Pb and suggests an anthropogenic origin for soil-Ca. The approximate location of the Alhandra cement plant, relative to the study area, is provided in the form of supplementary material (Fig. S1).

Aiming at assessing potential sources of Pb and PAHs mixed pollution, the spatial dispersion pattern of Σ16PAHs is combined with source apportionment data obtained for the eight soils under investigation (Fig. 5b). The dispersion pattern of PAHs shows a hot-spot spatially related to the location of the international airport of Lisbon and a second relevant hot-spot in the city

centre, which is coincident with that of Pb. In addition, concentrations of PAHs (sum of 10) range from 562 to 7264 µg kg^{-1} in samples having a predominant contribution from unleaded vehicle exhaust to the total Pb content. A comparison with the Dutch generic soil quality standards (Swartjes et al. 2012) for the sum of 10PAHs shows that the majority of the soils under study having an important contribution from vehicular traffic have PAHs concentrations close or slightly above the maximum permissible value (6.8 mg kg^{-1}) for "Residential" land use. Hence, the results suggest that unleaded vehicle exhaust is an important source of PAHs and Pb. Assuming that the major source of PAHs in the city is probably the airport of Lisbon (Fig.5b), which is not an important contributor to the soil Pb content, by its nearby location, the medical waste incinerator of Lisbon (Fig. 1) cannot be discarded as a probable source of these organic compounds. The "hot-spot" at the SW corner of the map cannot be considered significant due to the small number of samples used in the interpolation procedure.

3.3. Environmental factors that influence mobility and fate of Pb and PAHs

The assessment of which environmental factors most strongly influence the mobility of Pb and PAHs in the urban soils was carried out by means of a MLR analysis. The linear models obtained are shown in Table 4. R^2 indicates the proportion of the variance in total Pb and PAHs concentrations accounted for by each regression model. All regression models are statistically significant ($p < 0.005$).

However, the Durbin-Watson value of $d = 1.1$ obtained for PAHs models does not fall in the interval defined by the two critical values of $1.5 < d < 2.5$ and, therefore, we must assume that there is a first-order linear autocorrelation in our multiple linear regression data. Hereafter is not possible to conclude that TOC, CEC and TN are robust predictor variables of PAHs concentrations in the urban soils under study.

Stepwise MLR performed for Pb indicates that the predictor variables are soil concentrations of P and Mn, which account for 54% of the total variance. None of the measured soil properties arises as a good predictor of the total soil Pb content, indicating that properties such as TC, TOC and C_{inorg} are not key factors influencing the mobility of Pb, as previously suggested following the interpretation of the PCA results (section 3.1).

Whereas Pb is significantly correlated with P ($r_{Spearman} = 0.67$, p< 0.01) and uncorrelated with Mn ($r_{Spearman} = 0.21$, p> 0.05), further studies are required to better understand factors controlling the mobility of this PTE in the urban soils of Lisbon.

Currently, it is generally recognised that the particular behaviour of PTEs in soil is largely influenced by their specific physicochemical forms and distribution among the different fractions (Reis et al. 2012; Wragg & Cave 2012). Hence, information about the physicochemical forms of Pb in the soil samples is required to understand its environmental behaviour (mobility, pathways, and bioavailability). Thereupon, the solid-phase fractionation of Pb was determined in a subset of seven soil samples as previously described by Reis et al., (2014b). The data are now re-evaluated in the context of the study's recent developments. Distribution plots showing the amount of Pb (mg kg^{-1}) associated with each component extracted by each acid matrix are provided in the form of supplementary material (Figs S2 and S3).

A detailed discussion on the results obtained for the solid-phase fractionation of Pb in individual samples is provided in the form of supplementary material. In general, the CISED data indicates

that minor fractions of Pb are associated to easily extractable phases (residual soil pore-water, exchangeable and carbonate phases) while major fractions of this PTE usually occur in the aforementioned anthropogenic Ca-components. This result is in agreement with those of PCA that show a correlation between Pb and Ca, and further suggest that inorganic forms of carbon are likely controls of the dispersion of Pb The exceptions to this apparently usual distribution are soil US39, where Pb is mainly extracted with an organic soil component, and soils US18 and US47, where Pb is associated to Fe-components made up of Fe, Al, S, Si, Ca, Mg and K, with important amounts of Zn, Cu, Ba, Cr and Li. Recent studies have suggested that all these elements can be linked to vehicle exhaust. Minor components of motor vehicle exhaust particle matter include inorganic species such as sulphate while S is present as an impurity in fuel, and S, P, Ca and Mg are used in additives found in lubricating oil (Dallmann et al. 2014). Ba, Cu, and Fe have been referred as indicators of brake wear while tire wear seems to be an important source of Zn to the environment (Councell et al 2004; Gietl et al. 2010; Patinha et al. 2015b). The assumption that in soil US47 Pb is associated with anthropogenic soil components originated by vehicular traffic is supported by the source apportionment study, which indicates for this sample a 62% contribution (Table 3) from unleaded vehicle exhaust to its total Pb concentration.

Figure 6a displays a distribution plot showing the amount of Pb (mg kg−1) associated with the predominant soil components previously identified (residual soil-pore water, exchangeable, carbonates, Ca-dominated, and oxides), which are the ones assumed to represent the most common components of the urban soils of Lisbon. The plot results from the sum of equivalent soil fractions, sequentially extracted by equivalent acid matrices in soils US5, US8, US14, US18, and US33. Soils US39 and US47, where Pb shows a slightly different solid-phase fractionation, were not considered to estimate the distribution plot presented in Fig. 6. Through the combination of similar Pb distributions that occur in the majority of the studied samples, the graph aims at presenting the likely general trend for the solid-phase fractionation of Pb in the urban soils of Lisbon. A PTE in soil, distributed among different fractions in different forms, has different solubility and reactivity in relation to plant uptake that strongly influence its mobility and fate in the environment. Thus, in order to better understand the role of P and Mn, which were indicated as good predictors of the total soil Pb content in the MLR model (Table 4) and potential controlling factors of its dispersion, Fig 6 also shows the general trend in the solid-phase fractionation of P (Fig. 6b) and Mn (Fig 6c), which was obtained using the approach previously described.

Major fractions of P and Mn are extracted with components 3 and 4 that are assigned as Ca-carbonates and other Ca-dominated phases, respectively. The overall assessment of the distribution of Pb, P, and Mn, among the components extracted by the CISED procedure indicates a similar solid-phase fractionation in the studied soils. Major fractions of these elements are associated with component 4 (Ca, Mg, Al, Si) that is extracted over a broad range of average to strong acid concentrations and assigned as an anthropogenic phase, probably representing oxides and silicates in cement and concrete. Mn and P are minor elements while Ca, Mg, Al, and Si are major elements in cement clinker and lime phase chemistry (Hökfors 2014). Also, a variety of PTEs such as Pb is incorporated in the cement during its production (Schembri et al. 2010). This information, available from the literature, further supports the interpretation of the CISED results. Thereupon, it is reasonable to assume that the key factor influencing the dispersion and fate of Pb in the urban soils of Lisbon is its solid-phase distribution. The broad range of acid concentrations that extracted Pb associated to these Ca-dominated phases suggests metal fractions within different anthropogenic materials having a

distinct solubility, and consequently distinct bioavailability. This is in good agreement with the wide range of values for the bioaccessible fraction of Pb (24-100%) reported by Reis et al. (2014b) for the urban soils of Lisbon and further supports the assumption that soil ingestion is a pathway of exposure to environmental Pb for children while playing in urban recreational areas (Reis et al. 2014a).

The MLR models obtained for soil PAHs contents indicate that there is a first-order linear autocorrelation in our multiple linear regression data, therefore hindering the assumption that TOC, CEC, and TN are robust predictor variables of PAHs concentrations in the urban soils under study.

4. Conclusion

In this study, a combination of statistical analysis, spatial modelling, GIS, Pb stable isotopes and solid-phase fractionation studies is used to perform a source-pathway-fate analysis of Pb and PAHs in urban soils of Lisbon.

Unleaded vehicle exhaust and cement production show the largest relative contribution to the total soil-Pb, but their respective importance depends on factors such as location and urban landscape. Although the primary sources of PAHs to the urban soils are probably air and land traffic, by its nearby location, the medical waste incinerator of Lisbon cannot be discarded as a probable source of these organic compounds. No robust MLR model was obtained for the PAHs, impeding identifying environmental factors most likely to influence their dispersion in the urban soils. Whereas the solid-phase fractionation of Pb seems the key factor influencing its dispersion and fate, the use of a non-selective chemical extraction scheme coupled to chemometric analysis was crucial to discriminate Pb fractions associated with natural and anthropogenic components of the soil.

References

Álvarez-Iglesias, P., Rubio, B., Millos, J., 2012. Isotopic identification of natural vs. anthropogenic lead sources in marine sediments from the inner Ría de Vigo (NW Spain). Sci. Total Environ. 437, 22–35. doi:10.1016/j.scitotenv.2012.07.063

Alcoforado, M. J., 1992. O clima da região de Lisboa. Memória do Centro de Estudos Geográficos, 15, Centro de Estudos Geográficos, Lisboa. (in Portuguese)

Beriro, D.J., Cave, M.R., Wragg, J., Thomas, R., Wills, G., Evans, F., 2016. A review of the current state of the art of physiologically-based tests for measuring human dermal in vitro bioavailability of polycyclic aromatic hydrocarbons (PAH) in soil. J. Hazard. Mater. 305, 240–259. doi:10.1016/j.jhazmat.2015.11.010

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. doi:10.1016/j.scitotenv.2005.04.033

Cachada, A., Pato, P., Rocha-Santos, T., da Silva, E.F., Duarte, A.C., 2012. Levels, sources and potential human health risks of organic pollutants in urban soils. Sci. Total Environ. 430, 184–192. doi:10.1016/j.scitotenv.2012.04.075

Cachada, A., Dias, A.C., Pato, P., Mieiro, C., Rocha-Santos, T., Pereira, M.E., Da Silva, E.F., Duarte, A.C., 2013. Major inputs and mobility of potentially toxic elements contamination in urban areas. Environ. Monit. Assess. 185, 279–294. doi:10.1007/s10661-012-2553-9

Cao, S., Duan, X., Zhao, X., Wang, B., Ma, J., Fan, D., Sun, C., He, B., Wei, F., Jiang, G., 2014. Isotopic ratio based source apportionment of children's blood lead around coking plant area. Environ. Int. 73, 158–166. doi:10.1016/j.envint.2014.07.015

Cave, M.R., Milodowski, A.E., Friel, E.N., 2004. Evaluation of a method for identification of host physico-chemical phases for trace metals and measurement of their solid-phase partitioning in soil samples by nitric acid extraction and chemometric mixture resolution. Geochemistry Explor. Environ. Anal. 4, 71–86. doi:10.1144/1467-7873/03-025

Cave, M.R., Wragg, J., Harrison, H., 2013. Measurement Modelling and Mapping of Arsenic Bioaccessibility in Northampton, UK. J. Environ. Sci. Heal. PART A TOXIC Hazard. Subst. Environ. Eng. 48, 629–640.

Chen, J., Tan, M., Li, Y., Zhang, Y., Lu, W., Tong, Y., Zhang, G., Li, Y., 2005. A lead isotope record of Shanghai atmospheric lead emissions in total suspended particles during the period of phasing out of leaded gasoline. Atmos. Environ. 39, 1245–1253. doi:10.1016/j.atmosenv.2004.10.041

Chen, J., Tan, M., Lu, W., Li, Y., Zhang, G., Li, Y, 2005b, Measurements of Lead Isotope Ratio in Cement by Inductively Coupled Plasma Mass Spectrometry. Chinese Journal of Analytical Chemistry, 33(7): 943-946

Cheng, H., Hu, Y., 2010. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: A review. Environ. Pollut. 158, 1134–1146. doi:10.1016/j.envpol.2009.12.028

Chiaradia, M., Cupelin, F., 2000. Behaviour of airborne lead and temporal variations of its source effects in Geneva (Switzerland): Comparison of anthropogenic versus natural processes. Atmos. Environ. 34, 959–971. doi:10.1016/S1352-2310(99)00213-7

Chiodo, L.M., Covington, C., Sokol, R.J., Hannigan, J.H., Jannise, J., Ager, J., Greenwald, M., Delaney-black, V., 2007. Blood lead levels and specific attention effects in young children. Neurotoxicol. Teratol. 29, 538–546. doi:10.1016/j.ntt.2007.04.001

Cipurkovic, A., Trumic, I., Hodžic, Z., Selimbašic, V., Djozic, A., 2014. Distribution of heavy metals in Portland cement production process. Adv. Appl. Sci. Res. 5, 252–259.

Councell, T.B., Duckenfield, K.U., Landa, E.R., Callender, E., 2004. Tire-wear particles as a source of zinc to the environment. Environ. Sci. Technol. 38, 4206–4214. doi:10.1021/es034631f

Costa, C., Reis, A. P., Ferreira da Silva, E., Rocha, F., Patinha, C., Dias, A. C., Sequeira, C., Terroso, D., 2012. Assessing the control exerted by soil mineralogy in the fixation of potentially harmful elements in the urban soils of Lisbon, Portugal. Environ. Earth Sci. 65, 1133–1145. doi:10.1007/s12665-011-1362-8

Cox, S.F., Chelliah, M.C.M., McKinley, J.M., Palmer, S., Ofterdinger, U., Young, M.E., Cave, M.R., Wragg, J., 2013. The importance of solid-phase distribution on the oral bioaccessibility of Ni and Cr in soils overlying Palaeogene basalt lavas, Northern Ireland. Environ. Geochem. Health 35, 553–567. doi:10.1007/s10653-013-9539-6

Dallmann, T.R., Onasch, T.B., Kirchstetter, T.W., Worton, D.R., Fortner, E.C., Herndon, S.C., Wood, E.C., Franklin, J.P., Worsnop, D.R., Goldstein, A.H., Harley, R.A., 2014. Characterization of particulate matter emissions from on-road gasoline and diesel vehicles using a soot particle aerosol mass spectrometer. Atmos. Chem. Phys. 14, 7585–7599. doi:10.5194/acp-14-7585-2014

De Miguel, E., Iribarren, I., Chacón, E., Ordoñez, A., Charlesworth, S., 2007. Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere 66, 505–513. doi:10.1016/j.chemosphere.2006.05.065

De Miguel, E., Mingot, J., Chacón, E., Charlesworth, S., 2012. The relationship between soil geochemistry and the bioaccessibility of trace elements in playground soil. Environ. Geochem. Health 34, 677–687. doi:10.1007/s10653-012-9486-7

Denys, S., Caboche, J., Tack, K., Delalain, P., 2007. Bioaccessibility of lead in high carbonate soils. J. Environ. Sci. Health. A. Tox. Hazard. Subst. Environ. Eng. 42, 1331–9. doi:10.1080/10934520701435569

Díaz-Somoano, M., Kylander, M.E., López-Antón, M.A., Suárez - Ruiz, I., Martínez-Tarazona, M.R., Ferrat, M., Kober, B., Weiss, D.J., 2009. Stable lead isotope compositions in selected coals from around the world and implications for present day aerosol source tracing. Environ. Sci. Technol. 43, 1078–1085. doi:10.1021/es801818r

Duzgoren-Aydn, N.S., Weiss, A.L., 2008. Use and abuse of Pb-isotope fingerprinting technique and GIS mapping data to assess lead in environmental studies. Environ. Geochem. Health 30, 577–588. doi:10.1007/s10653-008-9179-4

Environment Agency, 2009. Human health toxicological assessment of contaminants in soil. Science Report — SC050021/SR2. UK: Environment Agency.

Ettler, V., Mihaljevič, M., Komárek, M., 2004. ICP-MS measurements of lead isotopic ratios in soils heavily contaminated by lead smelting: Tracing the sources of pollution. Anal. Bioanal. Chem. 378, 311–317. doi:10.1007/s00216-003-2229-y

Filippelli, G.M., Morrison, D., Cicchella, D., 2012. Urban Geochemistry and Human Health. ELEMENTS 8, 439–444. doi:10.2113/gselements.8.6.439

GEOFABRIK 2015. OpenStreetMap, Portugal. Available on-line from http://download.geofabrik.de/europe/portugal.html

Giergiczny, Z., Król, A., 2008. Immobilization of heavy metals (Pb, Cu, Cr, Zn, Cd, Mn) in the mineral additions containing concrete composites. J. Hazard. Mater. 160, 247–255. doi:10.1016/j.jhazmat.2008.03.007

Gietl, J.K., Lawrence, R., Thorpe, A.J., Harrison, R.M., 2010. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. Atmos. Environ. 44, 141–146. doi:10.1016/j.atmosenv.2009.10.016

Gleyzes, C., Tellier, S., Astruc, M., 2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. trends Anal. Chem. 21, 451–467.

Goovaerts, P., 1999. Geostatistics in soil science: state-of-the-art and perspectives. Geoderma 89, 1–45.

Haack, U.D.O.K., Heinrichs, H., Gutsche, F.H., Plessow, K., 2003. The isotopic composition of anthropogenic Pb in soil profiles of northern Germany: evidence for pollutant. Water. Air. Soil Pollut. 150, 113–134.

Hökfors, B., 2014. Phase chemistry in process models for cement clinker and lime production. Doctoral Thesis, Umeå Universitet, 1-76.

IUSS Working Group WRB. 2015. World Reference Base for Soil Resources 2014, update 2015 International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.

Jollife, I.T., 2002. Principal Component Analysis, second ed. Springer, NewYork.

Ketterer, M.E., Peters, M.J., Tisdale, P.J., 1991. Verification of a correction procedure for measurement of lead isotope ratios by inductively coupled plasma mass spectrometry. J. Anal. Atom Spectrom. 6, 439–443.

Khan, S., Munir, S., Sajjad, M., Li, G., 2016. Urban park soil contamination by potentially harmful elements and human health risk in Peshawar City, Khyber Pakhtunkhwa, Pakistan. J. Geochemical Explor. 165, 102–110. doi:10.1016/j.gexplo.2016.03.007

Komárek, M., Ettler, V., Chrastný, V., Mihaljevič, M., 2008. Lead isotopes in environmental sciences: A review. Environ. Int. 34, 562–577. doi:10.1016/j.envint.2007.10.005

Li, H.B., Yu, S., Li, G.L., Deng, H., Luo, X.S., 2011. Contamination and source differentiation of Pb in park soils along an urban-rural gradient in Shanghai. Environ. Pollut. 159, 3536–3544. doi:10.1016/j.envpol.2011.08.013

Li, H.B., Chen, K., Juhasz, A.L., Huang, L., Ma, L.Q., 2015. Childhood lead exposure in an industrial town in china: Coupling stable isotope ratios with bioaccessible lead. Environ. Sci. Technol. 49, 5080–5087. doi:10.1021/es5060622

Ljung, K., Oomen, A., Duits, M., Selinus, O., Berglund, M., 2007. Bioaccessibility of metals in urban playground soils. J. Environ. Sci. Health. A. Tox. Hazard. Subst. Environ. Eng. 42, 1241–50. doi:10.1080/10934520701435684

Ma, W.L., Li, Y.F., Sun, D.Z., Qi, H., 2009. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in topsoils of Harbin, China. Arch. Environ. Contam. Toxicol. 57, 670–678. doi:10.1007/s00244-009-9314-y

Mil-Homens, M., Caetano, M., Costa, A.M., Lebreiro, S., Richter, T., de Stigter, H., Trancoso, M.A., Brito, P., 2013. Temporal evolution of lead isotope ratios in sediments of the Central Portuguese Margin: A fingerprint of human activities. Mar. Pollut. Bull. 74, 274–284. doi:10.1016/j.marpolbul.2013.06.044

Monna, F., Lancelot, J., Croudace, I.W., Cundy, A.B., Lewis, J.T., 1997. Pb isotopic composition of airborne particulate material from France and the Southern United Kingdom: Implications for Pb pollution sources in urban areas. Environ. Sci. Technol. 31, 2277–2286. doi:10.1021/es960870+

Morillo, E., Romero, A.S., Madrid, L., Villaverde, J., Maqueda, C., 2008. Characterization and sources of PAHs and potentially toxic metals in urban environments of Sevilla (southern Spain). Water. Air. Soil Pollut. 187, 41–51. doi:10.1007/s11270-007-9495-9

Mosleh, M., Blau, P.J., Dumitrescu, D., 2004. Characteristics and morphology of wear particles from laboratory testing of disk brake materials. Wear 256, 1128–1134. doi:10.1016/j.wear.2003.07.007

Nadal, M., Schuhmacher, M., Domingo, J.L. 2007. Levels of metals, PCBs, PCNs and PAHs in soils of a highly industrialized chemical/petrochemical area: Temporal trend. Chemosphere, 66: 267-276.

Nam, J.J., Song, B.H., Eom, K.C., Lee, S.H., Smith, A., 2003. Distribution of polycyclic aromatic hydrocarbons in agricultural soils in South Korea. Chemosphere 50, 1281–1289. doi:10.1016/S0045-6535(02)00764-6

Norra, S., Lanka-Panditha, M., Kramar, U., Stüben, D., 2006. Mineralogical and geochemical patterns of urban surface soils, the example of Pforzheim, Germany. Appl. Geochemistry 21, 2064–2081. doi:10.1016/j.apgeochem.2006.06.014

Okorie, A., Entwistle, J., Dean, J.R., 2011. The application of in vitro gastrointestinal extraction to assess oral bioaccessibility of potentially toxic elements from an urban recreational site. Appl. Geochemistry 26, 789–796. doi:10.1016/j.apgeochem.2011.01.036

Ottesen, R.T., Alexander, J., Langedal, M., Haugland, T., Høygaard, E., 2008. Soil pollution in day-care centers and playgrounds in Norway: National action plan for mapping and remediation. Environ. Geochem. Health 30, 623–637. doi:10.1007/s10653-008-9181-x

Palumbo-Roe, B., Wragg, J., Cave, M.R., Wagner, D., 2013. Effect of weathering product assemblages on Pb bioaccessibility in mine waste: Implications for risk management. Environ. Sci. Pollut. Res. 20, 7699–7710. doi:10.1007/s11356-013-1515-2

Patinha, C., Reis, A.P., Dias, A.C., Abduljelil, A.A., Noack, Y., Robert, S., Cave, M., Ferreira da Silva, E., 2015. The mobility and human oral bioaccessibility of Zn and Pb in urban dusts of Estarreja (N Portugal). Environ. Geochem. Health 37, 115–131. doi:10.1007/s10653-014-9634-3

Patinha, C., Durães, N., Sousa, P., Dias, A.C., Reis, A.P., Noack, Y., Ferreira da Silva, E., 2015. Assessment of the influence of traffic-related particles in urban dust using sequential selective extraction and oral bioaccessibility tests. Environ. Geochem. Health 37, 707–724. doi:10.1007/s10653-015-9713-0

Peng, C., Chen, W., Liao, X., Wang, M., Ouyang, Z., Jiao, W., Bai, Y., 2011. Polycyclic aromatic hydrocarbons in urban soils of Beijing : Status , sources , distribution and potential risk. Environ. Pollut. 159, 802–808. doi:10.1016/j.envpol.2010.11.003

Radwan, M.M., El Hemaly, S.A.S., 2011. Hydration characteristics of tetracalcium alumino-ferrite phase in the presence calcium carbonate. Ceram. - Silikaty 55, 337–342.

Reimann, C., Flem, B., Fabian, K., Birke, M., Ladenberger, A., Négrel, P., Demetriades, A., Hoogewerff, J., Team, T.G.P., 2012. Lead and lead isotopes in agricultural soils of Europe - The continental perspective. Appl. Geochemistry 27, 532–542. doi:10.1016/j.apgeochem.2011.12.012

Reimann, C., Birke, M., Demetriades, A., Filzmoser, P., O'Connor, P. (eds.), 2014. Chemistry of Europe's agricultural soils. Part A: Methodology and interpretation of the GEMAS data set. Geologisches Jahrbuch, Reihe B, Heft 102, Schweizerbart, Stuttgart, 528pp

Reis, A.P., Menezes de Almeida, L., Ferreira da Silva, E., Sousa, A.J., Patinha, C., Fonseca, E.C., 2007. Assessing the geochemical inherent quality of natural soils in the Douro river basin for grapevine cultivation using data analysis and geostatistics. Geoderma 141, 370–383. doi:10.1016/j.geoderma.2007.07.003

Reis, A.P., Silva, E.F., Sousa, A.J., Patinha, C., Martins, E., Guimarães, C., Azevedo, M.R., Nogueira, P., 2009. Geochemical associations and their spatial patterns of variation in soil data from the Marrancos gold-tungsten deposit: a pilot analysis. Geochemistry Explor. Environ. Anal. 9, 319–340. doi:10.1144/1467-7873/09-199

Reis, A.P., Patinha, C., Ferreira da Silva, E., Sousa, A.J., 2012. Metal fractionation of cadmium, lead and arsenic of geogenic origin in topsoils from the Marrancos gold mineralisation, northern Portugal. Environ. Geochem. Health 34, 229–241. doi:10.1007/s10653-011-9433-z

Reis, A.P., Patinha, C., Wragg, J., Dias, A.C., Cave, M., Sousa, A.J., Batista, M.J., Prazeres, C., Costa, C., Ferreira da Silva, E., Rocha, F., 2014a. Urban geochemistry of lead in gardens, playgrounds and schoolyards of Lisbon, Portugal: Assessing exposure and risk to human health. Appl. Geochemistry 44, 45–53. doi:10.1016/j.apgeochem.2013.09.022

Reis, A.P., Patinha, C., Wragg, J., Dias, A.C., Cave, M., Sousa, A.J., Costa, C., Cachada, A., Ferreira, E., Rocha, F., Duarte, A., 2014b. Geochemistry, mineralogy, solid-phase fractionation and oral bioaccessibility of lead in urban soils of Lisbon. Environ. Geochem. Health 36, 867–881. doi:10.1007/s10653-014-9605-8

Reis, A.P., Costa, S., Santos, I., Patinha, C., Noack, Y., Wragg, J., Cave, M., Sousa, A.J., 2015. Investigating relationships between biomarkers of exposure and environmental copper and manganese levels in house dusts from a Portuguese industrial city. Environ. Geochem. Health 37, 725–744. doi:10.1007/s10653-015-9724-x

Richter, T.O., de Stigter, H.C., Boer, W., Jesus, C.C., van Weering, T.C.E., 2009. Dispersal of natural and anthropogenic lead through submarine canyons at the Portuguese margin. Deep. Res. Part I Oceanogr. Res. Pap. 56, 267–282. doi:10.1016/j.dsr.2008.09.006

Rodríguez-Seijo, A., Arenas-Lago, D., Andrade, M.L., Vega, F.A., 2015. Identifying sources of Pb pollution in urban soils by means of MC-ICP-MS and TOF-SIMS. Environ. Sci. Pollut. Res. 7859–7872. doi:10.1007/s11356-014-4027-9

Schembri, M., Peplow, G., Camilleri, J., 2010. Analyses of heavy metals in mineral trioxide aggregate and Portland cement. J. Endod. 36, 1210–1215. doi:10.1016/j.joen.2010.02.011

Schwarz, K., Pickett, S.T.A., Lathrop, R.G., Weathers, K.C., Pouyat, R. V, Cadenasso, M.L., 2012. The effects of the urban built environment on the spatial distribution of lead in residential soils. Environ. Pollut. 163, 32–39. doi:10.1016/j.envpol.2011.12.003

Siciliano, S.D., Laird, B.D., Lemieux, C.L., 2010. Polycyclic aromatic hydrocarbons are enriched but bioaccessibility reduced in brownfield soils adhered to human hands. Chemosphere 80, 1101–1108. doi:10.1016/j.chemosphere.2010.04.061

Swartjes, F.A., Rutgers, M., Lijzen, J.P.A., Janssen, P.J.C.M., Otte, P.F., Wintersen, A., Brand, E., Posthuma, L., 2012. State of the art of contaminated site management in The Netherlands: Policy framework and risk assessment tools. Sci. Total Environ. 427-428, 1–10. doi:10.1016/j.scitotenv.2012.02.078

Tan, M.G., Zhang, G.L., Li, X.L., Zhang, Y.X., Yue, W.S., Chen, J.M., Wang, Y.S., Li, A.G., Li, Y., Zhang, Y.M., Shan, Z.C., 2006. Comprehensive study of lead pollution in Shanghai by multiple techniques. Anal. Chem. 78, 8044–8050. doi:10.1021/ac061365q

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. Anal. Chem. 51, 844–851. doi:10.1021/ac50043a017

Thavamani, P., Megharaj, M., Krishnamurti, G.S.R., McFarland, R., Naidu, R., 2011. Finger printing of mixed contaminants from former manufactured gas plant (MGP) site soils: Implications to bioremediation. Environ. Int. 37, 184–189. doi:10.1016/j.envint.2010.08.017

Vieira, B.J., Biegalski, S.R., Freitas, M.C., Landsberger, S., 2006. Atmospheric trace metal characterization in industrial area of Lisbon, Portugal. J. Radioanal. Nucl. Chem. 270, 55–62. doi:10.1007/s10967-006-0309-0

Wang, W., Huang, M.-J., Kang, Y., Wang, H.-S., Leung, A.O.W., Cheung, K.C., Wong, M.H., 2011. Polycyclic aromatic hydrocarbons (PAHs) in urban surface dust of Guangzhou, China: Status, sources and human health risk assessment. Sci. Total Environ. 409, 4519–4527. doi:10.1016/j.scitotenv.2011.07.030

Wragg, J., Cave, M., 2012. Assessment of a geochemical extraction procedure to determine the solid phase fractionation and bioaccessibility of potentially harmful elements in soils: A case study using the NIST 2710 reference soil. Anal. Chim. Acta 722, 43–54. doi:10.1016/j.aca.2012.02.008

Yang, Y., Woodward, L.A., Li, Q.X., Wang, J., 2014. Concentrations , Source and Risk Assessment of Polycyclic Aromatic Hydrocarbons in Soils from Midway Atoll , North Pacific Ocean 9, 1–7. doi:10.1371/journal.pone.0086441

Yongming, H., Peixuan, D., Junji, C., Posmentier, E.S., 2006. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Sci. Total Environ. 355, 176–186. doi:10.1016/j.scitotenv.2005.02.026

Table 1. Summary statistics of selected physicochemical properties determined in the soil samples

	Min	Median	Max	Mean±SD
pH	5.46	7.02	7.56	7.00 ± 0.33
TOC	0.57	2.40	8.59	2.66 ± 1.51
C_{inorg}	0.05	1.37	15.92	1.858 ± 2.07
TC	0.69	4.08	24.47	4.51 ± 3.13
TN	0.002	0.33	1.22	0.38 ± 0.27
TH	0.02	0.74	2.81	0.84 ± 0.53
TS	0.004	0.05	1.02	0.06 ± 0.11
CEC	2.05	17.52	51.82	19.37 ± 11.22
ExchNa	0.15	0.71	3.33	0.91 ± 0.66
ExchK	0.06	0.86	20.55	1.21 ± 2.15
ExchMg	0.001	1.10	11.05	1.79 ± 2.05
ExchCa	1.90	17.71	67.80	19.88 ± 11.84
Sand	10.95	59.77	96.13	59.87 ± 16.56
Silt	2.87	27.27	48.44	26.44 ± 10.21
Clay	1.00	12.98	43.99	13.76 ± 8.33

TOC: total organic carbon; Cinorg: inorganic carbon; TC, TN, TH, TS: elemental C, N, H, S; CEC: cation exchange capacity; ExchNa, ExchK, ExchMg, ExchCa: exchangeable cations; Min: minimum; Max: maximum; SD: standard deviation; TOC, Cinorg, TC, TN, TH, TS, Sand, Silt and Clay are expressed as %; CEC and exchangeable cations are expressed as cmol/kg

Table 2. Summary statistics for total concentrations of Pb (mg kg^{-1}) and Σ16PAHs (µg kg^{-1}) determined in the soil samples under study; comparison with other relevant studies.

	Pb	Σ16PAHs	Study
Min	5	6	present study
Q1	29	192	"
Median	61	563	"
Q3	126	1269	"
Max	428	73395	"
Mean ± SD	88 ± 80	2717 ± 9777	"
Median	-	83	Cachada et al., 2012, Viseu, Portugal
Median	-	301	Ma et al 2009, Harbin, China
Median	-	688	Peng et al 2011, Beijing, China
Mean	-	438	Nadal et al 2007, Tarragona, Spain
Median	35	240	Ottensen et al 2008, Trondheim, Norway
Median	22	-	De Miguel et al 2012, Madrid, Spain
Median	4968	-	Okorie et al 2011, Newcastle, UK
Median	26	-	Ljung et al 2007, Uppsala, Sweden

Min: minimum; Q1: 1st quartile; Q3: 3rd quartile; Max: maximum; SD: standard deviation;

Table 3. Pb isotope ratios of possible Pb sources and urban soils in Lisbon.

Materials	Pb (mg kg^{-1})		^{206}Pb/^{207}Pb		^{208}Pb/^{206}Pb		Study
	Mean	Range	Mean	Range	Mean	Range	
UK Leaded petrol	-	-	1.066 ± 0.007	1.059- 1.079	2.194 ± 0.007	2.197 - 2.186	Monna et al. 1997
France Leaded petrol	-	-	1.084 ± 0 001	1.069 - 1.094	2.182 ± 0.11	2.198 - 2.171	Monna et al. 1998
Cement	221± 81	166 - 318	1.128 ± 0.005	1.122 - 1.133	2.138 ± 0.004	2.142 - 2.133	Chen et al. 2005b
Vehicle exhaust	217 ± 98	-	1.147 ± 0.0040	-	2.124 ± 0.018	-	Chen et al. 2005a
Spanish coal	43 ± 81	7 - 301	1.183 ± 0.015	1.155 - 1.244	2.083 ± 0.023	2.110- 2.033	Diaz-Somoano et al. 2009
Portuguese coal	14 ± 4	8 - 17	1.191 ± 0.012	1.178 - 1.201	2.074 ± 0.018	2.095 - 2.059	Diaz-Somoano et al. 2009
Canyon sediments	42 ± 8	29 - 58	1.183 ± 0.003	1.176 - 1.190	2.071 ± 0.006	2.082- 2.064	Richter et al. 2009
Open shelf sediments	14 ± 1	13 -16	1.205 ± 0.002	1.203 - 1.207	2.055 ± 0.003	2.058 - 2.051	Richter et al. 2009
Agricultural soil	25	-	1.205	-	2.047	-	Reimann et al. 2014
Waste incineration	2143*	-	1.153 ± 0.0004	1.153-1.154	2.107 ± 0.0004	2.107 - 2.106	this study
Soil samples Lisbon	136 ± 114	15 -294	1.165 ± 0.007	1.155 - 1.176	2.096 ± 0.008	2.103 - 2.081	this study

Table 4. Relative contributions (%) of anthropogenic (unleaded vehicle exhaust, leaded petrol and cement) and natural sources to the total soil Pb concentration in the sub-set of eight samples selected for Pb isotope analysis. The distance (m) from the soil sample location to the nearest high traffic density road is also presented.

Sample	Vehicle exhaust	Leaded Petrol	Cement	Natural	Distance
US11	0.00	26.42	20.70	52.89	100
US12	52.68	0.00	0.00	47.32	750
US20	0.00	1.53	51.76	46.71	350
US23	0.00	0.05	37.28	62.68	700
US27	74.25	0.00	0.00	25.75	100
US35	73.61	0.00	0.00	26.39	50
US47	61.60	0.00	0.00	38.40	80
US48	76.37	0.00	0.00	23.63	20

Table 5. Stepwise LMR models for predicting soil PAHs and Pb concentrations from soil parameters.

| Variable	MLR models	R^2
Σ16PAHs	[PAHs] = -3793 + 2498 [TOC]	13%
	[PAHs] = -2471 + 4627 [TOC] – 359 [CEC]	21%
	[PAHs] = -1720 + 5718 [TOC] – 324 [CEC] – 11213 [TN]	27%
Pb	[Total Pb] = 8.22 + 730.03 [P]	35%
	[Total Pb] = 18.25 + 1083.05 [P] – 0.16 [Mn]	54%
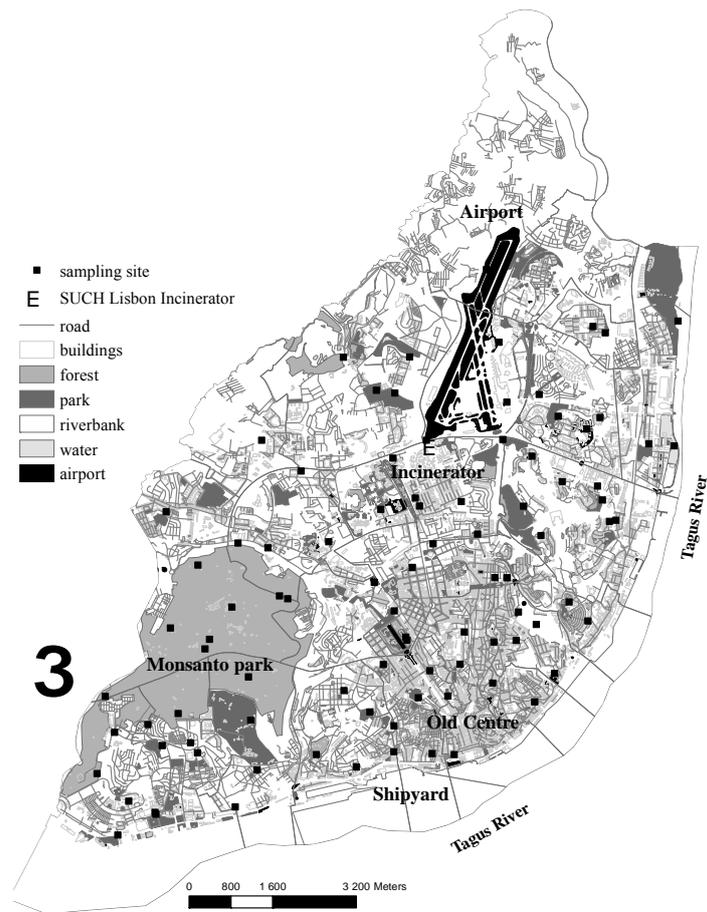
Fig. 1. Map of the study area where the sampling sites are identified by black squares. Housing density is represented by light grey lines while the roads are marked in black. Areas in grey tones represent green urban spaces such as parks and gardens (adapted from GEOFABRIK 2015).
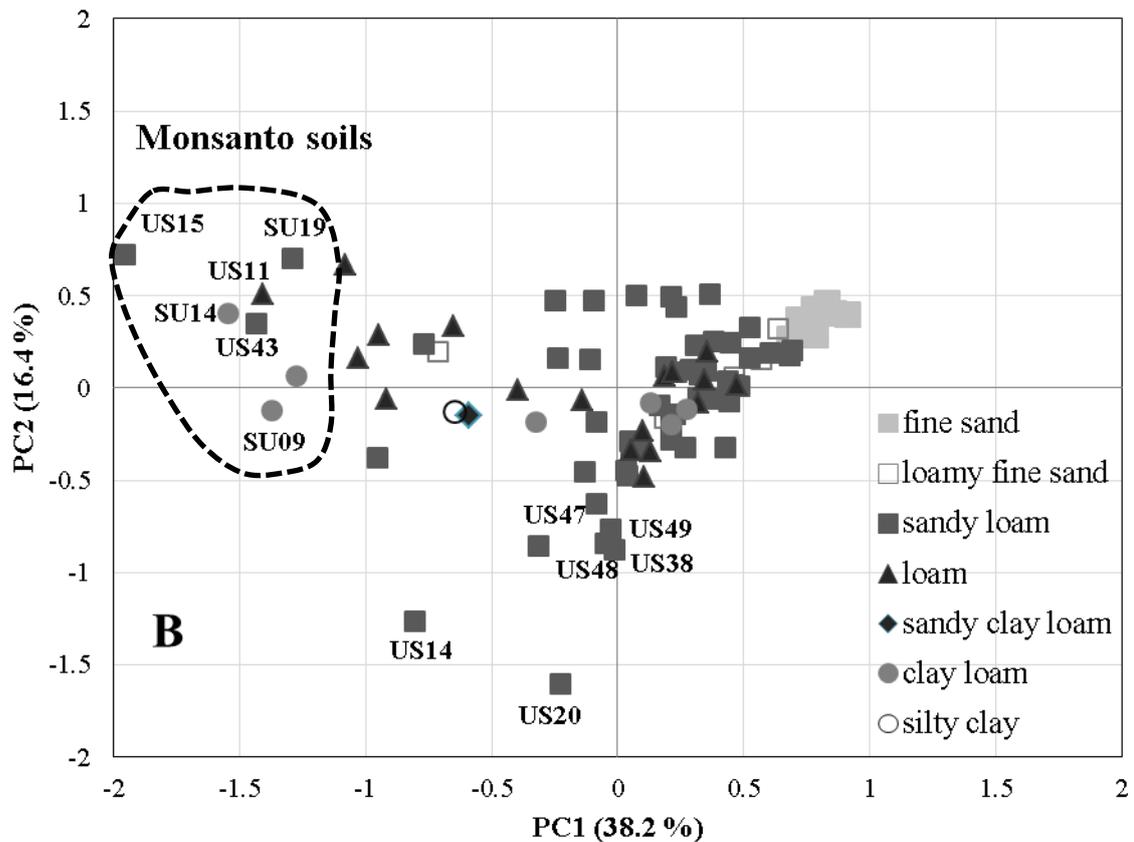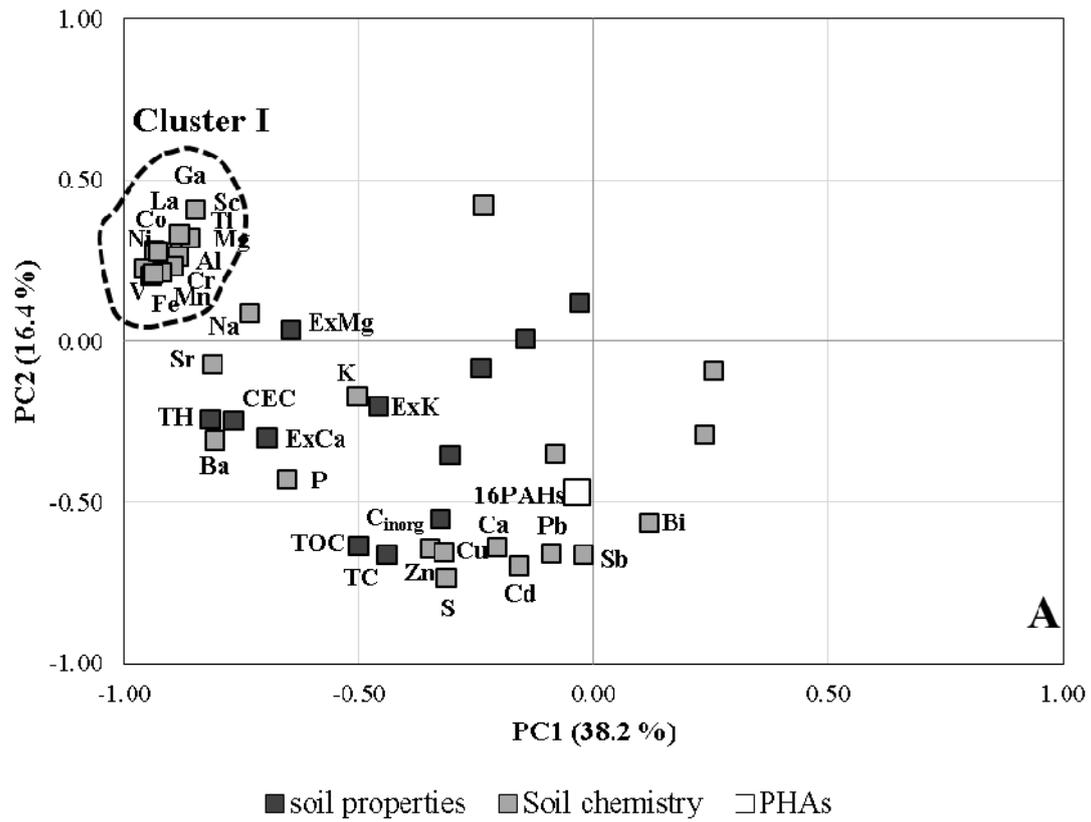
Fig. 2. Projections in the first principal component plane (PC1/PC2) of PCA analysis that accounts for ca. 55% of the total variance. Scatterplot 2A shows projections of variables (soil properties, PAHs and

chemical elements); in order to increase clarity, only variables that are well projected in the factorial plane are labelled. Scatterplot 2B shows projections of individuals (soil samples), discriminated according to their textural classification (symbols in the legend); only samples with high scores in PC1 and PC2 are labelled; Key: ExMg: exchangeable Mg; ExK: exchangeable K; ExCa: exchangeable Ca.
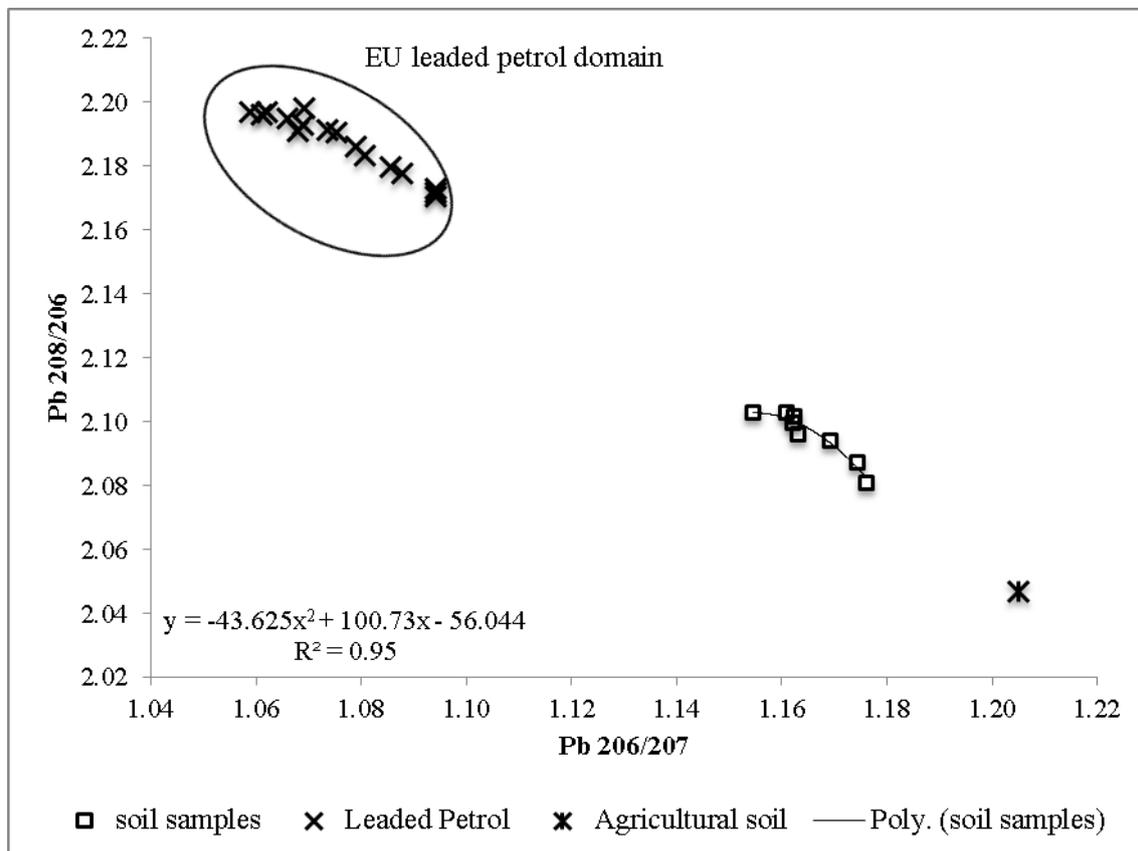
Fig 3. Three-isotope (^{206}Pb/^{207}Pb vs. ^{208}Pb/^{206}Pb) plot for soil samples compared with the values for European leaded petrol and one agricultural soil from the GEMAS project. The black line represents the polynomial correlation between the soil samples.
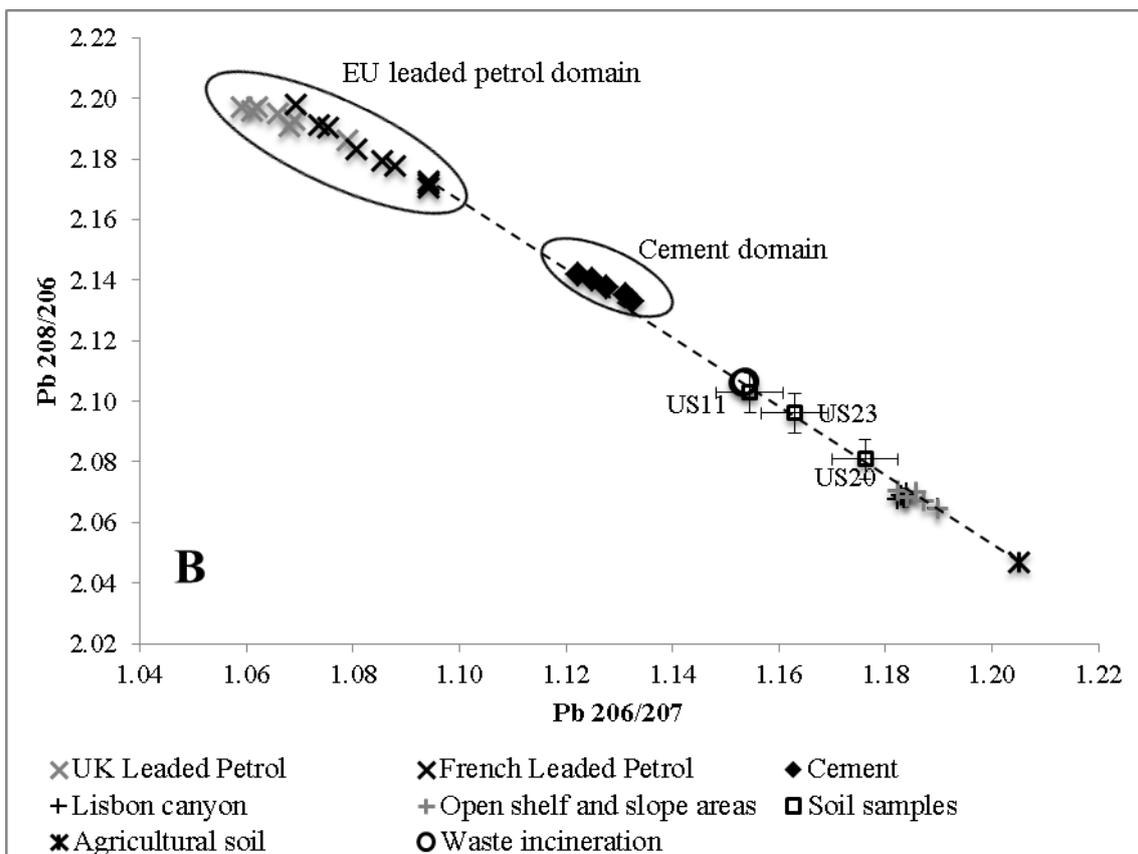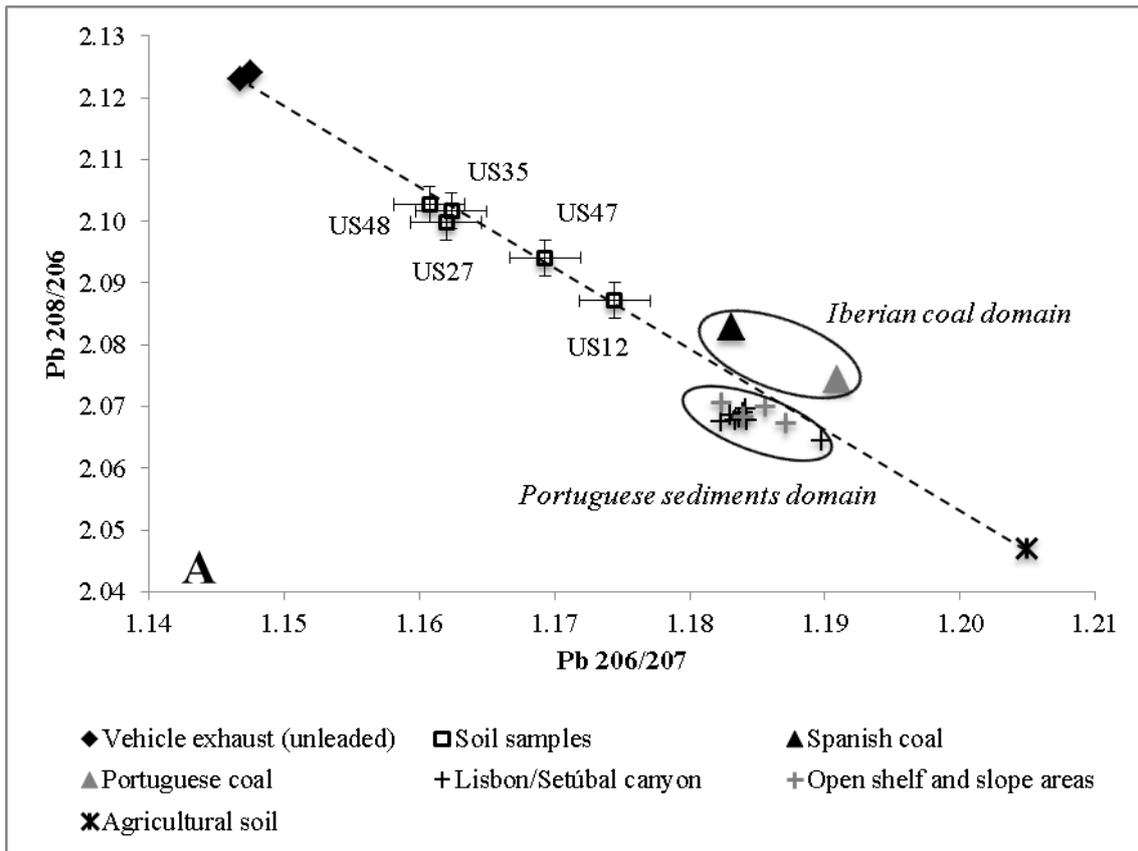
Fig 4. Three-isotope (206Pb/207Pb vs. 208Pb/206Pb) plot for soil samples. Plot A shows a two-end-member mixing line between unleaded vehicle exhaust (Chen et al. 2005a) and the agricultural soil (Reimann et al. 2014); data for Iberian coals (Diaz-Somoano et al. 2009) and Portuguese sediments

(Richter et al. 2009) are also plotted; Plot B shows a three-end-member mixing line between European leaded petrol (Monna et al. 1997), cement (Chen et al. 2005b) and the agricultural soil (Reimann et al. 2914); data for waste incineration and offshore Portuguese sediments (Richter et al. 2009) are also plotted.

a)

b)
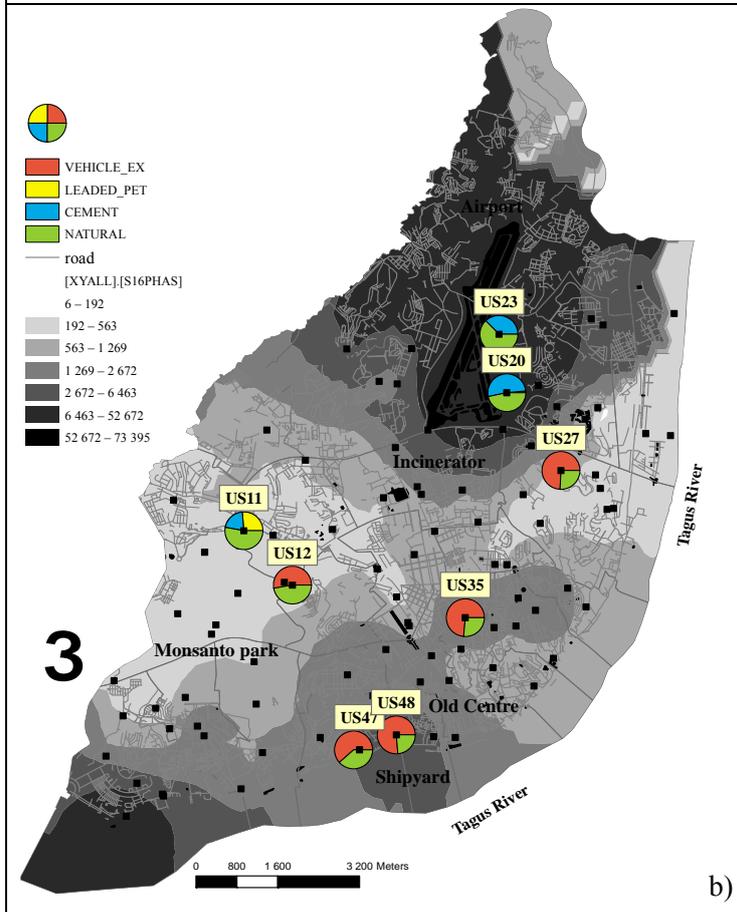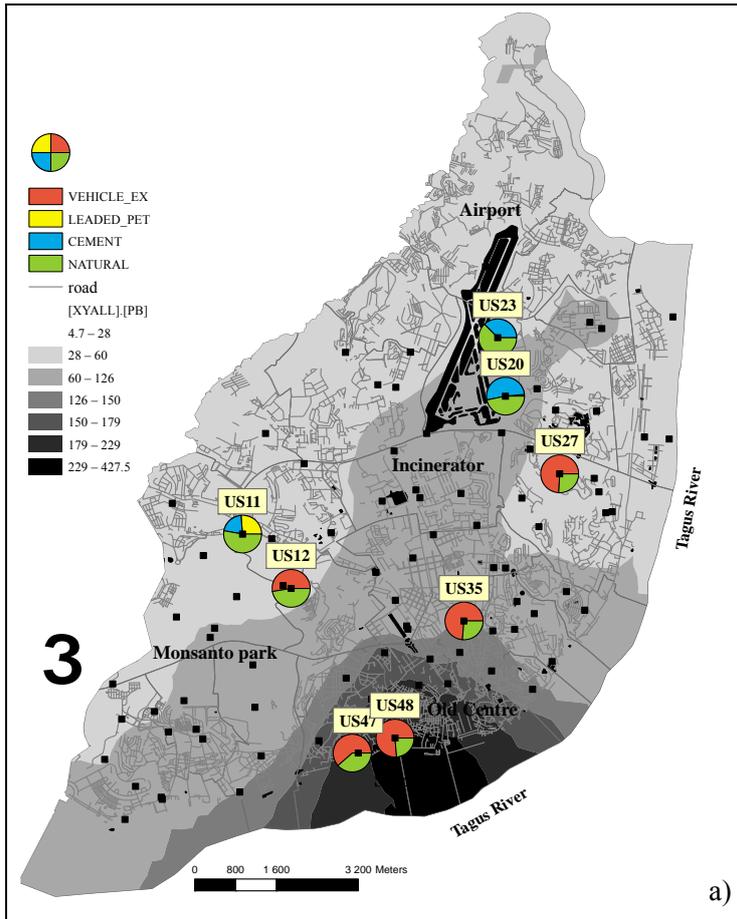
Fig. 5. Spatial dispersion patterns of Pb (Fig. 5a) and PAHs (Fig. 5b); relative contributions of potential Pb sources in the eight soils under study are displayed in colour pie plots.
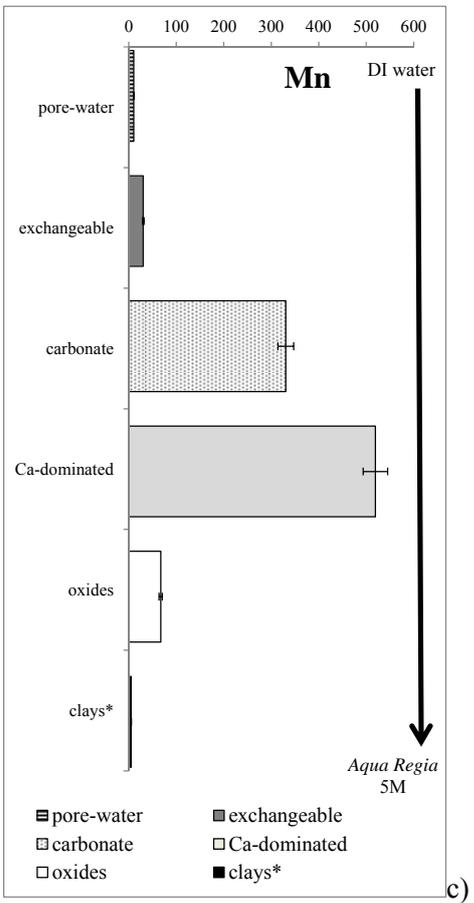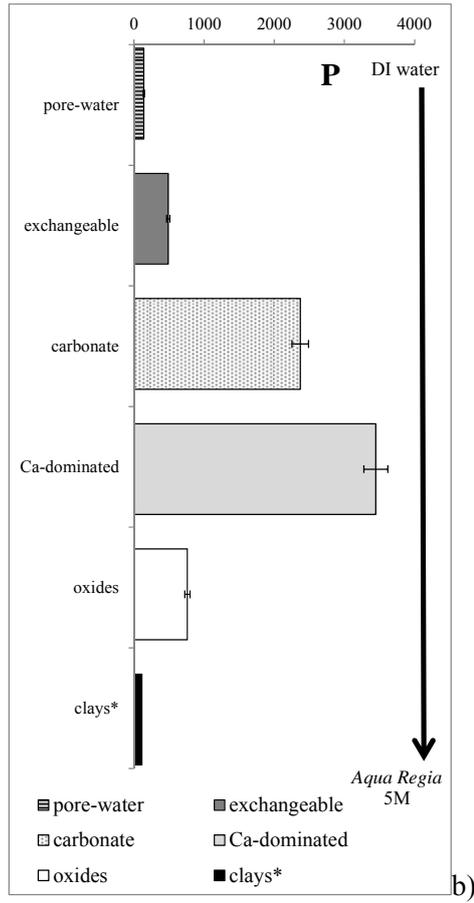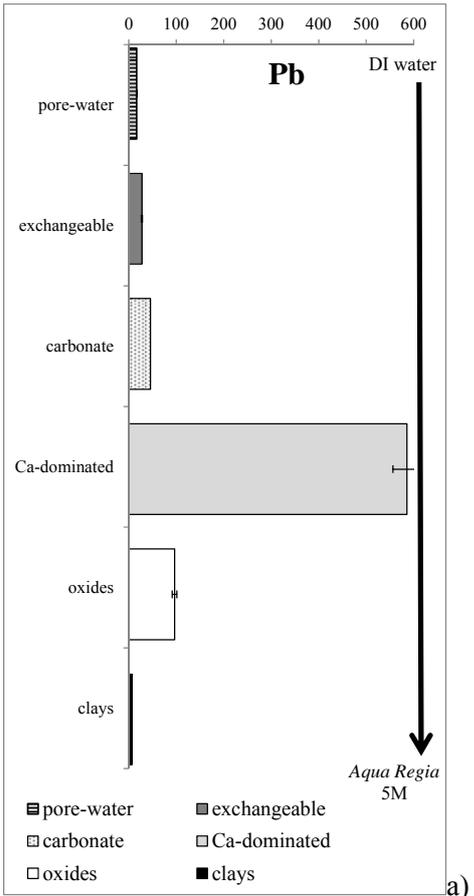
Fig. 6. Distribution plots showing the total amount of Pb, P and Mn (mg kg^{-1}, x-axis) associated with each component, sequentially extracted by the CISED procedure (y-axis) in soils US5, US8, US14, US18 and US33, the ones in which the chemical elements show a similar solid-phase fractionation. The arrow identifies increasing acid concentrations (DI water – *Aqua Regia* 5M). The error bars represent the upper and lower 95th percent confidence limits.