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

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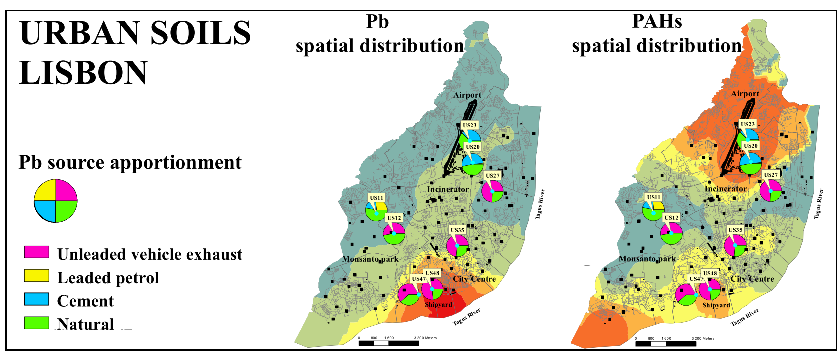
HIGHLIGHTS

- The biogeochemical cycles of Pb and PAHs in the urban soils influence human exposure.
- Sources-mobility-fate of contaminants were assessed by coupling various techniques.
- Links between atmosphere, anthroposphere and lithosphere are investigated.
- Pb stable isotope ratios were used for purposes of source apportionment.
- High levels of contaminants in soil are mainly associated to air and land traffic.

GRAPHICAL ABSTRACT



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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

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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.

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; Filippelli 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 (Filippelli 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, 2009). 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 and Hu, 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; Díaz-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., 2011).

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