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Metal(loid) distribution and Pb isotopic signatures in the urban environment of Athens, Greece☆

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ABSTRACT

Lead concentrations and isotopic compositions of contaminated urban soils and house dusts from Athens, Greece, have been determined to identify possible sources of Pb contamination and examine relationships between these two environmental media. Different soil particle sizes (<2000 μm, <200 μm, <100 μm, <70 μm, <32 μm) and chemical fractions (total, EDTA-extractable and acetic acid-extractable (HAc)) were analyzed for their Pb content and isotopic composition. Metal(loid)s (Pb, Zn, Cu, As, Ni, Cr, Mn, Fe) are significantly enriched in the finest fraction. The Pb isotopic compositions were similar for the different soil particle size fractions and different chemical extractions. The HAc extraction proved to be a useful procedure for tracing anthropogenic Pb in urban soil. The range of $^{206}Pb/^{207}Pb$ ratios (1.140–1.180) in Athens soil suggests that the Pb content represents an accumulated mixture of Pb deposited from past vehicular emissions and local natural sources. The contribution of anthropogenic Pb to total soil Pb ranged from 36% to 95%. The Pb isotopic composition of vacuum house dusts ($^{206}Pb/^{207}Pb$ = 1.1.38–1.167) from Athens residents is mostly comparable to that of urban soil suggesting that exterior soil particles are transferred into homes. As a result, anthropogenic Pb in house dust from Athens urban environment principally originated from soil particles containing Pb from automobile emissions (former use of leaded gasoline).

1. Introduction

Identification of contamination and source apportionment of potentially harmful elements within the surface urban environment is a challenging task mainly because of coexistence of multiple factors contributing to the elevated concentrations. In such environments, metals are typical contaminants of concern due to their ubiquitous historical uses by human societies, their non-degradable nature and potential harmful effects to the biosphere when in excess. Although they naturally occur in the environment, both diffuse and point anthropogenic sources commonly contribute to metal(loid) contamination of urban soil and dust. A classical example of diffuse source was the former use of leaded gasoline which, although it has been phased out for over two decades in most countries, is still considered to be a major contributory factor to urban soil contamination (Cheng and Hu, 2010; Erel et al., 1997; Farmer et al., 2000; Gulson et al., 1995; Monna et al., 1997). Other examples of vehicular traffic related metal contaminants are Zn and Cd originating from tire ware. Contamination hotspots are also present within the urban environment and might be related to specific point sources such as demolition and/or construction sites (Caravanos et al., 2006; Farfel et al., 2003, 2005). Specific sources of Pb in this instance include plumbing and leaded paint while a range of other metals (e.g. Zn, Cu, Sn, Cd) may originate from electrical and electronic appliances as well as other every day commodities.

Elevated Pb concentrations in the surface environment remain an important problem, not only because of the adverse health effects of this element, but also because of the historical legacy of its use. Indeed, Pb is a non-essential and toxic metal whose biogeochemical cycle has been affected by man to a great degree and has been used since antiquity in construction, containers, plumbing, insulation etc. Because of the complex character of Pb contamination regarding its origin, especially within urban areas, the identification of its sources is often complicated. Therefore, the use of Pb-isotope fingerprinting technique provides an excellent tool for

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source apportionment and has been used extensively in environmental studies globally (Komárek et al., 2008; Miller, 2013). However, the results of such analysis should be interpreted with caution as it is possible to overestimate or underestimate the contribution of specific sources of Pb in environments where Pb isotopic compositions of the natural and anthropogenic sources are similar (Duzgoren-Aydin and Weiss, 2008). Another reason could be that the isotopic measurements have been made by medium quality inductively coupled plasma mass spectrometry (Kamenov and Gulson, 2014).

It is well recognized that potentially harmful elements within the urban environment accumulate in the fine fraction of the soil and dust with consequences on the estimation of human and biota exposure to the contamination (Ajmone-Marsan et al., 2008; Qian et al., 1996; Sheppard and Evenden, 1994). As such, the effect of particle size in the collected samples cannot be overlooked and is another factor that needs to be taken into account especially in arid areas influenced by soil erosion (Hayes et al., 2012). Another important parameter for the estimation of the elemental sources and pathways is the fractionation of metal(loid)s in soils which also influences their mobility and environmental availability. A common way of testing this is the application of laboratory tests, using single or sequential extractions, based on chemical reagents capable of releasing metals bound to specific soil phases (Kelepertzis and Argyraki, 2015). To date only a few studies have looked into Pb isotopic ratios of different particle size fractions (Bi et al., 2013; Gulson et al., 1994; Luo et al., 2011) and tested the response of the Pb isotopic signal to different extraction methods (Ettler et al., 2006; Komárek et al., 2006; Li et al., 2011).

Redistribution and transport of metal-containing fine soil particulates has also been recognized to have a significant contribution to house dust, depending on a variety of site-specific factors and methodological approaches (Laidlaw et al., 2014; Rasmussen et al., 2001). House dust is also a significant contributor to blood lead especially in children (e.g. Lanphear and Roghmann, 1997). House dust is composed of finer particles, which are more mobile and metal enriched compared with external materials, and adhere to skin more effectively (Duggan and Inskip, 1985). It is thus a significant exposure medium for risk assessment and a number of researchers have investigated the sources of heavy metals and especially Pb in interior house dust (e.g., Brewer et al., 2015; Laidlaw et al., 2014; Rasmussen et al., 2013; Yoshinaga et al., 2014). In some of these studies Pb isotopic ratio analyses have been incorporated in order to distinguish the dominant source of contamination which has apparent implications for selecting the best option for risk elimination (Gulson et al., 1995; Laidlaw et al., 2014).

In addition to the limited information on Pb isotopic signature of different soil grain size and chemical fractions, comparative studies between soil and house dust in big cities targeting to Pb source apportionment based on Pb isotopes are rare (Gulson et al., 1995; Laidlaw et al., 2014). In the present study, we performed a combined investigation of Pb isotopic composition in different particle sizes and chemical fractions of urban soil in Athens, Greece. The data were compared with Pb isotopic ratios in samples of house dust as well as samples of rather confined settings, such as a vehicular tunnel, a lead battery recycling unit and background geological materials, in order to provide insight on source apportionment of Pb in the specific urban environment. Previous research on the environmental availability of potentially harmful elements indicated that the metals of anthropogenic origin in Athens soil, i.e., Pb, Zn, Cu and Cd are significantly mobile. It was shown, especially for Pb, that a considerable fraction of the element remains in a highly bioaccessible and reactive form in these soils (Kelepertzis and Argyraki, 2015). Within this frame, the specific objectives of the present study are: (a) to further constrain the factors that control metal enrichment in soils by examining their fractionation in different particle sizes, (b) to evaluate the sources of Pb in bulk soil as well as different particle size and chemical fractions, and (c) to compare soil and house dust with respect to Pb sources. In a wider context, this research contributes to the development of a comprehensive database of the surface environment of urban areas. Inclusion of Pb isotope data in such environments provides the basis for further actions in environmental risk assessment.

2. Materials and methods

2.1. Sampling and preparation of relevant materials

In environmental soil sciences, the isotopic ratios of ^{206}Pb, ^{207}Pb and ^{208}Pb can be used to pinpoint the source of Pb by comparing the Pb isotopic composition found in soil with those of potential contributing sources (Cheng and Hu, 2010). The sampling strategy of the present study included collection of samples from both unconfined and relatively confined settings within the urban environment of Athens with respect to dominant sources of Pb. The source-specific materials included a vehicular tunnel ceiling dust sample from Lagoumitzi Street located near the Athens centre (Fig. 1), a sludge sample originating from a battery recycling industrial unit outside Athens and samples of local rocks representing natural sources of Pb. Despite the phasing out of leaded gasoline in the 1990s, we also incorporated in our discussion its contribution as a long lasting source of Pb in the urban environment. The vehicular tunnel of Lagoumitzi Street was opened to the public before leaded gasoline was phased out in Greece, thus the Pb isotopic ratio of the collected ceiling dust sample represents a mixture of leaded and unleaded fuel time periods. Lead isotopic compositions of regional natural sources were assessed based on schist and limestone bedrock samples from Athens as well as a galena sample originating from the Lavrion mixed sulfide ore deposit occurring about 45 km south of the city center.

Surface soil samples and house dusts represented unconfined urban settings. Eight composite soil samples (0–10 cm depth) were selected from the sample database of an earlier systematic soil geochemical survey based on their Pb contamination. Details on the sampling methodology are provided in Argyraki and Kelepertzis (2014). The selected samples included medium and high levels of metals covering both the periphery and the city core of Athens (Fig. 1). Specific land uses of the selected sample sites included road and railway verges (samples J12 and L12) as well as woodland and park areas (samples J10, L20, M10, K10, J11, H12). Total organic carbon content in bulk samples ranged from 1.3 to 2.5%, clay content ranged from 10 to 18%, silt from 24 to 32% and sand from 53 to 64%. All samples were mildly alkaline with an average pH of 8 (Kelepertzis and Argyraki, 2015). Soil particle size fractionation was achieved by dry sieving of air-dried field samples after thorough, gentle disaggregation using a porcelain pestle and mortar. A series of nylon sieves was subsequently used to separate particle size fractions of <2 mm, <200 μm, <100 μm, <70 μm and <32 μm. From these, analytical samples were prepared by grinding the two coarser fractions (<2 mm and <200 μm) in an automated agate mill in order to ensure sufficient acid dissolution, while finer fractions were presented for analysis without further grinding.

House dust samples were collected from 45 residences selected at random from the city of Athens. House residents collected the samples themselves by vacuuming repeatedly hard floor surfaces using a common protocol within a specified time period of eight weeks from September to November 2014. Laboratory preparation of the samples included manual removal of large objects and