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Environmental availability of trace elements (Pb, Cd, Zn, Cu) in soil from urban, suburban, rural and mining areas of Attica, Hellas

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ABSTRACT

The environmental availability of trace elements (Pb, Cd, Zn, Cu) in soil samples from the urban area of Athens and Piraeus is compared to that from samples of suburban, uncontaminated rural and the nearby historical mining area of Lavrion in Attica. These trace elements had been previously shown to be related to anthropogenic activities in the urban chemical environment of Athens. Trace element environmental availability is determined by using three single stage chemical extractions of (i) nitric acid (HNO_3), (ii) ethylenediaminetetraacetic acid (EDTA) and (iii) acetic acid (CH_3COOH), and the respective extractabilities are calculated as ratios relative to total element concentrations. All elements showed the same decreasing concentration trend in the order mining > urban > suburban ≈ rural soil categories. Median concentration, based on aqua regia dissolution, are 185, 173, 86, 0.4 mg/kg and 2.26% for Pb, Zn, Cu, Cd and Fe, respectively, for the urban soil samples. Whereas, the corresponding median concentrations of Pb, Zn and Cd in Lavrion soil are over ten times higher. The ratios of the extractable concentrations of Pb, Zn and Cd, relative to the aqua regia extractable content in soil, are also higher for the mining soil category. Extractable concentrations for all the studied elements are highly dependent on their respective aqua regia extractable values in all land use categories; extractability ratios are also controlled by HNO_3 extractable Fe in soil. For the two toxic elements, Pb and Cd, the data of this study suggest that environmental availability has to be assessed on a site-specific basis as local conditions, and in particular the mineralogical composition of soil, may influence their relative extractability.

1. Introduction

The increasing dominance of urban environments worldwide has led to accelerated emission and amplified exposure of biota to contaminants with implications to human and ecosystem health (Wong et al., 2006; Johnson and Demetriades, 2011). Soil acts as a sink for trace elements and, thus, constitutes an important indicator of long term ecosystem exposure to these contaminants within the urban environment. A recent study by McIlwaine et al. (2016) has shown that potentially harmful elements (PHEs) can be used as urbanisation tracers based on data from two British cities. As big cities are expanding into their rural surroundings, it is important to know what the current load of these elements is in order to have a base for future comparison within such fast changing human environment.

Many studies have been conducted with a focus on geochemical mapping of trace elements in soil from urban and rural areas (e.g., Acosta et al., 2011; Massas et al., 2013; Hu et al., 2013; Vazquez de la Cueva et al., 2014), and performance of environmental risk assessment by considering the effect of different land uses on concentrations of trace elements (e.g., Pelfrêne et al., 2013). Of particular interest is the assessment of Pb bioaccessibility in urban and rural contaminated soil (Rodrigues et al., 2010; Smith et al., 2011; Pelfrêne et al., 2012; Appleton et al., 2013), because of the recognised toxic effects of this element in the environment. These studies have demonstrated that potentially toxic trace elements are associated with soil components in a variety of ways, which affect their mobility and environmental availability. Thus, the chemical form and solubility of elements of concern, which in turn can be related to a number of soil properties, such as soil pH, organic matter and mineralogy, has an influence on their reactivity and environmental availability (Rodrigues et al., 2012).

Contamination sources play a significant role, not only in determining the levels of soil enrichment with trace elements, but also in controlling their form and speciation. Notably in urban environments, mixed and continuously changing land uses can result in soil impacted

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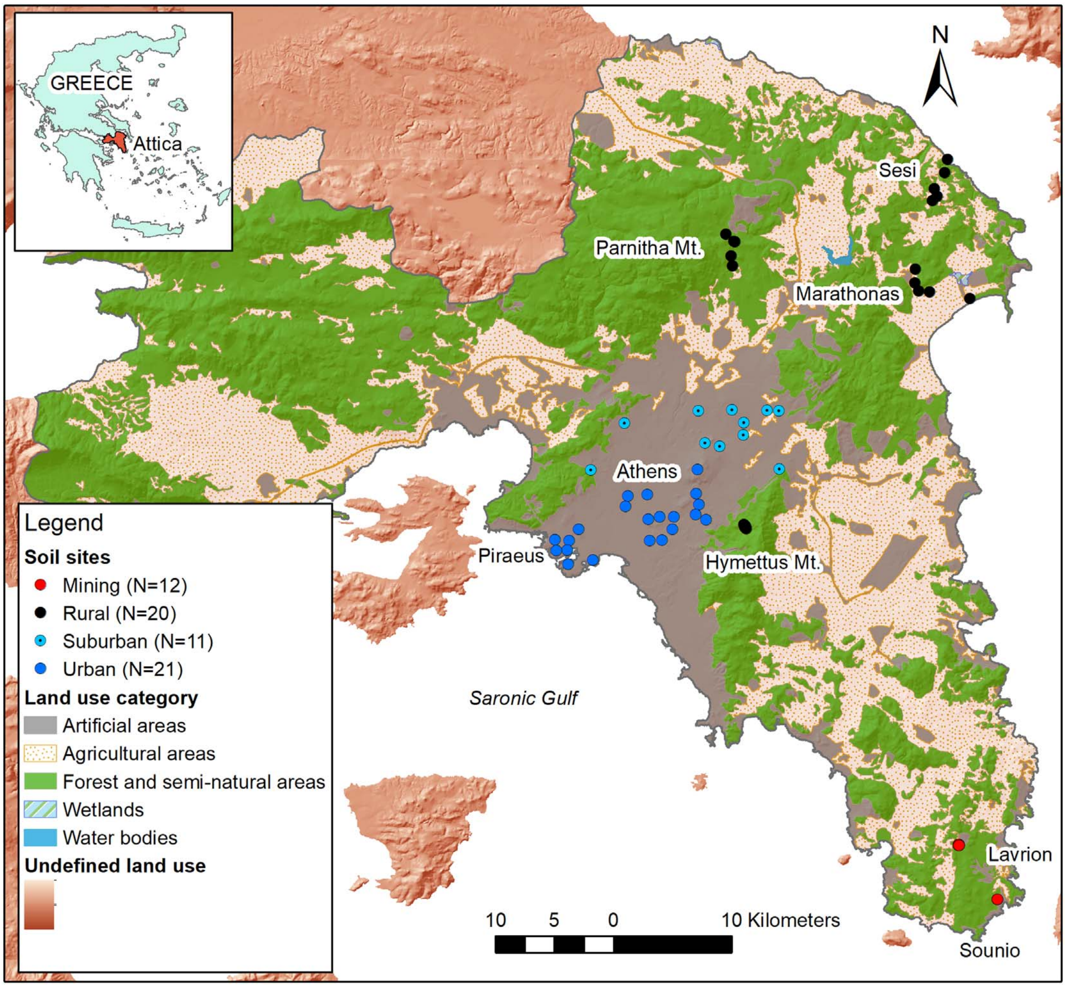

Fig. 1. Location map of the study area showing urban, suburban, rural and mining sampling sites on the Corine Land Cover (CLC) map, Attica, Hellas. The urban and suburban soil samples are those collected for a previous study (Argyraki and Kelepertzis, 2014), while the rural and mining soil samples were collected for this study. N = the number of samples of each group. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

by trace elements originating from various anthropogenic sources, such as industrial activities, coal and fuel combustion, vehicle emissions and municipal waste disposal (Islam et al., 2015; McIlwaine et al., 2016). Numerous sources of contamination by trace elements have been identified in rural regions, acting over disparate spatial scales. Point sources include factories, gas works, waste deposits, and applications of sewage sludge (Vazquez de la Cueva et al., 2014). Cadmium, Cu, Pb, and Zn are the most widespread anthropogenic contaminant elements in urban soil (Johnson and Demetriades, 2011; Hu et al., 2013). However, the major contaminant sources of these elements in the environment are mining and smelting activities. For this reason comparison of the environmental availability of these elements between mining and urban areas provides some insight into the geochemical controls in the contrasting soil types (Appleton et al., 2013).

The geochemical soil environment of the Athens basin in Attica, the plain that hosts the metropolitan area of Athens and Piraeus (Fig. 1), has been recently studied in a systematic way by Argyraki and Kelepertzis (2014). This study demonstrated that the major factor controlling variability of the chemical composition of surface soil was the bedrock chemistry, resulting in significant enrichment of soil Ni, Cr, Co and possibly As (four-acid (HNO_3, $HClO_4$, HF, HCl) extractable concentration medians of 102, 141, 16 and 24 mg/kg, respectively). Further work, by applying single step weak extractions on a sub-set of the soil samples, indicated that despite the elevated near-total concentrations of the geogenic elements (Ni, Cr, As and Co) in Athens soil, their availability is limited because of their sequestration in stable mineral phases (Kelepertzis and Argyraki, 2015). Anthropogenic influences were also significant, controlling a spectrum of elements that are typical of human activities (classical urban contaminants), i.e., Pb, Zn, Cu, Cd, Sb, and Sn. Significant correlations are identified between concentrations of these elements and urbanisation indicators, including vehicular traffic, urban land use, population density, and the history of urbanisation. The highest concentrations of the classical urban contaminants were observed in surface soil from roadside verges and in the older parts of the city, as well as the densely populated areas. Spatial distribution patterns of PHEs demonstrated an increase in concentrations of the anthropogenically induced elements towards the central part of the city and the port of Piraeus. Soil content of the typical anthropogenic elements in Athens soil was found to be comparable and somewhat lower than most cities (four-acid extractable concentration medians of 39 mg/kg, 45 mg/kg, 0.3 mg/kg and 98 mg/kg, for Cu, Pb, Cd and Zn respectively). Although the relatively low concentrations of typical anthropogenic elements reflect the lack of historical industrial legacy in Athens, significantly higher extractabilities were observed in comparison to the geogenic elements based on data from weaker extractions. This is indicative of the enhanced environmental availability of the specific elements in the urban area of Athens due to their association with relatively chemically unstable soil phases, such as Fe and Mn oxides. The aqua regia extractable content of the anthropogenic group of elements (Pb, Zn, Cu, Cd) was found to be the pre-dominant factor controlling their availability (Kelepertzis and Argyraki, 2015).

The soil environment of urban areas in Attica, the wider region

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