



Geochemical associations for evaluating the availability of potentially harmful elements in urban soils: Lessons learnt from Athens, Greece



Efstratios Kelepertzis*, Ariadne Argyraki

Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens, Panepistimiopolis, Zographou, 157 84 Athens, Greece

ARTICLE INFO

Article history:

Available online 6 April 2015

Editorial handling by M. Kersten

ABSTRACT

The estimation of potentially harmful element (PHE) availability in urban soil is essential for evaluating impending risks for human and ecosystem health. In the present study five single extraction procedures were evaluated based on the analysis of 45 urban top-soil samples from Athens, Greece. The pseudototal (aqua regia), potentially phytoavailable (0.05 M EDTA), mobilizable (0.43 M HAc), bioaccessible (0.4 M glycine) and reactive pools (0.43 M HNO₃) of PHEs were determined. In general, geogenic elements in Athens soil (Ni, Cr, Co, As) are relatively less available than typical tracers of anthropogenic contamination (Pb, Zn, Cu, Cd). Results of principal component analysis (PCA) indicate an association between available fractions of Pb, Cu, Zn, Cd and amorphous Fe oxides, whereas amorphous Mn oxides account for the available concentrations of Mn, Ni and Co. Empirical multiple linear regression models demonstrate that pseudototal concentration is the predominant explanatory factor of variability for the available pools of the anthropogenic elements. Major elemental composition and total organic carbon (TOC) improve the predictions for the geogenic group of elements, although the explained variability remains low. Dilute HNO₃ is a better predictor of Zn, Ni, As and Mn availability, whereas Pb and Cu available fractions are predicted more accurately by the classical aqua regia protocol. This study contributes to the international database on the environmental behavior of PHEs and provides additional knowledge that can be used toward the harmonization of chemical extraction methodology in urban soil.

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1. Introduction

Urban soil is a complex component of the urban landscape that is influenced by both natural and anthropogenic factors. Potentially harmful elements (PHEs), such as heavy metals and metalloids, are among the most common chemical constituents in soil that are associated with human activities (Rodríguez Martín et al., 2015). As a result elevated concentrations of PHEs in urban soil have been reported for various cities around the world (e.g. Shi et al., 2008; Cannon and Horton, 2009). Some PHEs, for example zinc (Zn), copper (Cu), manganese (Mn), chromium (Cr), nickel (Ni) and cobalt (Co), are essential for living organisms in trace amounts while others such as lead (Pb), arsenic (As) and cadmium (Cd) are considered toxic even at low concentrations.

Determination of total or pseudototal concentrations of PHEs in urban soil is of little significance for evaluating potential risks for the environment because it is assumed that 100% of the contaminant is released from the soil and subsequently involved in chemical and biological processes. PHEs in soil are distributed among

different fractions and forms with different solubility and reactivity in relation to plant uptake, leaching to groundwater and absorption by the human body (Rodrigues et al., 2010). These so-called plant available, mobilizable and oral bioaccessible fractions define the availability of PHEs in urban soil (Luo et al., 2012).

Chemical methods for evaluating the availability of PHEs include single extraction procedures and in vitro digestion models that have been developed to provide a conservative measure of the relative hazard to ecological and human receptors. Potential phytoavailability and mobility are commonly determined by chelating agents including ethylenediamine tetraacetic acid (EDTA) and dilute acetic acid (HAc), respectively (Madrid et al., 2008; Poggio et al., 2009; Li and Zhang, 2013). Human oral bioaccessibility is assessed by physiologically based extraction tests (PBET) originally developed by Ruby et al. (1996) simulating the chemical environment of the human gastrointestinal system. Due to its complexity, a simplified extraction test (SBET) has been alternatively applied to several studies providing useful information on solubility of PHEs in a medium compositionally similar to acid gastric fluids (Morman et al., 2009; Poggio et al., 2009). Moreover, Römkens et al. (2009) introduced the concept of *reactive metal fraction* representing the pools of PHEs that are associated with adsorption-desorption phenomena and might be taken up by plants

* Corresponding author. Tel.: +30 210 7274867.

E-mail address: kelepert@geol.uoa.gr (E. Kelepertzis).

and organisms. Determination of this fraction can be achieved by a 0.43 M nitric acid (HNO_3) extraction test (Römkens et al., 2009). Interestingly, Rodrigues et al. (2013) concluded that the reactive pools of Cd, Cu, Pb and Zn were robust predictors of their respective availabilities in urban soils from Porto, Portugal. Following from these findings, the applicability of the 0.43 M HNO_3 soil extraction for assessing the availability of a considerable suite of PHEs in urban soil requires further investigation.

Previous research in PHEs availability has shown that various soil parameters such as pH, organic carbon and soil texture, as well as the bulk chemical composition and mineralogy typically control the available PHEs fractions (Kelepertzis and Stathopoulou, 2013; Römkens et al., 2009), especially the orally bioaccessible pools (Cox et al., 2013; Palmer et al., 2014). However, the majority of urban soil investigations that aimed to evaluate the potential transfer of pollutants to the groundwater, the plants and the health risks to humans by combining major soil properties and chemical extractions has principally focused on the risks associated with PHEs of anthropogenic origin (Luo et al., 2012; Rodrigues et al., 2013); there is undoubtedly a gap of knowledge regarding the availability of naturally enriched PHEs in urban soil. Recent investigations highlighted the significant contribution of geogenic PHEs in the chemistry of topsoil in many European cities, for example Athens, Greece (Argyraki and Kelepertzis, 2014), Thiva, Greece (Kelepertzis, 2014), Northampton, UK (Cave et al., 2013) and Grugliasco, Italy (Poggio et al., 2009).

In this article, we provide insights in the reactivity and availability of PHEs of both natural and anthropogenic origin using an urban data set of Athens topsoil (Argyraki and Kelepertzis, 2014). We determine the pseudototal (aqua regia), potentially phytoavailable (0.05 M EDTA, pH 7.0), mobilizable (0.43 M HAc), bioaccessible (0.4 M glycine, pH 1.5) and reactive (0.43 M HNO_3) pools of PHEs. It is noted that the bioaccessible pool measured in this study refers only to the oral exposure pathway. Soil properties were also examined including pH, total organic carbon, soil texture and amorphous iron (Fe) and Mn oxides content. The various concentrations of extractable PHEs are expressed as a function of pseudototal content and geochemical variables. The results were statistically interpreted with a view to better understand the soil factors that influence PHEs available fractions and possibly link the chemical forms of the studied elements to their availability.

The specific objectives of the present study are: (a) to evaluate the availability and reactivity of various PHEs in selected urban soils from Athens and to compare these to the pseudototal content, (b) to assess the soil factors that control the PHEs available fractions by applying multivariate principal component analysis (PCA) and multiple linear regression, (c) to explore the possibility of implementing the fast and easily applicable 0.43 M HNO_3 leaching method for characterizing the availability of PHEs in Athens soil.

2. Materials and methods

2.1. Sample selection and preparation for analysis

Athens is a European city with a very long history concentrating about one third of the Greek population (around 3,000,000 city residents), as well as a major part of economic and commercial activities of the whole country. Forty-five composite soil samples (0–10 cm depth) were selected from the sample database of an earlier systematic soil geochemical survey. Details on the sampling methodology are provided in the study of Argyraki and Kelepertzis (2014). The criteria for sample selection were the total content of PHEs as determined by a strong acid mixture dissolution and the spatial variability of soil chemical composition. The selected samples included low, medium and high levels of PHEs

covering both the periphery and the city core of Athens (Fig. 1). The importance of local geology has been shown to control the distribution of a specific group of elements including Ni, Cr, Co, Mn and As; anthropogenic soil enrichment was identified for Pb, Zn, Cu, Cd in the urban environment of Athens (Argyraki and Kelepertzis, 2014).

2.2. Laboratory experimental work

The soil samples were air-dried, disaggregated and sieved to <2 mm fraction. Representative portions of each soil sample were further sieved through a nylon 100- μm sieve and stored in room temperature. Major physicochemical properties including pH, total organic carbon (TOC) and texture (sand, silt, clay) were determined. Soil pH was measured in a soil to deionized water suspension of 1:2.5 (w/v) based on the <2 mm sample fraction (ISO, 1994). Total organic carbon (TOC%) was determined on the <100 μm fraction according to the volumetric method described by Walkley and Black (1934). Grain size distribution (vol.%) in the sand, silt and clay fractions was determined using the hydrometer sedimentation method (Bouyoucos, 1962). Amorphous Fe oxides (Fe_{ox}) and Mn oxides (Mn_{ox}) were determined by the acid ammonium oxalate extraction in the dark (Schwertmann, 1964). Iron and Mn concentrations in the filtrates were analyzed by flame atomic absorption spectrometry (FAAS) at the Laboratory of Economic Geology and Geochemistry, University of Athens, and the results are presented in mg/kg. Scanning electron microscopy (SEM) and energy dispersive spectra (EDS) analysis were carried out on free surfaces of carbon-coated soil grains, using a Jeol JSM 5600 SEM instrument, equipped with an Oxford ISIS 300 micro-analytical device. The SEM study was performed on the high-density (specific gravity >2.96) fraction of selected soil samples after gravity separation in sodium polytungstate. Examination in the backscattered electron (BSE) mode permitted the localization of areas where heavy metals were concentrated.

Chemical analysis was performed on the <100 μm fraction because it has been demonstrated that this soil particle fraction is of major significance for assessing potential environmental risks in urban areas (Luo et al., 2011). The pseudototal content of PHEs was determined after digestion by aqua regia at the Acme Analytical Laboratories Ltd of Canada using ICP-MS and was used to establish the availability and reactivity ratio, i.e. per cent availability and reactivity. Results for the major elements (calcium (Ca), magnesium (Mg), aluminum (Al), Fe) are also presented and the concentrations are expressed in %. Replicates, in-house reference materials and reagent blanks were used for quality control. The availability of PHEs was assessed by applying the widely adopted extraction methods of EDTA, HAc and SBET. The metal fractions obtained by these analytical procedures were operationally defined as potentially phytoavailable (Madrid et al., 2008; Li and Zhang, 2013), mobilizable (Gupta et al., 1996; Sahuquillo et al., 2003) and orally bioaccessible (Luo et al., 2012; Popescu et al., 2013), respectively. Following results recently presented by Rodrigues et al. (2013), the soil reactive content of PHEs was determined after extraction with dilute HNO_3 .

The EDTA extractable content was obtained from subsamples of 4 g of soil leached with 40 ml of 0.05 M EDTA solution (adjusted to pH 7) for 1 h at room temperature (Ure et al., 1993). The mobilizable pools of PHEs were determined by treating 1 g of soil sample with 40 ml of 0.43 M HAc solution for 16 h at room temperature (Houba et al., 1996). The reactive forms of PHEs were extracted by mixing 1 g of soil material with 40 ml of a 0.43 M HNO_3 solution and shaken for 2 h at room temperature. We modified the proposed 1/10 (w:v) ratio of Rodrigues et al. (2010) because of the calcareous nature of Athens soil ensuring that pH values of the final extraction fluids were within the range 0.8–1.0. All the mixtures from these

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