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Urban soil geochemistry in Athens, Greece: The importance of local geology in controlling the distribution of potentially harmful trace elements

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HIGHLIGHTS

- A systematic geochemical survey of Athens soil is presented for the first time.
- Sources and spatial distribution of chemical elements in soil were examined.
- Geology defined the spatial signature of major elements, and Ni, Cr, Co, As.
- Urbanization controlled the geochemical pattern of Pb, Zn, Cu, Cd, Sb, and Sn.
- Urban topsoil exhibited significant loadings of geogenic PHEs.

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ABSTRACT

Understanding urban soil geochemistry is a challenging task because of the complicated layering of the urban landscape and the profound impact of large cities on the chemical dispersion of harmful trace elements. A systematic geochemical soil survey was performed across Greater Athens and Piraeus, Greece. Surface soil samples (0–10 cm) were collected from 238 sampling sites on a regular 1 × 1 km grid and were digested by a HNO_3–HCl–$HClO_4$–HF mixture. A combination of multivariate statistics and Geographical Information System approaches was applied for discriminating natural from anthropogenic sources using 4 major elements, 9 trace metals, and 2 metalloids. Based on these analyses the lack of heavy industry in Athens was demonstrated by the influence of geology on the local soil chemistry with this accounting for 49% of the variability in the major elements, as well as Cr, Ni, Co, and possibly As (median values of 102, 141, 16 and 24 mg kg^{-1} respectively). The contribution to soil chemistry of classical urban contaminants including Pb, Cu, Zn, Sn, Sb, and Cd (medians of 45, 39, 98, 3.6, 1.7 and 0.3 mg kg^{-1} respectively) was also observed; significant correlations were identified between concentrations and urbanization indicators, including vehicular traffic, urban land use, population density, and timing of urbanization. Analysis of soil heterogeneity and spatial variability of soil composition in the Greater Athens and Piraeus area provided a representation of the extent of anthropogenic modifications on natural element loadings. The concentrations of Ni, Cr, and As were relatively high compared to those in other cities around the world, and further investigation should characterize and evaluate their geochemical reactivity.

1. Introduction

The rapid urbanization and industrial growth that has occurred in many places around the world during the last decades has resulted in modification of the urban chemical environment (cf. Johnson and Demetriades, 2011). Urban soil constitutes an integral part of the city landscape, presenting unique characteristics that differentiate it from naturally developed soil. For instance, urban soil, frequently, does not present the classical vertical stratification, classified as horizons A, B and C, and may not even reflect the mineralogical and chemical composition of the parent material (Wong et al., 2006); however, several studies highlighted the influence of natural geochemical factors on the soil chemistry even in strongly urbanized areas (e.g. Manta et al., 2002; Rodrigues et al., 2009).

Most published urban soil investigations involve the characterization of potentially harmful elements (PHEs), e.g. heavy metals and metalloids, because of their non-biodegradable nature and their tendency to accumulate in the human body (Ajmone-Marsan and Biasioli, 2010). The sources of PHEs in the urban environment can be either natural, i.e. inherited materials from the underlying parent materials (e.g., rocks, alluvium, etc.), or anthropogenic (Wong et al.,

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2006; Wei and Yang, 2010; Luo et al., 2012). Anthropogenic metal signatures in soil can persist for many decades after termination of point and nonpoint source emissions due to the long residence times of metals in soil (Yesilonis et al., 2008). Both multivariate statistics and geostatistics are invaluable tools for identifying sources of PHEs on the urban scale and evaluating the significance of geochemical anomalies in relation to lithological characteristics and human activities (Zhang, 2006; Cicchella et al., 2008; Davis et al., 2009).

A few publications exist on the soil geochemistry of urban areas in Attica, the wider area around Athens (Fig. 1) (Demetriades, 2010, 2011, Demetriades et al., 2010; Massas et al., 2010, 2013; Kaitantzian et al., 2013); however, there are no published systematic geochemical maps of urban soil for any of the major Greek cities. Furthermore, earlier studies with reference to heavy metal concentrations in urban soil of Athens were focused on specific land uses, i.e. playgrounds and roads (Yassoglou et al., 1987; Chronopoulos et al., 1997; Riga-Karandinos et al., 2006; Massas et al., 2010). These studies have adopted various methodologies depending on their primary objectives. Assessment of previous research highlights the necessity for an extensive, systematic urban soil geochemical survey aiming to determine spatial distribution patterns of both major and trace elements.

Greek soil is naturally enriched in Cr, Ni, Co and Mn as a result of the widespread occurrence of basic and ultrabasic rocks (Vardaki and Kelepertsis, 1999; Kelepertzis et al., 2013; Kanellopoulos and Argyraki, 2013). Furthermore, elevated As concentrations in soil and natural waters have been linked to metamorphic rocks in Greece (Gamaletsos et al., 2013). Bearing in mind the historical absence of heavy industry within the Greater Athens and Piraeus area, it is hypothesized that local geology is important in controlling the distribution of potentially harmful trace elements in urban soil.

In this paper we investigate the concentrations of major and trace elements in urban soil from Athens, using a systematic sampling strategy with the primary objectives being: (a) to produce geochemical maps of the investigated elements within the Greater Athens and Piraeus area; (b) to define the natural or anthropogenic origin of the chemical elements by combining multivariate statistics and GIS approaches; and (c) to evaluate the influence of specific urbanization indicators, i.e. urban land use, population density, timing of urbanization and vehicular traffic, on soil chemistry, and over time. Thus, a systematic geochemical baseline data set for the soil chemical environment of Greater Athens and Piraeus is presented, and this contributes to the international database of surveys on the distribution and sources of chemical elements and compounds in urban soil. Whereas many studies have addressed the problem of distinguishing the sources of PHEs, only a few have examined the influence of urbanization indicators on soil chemistry (Yesilonis et al., 2008; Chen et al., 2010; Peng et al., 2013). Furthermore, an estimation method and quantitative data on the influence of short scale soil heterogeneity on urban geochemical mapping are presented.

2. Materials and methods

2.1. Description of the study area

The city of Athens lies within the Athens Basin, which is located in Attica on the south-east tip of mainland Greece (Fig. 1). The Athens Basin is highly urbanized with elevated vehicular traffic loads in the city core and the wider area of Piraeus port, located south-west of Athens Centre. Although Piraeus and Athens are joined nowadays, they are actually two different cities historically and administratively. The Greater Athens comprises four regional units while the regional unit of Piraeus forms Greater Piraeus. Together they make up the contiguous built up urban area of the Greek capital. Most surfaces are asphalt, residential and commercial buildings, while park areas are limited. Unlike most European capitals, the urbanization of modern Athens was not related to the Industrial Revolution. The city experienced rapid population growth from ~400,000 people in 1925 to >1,000,000 by 1950. The population increase of modern Athens is marked by the return of Greek refugees from Asia Minor in the 1920s after World War I and extensive internal migration after World War II. Today, the urban areas of Greater Athens and Piraeus have a population of ~3.2 million over an area of 412 km^2. This constitutes ~1/3rd of the Greek population. In addition, this area is the center of economic and commercial activities for the country. The population density (people per km^2) is approximately 7,500, and over 20,000 in a few municipalities with a high incidence of residential, commercial, and business activities (Fig. S1, Supplementary material). There is no large scale industry in Athens. Some industrial support services including depots, trade transport companies and building material stocking yards are located between the Athens Centre and Piraeus. Previous industries during the past decades included pottery making, textile production, shoe making, tanneries, and metal plating.

The bedrock geology of Athens is comprised of 4 different geotectonic units that form and outcrop in the mountains surrounding the city, as well as in hills within the Athens Basin (Papanikolaou et al., 2004a) (Fig. 2): (a) the lowest basement unit is composed of metamorphic rocks, including marble, dolomite, and mica-schist; (b) this is tectonically overlain by the Alepovouni unit that is also comprised of metamorphic rocks, including crystalline limestone, schist and greenstone; (c) the Athens Unit, which outcrops in the hills of western and central Athens Basin, is an Upper Cretaceous mélange that includes pelagic sediments consisting of marly limestone, shale, sandstone, tuff and ophiolithic blocks and neritic limestone (Papanikolaou et al. 2004b); and (d) the Sub-Pelagonian unit, which mainly consists of limestone and dolomitic limestone. Serpentinized blocks of varying dimensions are embedded within the lithology of all alpine units occurring in Athens (Basement unit, Athens unit, Alepovouni unit), not all of them are shown on the geological map.

Post-orogenic Neogene to Quaternary deposits cover the alpine bedrock. Lithologically, these include Neogene coastal marine, continental and lacustrine carbonate and clastic sediments, and thick Quaternary alluvial fans at the foothills of the surrounding mountains. Alluvial soils, derived from the surrounding mountains are enriched in Cr, Ni, and Co via mechanical and chemical weathering processes (Kelepertzis et al. 2013). Natural soil within the city is generally thin. Soil types range from Calcaric–Lithic–Leptosols (renzinas) on the mountainous margins of the basin to Calcaric Fluvisols and Regosols in the western part of the study area and Rhodic Luvisols over the eastern part of the basin (ESDB, 2013; Soil Atlas of Europe).

2.2. Sampling methodology

The area where soil sampling was performed occupies more than 220 km^2 (Fig. 1) and was divided into 218 cells of 1 × 1 km in size. A sampling density of 1 sample per km^2 was adopted and the center of the cell was preferably determined as the sampling location. If no open soil was present, the sampling location was moved to the nearest available space of soil material. We targeted areas with land use categories such as parks, recreational areas, playgrounds, and school yards. Whenever sampling in these categories was not feasible, soil from road verges was collected. Sampling was carried out where plants with superficial roots were not present. A total of 238 composite topsoil (0–10 cm) samples were collected in the spring and summer of 2012. Using a plastic spatula, five subsamples were collected from the center and corners of a 10 m square site to obtain a representative sample from each sampling location. If this was not possible, the composite sample was obtained by collecting material from 5 points with at least 5 m distance from each other. At 20 randomly selected sampling sites a second sample was recovered at approximately 200 m distance from the original sampling location, but within the same 1 × 1 km sampling cell. The data from these samples were utilized for estimating the within sampling-cell variability of elemental concentrations in soil. The exact