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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

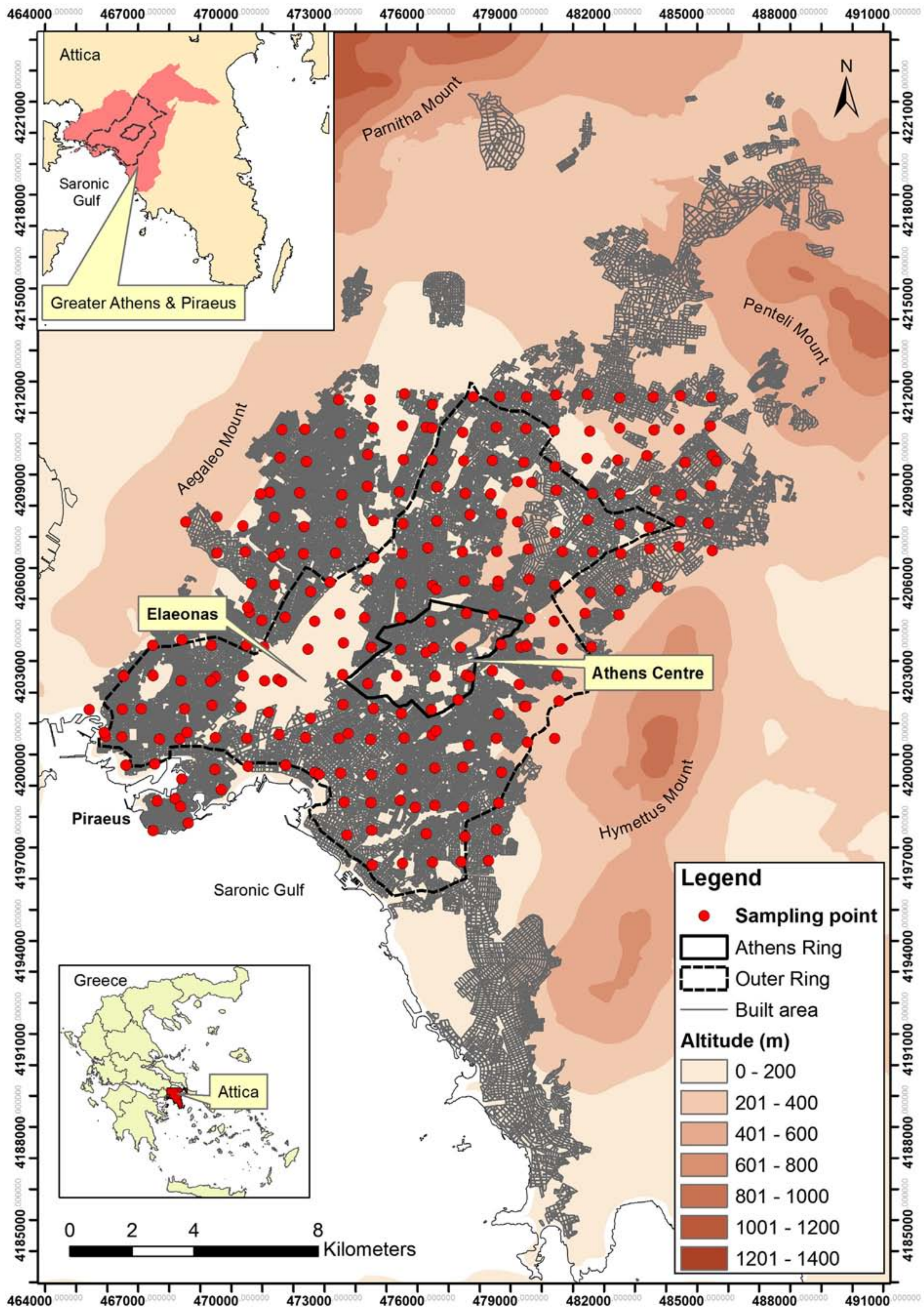

Fig. 1. Topographical map showing the sampling site locations within the urban area of Greater Athens and Piraeus.

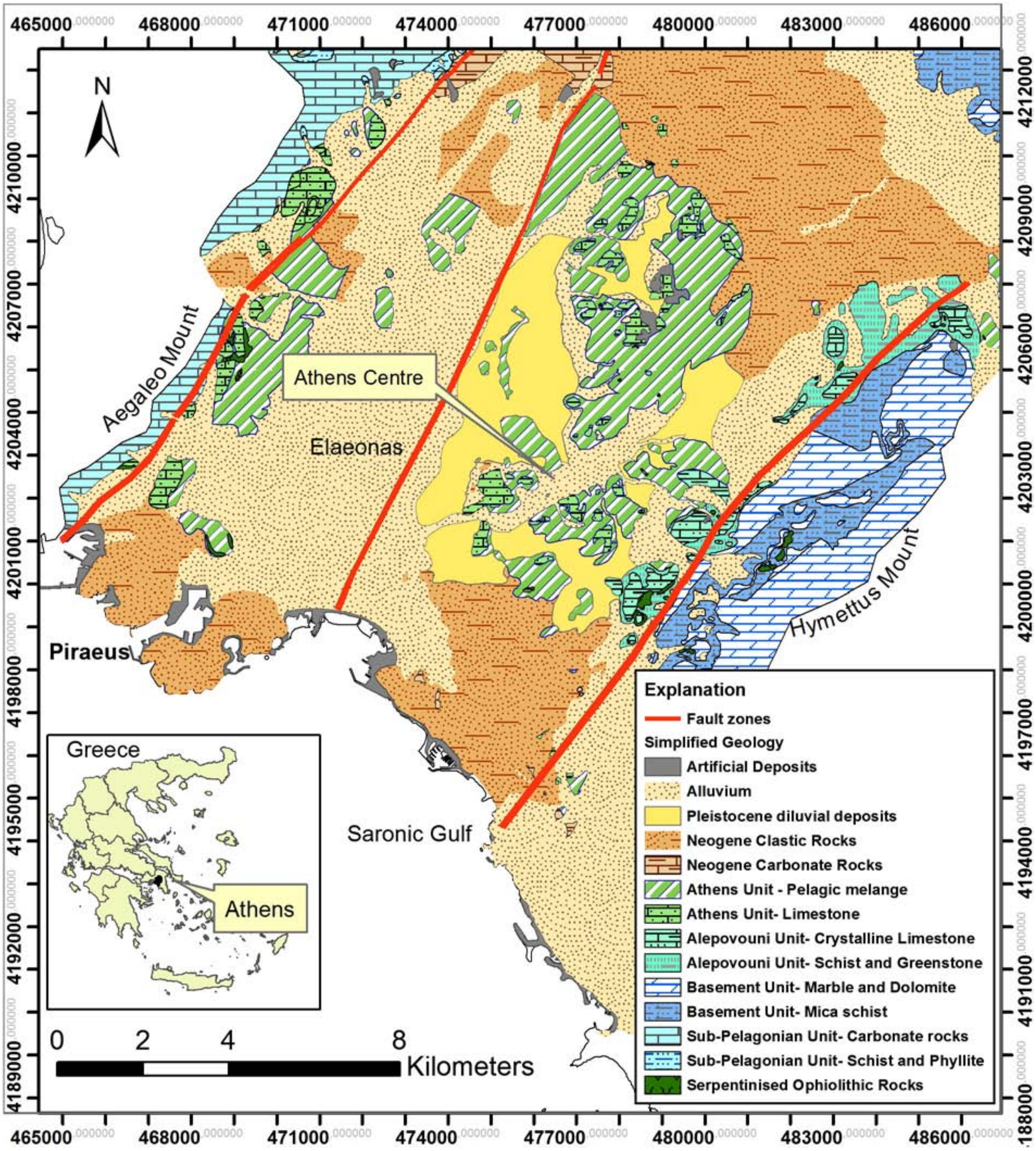

Fig. 2. Simplified geological map of the study area modified after Papanikolaou et al. (2004a).

geographical coordinates for each soil sample were recorded by Geographic Positioning System (GPS: Garmin e-Trex Vista HCx) and field observations were archived. Sampling sites were also photographed for reference.

The soil samples were stored in plastic bags for transportation and storage, and were air dried at a constant temperature of 50 °C for 3 days in a thermostatically controlled oven. They were subsequently gently disaggregated in a porcelain mortar and sieved to <2 mm fraction, using a nylon screen to remove coarse material. Each soil sample was further sieved through a nylon 100-μm sieve in order to focus on geochemically reactive particles and stored at room temperature in a dark storeroom. The <100 μm fraction was used for chemical analyses. All utensils were thoroughly cleaned between the samples to avoid cross contamination.

2.3. Analytical procedure

The total pool of Cu, Zn, Pb, Sn, Sb, Cd, Ni, Cr, Co, As and Mn in soil was determined by a 4-acid (HNO_3, $HClO_4$, HF, HCl) digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) at the accredited ACME analytical laboratories in Vancouver, Canada. Geochemical results for the major elements Fe, Al, K, and Ca were also measured by ICP-MS and included to assist in the source apportionment of metals. This strong acid attack is often used in survey-type geochemical programs (Allen et al., 2011). In the present study it was selected on the basis of local geology, comprising silicate rocks that are more effectively dissolved by this method. Thus, it was anticipated that the near total dissolution would provide a more realistic representation of the geochemical baseline of both geogenic and anthropogenic elements. It is noted that the 4-acid attack is regarded near total for some elements like Cr, because it cannot completely dissolve certain refractory minerals like chromite (Goldhaber et al., 2009). The pH of each soil sample was measured in a soil to deionized water suspension of 1:2.5 (w/v) (ISO, 1994).

The accuracy of chemical analyses was evaluated using two certified reference materials (United States National Institute of Standards NIST 2709 and 2711) and some in-house reference materials (STD OREAS24P, STD OREAS45E) developed by the ACME laboratories for its own internal use. Recovery rates ranged from 80% to 120% for most elements. Seven analytical duplicates were randomly included and yielded relative per cent differences of less than 10%. Reagent blanks were also included throughout the batches as part of the quality control procedure. Details on the quality control results including measured and certified concentrations of the reference materials, analytical precision and detection limits for the 15 studied elements are presented in Table S1 of the Supplementary material.

2.4. Geochemical mapping and statistical treatment of the data

The first step in spatial analysis was the integration of all the available and generated information in a geographical information system (GIS) using ArcMap v.10.0 (ArcGIS). The GIS-based platform incorporated the geo-referenced sampling points, simplified geology of the area, elevation contour lines, municipality borders, and city extent borders for different historical periods. Road network data, corresponding to vehicular traffic restrictions area boundaries were also added. Traffic restrictions have been enforced since 1982 in the city center, the ‘Athens Ring’, by allowing alternatively odd/even plate number vehicles to enter on subsequent days. During intense air pollution events, traffic restrictions are extended to a wider area of Athens, the ‘Outer Ring’ (Fig. 1). Enrichment factors of Pb, Zn and Cu were calculated as ratios of average concentrations in samples within the inner and outer rings ($n = 138$) to average concentrations in the rest of the sampled area.

Data of several urbanization indicators, including urban land use, population density (ELSTAT, 2013), timing of urbanization (Diakakis et al., in press), and vehicular traffic, were linked to the spatial data. These specific indicators have been shown to govern metal distribution patterns in the urban environment (Wang et al., 2012; Peng et al., 2013). Soil samples were grouped based on their respective spatial index with respect to selected urbanization indicators in the GIS. One-way ANOVA followed by post hoc analysis (LSD test) was subsequently applied on the normal score transformed concentration data in order to identify statistically significant differences between the groups.

The geochemical maps showing the overall spatial distribution patterns of elemental concentrations were plotted by using the Geostatistical Analyst tool for ArcMap (ArcGIS) and the Inverse Distance Weighted (IDW) interpolation method with a power of 2. Geographically Weighted Regression (GWR) was used to evaluate the spatial correlations between the studied elements. GWR is a local form of linear regression used to model spatially varying relationships by fitting a regression equation to every feature in the dataset. The method was implemented by using the Spatial Statistics tool for ArcMap (ArcGIS).

Multivariate statistical analysis was carried out using Minitab v.15.0 and SPSS for Windows v.20. Principal component analysis (PCA) and cluster analysis (CA) using the average neighbor linkage were applied to the elemental data after normal score transformation of the raw values. This ensured the normal distribution for all the elements and reduced the influence of high values on the output results. The varimax rotation method was used in PCA in order to extract key components responsible for variation in elemental concentrations. The obtained component factors were interpreted in terms of the assumed origin (geogenic or anthropogenic) or geochemical behavior of the relevant elements.

One-way robust analysis of variance (RANOVA) was applied on the results from the 20 cells containing a second sample in order to estimate the within sampling cell data variability. The technique was implemented using the computer program ROBAN. EXE, adapted from a published program (Analytical Methods Committee (AMC), 2001) and available from the (UK) Royal Society of Chemistry web site.

3. Results and discussion

3.1. Elemental concentrations in urban soil from Athens

The descriptive statistics of the raw data are shown in Table 1. Although the mean value should not be used for compositional data (Reimann et al., 2008, 2012), it is given to facilitate comparison with older urban geochemical studies. All elements display wide variability in their concentrations, reflecting the variety in lithological types as well as anthropogenic impacts like vehicular traffic emissions, soil excavation, transport and redistribution.

Concentrations of the major elements reflect the contribution of underlying geology on soil chemistry. Athens soil is rich in Ca (median 13%, max 38%) due to the high $CaCO_3$ content of both the alpine and post-alpine lithologies. This is also verified by the alkaline soil pH, ranging from 7.1 to 9.2, as well as the abundant presence of calcite in all the samples that were analyzed by X-ray diffraction (data not included here). Aluminum, K, and Fe concentrations reflect the high aluminosilicate mineral content of underlying rocks, especially those of the Athens Unit and the metamorphic rocks outcropping mainly in the central and western part of the basin.

Of the PHEs chromium and Ni displayed the highest medians of 141 mg kg^{-1} and 102 mg kg^{-1} respectively, as well as a wide spread range in their concentrations (Fig. 3). High concentrations of these elements in soil are associated with serpentinized ophiolithic rock (Oze et al., 2004 and references therein). However, the highest variation in concentration was displayed by Pb with a range of 2761 mg kg^{-1}, indicating that in addition to diffused contamination of this element within the urban environment, distinct point sources such as building demolition material and transported contaminated soil give rise to high concentrations.

In comparison with other cities around the world (Table 2), surface soil from Athens showed comparable and somewhat lower concentrations of Cu, Pb, Cd and Zn than most cities (medians of 39, 45, 0.3 and 98 mg kg^{-1}, respectively), but is enriched in Ni, Cr, Co and As with medians of 102, 141, 16 and 24 mg kg^{-1}, respectively. Despite the various analytical methods used to determine the PHEs, the total concentration values of Cu, Pb, Cd, and Zn reported in this research are still low compared to results from many other studies that used a weaker extraction (see Table 2). The relatively low concentration of these typical anthropogenic elements reflects the lack of historical industrial legacy in Athens. The elevated concentrations of Ni, Cr, and Co are attributed to the natural enrichment of soil derived from serpentinized ophiolites, a typical geochemical feature in areas of ophiolite occurrences in Greece (Vardaki and Kelepertsis, 1999; Kelepertzis et al., 2013). This is in agreement with the elevated geochemical background of these elements observed over the whole country in the FOREGS and GEMAS Geochemical Atlases of Europe (Salminen et al., 2005; Reimann et al., 2014).

3.2. Elemental spatial distribution patterns

Geochemical maps were plotted in order to depict the spatial distribution of the studied elements in soil (Fig. 4). Class intervals were defined by natural breaks in the histograms of the original data, and elemental concentrations were plotted as circles with size increasing as a function of concentration. The interpolated surfaces were added in the background for better visual inspection of the spatial trends (brown being higher and yellow being lower). However, it must be noted that interpolated maps must be used with caution due to the variability between the sampling locations.

Table 1
Statistical summary of elemental concentrations ($n = 238$) and pH of urban soils in Athens (in mg kg^{-1} except for Ca, K, Al, Fe in %). RSD$_{samp}$ (%) denotes the robust relative standard deviation of 20 samples collected 200 m away from the original sampling location and expresses soil heterogeneity within the 1 km sampling cells.

Parameter	Mean	SD	Q1	Median	Q3	Minimum	Maximum	RSD$_{samp}$ (%)
Ca	13.5	5.1	11.4	13.0	15.8	1.2	38.0	39.1
K	1.1	0.3	0.9	1.1	1.3	0.3	1.9	20.5
Al	4.5	1.2	3.9	4.5	5.1	1.0	8.2	16.6
Fe	2.4	0.7	2.0	2.4	2.7	0.6	4.8	16.1
Mn	587	237	484	554	662	168	2731	16.9
Cu	48	41	30	39	50	11	410	44.7
Pb	77	194	29	45	70	3	2764	50.0
Zn	122	101	73	98	135	18	1089	43.9
Ni	111	70	83	102	121	27	727	25.9
Cr	163	151	114	141	167	43	1586	24.2
Co	16	5	14	16	18	4	54	19.9
As	29	21	19	24	31	6	204	27.4
Sb	2.4	3.9	1.3	1.7	2.4	0.1	41.7	42.2
Sn	5.5	10.9	2.7	3.6	5.1	0.6	156	39.7
Cd	0.4	0.3	0.2	0.3	0.4	0.1	3.5	35.9
pH	8.3	0.3	8.1	8.3	8.5	7.1	9.2	

Notation: *SD* standard deviation, *Q1* first quartile, *Q3* third quartile.

Urban soil is subject to hundreds of human-driven pressures, resulting in wide differences in elemental concentrations inside the urban net even at short distances (Hursthouse et al., 2004; Albanese et al., 2008; Bain et al., 2012). This impacts continuity between the classes of the parameters mapped and introduces a degree of uncertainty in concentrations between the known sample points. One-way to overcome this issue is to reduce the distance between sampling locations, but this would increase both sampling and analytical research costs. Furthermore, predetermined sampling locations are often moved in order to find soil not covered by buildings and infrastructures. All of the above call for the need of finding other means of quantifying the inherited uncertainty, mainly caused by small-scale soil heterogeneity within the urban environment.

In this study, soil heterogeneity at distances shorter than 1 km was estimated by calculating the robust relative standard deviation (RSD$_{samp}$) of 20 samples collected 200 m away from the original sampling location (Table 1). Prior to this, the analytical repeatability precision was subtracted from the measurement variance. Calculated percentages are exceeding 10% for all studied elements. Furthermore, the calculated RSD$_{samp}$ of the lithogenic group of elements (Ca, K, Al, Fe, Mn, Ni, Cr, Co and As) varying from 16.1% for Fe to 39.1% for Ca is systematically lower than that of typical anthropogenic elements (Cu, Pb, Zn, Sb, Sn, Cd) varying from 35.9% for Cd to 50% for Pb. This provides an additional indication of the origin and mode of deposition of PHEs.

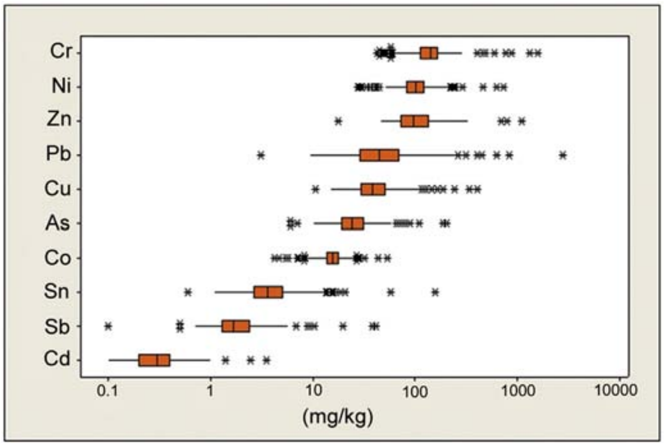

Fig. 3. Boxplot comparison of PHEs concentration and variation in Athens topsoil samples for log-transformed data. Elements are ordered according to decreasing median value. The scale is back-transformed to show concentrations in mg kg^{-1}.

The finding is in agreement with unpublished data from a previous study in an Athens park area. That study employed the collection of topsoil samples at separation distances of 2 m, 25 m, 50 m and 400 m from 8 locations for each distance within the total sampled area of 12,000 m^2 in the park. The sampling precision was subsequently estimated for each distance. Heterogeneity factors were calculated as % RSD$_{samp}$ at the 68% confidence level for Pb and Cr by adopting the method of Ramsey et al. (2013). Results indicate that the heterogeneity of both elements varied systematically with scale. Heterogeneity of Pb, ranging from 10% to 46% over the studied distances, was systematically higher by 10% compared to Cr (heterogeneity factors from 4% to 36%) over the same spatial scales. Although this finding cannot be generalized for the total sampled area across the city of Athens, it indicates a high magnitude of soil heterogeneity even at small sample separation distances, especially for the anthropogenic elements like Pb.

The influence of geology is apparent with respect to the spatial distribution of the major elements Ca, Al and Fe as well as Mn. The highest concentrations of Ca occur mainly in the northern and western parts of the study area (Fig. 4a), which are influenced by non-metamorphic carbonate rocks. The highest values of Al, Fe and Mn appear in the central and eastern parts of the basin that are influenced by the weathering of aluminosilicate rich mélange of the Athens Unit, and the metamorphic rocks of Penteli and Hymettus mountains. Chromium and Ni are enriched mainly in samples located at the periphery of the Athens Basin, along two axes running parallel to the foot hills of Aegaleo and Hymettus Mountains. These areas are characterized not only by outcrops of Alpine rocks, but also by the presence of serpentinized members of ophiolithic sequences. However, a few isolated samples with elevated concentrations of the 2 elements possibly indicate anthropogenic origin of high concentrations. These samples are located in the area of Elaeonas, between the Athens Centre and Piraeus (Fig. 1), where small scale industrial activities take place.

The spatial distribution of As also displays a distinct spatial pattern extending along a NE–SW axis. Arsenic concentrations exceed 100 mg kg^{-1} in several samples along this axis that coincides with the hilly areas built by alpine rocks of the Athens Unit in the center of the basin. Despite the known geochemical affinity between As and Sb, results of GWR indicated that the two metalloids are not spatially correlated in Athens soil. Antimony explained only a small percentage of As spatial variability ($R^2_{adjusted} = 24\%$).

Maximum concentrations of Cu, Zn, Pb, Sn, and Sb were measured in the core area of the city of Athens, within the 'Athens Ring' as well as around Piraeus Port. Relatively high concentrations also extend towards the western part of the city in the area of Elaeonas, while some isolated high values were observed in the periphery of the study area. The lowest concentrations occurred in the north and north-eastern suburbs

Table 2
Literature data on published PHE median concentrations (mg kg^{-1}) in urban soil from various cities around the world.

City	Pb	Zn	Cu	Ni	Cr	Cd	Co	As	Sb	Mn	Analytical method	Reference
Sicily (Italy)	202	138	63	17.8	34	0.68	5.2		3	519	$HNO_3 + HCl$	Manta et al. (2002)
Mexico City	82	219	54	39	116						XRF, $HClO_4 + HF$	Morton-Bermea et al. (2009)
Hong Kong (China)	77.2	92.1	16	11.2	21.6	0.52	3.02				$HNO_3 + HClO_4$	Li et al. (2004)
Galway (Ireland)	58	85	27	22	35		6	8		539	$HNO_3 + HCl + HClO_4 + HF$	Zhang 2006
Napoli (Italy)	141	158	74	8.9	11.2	0.37	6.3	11.9	2	635	$HNO_3 + HCl$	Cicchella et al. (2008)
Damascus (Syria)	10	84	30	35	51		10				$HNO_3 + HCl$	Möller et al. (2005)
Berlin (Germany)	76.6	129	31.2	7.7	25.1	0.35		3.9			XRF, $HNO_3 + HCl$	Birke and Rauch (2000)
Oslo (Norway)	33.9	130	23.5	24.1	28.5	0.34	9.74	4.5		438	HNO_3	Tijhuis et al. (2002)
Bristol (UK)	210.1	272.6	60.1	21	23.1	1.1		21.7			$HNO_3 + HCl$	Giusti (2011)
Zagreb (Croatia)	23	69.7	17.8	48.7		0.5				605	$HNO_3 + HCl$	Romic and Romic (2003)
Lisbon (Portugal)	62	88	29	20	16		6.8	4.4	0.7	218	$HNO_3 + HCl$	Cachada et al. (2013)
Trondheim (Norway)	32	80	32	43	58	0.12		3.3			HNO_3	Andersson et al. (2010)
Annaba (Algeria)	42.3	64.7	23.8		28.3	0.3				405.9	HNO_3	Maas et al. (2010)
Ibadan (Nigeria)	47	93.5	32	16.5	55.5	0.15		3		993	$HNO_3 + HCl$	Odewande and Abimbola (2008)
Sevilla (Spain)	103	86	41.7	23.1	42					468	$HNO_3 + HCl$	Madrid et al. (2004)
Beijing (Cjina)	19.3	84.5	26.1	23.8	60	0.11					$HNO_3 + HCl + HClO_4 + HF$	Wang et al. (2012)
Baltimore (USA)	89.3	80.7	35.2	18.4	38.3	0.89	12.1			422	$HNO_3 + H_2O_2 + HCl$	Yesilonis et al. (2008)
Chicago (USA)	198	235	59	31	65		11	13.2		495	$HClO_4 + H_2SO_4 + HF + HCl$	Cannon and Horton (2009)
Greater Athens and Piraeus (Greece)	45	98	39	102	141	0.3	16	24	1.7	554	$HNO_3 + HCl + HClO_4 + HF$	This study

of the city where urbanization has an almost exclusively residential character.

3.3. Multivariate analysis results

The PCA results are presented in Table 3 and in Fig. S2 (Supplementary material) as a biplot. Three principal components were identified accounting for 78% of the total variance. This percentage is not very high because other parameters, such as soil pH and texture, organic content and cation exchange capacity, probably contribute to the total elemental variability. The first component (PC1) includes Al, K, Fe and Mn with high positive values and is interpreted as a geogenic source associated with the major rock-forming elements in soil. The typical contamination indicators Pb, Zn, Cu, Sn, Cd, and Sb are strongly associated in the second component (PC2), while the third component (PC3) includes Ni, Cr and Co, indicating the ophiolithic parent rocks as their common, geogenic source. Arsenic is not included in any of the principal components; however, it presents its highest loadings in PC1.

Based on their concentrations, the studied elements were hierarchically grouped by using cluster analysis. The distance measure was the Pearson correlation coefficient at the 95% confidence level. The results are presented in the dendrogram of Fig. 5. The similarity axis represents the degree of association between the elements, the greater the value the more significant the association. Three distinct clusters are identified, based on a criterion for similarity of >60%. The results of CA complement those of PCA and thus, verify interpretation of the data. Specifically, Ca is the main cluster that reflects the dominance of carbonate containing rocks in the area. This is then divided into two clusters, one containing Cu, Zn, Pb, Sn, Sb, and Cd that reflects local anthropogenic pollution, and another that reflects local geology and includes Ni, Cr, and Co, Mn, Fe, Al, and K, and As as three groupings. These three groupings likely represent enrichment of these elements in specific rock types. The Ni, Cr, Co group is controlled by the contribution of ophiolithic rocks to soil chemistry. The Mn, Fe, Al, K group contains elements associated with the weathering processes of aluminosilicate minerals and pedogenesis, and finally As, displays high similarity with the lithogenic elements within the Athens Unit. Overall, the results of multivariate analysis are in good agreement with the elemental spatial distribution patterns.

3.4. Influence of urbanization indicators on soil chemistry and sources of PHEs

Data for the evaluation of PHE geochemistry with respect to urbanization indicators, including urban land uses, population density and timing of urbanization are presented in Table 4. Statistically significant ($p < 0.05$) higher concentrations of Cu, Pb, and Zn are detected in road verge soil compared to other land use categories. This is in agreement with many previous studies (e.g., Li et al., 2001, 2004; Möller et al., 2005; Morton-Bermea et al., 2009; Andersson et al., 2010), indicating vehicular traffic as the major contributory factor in urban soil contamination by the typical anthropogenic elements. Leaded fuel for Pb, tire wear for Zn and Cd, and brake pads for Sb have been recognized as specific vehicular traffic-related sources (Albanese and Breward, 2011). The significant contribution of vehicular traffic on the distribution of these elements in soil is also reflected in the enrichment factors of 1.90, 1.27 and 1.40 for Pb, Cu, and Zn respectively in the city core area. It is noted that the city center is characterized by low average vehicular speeds and more vehicles (Region of Attica, Athens Traffic Management Centre, 2013).

Distinct point sources also contribute to hot-spots of these elements in soil. In the city of Athens, such hot-spots were identified at the west end of the center and were attributed to the small scale industrial activity in this area. For example an indicator of urban contamination is Sn, because of its very low (<5 mg kg^{-1}) natural concentration levels and limited mobility. Old paint, glazed pottery, electrical solder, and tin plate (food cans) are sources of Sn in the urban environment (Albanese and Breward, 2011). In the present study a high proportion of the spatial variability of Sn was predicted by Pb as estimated by the GWR analysis ($R^2_{\text{adjusted}} = 87\%$), providing further evidence on common sources of these 2 elements. Interestingly, Pb concentrations in park and woodland areas are also significantly higher than other land use categories. This indicates either greater deposition of airborne Pb in soil of vegetated areas (Ukonmaanaho et al., 2001; Michopoulos et al., 2005), or the effect of distinct point sources within park and woodland areas. The same pattern is observed for As, while no significant differences are detected for Cr, Ni and Co among different land use categories (ANOVA, $p > 0.05$ in all cases).

Population density data, disaggregated to municipality level, also displayed significant differences between the densely populated areas of central Athens and Piraeus, and the less populated north and north-eastern suburbs with respect to Pb, Cu, and Zn concentrations. The data were classified into four categories of (i) low (967–7584 people/km^2), (ii) medium (7585–10,924 people/km^2), (iii) high (10,925–16,830 people/km^2) and (iv) very high (16,831–21,068 people/km^2) population density (see Fig. S1 in Supplementary material). These classes were based on area coverage estimated by the GIS software and correspond to population densities within approximately equal areas. Statistically significant differences ($p < 0.003$) were identified between the categories low and high–very high for the elements Pb, Cu, and Zn.

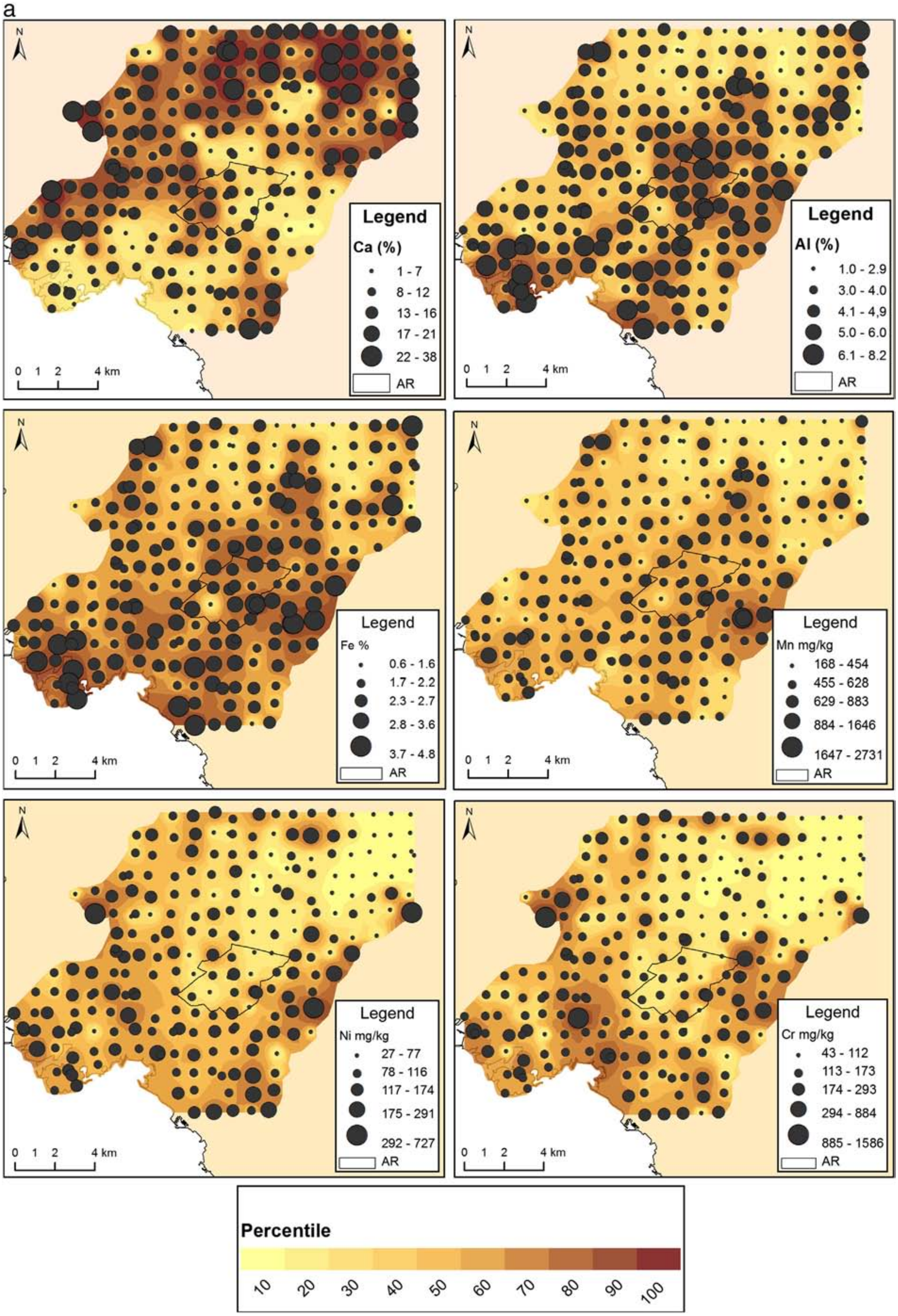

Fig. 4. a. Geochemical maps showing the spatial distribution patterns of mainly geogenic chemical elements (Al, Ca, Fe, Mn, Co, Cr) in urban soil in the city of Athens (AR = 'Athens Ring'). b. Geochemical maps showing the spatial distribution patterns of mainly anthropogenic chemical elements (Pb, Zn, Cd, Cu, Sb) and As in urban soil in the city of Athens (AR = 'Athens Ring').

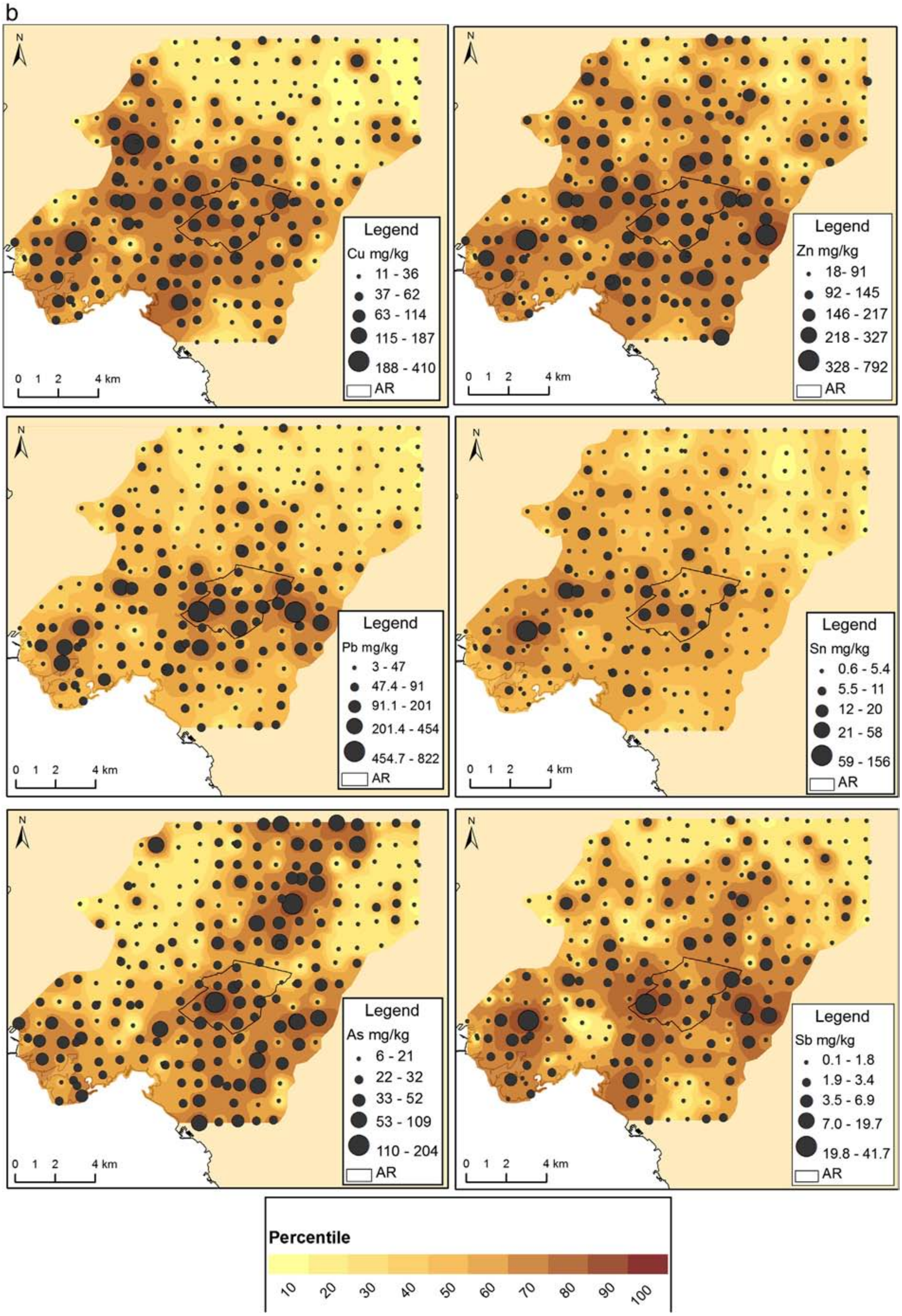

Fig. 4 (*continued*).

Table 3
Total variance explained and matrix of principal component analysis for normalized elemental concentrations of urban soil in Athens. Significant principal component loadings are indicated in italics.

Element	Rotated component matrix		
	PC1	PC2	PC3
Cu	0.215	*0.842*	0.178
Pb	0.130	*0.898*	0.049
Zn	0.125	*0.894*	0.056
Ni	0.143	0.019	*0.961*
Co	0.593	0.071	*0.745*
Mn	*0.789*	0.182	0.333
Fe	*0.874*	0.111	0.348
As	0.421	0.272	0.192
Sb	0.202	*0.835*	0.046
Ca	−0.840	−0.058	−0.242
Cr	0.162	0.131	*0.933*
Al	*0.971*	0.057	0.017
K	*0.934*	0.141	−0.091
Sn	0.129	*0.854*	−0.037
Cd	−0.076	*0.633*	0.046
Eigenvalue	4.62	4.31	2.73
% variance explained	30.8	28.7	18.2
Cumulative % variance	30.8	59.5	77.7

A similar analysis of geochemical data concerning the age of parts of the city was based on the spatial extent of the urban net during three time periods: 1834–1920, 1920–1945 and 1945–1980 (Diakakis et al., in press) (see Fig. S3 in Supplementary material). Concentrations of Pb, Cu, Zn, as well as Sb and Sn, are systematically higher in the older parts of the city. Statistically significantly lower concentrations ($p < 0.05$) were observed in areas where the latest expansion spread, i.e., after World War II. No systematically significant differences between areas developed in different time periods were observed for Ni, Cr, Co, and As, providing further evidence that the spatial distribution of these elements is more strongly influenced by their geogenic signature.

Arsenic and Cd are often associated with coal combustion and point-sourced industrial discharges respectively (Shi et al., 2008; Yang et al., 2011). In Athens surface soil Cd concentrations are rather low, close to detection limit. However, As was found to be enriched in a number of samples reaching a maximum of 204 mg kg^{-1} and displays a distinct spatial pattern (Fig. 4b). Multivariate cluster analysis of the Athens geochemical data implied a geogenic source for As, showing higher similarity with major elements related to pedogenesis. It is well established that As adsorbs very easily, either as As (III) or As (V), on different soil components such as Fe and Al oxides, and clay minerals (Smedley and Kinniburgh, 2002). Existing data on the geological sources of As in Greece have been reviewed by Gamaletsos et al. (2013). In their review, As-bearing Mn-silicates are reported as possible hosts of As in metamorphic rocks found in NE Attica. Moreover, concentration of As ranges from 61 to 210 mg kg^{-1} and 33 to 430 mg kg^{-1} in limestone and related soil from NE Attica respectively (Kampouloglou and Economou-Eliopoulos, 2013). However, we must reserve judgment on the natural origin of this element in Athens soil, as the statistically significantly higher concentrations that were detected in parks and woodland areas might be indicative of anthropogenic airborne sources of As. The use of As-based pesticides in the past cannot be excluded. Further research, focused on comparisons of chemistry of the underlying rocks, as well as As speciation in soil, is needed in order to clarify the origin of this element.

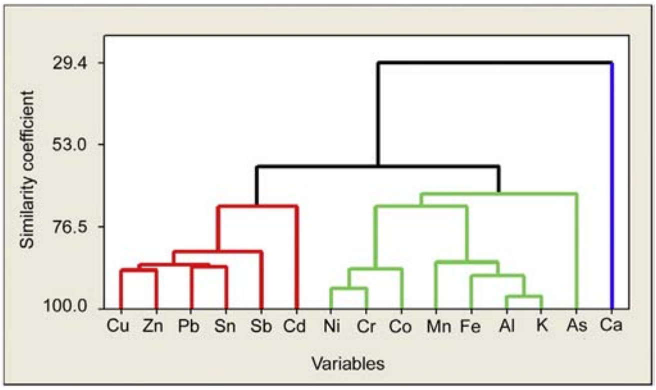

Fig. 5. Cluster analysis dendrogram based on the linear correlation coefficients using the average neighbor linkage method and correlation coefficient distance.

Nickel concentrations in urban soil may be controlled either by parent rock materials (Chen et al., 2005), or by atmospheric deposition of vehicle emissions (Cannon and Horton, 2009). Chromium and Co are routinely attributed to weathering processes and their amounts in urban soil are usually too low to reach contamination levels (Manta et al., 2002; Lee et al., 2006). In Athens, all 3 elements were enriched in soil, exceeding reported concentrations in other cities worldwide (Table 2). Although the anthropogenic influence cannot be totally excluded, the presence of serpentinized ophiolithic rocks in local geology, coupled with their strong statistical similarity (Fig. 5 and Table 3), points to their common, natural source.

Elevated concentrations of Cr and Ni, with median values of 141 mg kg^{-1} and 102 mg kg^{-1} respectively, might indicate a potential environmental hazard, although their speciation and bioaccessibility, rather than simply their total concentrations, have to be addressed first (Gupta et al., 1996). A recent study on urban soil from Thiva, a Greek town 90 km north of Athens with geochemical influence by ultramafic rocks, demonstrated that pseudototal concentrations of Cr and Ni, derived with aqua regia, were not indicative of metal bioaccessibility (Kelepertzis and Stathopoulou, 2013).

4. Conclusions

A geochemical baseline study of surface soil in Athens, based on a systematic sampling survey covering the Greater Athens and Piraeus area, was done. The contents of the major elements Fe, Al, K, and Ca, and potentially harmful elements (PHEs) Ni, Cr, Co, Mn, As, Pb, Zn, Cu, Cd, Sb, and Sn were determined. Principal component analysis and cluster analysis, combined with analysis of soil heterogeneity and spatial variability, were implemented in order to distinguish the sources of elements and their classification as geogenic or anthropogenic. It was found that the major factor controlling variability of the chemical composition of surface soil was the bedrock chemistry, resulting in a significant enrichment in concentrations of Ni, Cr, Co and possibly As.

Anthropogenic influences were also significant, controlling a spectrum of elements that are typical of human activities, i.e. Pb, Zn, Cu, Cd, Sb, and Sn. The highest concentrations of the classical urban contaminants were observed in the surface soil from roadside verges and in the older parts of the city, as well as the densely populated areas. A prominent feature of soil chemistry throughout the city is the enrichment of Pb and As in parks and woodland areas. Spatial distribution patterns of PHEs demonstrated an increase in concentrations of the anthropogenically induced metals towards the city core and the port of Piraeus. On the contrary, the naturally derived Ni, Cr and Co are mainly enriched in the periphery of Athens Basin.

Taking into account the salient enrichment of geogenic metals in Athens soil, comparing with concentrations measured in other cities around the world, this study provides a baseline for understanding PHE mobility and bioaccessibility. This work is important, for under the current economic conditions, the development of urban agriculture is an emerging initiative of several municipalities.

Conflict of interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant

Table 4
Median concentrations and range of values (mg kg^{-1}) for selected PHEs in urban soil from Athens according to land use, population density and age of urban area.

	Cu	Pb	Zn	Ni	Cr	As
Land use						
RV ($n = 65$)	49 (16–188)	56 (17–621)	126 (53–327)	105 (28–224)	148 (48–884)	24 (10–65)
PS/P/S ($n = 88$)	38 (15–410)	44 (9.3–252)	91 (48–290)	102 (30–291)	139 (50–1586)	23 (6–81)
US ($n = 43$)	30 (11–336)	28 (3.1–455)	80 (18–792)	92 (27–727)	122 (43–1328)	24 (6–189)
P/W ($n = 41$)	40 (18–90)	60 (11–823)	104 (48–692)	95 (28–622)	129 (50–1586)	29 (12–204)
Population density						
Low ($n = 68$)	32 (11–93)	36 (3.1–233)	80 (18–692)	90 (27–727)	119 (43–1328)	23 (6–109)
Medium ($n = 61$)	40 (15–128)	42 (9.3–261)	95 (48–327)	108 (30–291)	154 (50–1586)	23 (6–65)
High ($n = 98$)	42 (17–410)	51 (11–823)	108 (46–792)	102 (28–186)	139 (45–763)	26 (12–204)
Very high ($n = 10$)	49 (32–115)	66 (35–312)	120 (98–238)	103 (84–224)	152 (127–884)	27 (13–33)
Age of urban area						
1834–1920 ($n = 34$)	46 (28–147)	56 (22–252)	115 (61–279)	103 (65–159)	144 (84–262)	27 (15–204)
1920–1945 ($n = 83$)	41 (15–336)	51 (9.3–823)	106 (48–792)	103 (28–727)	144 (45–1586)	23 (6–189)
1945–1980 ($n = 99$)	34 (11–410)	36 (3.1–189)	87 (18–290)	100 (27–460)	134 (53–481)	23 (6–109)

Notation: RV = road verge; PS/P/S = public squares, playgrounds and school yards; US = unbuilt spaces; P/W = parks and woodland.

financial support for this work that could have influenced its outcome. We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

We understand that the Corresponding Author, Ariadne Arygraki, is the sole contact for the Editorial process (including Editorial Manager and direct communications with the office). She is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs. We confirm that we have provided a current, correct email address which is accessible by the Corresponding Author and which has been configured to accept email from argyraki@geol.uoa.gr.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2014.02.133. These data include Google map of the most important areas described in this article.

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