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GEOCHEMICAL MAPPING OF URBAN SOILS IN ATHENS, GREECE- PRELIMINARY RESULTS

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Abstract

Urban geochemistry is a fast growing scientific discipline mainly because of the profound impact of large cities on the environment as well as the increase in the world's urban population. The present study aims to produce the urban geochemical map of Athens, based on multi-element analysis of surface soils (0-10 cm) with emphasis in the spatial distribution of potentially harmful elements (PHEs). Soil sampling was based on a regular 1km x 1km grid, laid over the survey area covering more than 200 km^2. Sampling locations within the grid cells were selected giving priority to playgrounds, schools and urban parks. The < 100 μm fraction of a total of 320 soil samples were analysed by Flame Atomic Absorption Spectroscopy for Pb, Zn, Cu, Cd, Cr, Ni, Co and Mn after aqua regia dissolution. Average content of Pb (62 mg/kg), Cu (36 mg/kg), Zn (91 mg/kg) and Mn (465 mg/kg) in soil was lower than reported concentrations from other European cities while Cr (74 mg/kg), Ni (89 mg/kg) and Co (16 mg/kg) were relatively enriched. Geochemical maps were plotted within GIS enabling recognition of spatial trends in elemental concentrations and potential sources of the elements. The research outcome will contribute to the evaluation of quality characteristics of urban soils in Athens and drive attention to areas of any environmental or health risks.

Key words: *Heavy metals, environmental contamination, GIS.*

Περίληψη

Η αστική γεωχημεία είναι ένας αναπτυσσόμενος επιστημονικός τομέας κυρίως λόγω των περιβαλλοντικών επιπτώσεων από την εξάπλωση των πόλεων και την αύξηση του αστικού πληθυσμού. Η παρούσα εργασία έχει ως στόχο τη γεωχημική χαρτογράφηση των επιφανειακών (0-10 cm) εδαφών της Αθήνας με έμφαση στη χωρική κατανομή δυνητικά βλαβερών χημικών στοιχείων. Η δειγματοληψία υπαίθρου πραγματοποιήθηκε βάσει τετραγωνικού κανάβου ισοδιάστασης 1 km και κάλυψε συνολική έκταση περίπου 200 km^2, με προτεραιότητα σε παιδικές χαρές, σχολεία και πάρκα. Αναλύθηκαν320 εδαφικά δείγματα κοκκομετρίας < 100 μm με την τεχνική της φασματοσκοπίας ατομικής απορρόφησης μετά από διαλυτοποίηση με βασιλικό ύδωρ και προσδιορίστηκαν τα στοιχεία Pb, Zn, Cu, Cd, Cr, Ni, Co και Mn. Οι μέσες συγκεντρώσεις των στοιχείων Pb (62 mg/kg), Cu (36 mg/kg), Zn (91 mg/kg) και Mn (465 mg/kg) είναι χαμηλότερες των αντίστοιχων συγκεντρώσεων άλλων Ευρωπαϊκών πόλεων ενώ οι

συγκεντρώσεις των Cr (74 mg/kg), Ni (89 mg/kg) και Co (16 mg/kg) υψηλότερες. Το γεωχημικό ανάγλυφο αποτυπώθηκε σε περιβάλλον ΓΣΠ δίνοντας τη δυνατότητα προσδιορισμού διαφορετικών πηγών των στοιχείων. Τα αποτελέσματα της έρευνας συμβάλουν στην εκτίμηση της ποιότητας των εδαφών της Αθήνας και αποτελούν πολύτιμο εργαλείο στην αναγνώριση περιοχών περιβαλλοντικής επικινδυνότητας.
Λέξεις κλειδιά: *Βαρέα μέταλλα, περιβαλλοντική ρύπανση, ΓΣΠ.*

1. Introduction

Urban geochemical mapping studies are useful for establishing a baseline for the urban environment, satisfying the legislative-driven demand for geochemical information on the urban chemical environment, locating polluted areas, assessing the contribution of parent materials and anthropogenic activity to the geochemical baseline, assessing risks to other compartments of the urban environment (e.g. groundwater) and identifying sources of potentially harmful elements (PHEs) (Johnson and Ander, 2008). Within this frame many cities around the world have been mapped with respect to PHEs content in soil (Kelly et al., 1996; Li et al., 2004; Madrid et al., 2002; Cicchella et al., 2008; Andersson et al., 2010). In Greece, a few publications exist on the soil geochemistry of urban areas (Demetriades, 2010; Massas et al. 2010; Massas et al. 2013) however systematic geochemical maps of urban soils do not exist for any of the major cities.

The present study aims to produce the urban geochemical map of Athens, the capital city of Greece with population exceeding 3 million (2011). The study was implemented by multi-element analysis of surface soils (0-10 cm) and this paper is focused on the spatial distribution of PHEs. Geochemical maps were plotted within GIS enabling recognition of spatial trends in elemental concentrations and potential sources of the elements. The preliminary results presented here, enable the identification of spatial patterns in elemental concentration corresponding to lithology and anthopogenic activity. The research outcome will contribute to the evaluation of quality characteristics of urban soils in Athens and drive attention to areas of any environmental or health risks.

2. Materials and Methods

2.1. Soil Sampling and Chemical Analysis

Soil sampling was based on a regular 1km x 1km grid, laid over the survey area covering more than 200 km^2. The 281 sampling locations within the grid cells were selected giving priority to playgrounds, schools and urban parks. Sampling depth was 0-10 cm. At each sampling site, samples were collected in sealable plastic bags after removing debris and surface vegetation. Five-fold composite samples were collected by mixing sample increments from the four corners and the centre of a 10 m square. Sampling duplicates were collected from 20 random sites by collecting a second soil sample about 200 m away from the original point at random direction but within the same 1km^2 sampling cell. A balanced Analysis of Variance (ANOVA) experimental design was subsequently applied by performing duplicate analysis for each of the field duplicate samples. This allowed the estimation of *geochemical* (between sampling sites), *sampling* (between sampling duplicates) and *analytical* (between analytical duplicates) variances as proportions of the total variability in the data set (Ramsey and Elisson, 2007; Argyraki, 2010).

The < 100 μm fraction of a total of 341 soil samples was analysed by Flame Atomic Absorption Spectroscopy for Pb, Zn, Cu, Cd, Cr, Ni, Co and Mn after *aqua regia* dissolution. All analytical procedures were performed in the Laboratory of Economic Geology and Geochemistry, University of Athens. Sampling and analytical quality was assessed by applying the duplicate method (Ramsey and Elisson, 2007) and inclusion of blanks and 3 certified reference materials (NIST SRM2709, NIST SRM2711 and ISE921) in random positions within the analytical batches.

2.2. Data Processing and GIS Application

Analytical results were inspected for systematic differences between batches and for outlying values. Subsequent statistical analysis was performed by calculating the basic descriptive statistics for the measured parameters including minimum, maximum, mean, median and standard deviation values. Factor analysis, a multivariate statistical method, was applied on the normal scores of concentration values in order to group the studied elements according to their inter-correlations and define geochemical processes that control their distribution in soil. Presentation and interpretation of the spatial patterns in PHEs soil content was enabled by using a GIS system within the ArcMap platform. Apart from the geochemical data, layers of spatial information that were inserted in the GIS included the topography and local geology of Athens. These data were provided by the Department of Dynamic Geology of UoA.

3. Results and Discussion

3.1. Descriptive Statistics

The descriptive statistics of heavy metal concentrations are presented in Table 1. Average concentrations reported in the literature for other European cities are also provided for comparison.

All elements showed positively skewed distributions- median values were always lower than means. Athens soils showed relatively lower concentrations in Mn, Cu, Pb and Zn than most European cities but were enriched in Ni, Cr and Co. Further statistical processing of the data by applying factor analysis grouped the elements in 3 groups accounting for 85% of the total variation (Table 2). The first factor included Ni, Cr and Co with high positive loadings and was interpreted as lithogenic, the second included Cu, Pb and Zn and the third Mn. Copper, Pb, Zn and Mn are typical elements indicating the influence of anthropogenic activities on soil characteristics in urban environments since they were used extensively throughout history (Albanese and Cicchella, 2012). Especially Pb was one of the most significant contaminants in urban environments throughout the 20^{th} century as a consequence of its use in urban smelters, in paint and its presence as tetraethyl lead in gasoline.

Table 1 - Statistical summary of heavy metal concentrations (mg/ kg) in urban soils from Athens extracted by aqua regia dissolution (n=281). Average concentrations for some European cities are also given for comparison purposes.

	Ni	Cr	Co	Mn	Cu	Pb	Zn
Mean	89	74	16	465	36	62	91
Standard Deviation	56	41	3.3	185	32	125	77
First quartile	63	51	14	377	22	32	54
Median	82	68	16	445	29	41	72
Third quartile	99	88	17	525	37	57	104
Minimum	26	19	5.8	121	8.5	9	14
Maximum	616	500	41	2200	316	1930	833
Trondheim (Norway)[1]	45	65			39	81	112
Napoli (Italy)[2]	11.6	15.3	7.3	683	94	204	223
Sevilla (Spain)[3]	21.9	39.4		471	68.2	137	145
Galway (Ireland)[4]	20.7	33.3	5.6	674	33.2	78.4	99.3

[1]Andersson et al., 2010, [2]Cicchella et al., 2008, [3]Madrid et al., 2002, [4]Zhang 2006

Table 2 – Rotated factor loadings and communalities based on normal score data of heavy metal concentrations in 281 urban soils of Athens.

Variable	Factor 1	Factor 2	Factor 3	Communality
Ni	0.935	0.058	0.157	0.902
Cr	0.912	0.146	0.077	0.859
Co	0.820	0.090	0.333	0.791
Mn	0.310	0.143	0.929	0.980
Cu	0.263	0.851	0.182	0.826
Pb	0.088	0.879	-0.030	0.781
Zn	-0.029	0.883	0.110	0.793
% Variance	0.364	0.333	0.150	0.847

3.2. Spatial Heterogeneity within the Sampling Cells

One-way analysis of variance was applied on the results from duplicate sampling and analysis. The technique was implemented using the computer program ROBAN. EXE, adapted from a published program (AMC, 1989) and available from the (UK) Royal Society of Chemistry web site. It was found that while analytical variance was within acceptable limits, accounting for small proportions (1.8 % - 12 %) of the total variance for all the elements, sampling variance contributed higher percentages than the geochemical variance in most instances. This was attributed to the high degree of soil heterogeneity within the separation distance of sampling duplicates (about 200 m). Indeed urban soils are subject to hundreds of human-driven forcings resulting in wide differences in elemental concentrations inside the urban net (Hursthouse et al. 2004; Bain et al. 2012). Densely populated areas amplify human-driven fluxes through waste generation at spots or through abrupt changes in land use within areas smaller than 1 km^2 which was the used sampling spacing in this study. Based on these facts it was decided not to interpolate the concentration values, as this would result in an erroneous smoothing effect, but rather present them as graduated size symbols on the constructed maps.

3.3. Spatial Distribution of PHEs

The spatial distribution of the studied elements is presented in two maps as integrated indexes of the lithogenic (Cr+ Ni +Co) (Figure 1) and anthropogenic (Pb + Zn +Cu) (Figure 2) elements. The grouping of elements was based on results from the factor analysis and the class intervals were defined based on natural breaks in the histograms of integrated data. Distinct patterns were observed between the two maps. Specifically, the lithogenic elements displayed maximum concentrations towards the periphery of the Athens Basin, along two axes running parallel to the foot hills of Agaleo and Hymettus Mountains. These areas are characterised not only by outcropping of Alpine rocks but also by the presence of serpentinised members of ophiolithic sequences (Papanikolaou et al. 2004) (Figure 3). The spatial correlation between maximum concentrations of Cr, Ni and Co and these lithological types provides further evidence on the geogenic origin of these elements. On the contrary maximum concentrations of Pb, Zn and Cu are plotted in the core area of the city of Athens, around the hills of Acropolis and Lycabetus as well as around Piraeus Port.

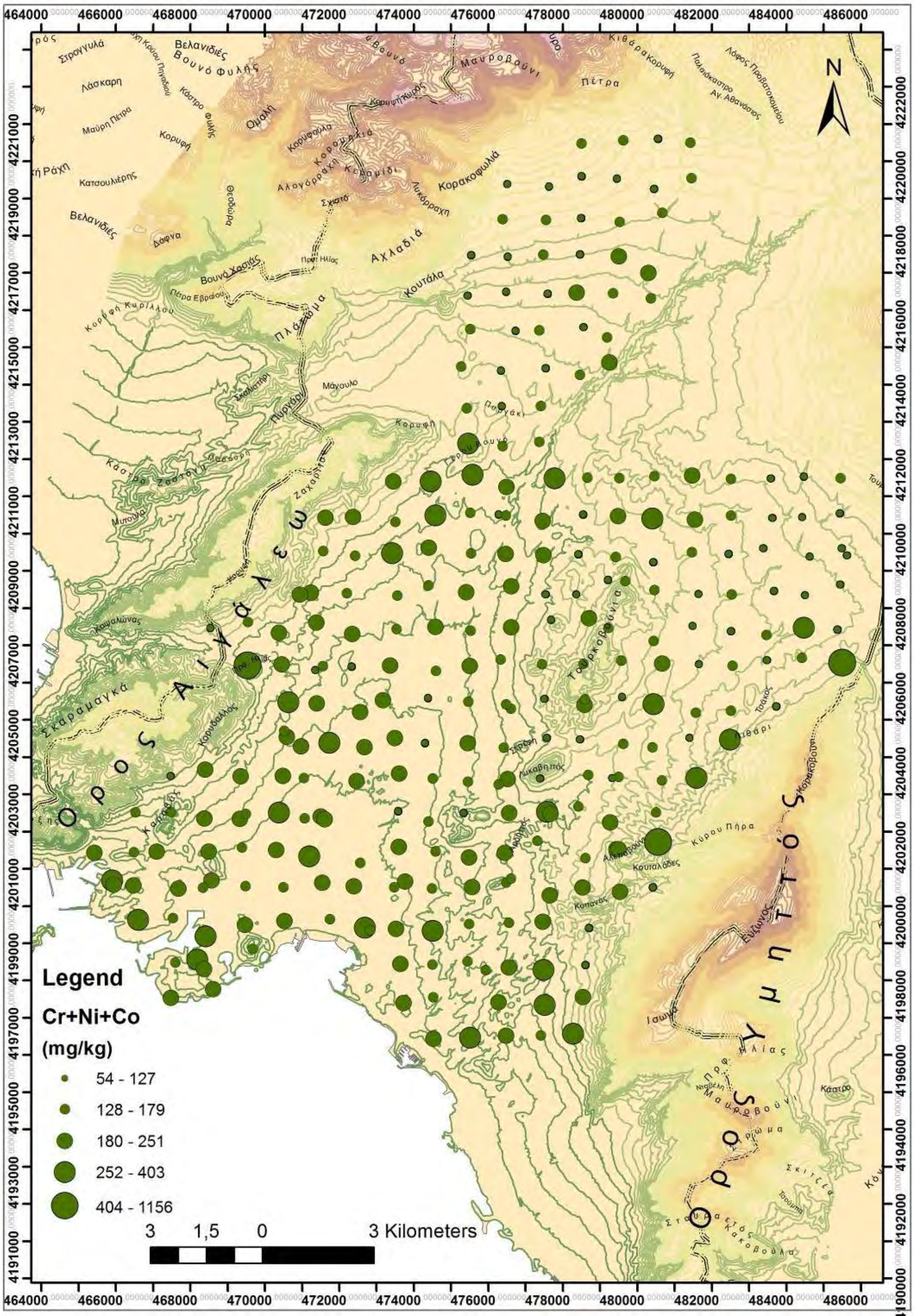

Figure 1 - Graduated symbol map showing the spatial distribution of the integrated index for the lithogenic elements Cr, Ni and Co in Athens soils.

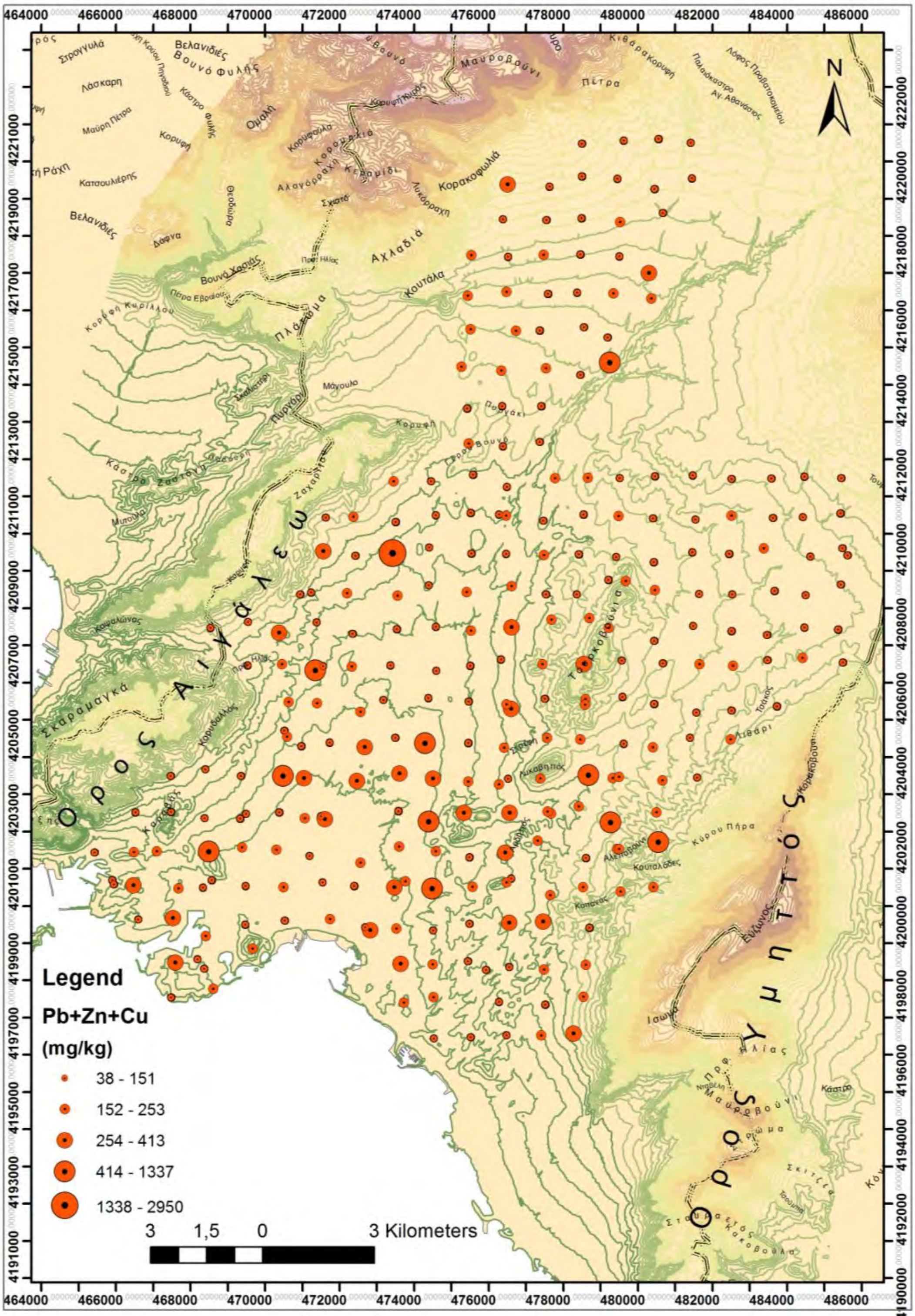

Figure 2 - Graduated symbol map showing the spatial distribution of the integrated index for the anthropogenic elements Pb, Zn and Cu in Athens soils.

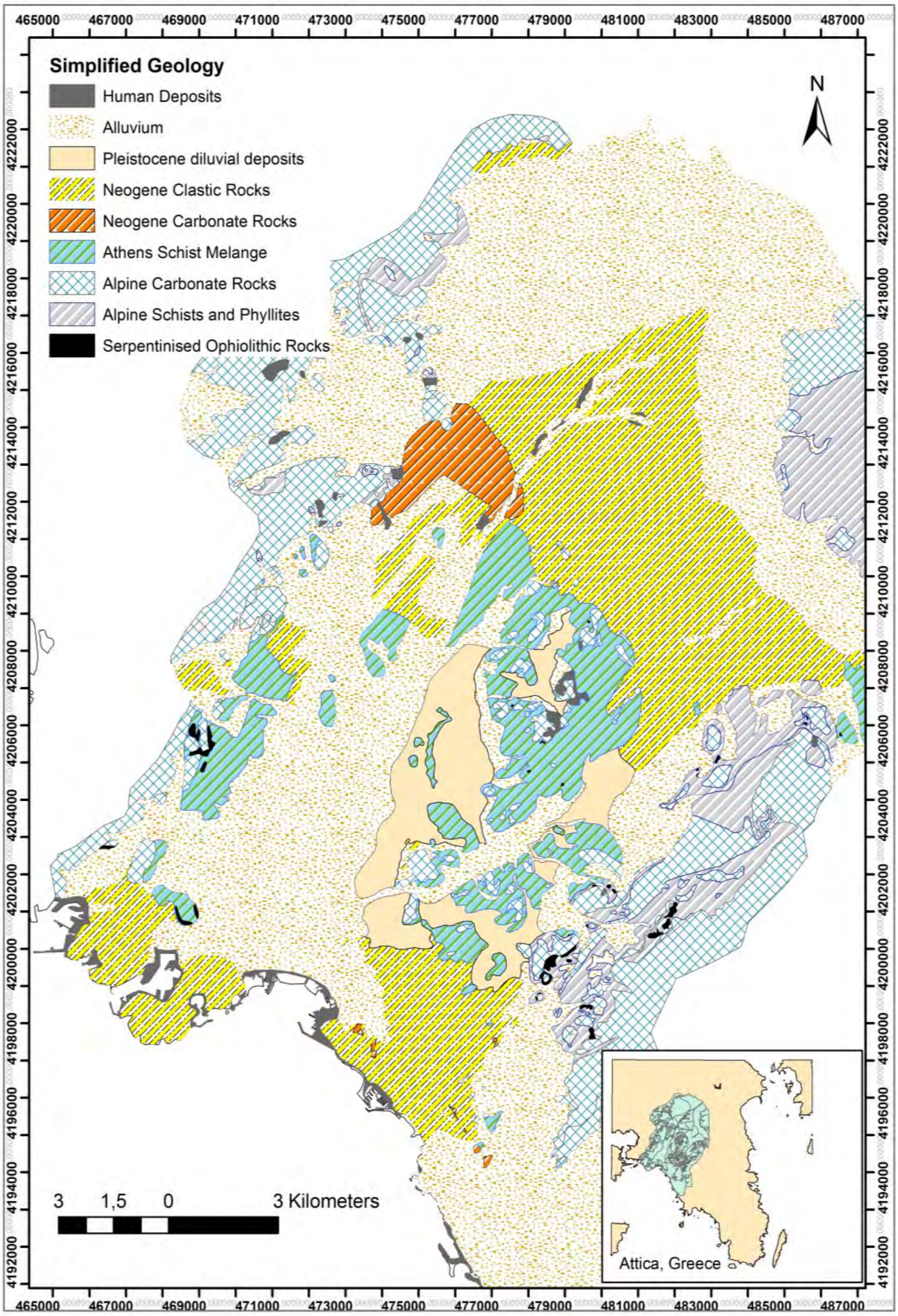

Figure 3 - Simplified geological map of the Athens Basin. Modified from Papanikolaou et al. 2004.

High concentrations of this group of elements extend towards the western part of the city in the industrial areas of Elaionas, while some isolated high values are observed in the periphery of the study area. Although the results presented here are preliminary, the spatial trend of Pb, Zn and Cu is probably linked to factors such as timing of urbanization, age of infrastructure, population density, vehicular traffic and amount of green spaces (Lyons and Harmon, 2012). In general, Pb, Zn and Cu have been repeatedly shown to be related to vehicular pollution (Li et al., 2004; Morton-Bermea et al., 2009). Further work will explore these relationships by utilizing statistical techniques and GIS in order to define the most significant of the contributing factors. Also, urban soils are considered to be sinks of PHEs deposited by atmospheric fallout, usually as adsorbed species onto particulate matter. Such secondary enrichment results in enhanced extractability and high bioavailability (Kierczak et al., 2008; Albanese and Ciccella, 2012) and calls for evaluation of the significance of geochemical anomalies in relation to lithological characteristics and human activities.

4. Conclusions

Systematic data on soil geochemistry of the city of Athens, covering the total extend of the metropolitan area are presented for the first time. In this study preliminary results on aqua regia extracted concentrations of PHEs were evaluated and compared to reported literature data from other European cities. It was found that Athens soils had lower concentrations of Pb, Cu, Zn and Mn but were relatively enriched in Cr, Ni and Co. Geochemical maps were plotted within GIS enabling recognition of spatial trends in elemental concentrations and potential sources of the elements. The group of Cr, Ni and Co was interpreted as being of geogenic origin and displayed spatial association of maximum values with ophiolithic rock outcrops in the periphery of the Athens Basin, while the group of Pb, Cu and Zn showed maximum concentrations in the centre of the city indicating anthropogenic influence. Further work within the GIS will exemplify relationships between spatial data such as population density, age of urban development and automobile traffic intensity and heavy metal concentrations in soil. The research outcome will contribute to the evaluation of quality characteristics of urban soils in Athens and drive attention to areas of any environmental or health risks.

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