15th International Congress of the Geological Society of Greece
Athens, 22-24 May, 2019 | Harokopio University of Athens, Greece
Bulletin of the Geological Society of Greece, Sp. Pub. **7** Ext. Abs. GSG2019-274

Combining Geochemical Mapping with Mineralogical and Chemical Data for Improved Interpretation of Elemental Mobility in the Urban Environment

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The environmental impact of urban development is a major concern of our times and the management of contaminated urban areas is a significant societal challenge at global scale with legal, financial and possible human health implications as over 50% of the global population resides in cities. Potentially harmful elements (PHEs) including trace metals and metalloids are always high in the agenda of urban environmental studies because of: a) their multiple industrial, domestic, medical and technological applications that have led to their wide distribution in urban environments, and b) their non-degradable character. An increasing body of scientific evidence suggests that measuring the total concentration of PHEs in soil and other environmental compartments in big cities does not provide an effective basis for the evaluation of potential adverse effects to humans and the environment, and tends to overestimate the risks and induce unnecessary remediation costs (Cipullo *et al*., 2018 and references therein). Rather, the elemental mobility and bioaccessibility of the contaminants have a central role in understanding human exposure, as the chemical structure of PHEs and associated mineral phases affect their solubility in physiological fluids and influence the absorption capacity of the human body. Risk-based environmental management decisions can also be impaired due to the fact that exposure to contaminant mixtures is often overlooked and receptor population vulnerabilities that can be profound in big cities are not taken into account. Here, we present results from a series of studies concerning the urban environment of Athens (Greece) with the aim to demonstrate how geochemical mapping at different spatial scales, combined with chemical methods and mineralogy can provide insights for better interpretation of PHEs environmental mobility. The ultimate aim is to contribute to improved planning and management of the urban development of Athens, the capital city of Greece with a population of over 3 million people.

Initially, a geochemical baseline study of surface soil, based on a systematic sampling survey covering the Greater Athens and Piraeus area, was implemented (Argyraki and Kelepertzis, 2014). The near total concentrations of the major elements Fe, Al, K and Ca, and PHEs Ni, Cr, Co, Mn, As, Pb, Zn, Cu, Cd, Sb and Sn were determined. Principle 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. The geochemical maps, showing the overall spatial distribution patterns of elemental concentrations, were plotted using a GIS and the Inverse Distance Weighted (IDW) interpolation method with a power of 2. Geographically Weighted Regression was used to evaluate the spatial correlations between the studied elements. It was found that the major factor controlling variability of the chemical composition of surface soil is the bedrock chemistry, resulting in a significant enrichment in concentrations of Ni, Cr, Co and possibly As. Anthropogenic influences are also significant, controlling elements that are typical of human activities, i.e., Pb, Zn, Cu, Cd, Sb, and Sn. The highest concentrations of the classical urban contaminants are observed in the 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 anthropogenic PHEs towards the city core (Fig. 1). The *aqua regia* extracted (pseudo-total), potentially phytoavailable, mobilisable, orally bioaccessible and reactive pools of PHEs were subsequently operationally defined by applying adequate chemical reagents on 45 urban top-soil samples (Kelepertzis and Argyraki, 2015). Despite the elevated pseudototal concentrations of geogenic elements (Ni, Cr, As and Co) in Athens soil, their availability is limited because of their sequestration in stable mineral phases. The pseudototal content of the anthropogenic group of elements (Pb, Zn, Cu, Cd) is the predominant factor controlling their availability. An association between available fractions of this group of elements and amorphous Fe oxides has been observed based on detailed mineralogical analysis of soil grains by Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) (Fig. 2). The study of Pb isotopic ratios in selected soil and house dust samples indicated that Pb in Athens soil is a mixture of local soil background Pb with high $^{206}Pb/^{207}Pb$ ratios, and Pb derived from the re-suspension of particulates deposited from past vehicular exhaust emissions of leaded petrol with a low $^{206}Pb/^{207}Pb$ ratio (Kelepertzis *et al.*, 2016). House dust exhibits anthropogenic enrichment of vehicular traffic-related Pb, Zn and Cu in relation to the urban soil. Furthermore, anthropogenic PHEs in house dust were found to be associated with the magnetic fraction that is enriched in magnetite (Kelepertzis *et al.*, 2019). Examination of selected spherules (size >30 μm) by electron back scatter diffraction (EBSD) in a Field Emission SEM instrument produced pattern image quality maps that helped to verify the magnetite crystal phases, while the focused ion beam (FIB) technique confirmed the high-temperature industrial origin of the magnetite spheres (Fig. 3). Such spherical particles have also been identified in the exterior soil indicating that they are ubiquitous in the urban chemical environment of Athens. The similarity in the Pb isotope results and the microstructure of particles between the urban soil and the house dust material suggests that these two environmental sampling media share common industrial and traffic-related sources.

We conclude that combining data of geochemical mapping from micro- to macro-scale with chemical data and detailed mineralogical observations can provide invaluable information for further studies of exposure assessment and environmental management in urban areas.

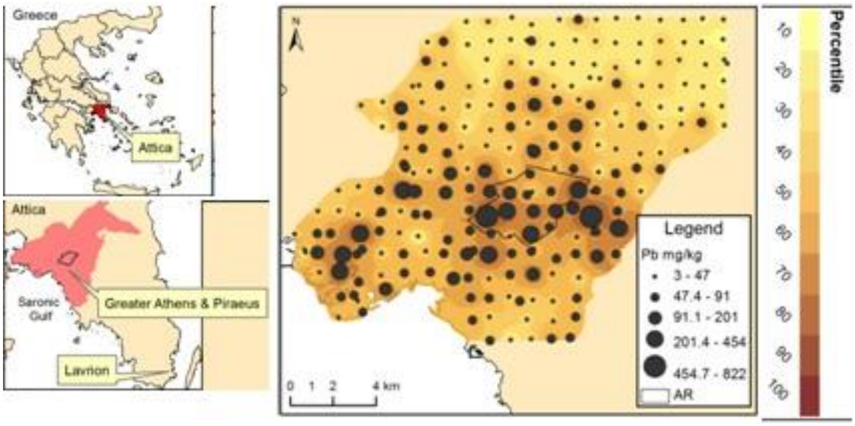

Figure 1. Lead distribution in Athens soil. AR denotes the centre of the city.

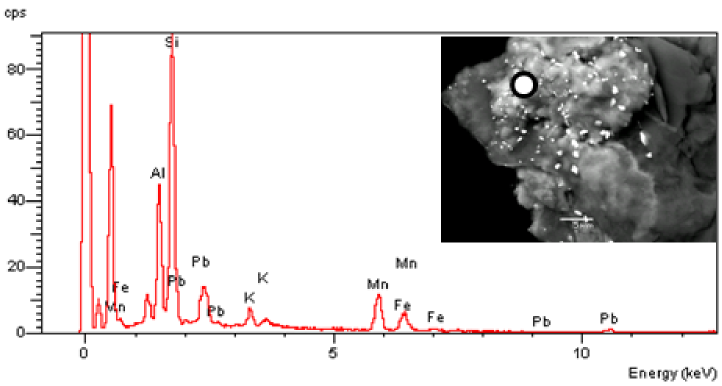

Figure 2. Microphotograph of PHE-bearing soil grain showing Mn-Fe oxide phase (bright) enriched in Pb and Sb.

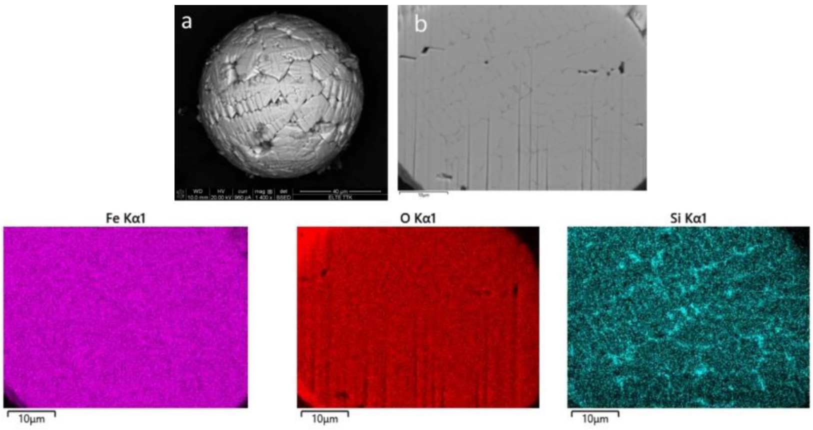

Figure 3. FIB-SEM images of an anthropogenic magnetite sphere in house dust and corresponding EDS elemental mapping.

Acknowledgements

We acknowledge the graduate and postgraduate students of the Department of Geology and Geoenvironment, NKUA, that have contributed to this research through their dissertation projects.

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