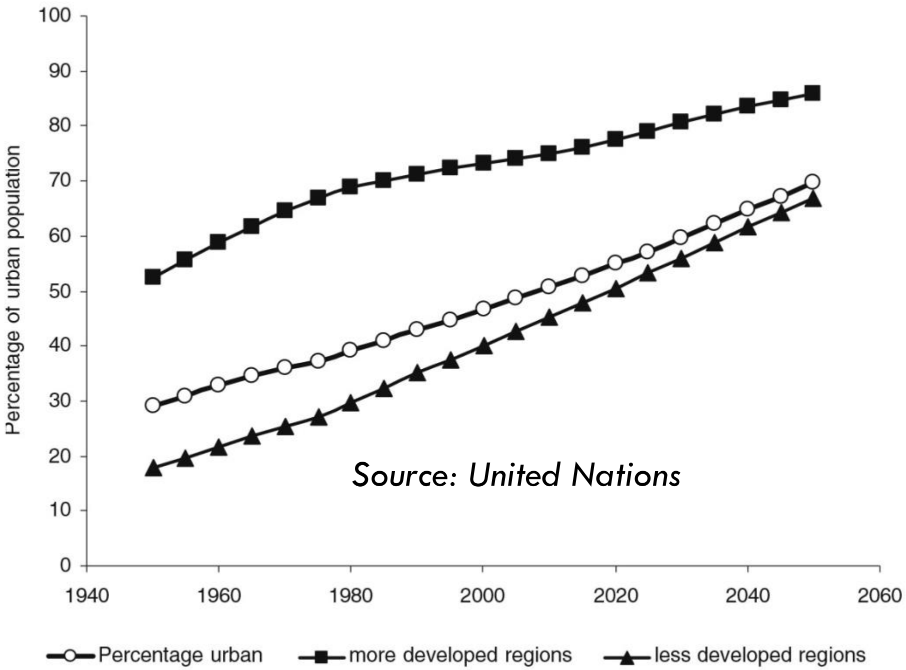
URBAN SOIL GEOCHEMISTRY OF TRACE ELEMENTS

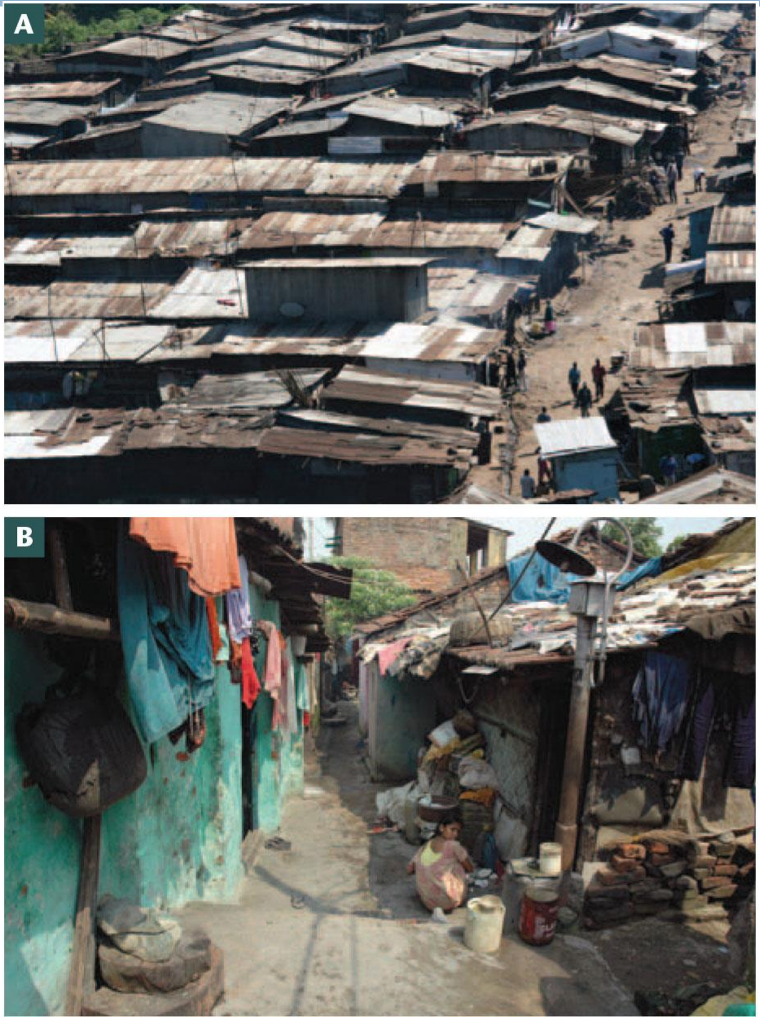
Efstratios Kelepertzis

Why urban geochemistry



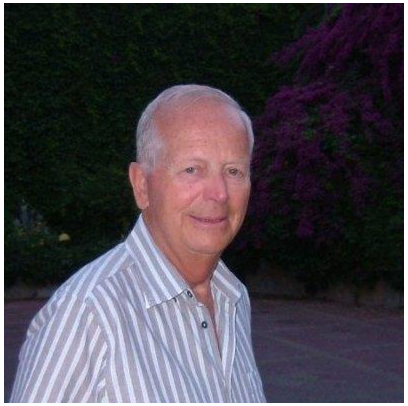
Urban areas comprise only 2% of the Earth's surface but are responsible for:

-80% of the world's gross domestic products
- 70% of the global energy consumption
- 80% of CO_2 emissions



Urban slums in Kenya (A) and India (B):
Lyons and Harmon, 2012

Development of urban geochemistry



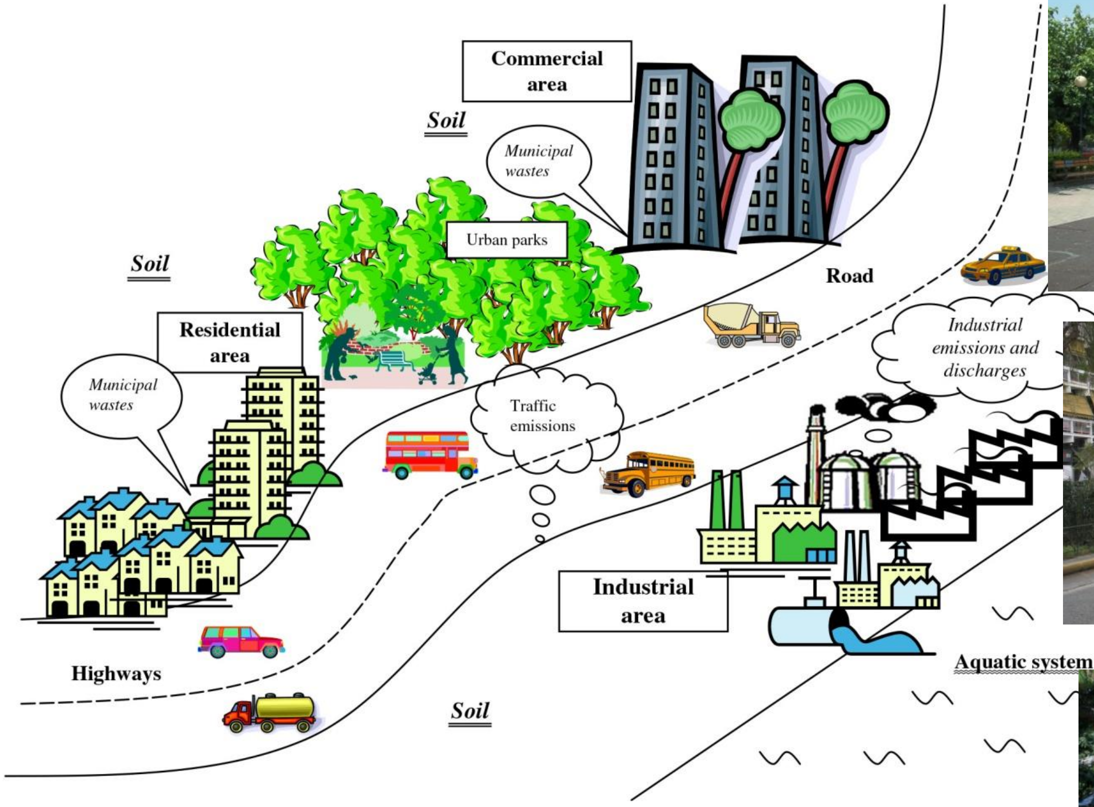
Professor Iain Thornton was the first who used the term *urban geochemistry*

Urban environmental geochemistry can be defined as the field of scientific study that uses the chemistry of solid earth, its aqueous and gaseous components, to examine the physical, chemical and biological conditions of an urbanized environment (*Siegel, 2002*)

- Anthropogenic Pb contamination of the urban environments and associated health implications were denoted in the 1970s
- Some early studies assessed Pb contamination in soil, dust and atmospheric particulates
- Technological advances in analytical equipment had as a result the inclusion of other metals, typical tracers of anthropogenic contamination (Zn, Cu, Hg, Sb)
- Towards the end of 1980s, developing regions experienced rapid urbanization and industrialization

Today, urban geochemical studies have developed into a global phenomenon

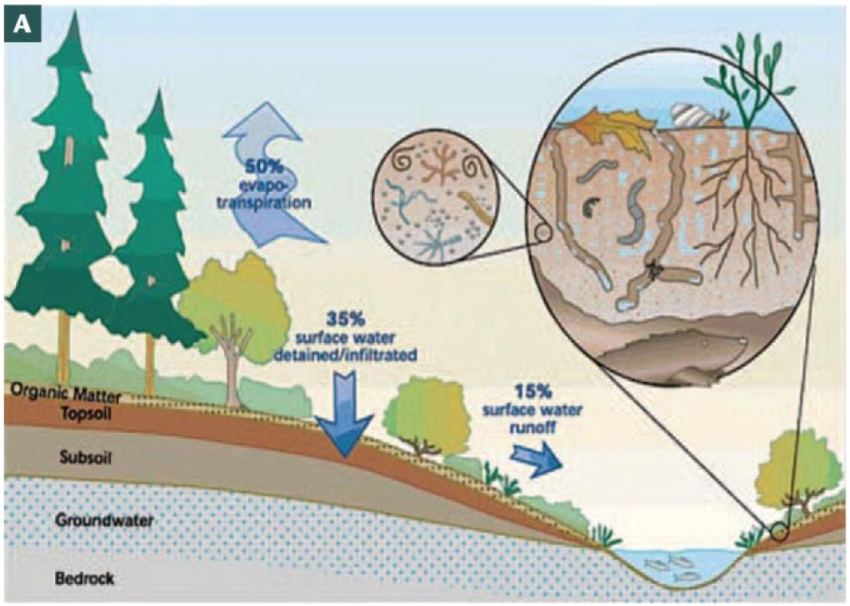
Urban soil



The major compartments of an urban environment

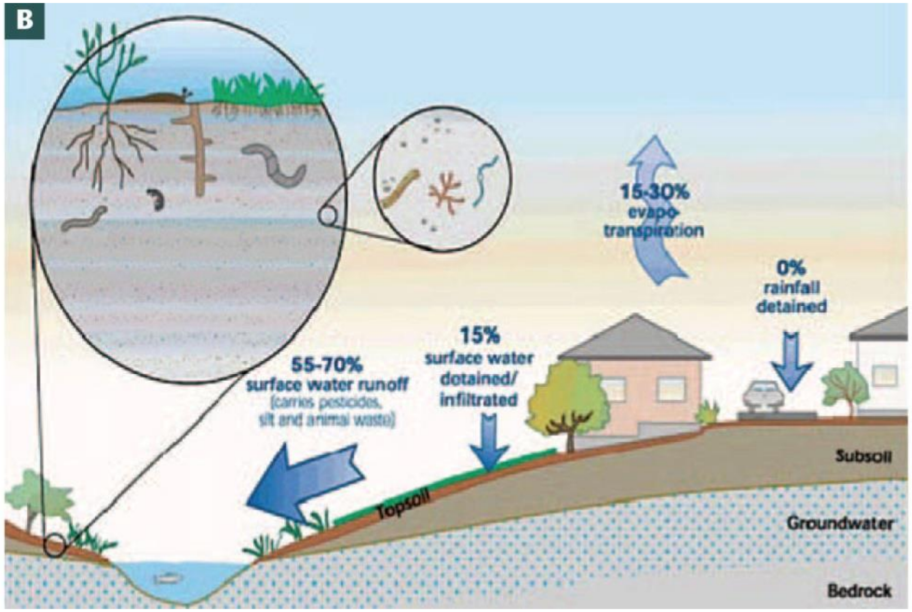
(*Wong et al., 2006*)

Characteristics of urban soil



Water movement on a natural landscape

(*Scheyer and Hipple, 2005*)

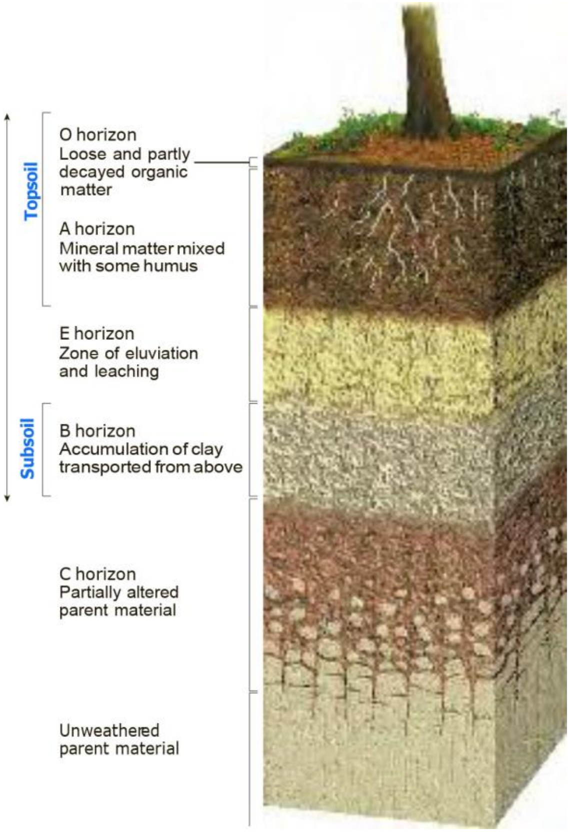


Water movement on a disturbed urban landscape with limited vegetation

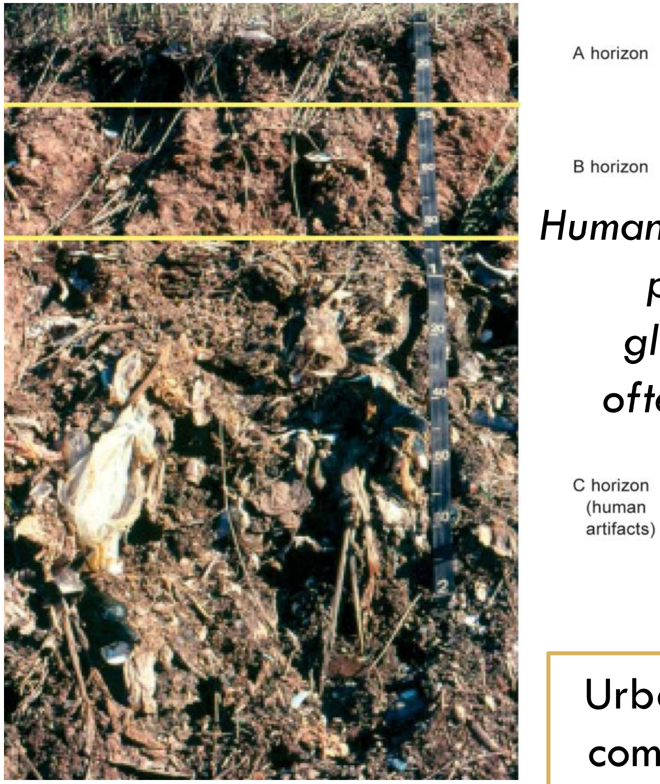
More water moves into the soil on natural landscapes than on disturbed landscapes, such as those in urban areas

Limited ability of the urban terrestrial environment to immobilize metal pollutants

Characteristics of urban soil



Natural soil profile with major horizons



Urban soil profile
(*Scheyer and Hipple, 2005*)

Human artifacts, such as bricks, bottles, pieces of concrete, plastics, glass, pesticides, garbage are often components of urban soils

Urban soils have been excavated, compacted, disturbed, and mixed and may no longer possess their natural soil properties and features

Sources of trace elements in urban soil

Heavy metals and metalloids associated with urban – industrial sources

(*Albanese and Breward, 2011*)

INDUSTRY/SOURCE	Cu	Pb	Zn	Sn	Cd	Hg	Ni	V	Cr	As	Sb	Others
General urban activity	+	+	+	+								
Mining (coal)		+		+			+					
Smelting (nonferrous)	+	+	+	+	+	+	+			+	+	
Iron-and-steel work	+			+			+	+	+	+		Ca, P_2O_5
Heavy engineering, toolmaking	+		+				+	+	+			Mn, Mo, W
Metal plating and fining	+		+	+	+		+		+			
Electronics	+				+	+	+			+	+	REEs, rarer elements
Ceramics, glass		+		+							+	Mn, Co, U, REEs
Incinerators						+				+		
Domestic coal-burning and coal-fired power stations (ashes)		+		+	+			+			+	
Vehicles, transport	+	+	+	+				+			+	Ba, Mn
Crematoria						+						

Emissions from traffic are caused by tire wear off, brake pads, wear of individual vehicular components such as the car body, clutch of motor parts and exhaust, oil leaking from engine and fuel additives

Significance of geology

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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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H I G H L I G H T S

- 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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A B S T R A C T

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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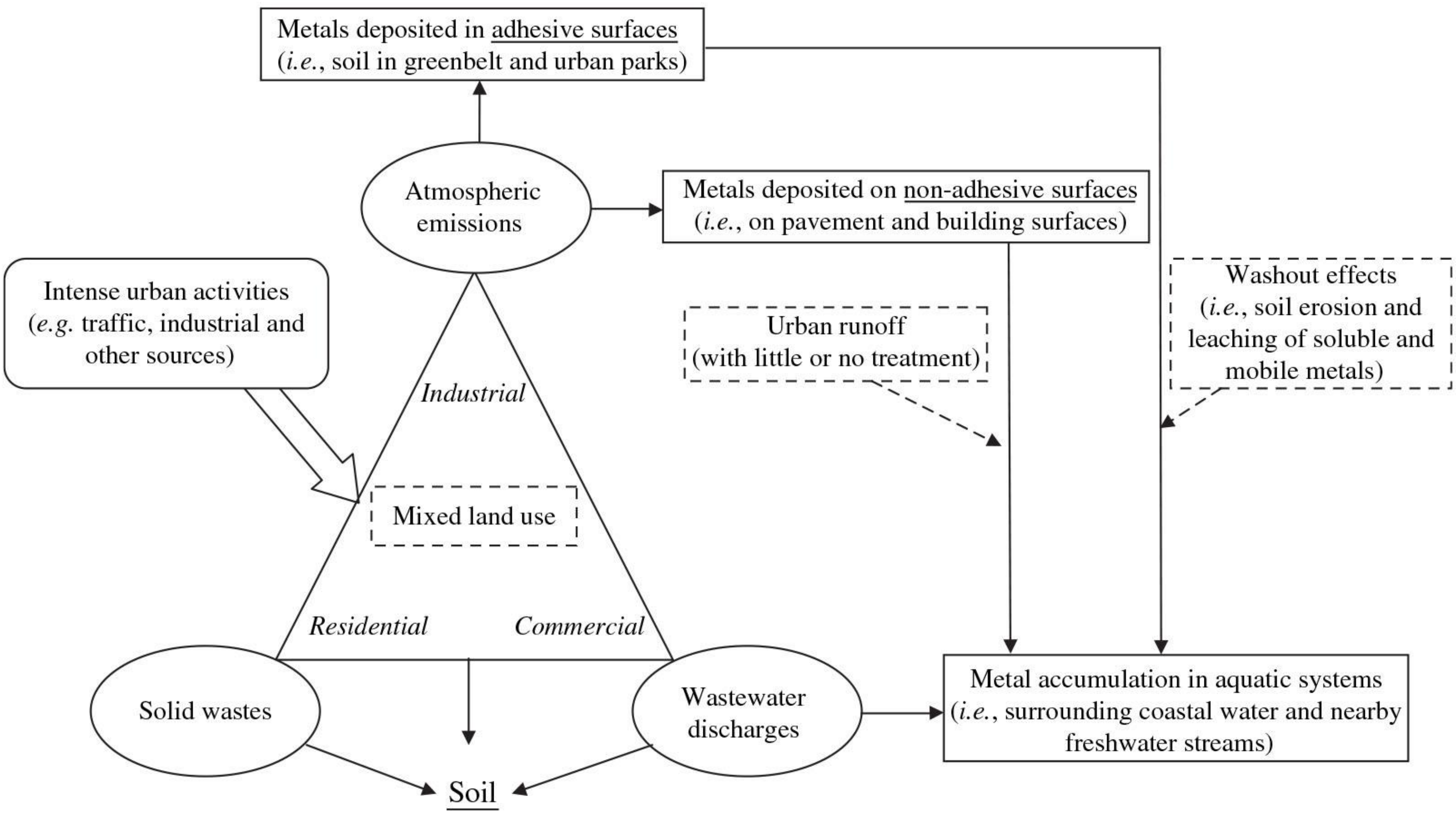
Elevated levels of potentially toxic metals can also be of natural (geogenic) origin due to variations in the bedrock geology:

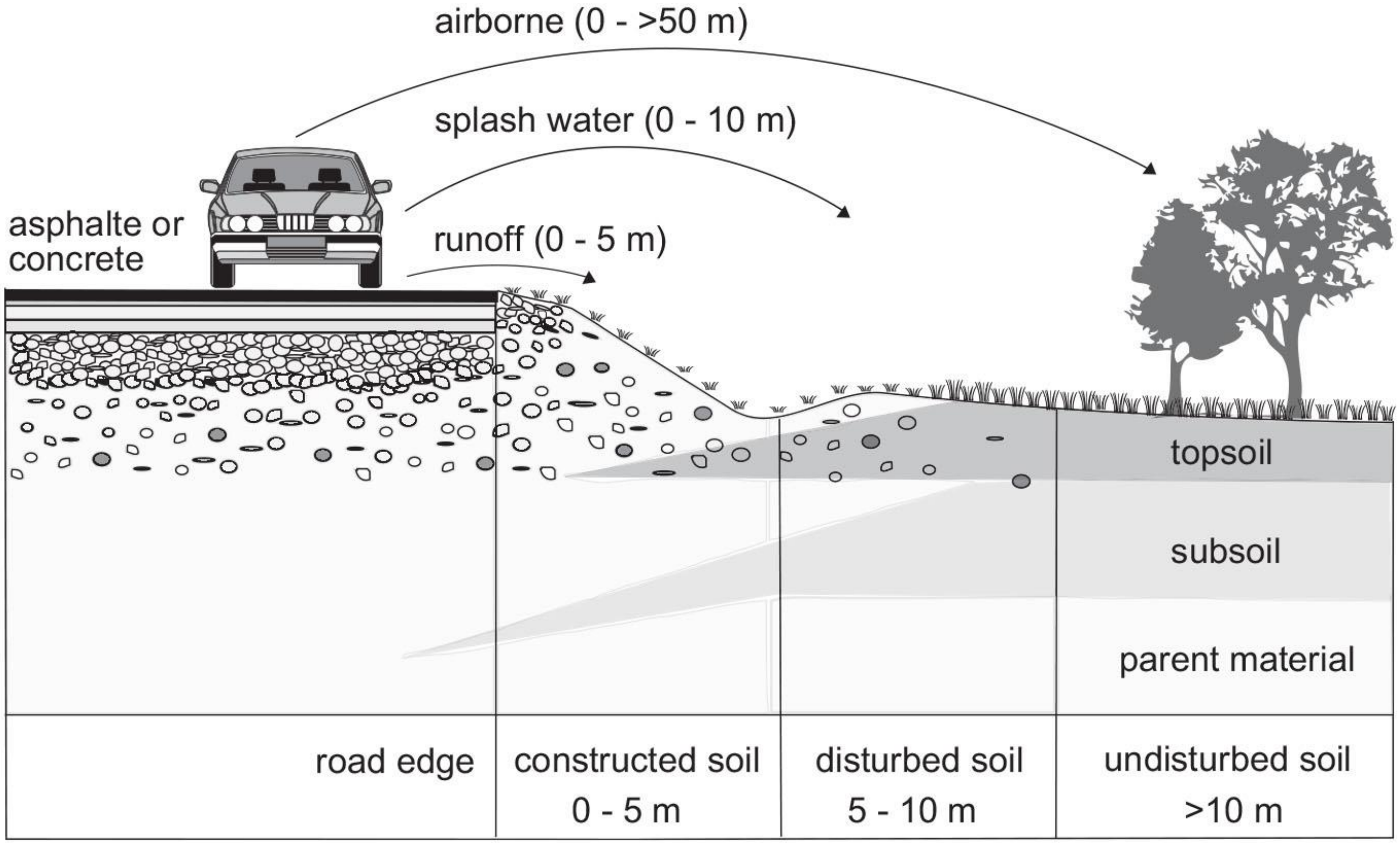
- sedimentary ironstones containing increased concentrations of As
- mafic – ultramafic rocks exhibiting elevated levels of Ni and Cr
- black shale lithologies often contain high concentrations of Cu, Cd and Mo

Dispersion of trace metals



Transport and deposition of metals in urban settings (*Wong et al., 2006*)

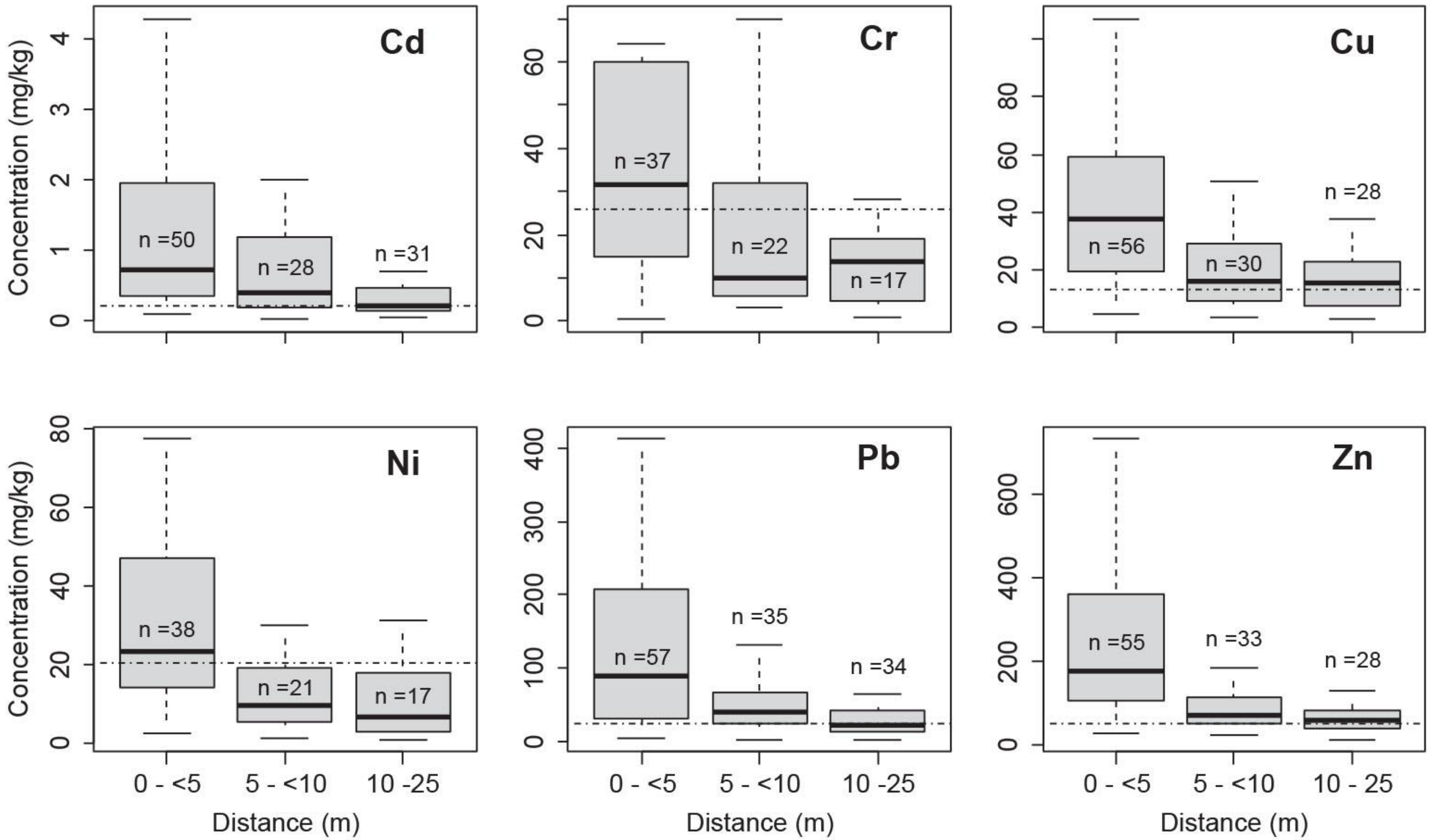
The roadside environment



Pathways of metal transport in a roadside environment (*Werkenthin et al., 2014*)

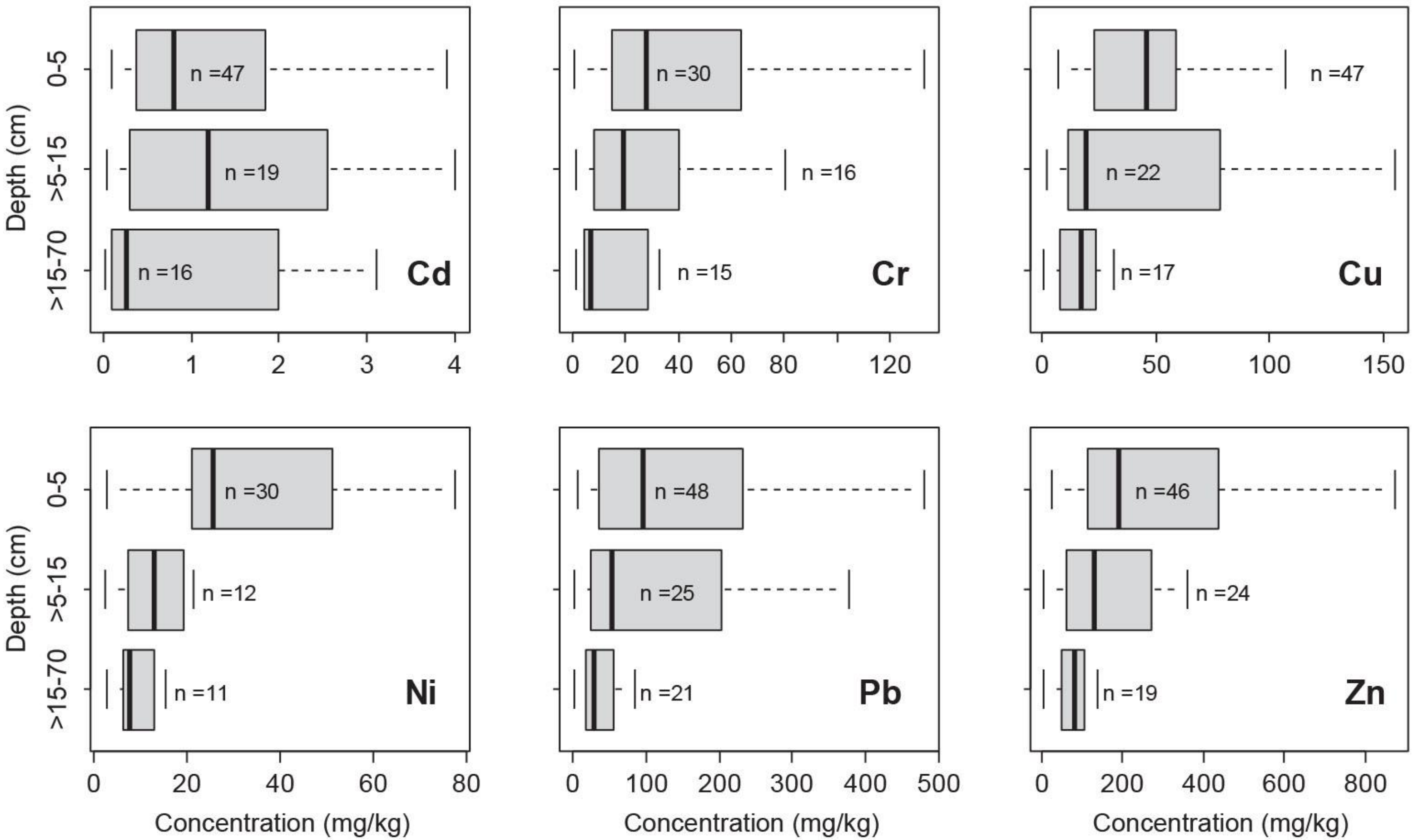
Emissions are influenced by road design, volume of traffic, intersections and driving speed

Influence of distance



Concentrations of metals in European roadside topsoils as a function of distance to the road edge (*Werkenthin et al., 2014*)

Influence of soil depth



Concentrations of metals in European roadside soils (distance 0-5 m) as a function of soil depth (*Werkenthin et al., 2014*)

Urban Geochemical Mapping

<u>Definition</u>

Geochemical mapping is a technique developed in the 1950s to give information on the spatial distribution of chemical elements at the Earth's surface. It was initially applied for the purposes of mineral exploration

<u>Aims</u>

• establishing a baseline for the urban environment
• identify contaminated areas
• assessing the contribution of parent materials and anthropogenic activities to the geochemical baseline and identifying the sources of elements
• assessing risk to other compartment of the urban environment (e.g. groundwaters, plants, human population)

Classification

Classification of urban geochemical mapping studies (*Johnson and Ander, 2008*)

Systematic survey	Targeted survey
Entire urban area	Targeted land use/area
Interpreted in the context of regional baseline	Interpreted in the context of guideline values
Ubiquitous sample medium	Variety of sample media
100s-1000s samples	1s-10s samples
Full range of elements	Selected elements
1-4 samples per km^2	4-50 samples per km^2
Done by national/public organisations	Done by research organisations/universities

Definitions of geochemical baseline and background

<u>Definition of geochemical baseline</u>

The concentration at a specific point in time of a chemical parameter in a sample of geological material. It is a fluctuating surface rather than a given value

Baseline X = f { A, B, C, D}

A = a defined media type, B = a documented sampling method, C = a documented sample preparation, D = a documented analytical method

<u>Definition of geochemical background</u>

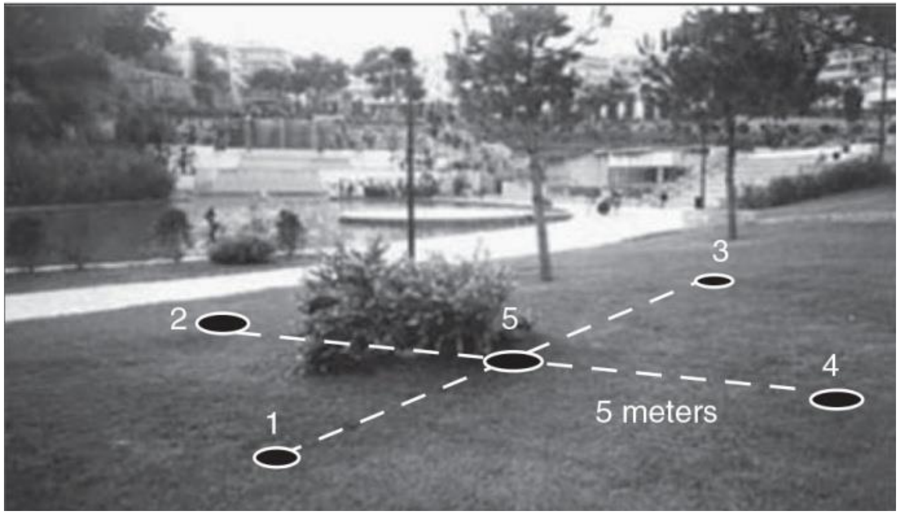
A relative measure to distinguish between natural element concentrations and anthropogenically-influenced concentrations

Baseline = Background + contribution

Background, unlike a baseline, is determined by interpreting and statistically treating the geochemical data

Planning urban geochemical mapping

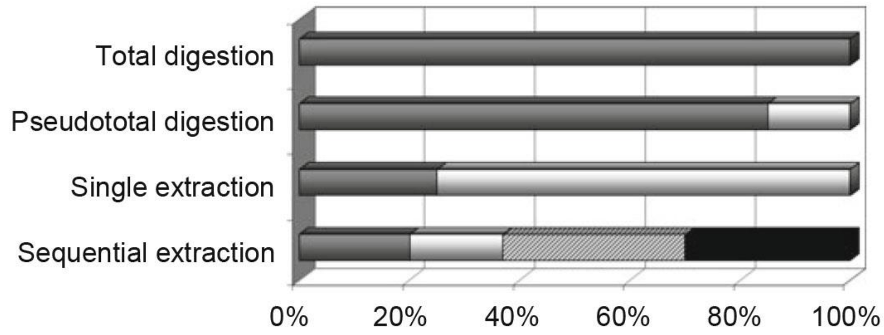
1) Sampling grid: The urban area has to be defined by a sampling grid (square or triangular cells) ⟶ sampling cells with larger dimensions for areas with low anthropic pressure
2) Sampling protocol according to international scientific community guidance. Important considerations:
   a) depth
   b) collection of sample from near to the centre of each sampling cell
   c) composite sample based on 3 to 5 subsamples with a minimum distance of between any two subsamples of not < 5 m



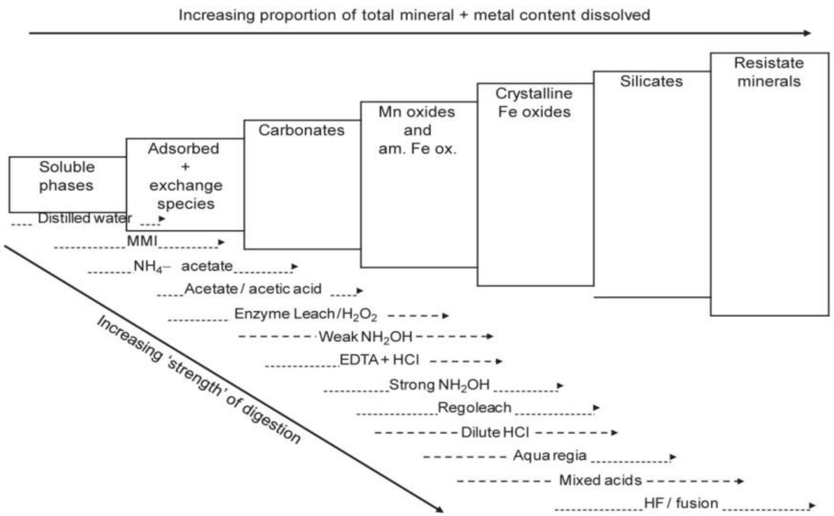
Field composite soil sample collected at an urban site

Sample analysis – Extraction techniques

Digestion of the soil samples is a necessity for most instrumental method of analysis

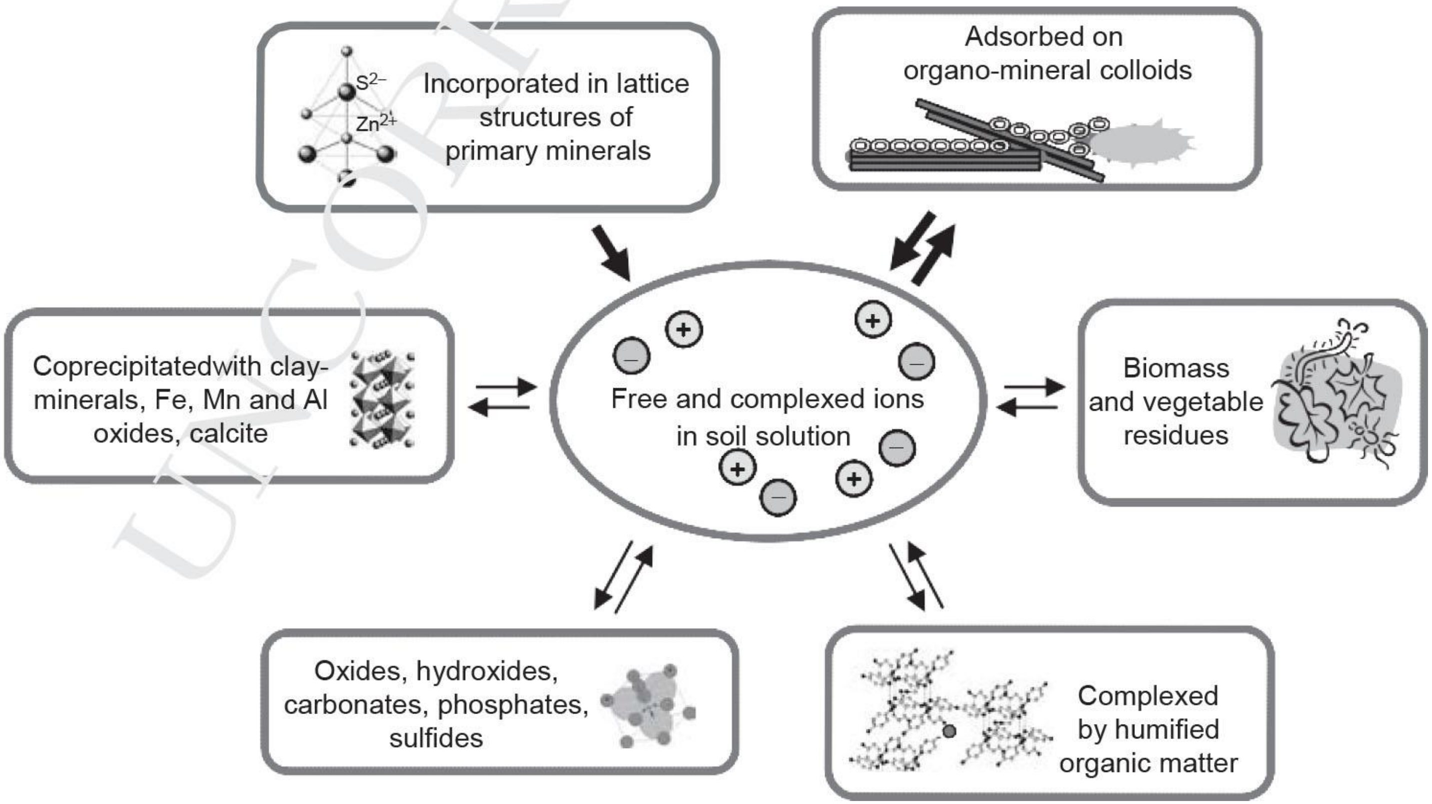


Approaches for the determination of heavy metals in soils (*Davidson, 2013*).



The relationship between various chemical extractions and the extent of mineral components attacked (*Cohen et al., 2010*).

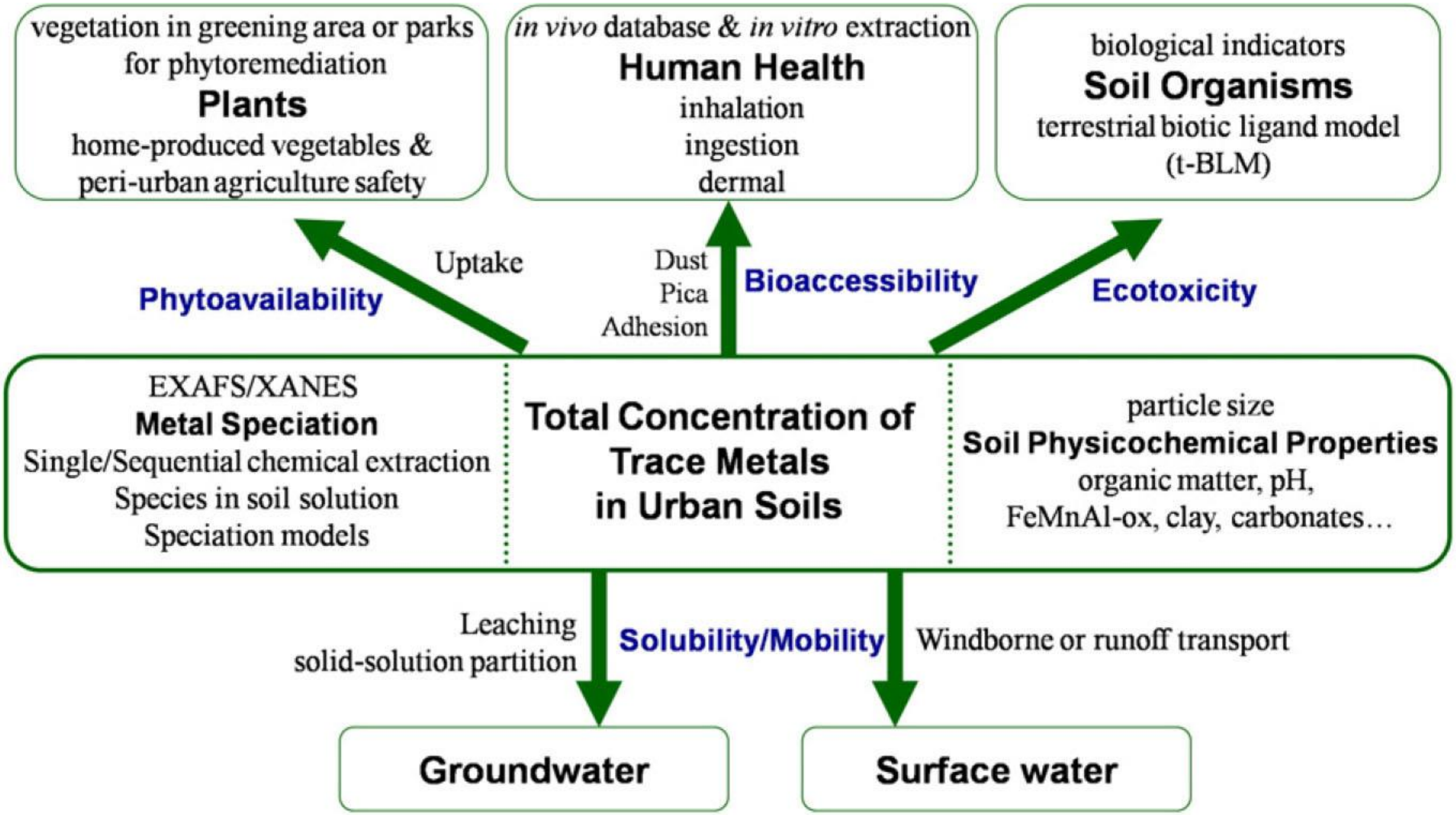
Geochemical forms of trace elements



(*Adamo and Zampella, 2008*)

Controlling factors for the alteration of metal forms are pH, redox potential, ionic strength of the soil solution, the solid components and their relative affinity for an element.

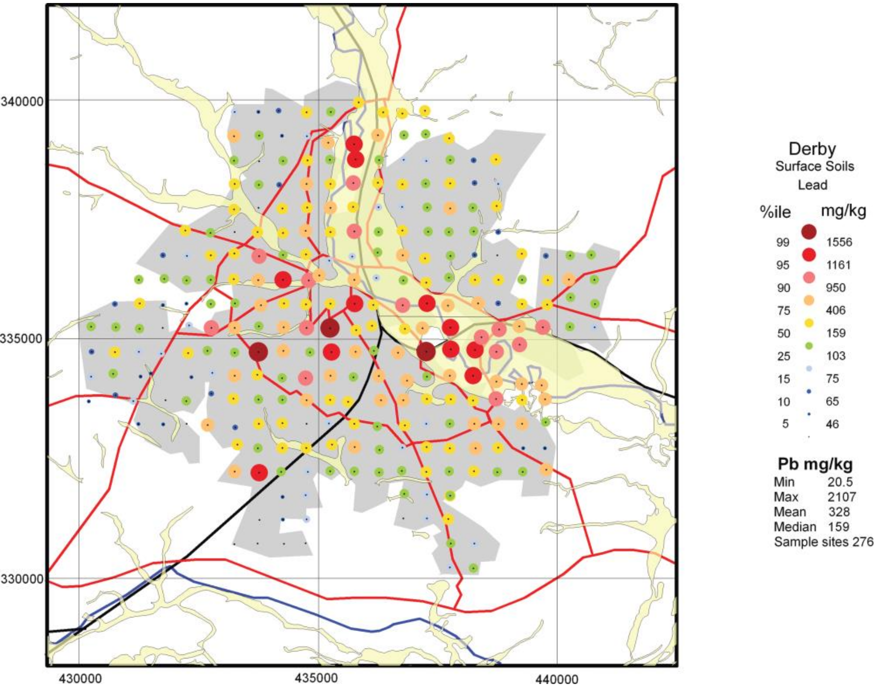
Characterization of trace metals in urban soil



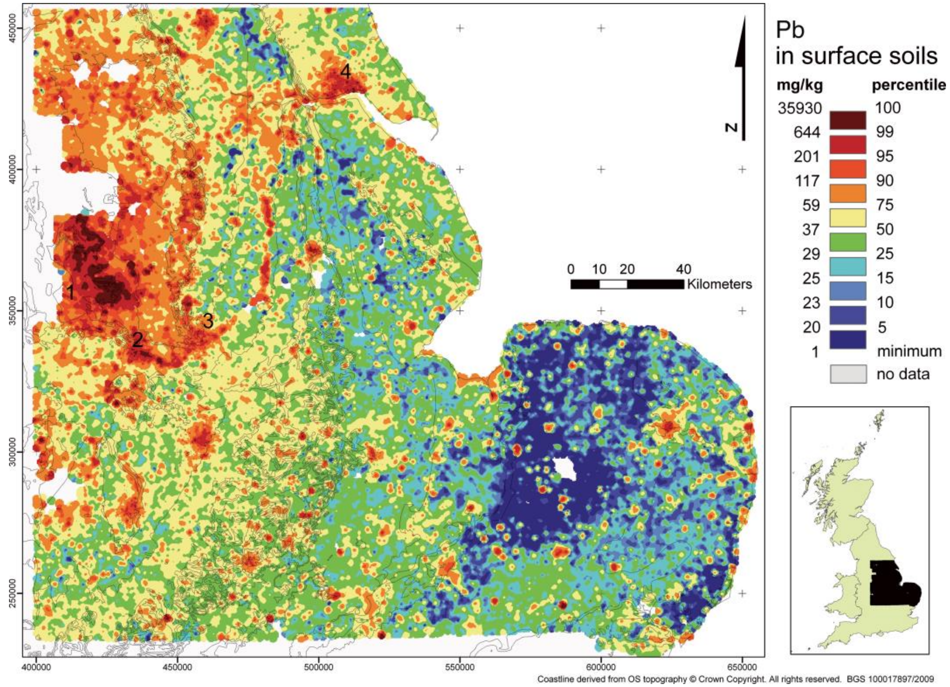
Implications for risk assessment and human and ecological health risks of urban soils

(*Luo et al., 2012*)

Geochemical data presentation



Dot distribution map of Pb (n=*276*) in surface soils of Derby, UK (*Flight and Scheib, 2011*)



Interpolated geochemical map of Pb in soils of eastern and central England (*Flight and Scheib, 2011*)

Multivariate analysis

<u>Aims</u>

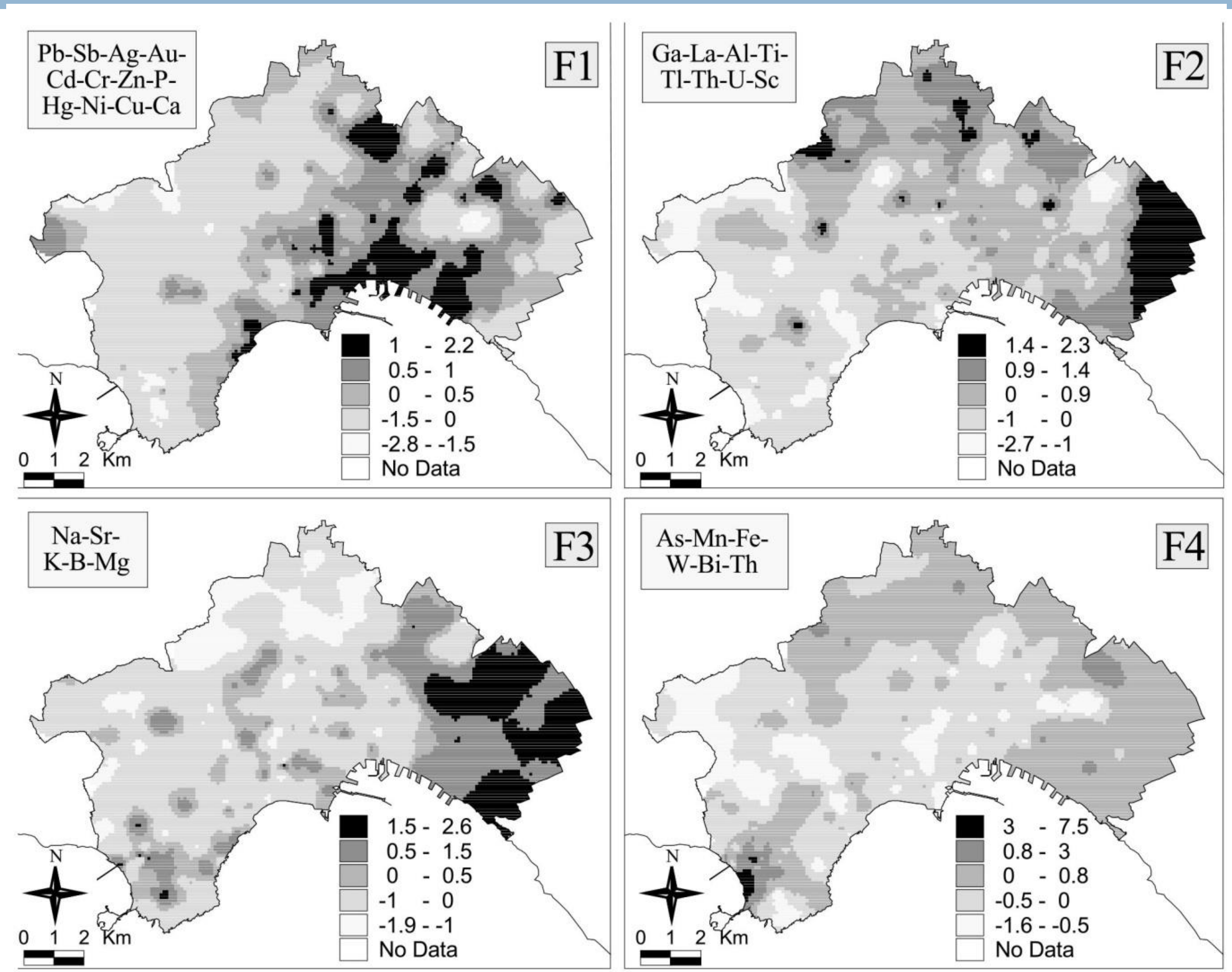
to identify correlations between groups of elements (lithological characteristics, enrichment phenomena, anthropogenic pollution) and reduce a multidimensional data set to a few basic components.

Factor analysis

Cluster analysis

The geochemist has to interpret correctly the correlations and relate each elemental association to specific phenomena (e.g. contamination sources, geology, geochemical processes)

Multivariate analysis



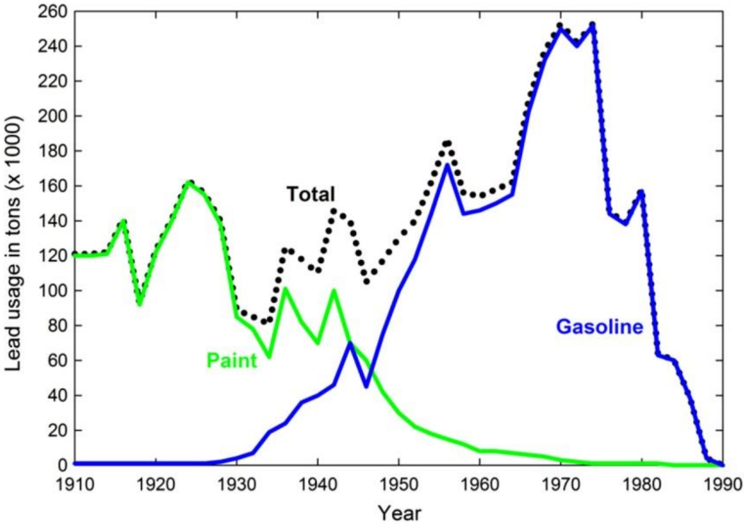
Distribution map of factor scores for soils of Naples area (*Cicchella et al.,2008*)

Source identification of Pb based on Pb isotopes

• Lead enters the environment during production (mining), use (batteries, ceramics, plastics), combustion of fuels (coal, former use of leaded gasoline), use of mineral fertilizers, lead-based paints.

•Lead in gasoline accounts for most of the Pb present in the human environment. About 75% of the gasoline lead was emitted from the exhaust pipes in the form a fine lead dust.

• Lead was used in gasoline as antiknock additive: $Pb(C_2H_5)_4$ = tetraethyllead, $Pb(CH_3)_4$ = tetramethyllead



History of Pb usage in paints and gasoline in the US during most of the 20th century (*Mielke, 1999*)

Source identification of Pb based on Pb isotopes

Radioactive isotopes are characterized by atoms of unstable nuclei that undergo radioactive decay to daughter isotopes, which, because they from by radioactive decay, are termed **radiogenic**. These daughter products may also be radioactive, or they may be stable. Radioactive decay produces a change in both Z (number of protons) and N (number of neutrons) from parent to daughter isotope.

✓Lead has 4 naturally stable isotopes, three of which are produced by decay of U or Th:
$^{232}Th \rightarrow {}^{208}Pb$, $^{235}U \rightarrow {}^{207}Pb$, $^{238}U \rightarrow {}^{206}Pb$

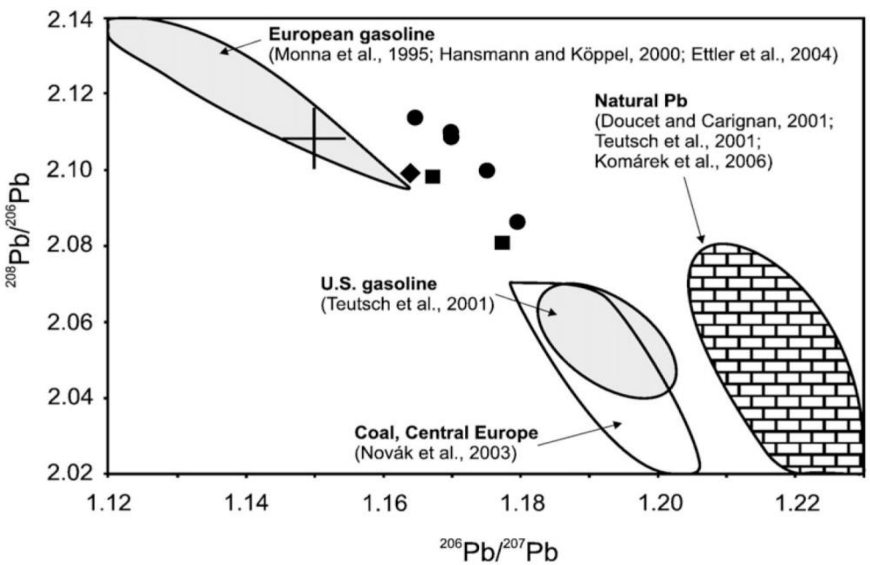
✓ Relative abundance of Pb isotopes are ~52% for ^{208}Pb, ~ 24% for ^{206}Pb and 23% for ^{207}Pb

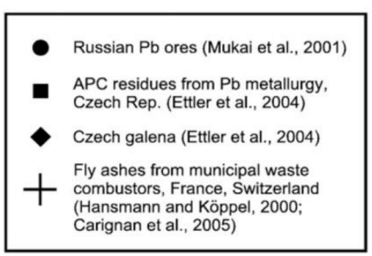
✓ Many different types of Pb ore deposits and anthropogenic sources of Pb have distinct isotope signature

✓The Pb isotopic composition of an ore body or anthropogenic source does not change during transition to a secondary weathering environment unless there is mixing with secondary Pb sources

Source identification of Pb based on Pb isotopes

Radiogenic Pb isotopes (particularly the ratio $^{206}Pb/^{207}Pb$) have been used to determine the source of atmospheric Pb contamination. It is possible to identify the source of Pb by comparing the Pb isotopic composition found at a site with those of potential sources



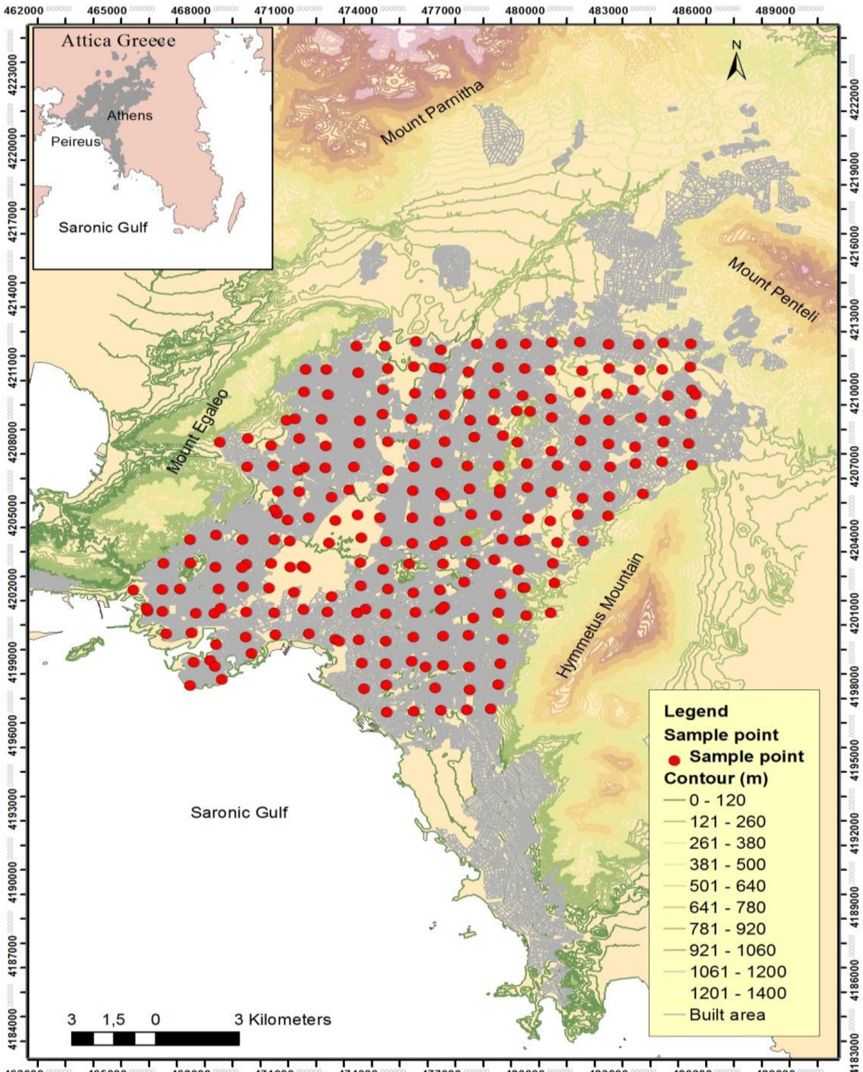


Isotope plot showing the isotopic compositions of different Pb sources (Komárek et al., 2008)

- Both China and Europe used alkyllead additives manufactured from the Pb source ore from Broken Hill, Australia ($^{206}Pb/^{207}Pb = 1.04$)

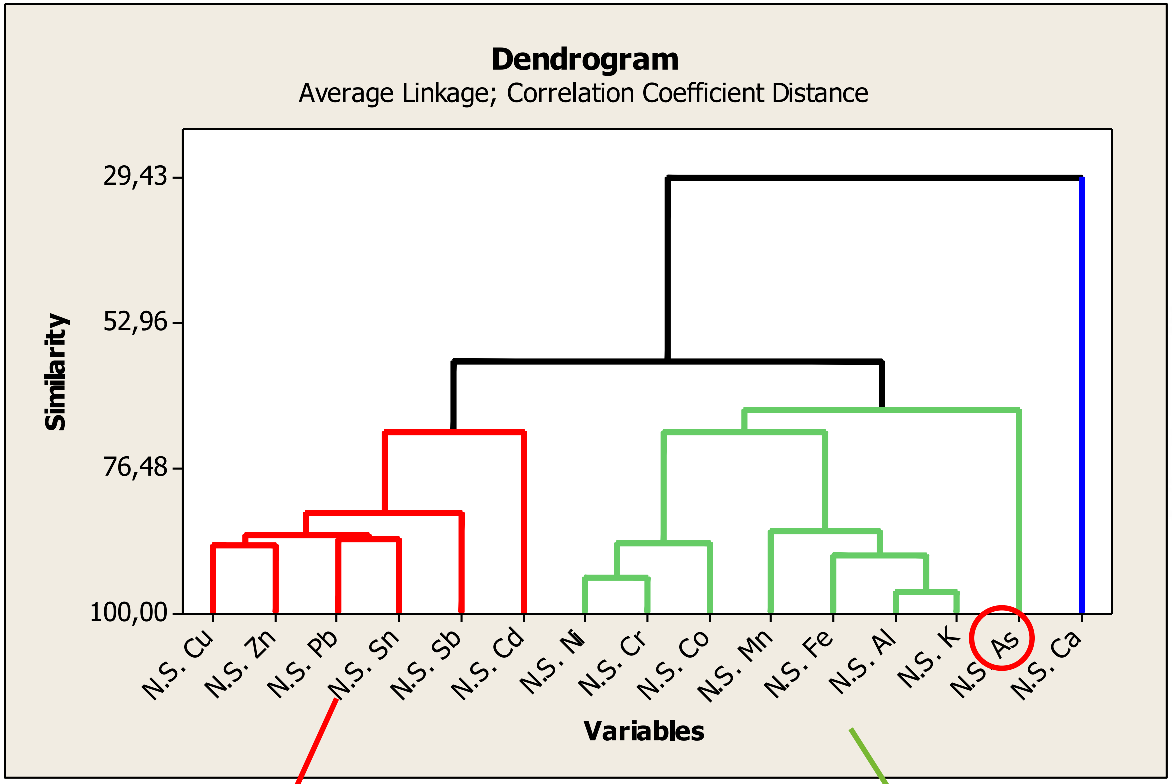
- The primary source for Pb additives in the U.S (before 1980s) was from Missouri and Mississippi Valley deposits ($^{206}Pb/^{207}Pb = 1.31\text{-}1.35$)

Soil geochemistry in Athens
Part a: Geochemical mapping

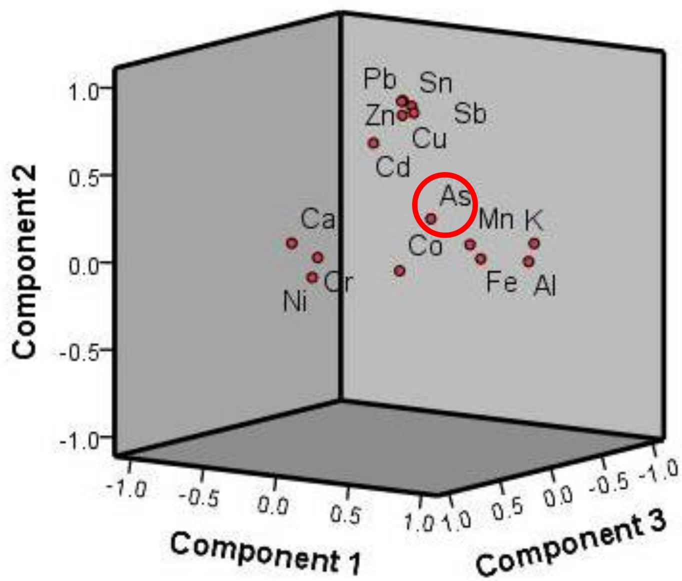


- Processed samples cover area = 240 km^2
  - Sampling grid 1 km x 1km
    - 238 soil samples
- 4- acid attack to determine total elemental content
  - Measurements by ICP-MS
  - Duplicate analysis and 2 NIST CRMs

Multivariate grouping of elements



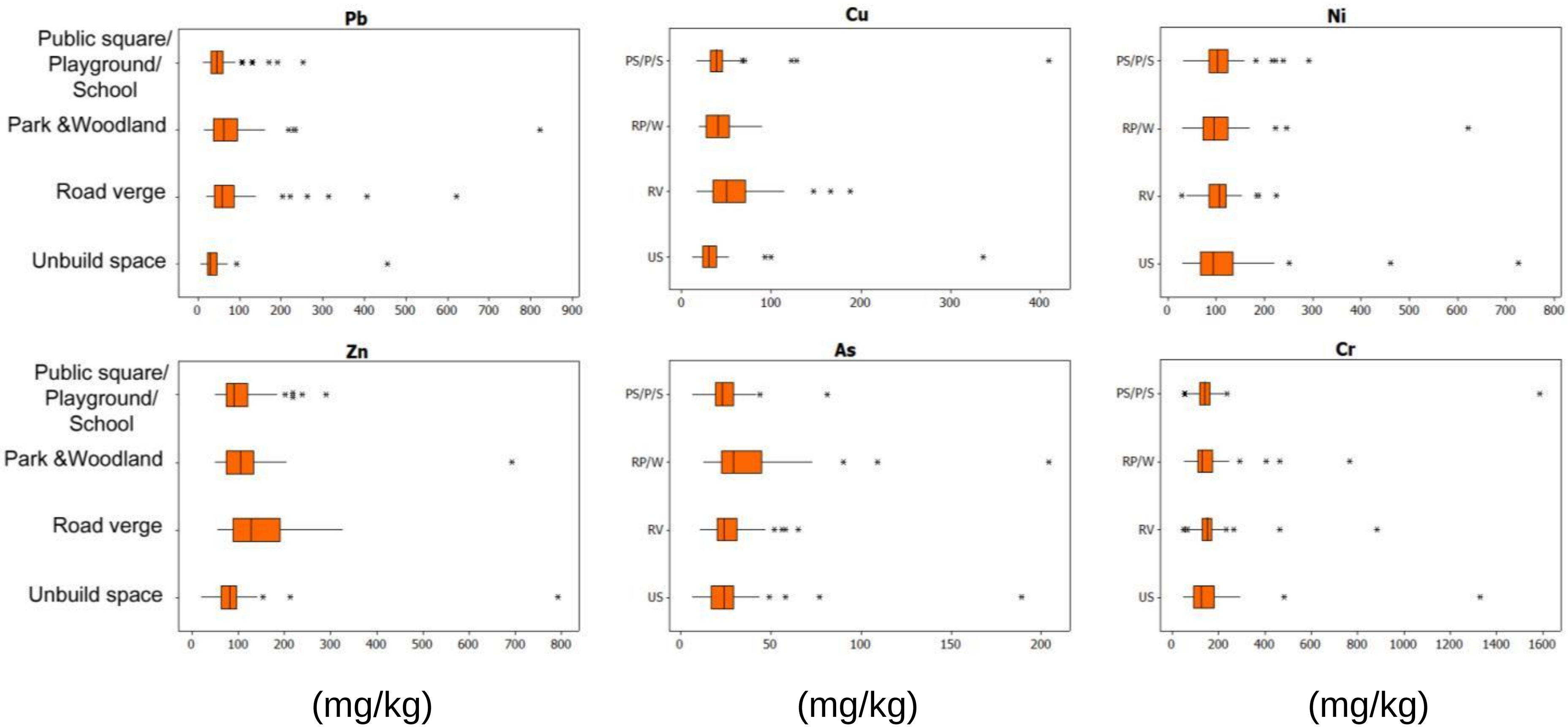
PCA plot



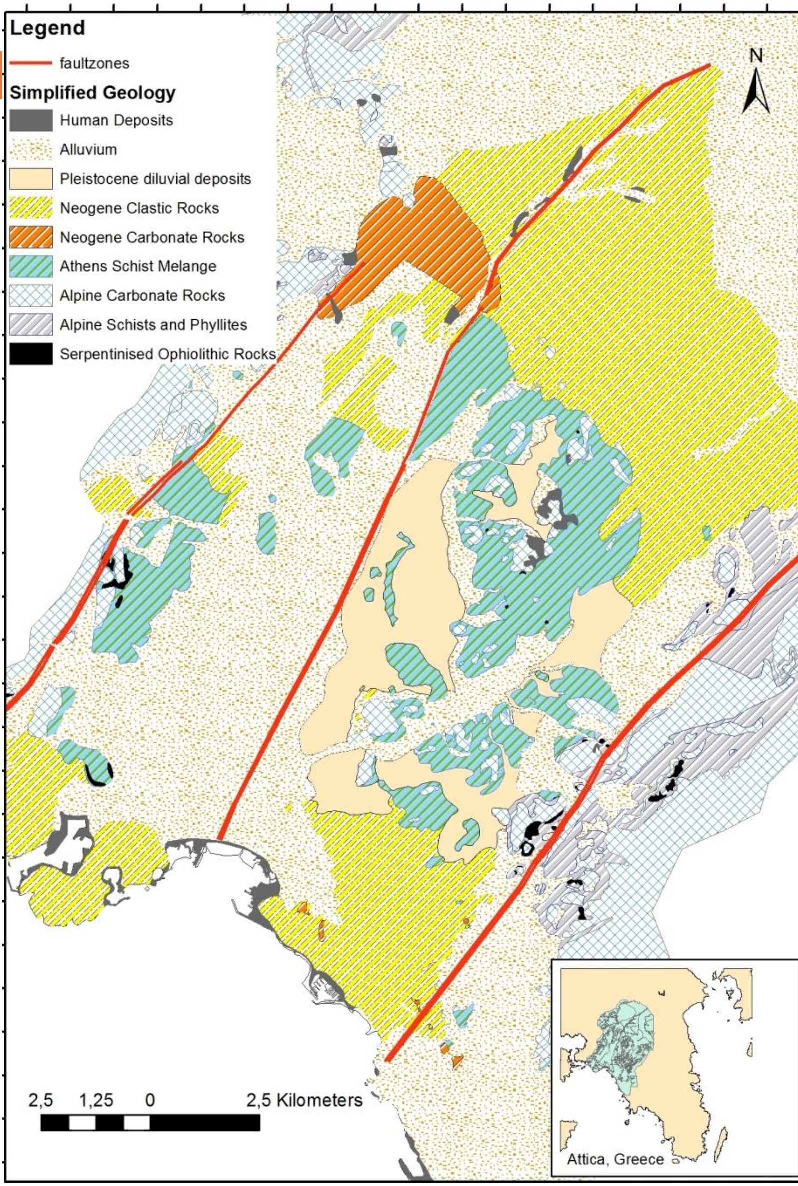
Anthropogenic sources

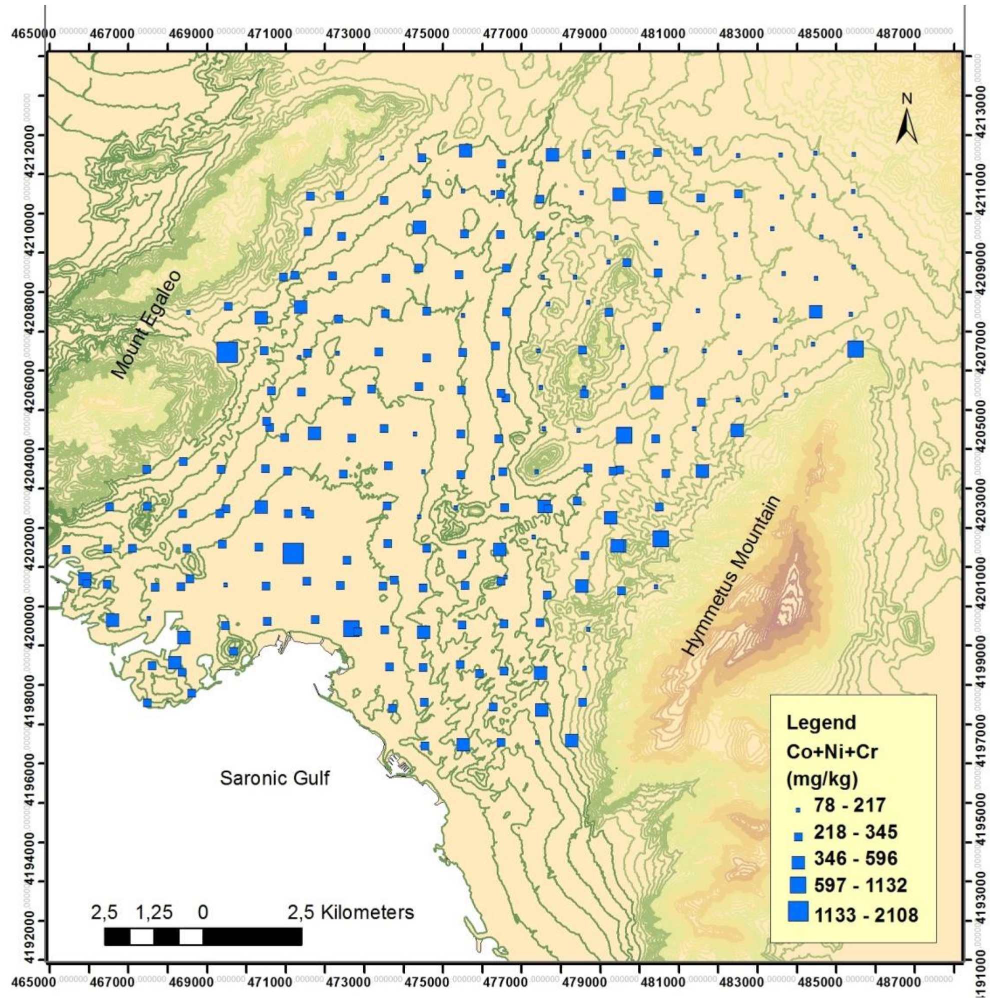
Natural sources

Concentration by land use



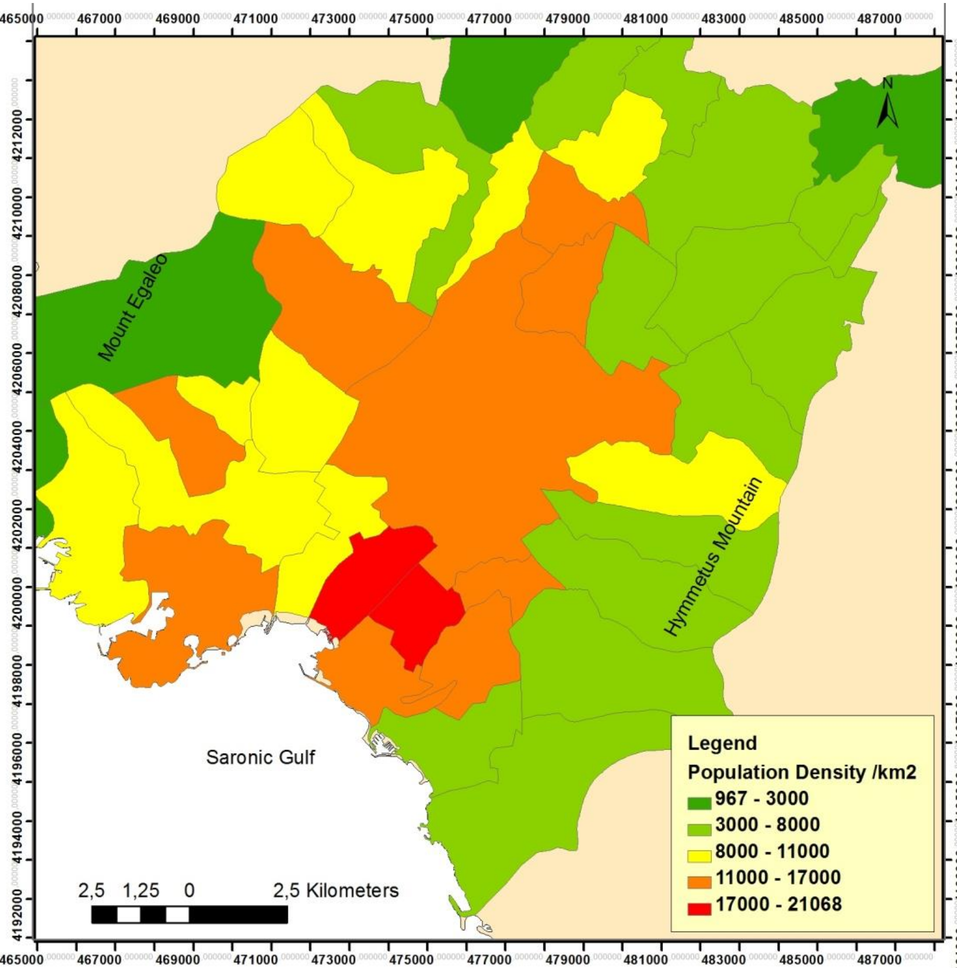
Spatial pattern of geogenic PHE elements



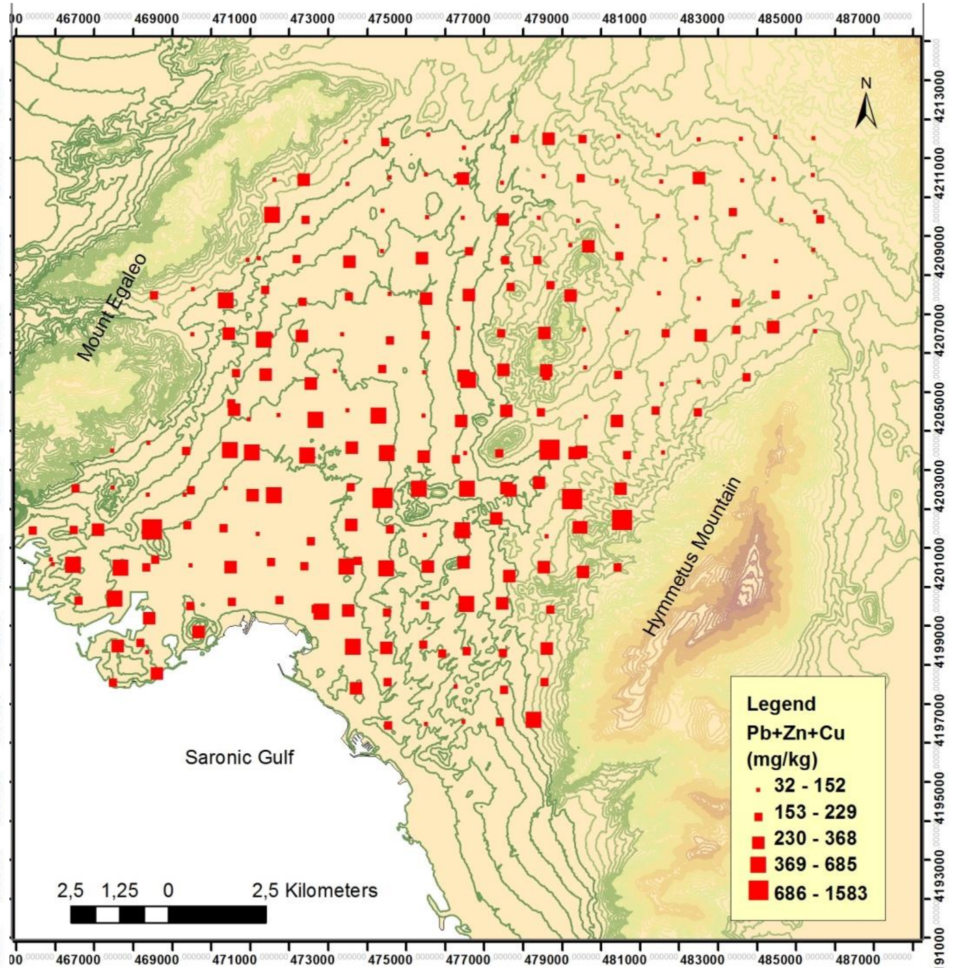


Spatial pattern of anthropogenic PHE elements

Population density by municipalities

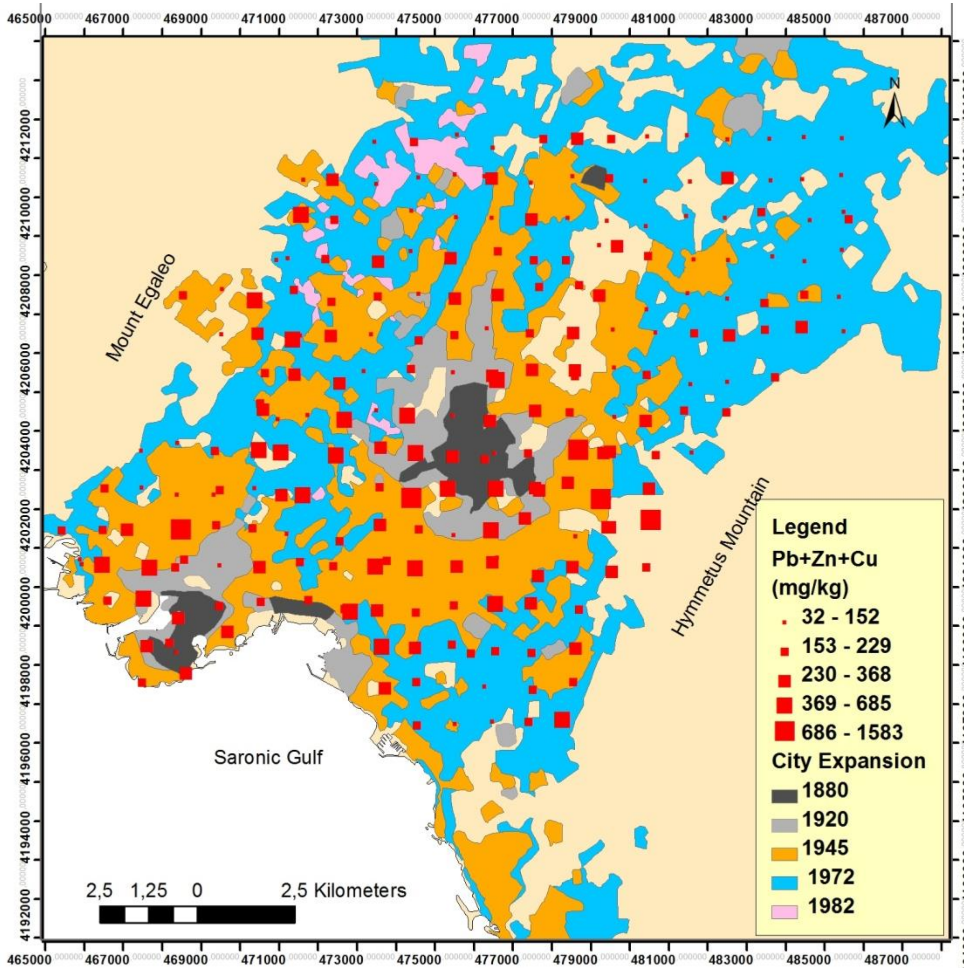


Pb+Zn+Cu concentration index

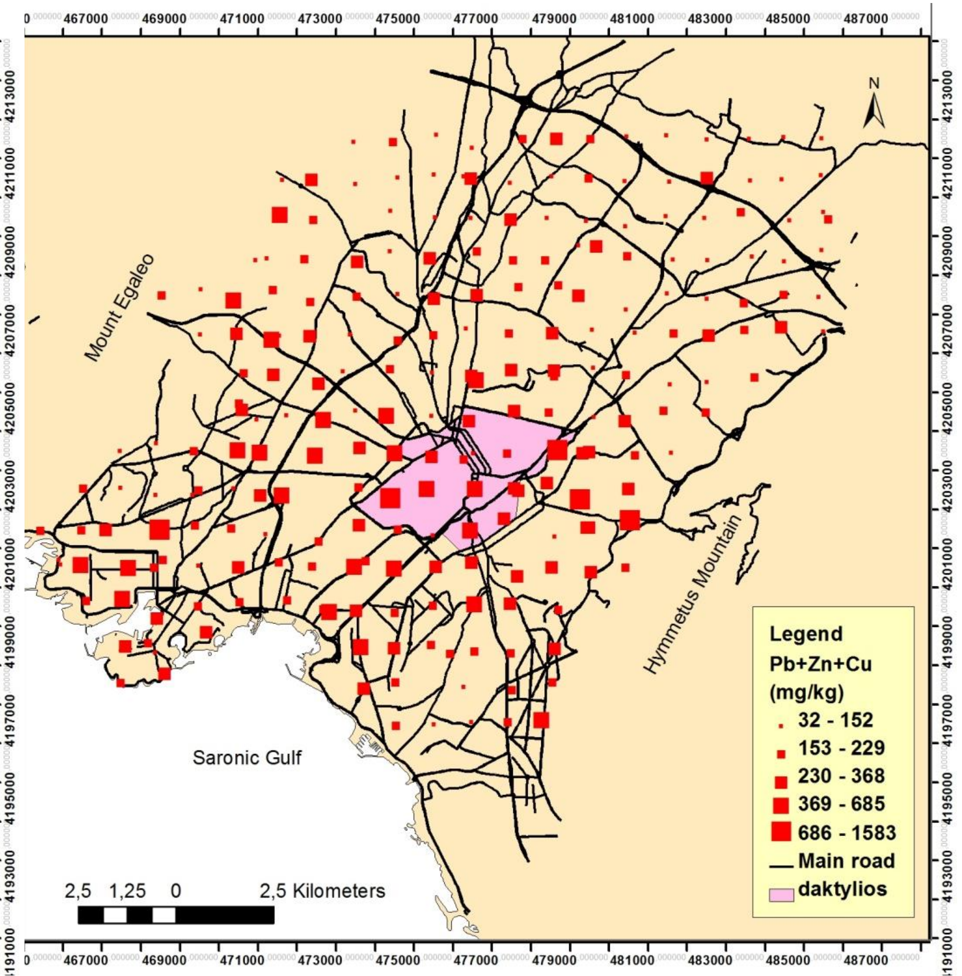


Other possible controlling factors

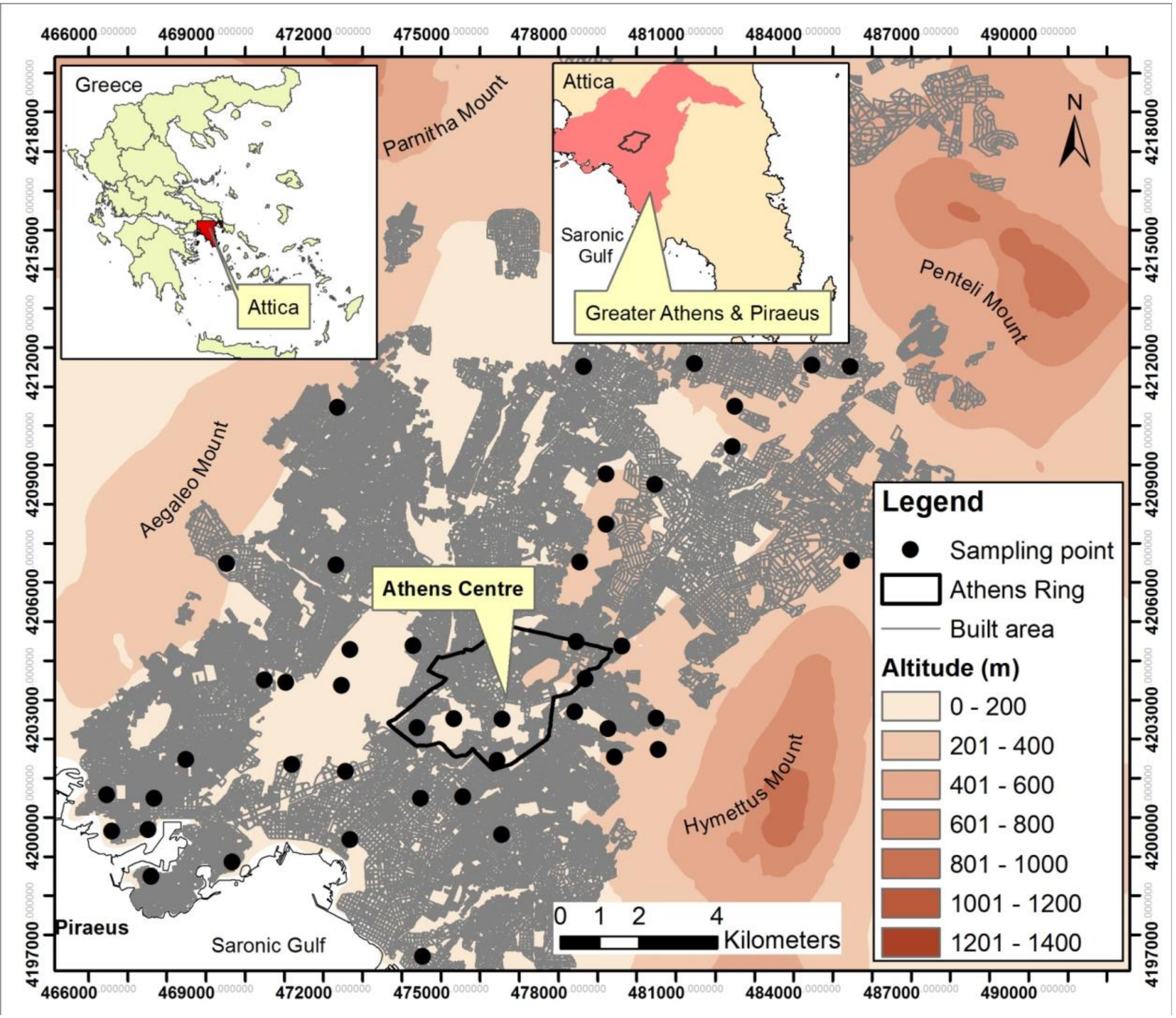
History of city expansion



Traffic



Soil geochemistry in Athens
Part b: Geochemical reactivity of trace elements



Selection: 45 topsoil samples

Criteria:

Total content of PHEs and the spatial variability of chemical composition

Low, medium and high levels of concentrations of both anthropogenic and geogenic elements

Chemical extractions

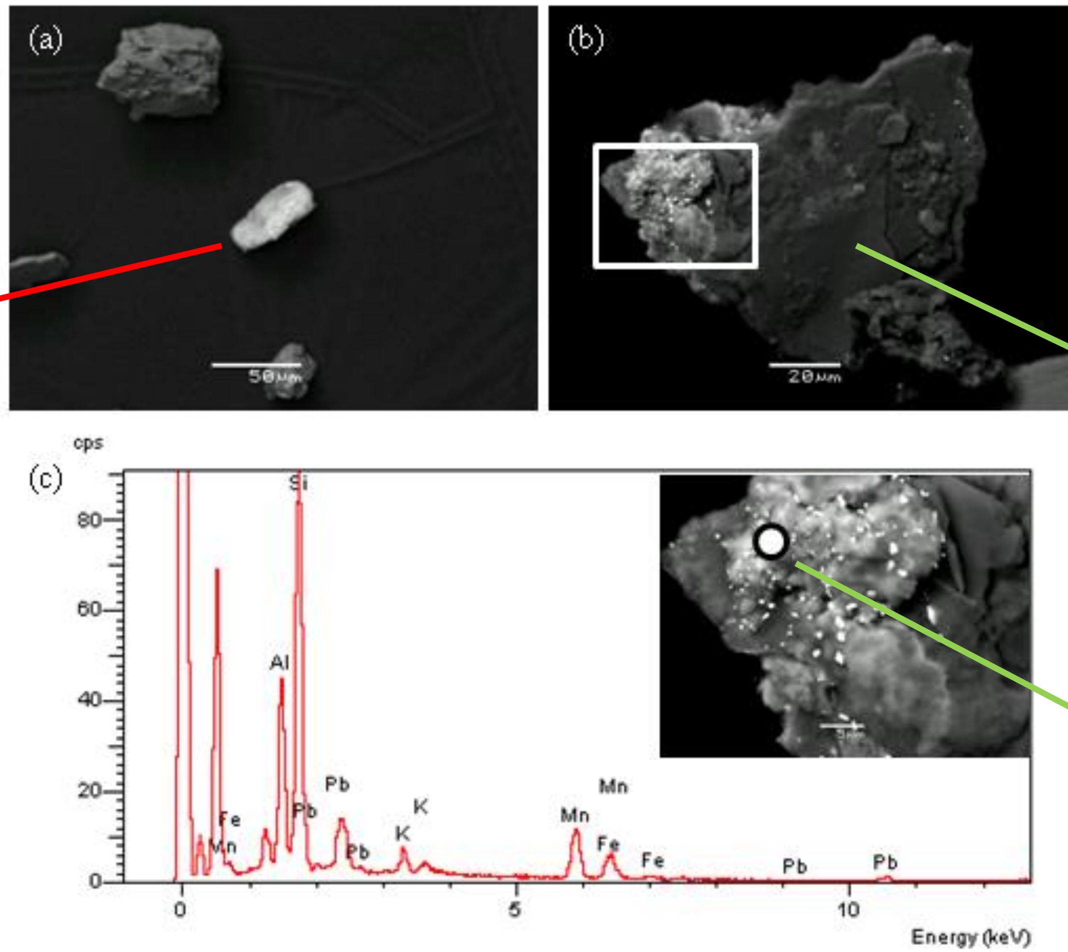
Pseudototal content (aqua regia)	Reactive fraction (0.43 M HNO_3)	Available fraction

Availability of PHEs was assessed by:

- 0.05 M EDTA (pH=7) → Potential phytoavailability
- 0.43 M CH_3COOH → Mobilizable fraction
- 0.4 M glycine (SBET) → Oral bioaccessibility

SEM-EDS results

Fe oxide phase enriched in Pb (1.41wt%) and Zn (2.32 wt%)

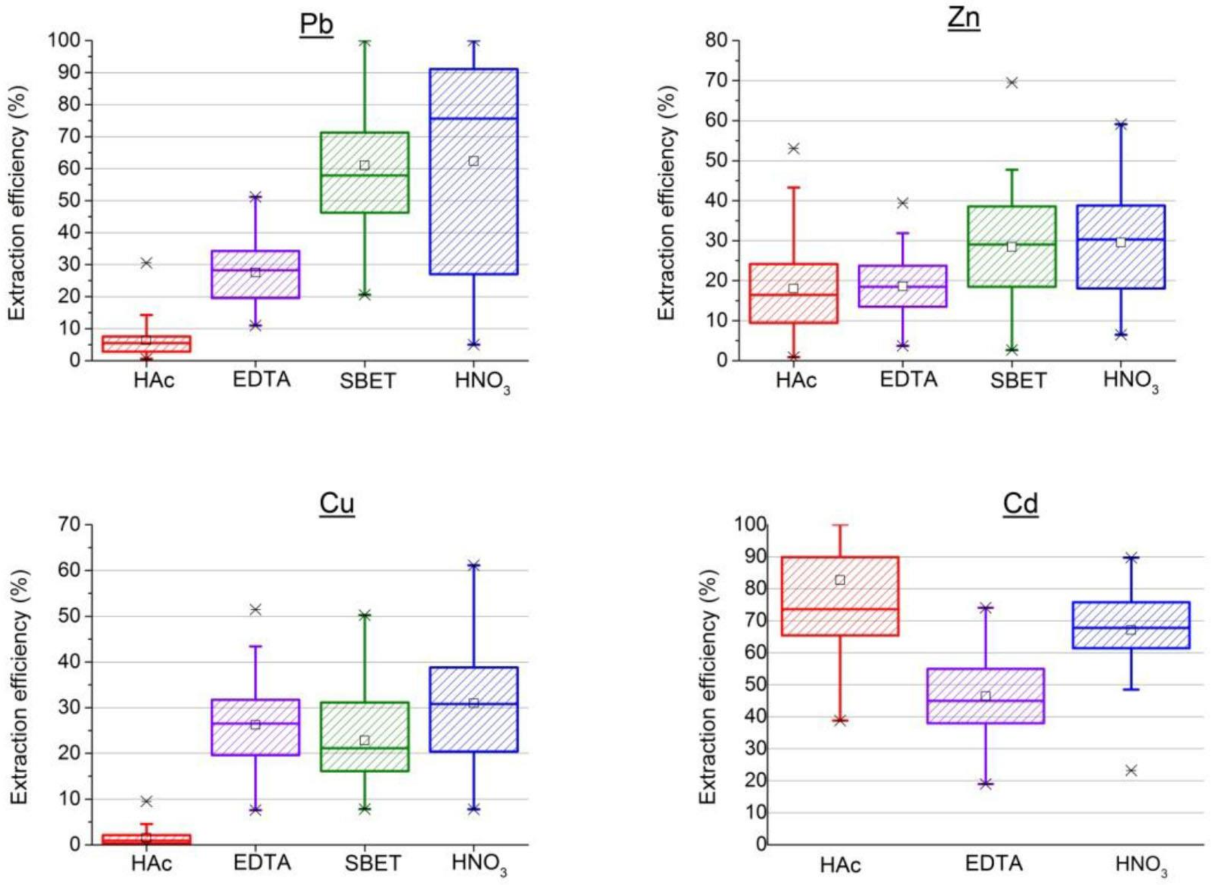


Aluminosilicate grain

Mn-Fe oxides coatings enriched in Pb (14.2 wt%) and Sb (2 wt%)

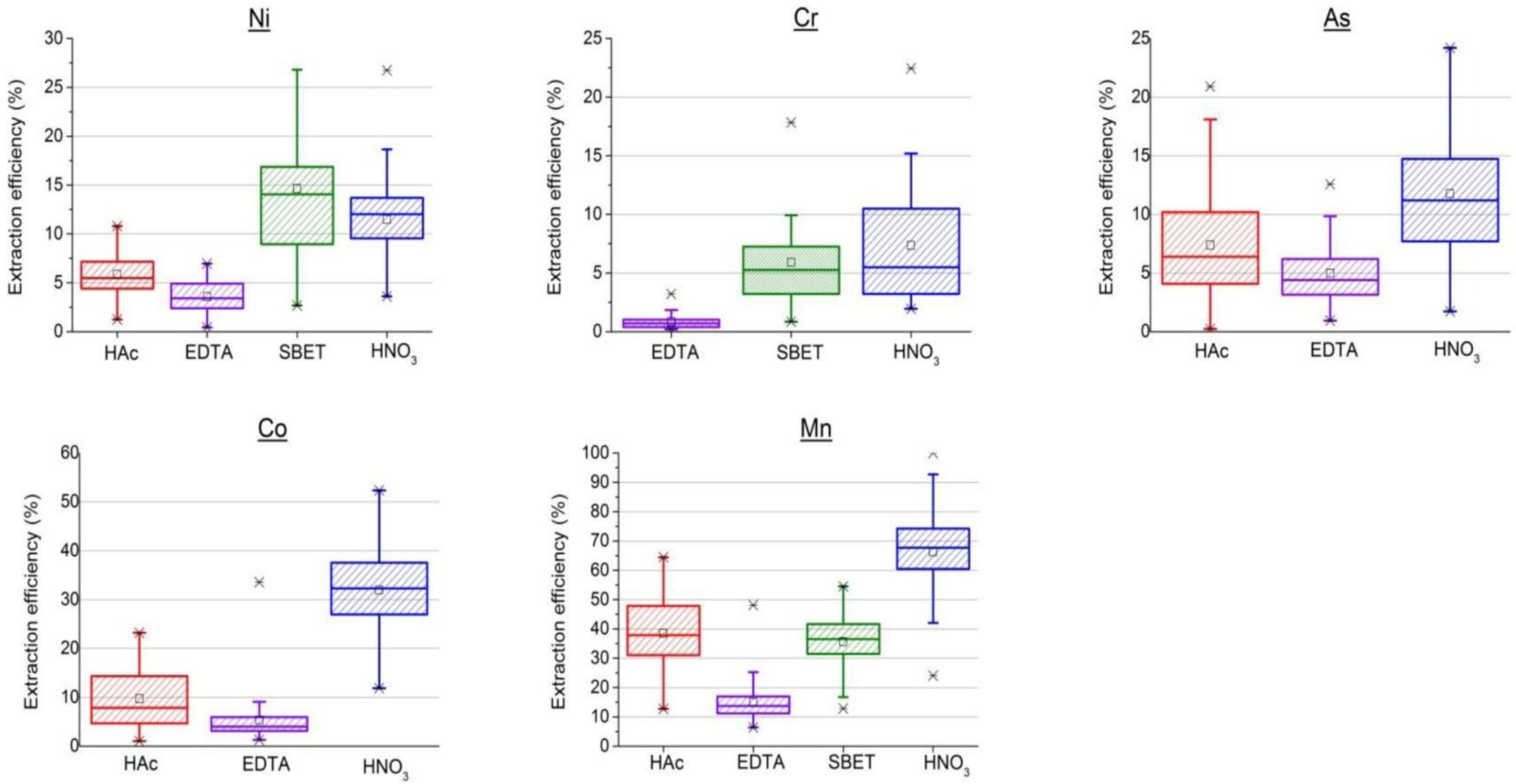
Single extraction results

Anthropogenic trace elements

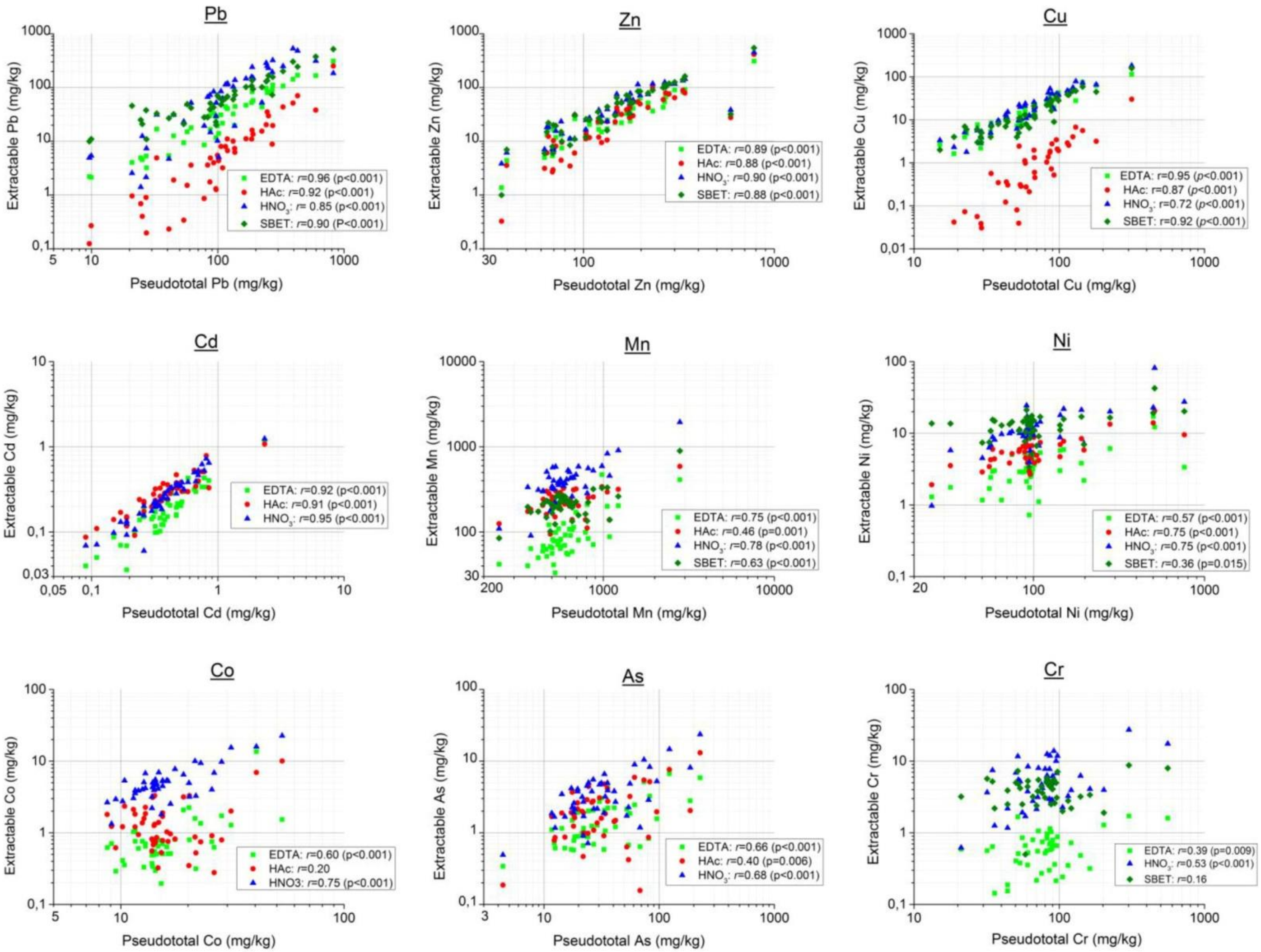


Single extraction results

<u>Geogenic trace elements</u>



Influence of pseudototal content



Regression analysis

<u>Based on pseudototal content</u>

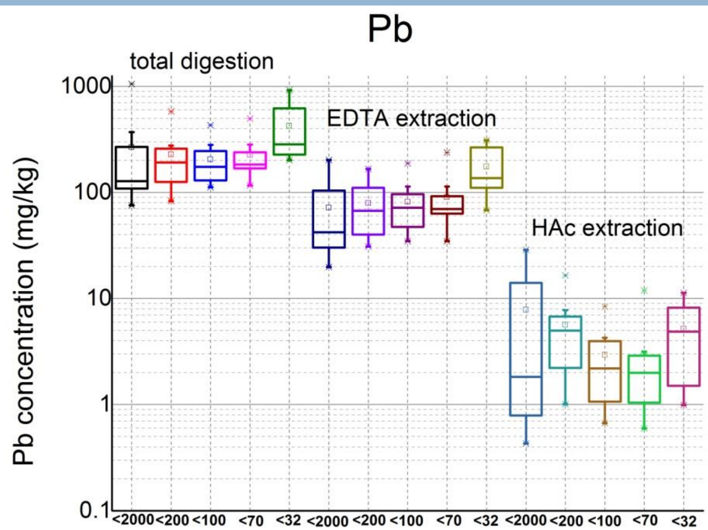
	R^2_{adj}
EDTA	
Pb	91.9
Zn	79.2
Cu	90
Cd	84.1
Ni	31.2
HAc	
Pb	83.3
Zn	77
Cu	75.5
Mn	19.3
Ni	55.9
As	14.2
SBET	
Pb	81.2
Zn	76.3
Cu	83.8
Mn	40.9

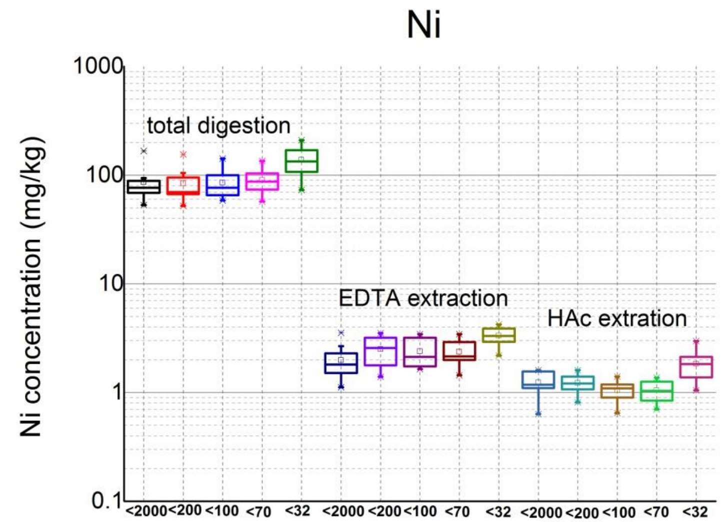
- ❑ Aqua regia is a better predictor for Pb and Cu availability
- ❑ Dilute HNO_3 is a better predictor for Zn, Ni, As and Mn availability
- ❑ Only for Zn and As there is a substantial improvement on the explained variance

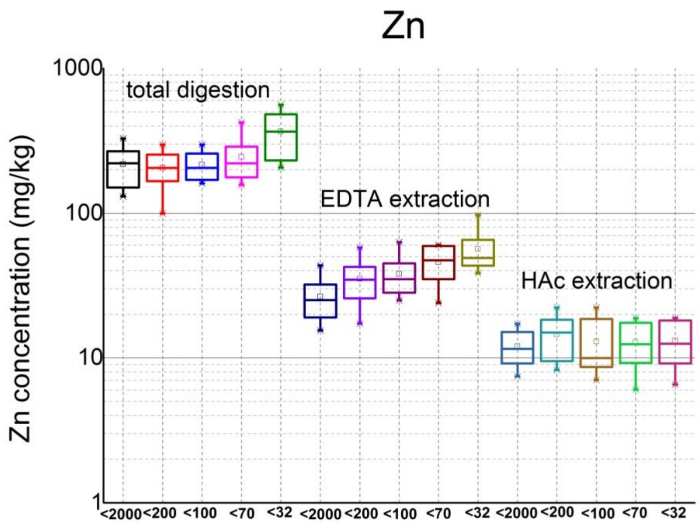
<u>Based on reactive content</u>

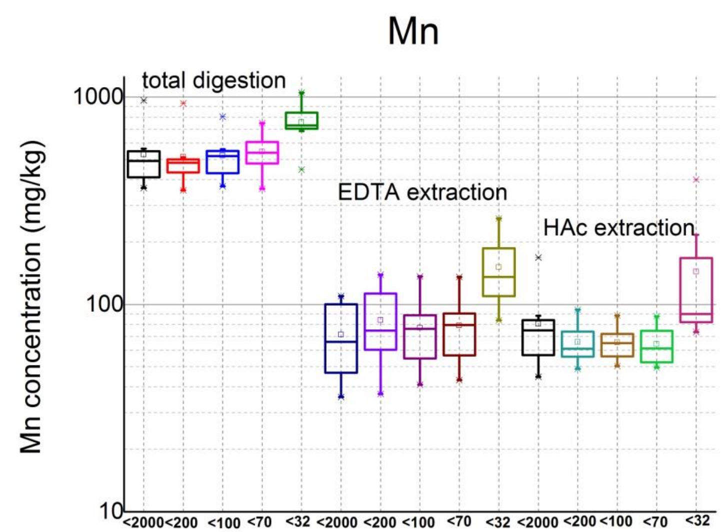
	R^2_{adj}
EDTA	
Pb	83.4
Zn	88.2
Cu	65.1
Cd	74.2
Ni	45
As	67.1
HAc	
Pb	64.8
Zn	89.1
Cu	71
Mn	50.2
Ni	74.8
As	74.6
SBET	
Pb	52.4
Zn	92.4
Cu	65.4
Mn	59.7

Concentrations of trace elements in different soil particle size fractions in Athens soil (Kelepertzis et al., 2016)

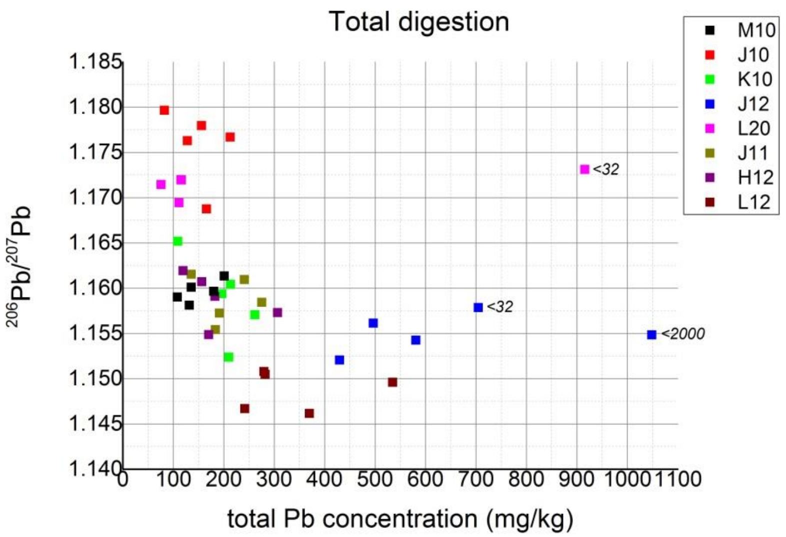


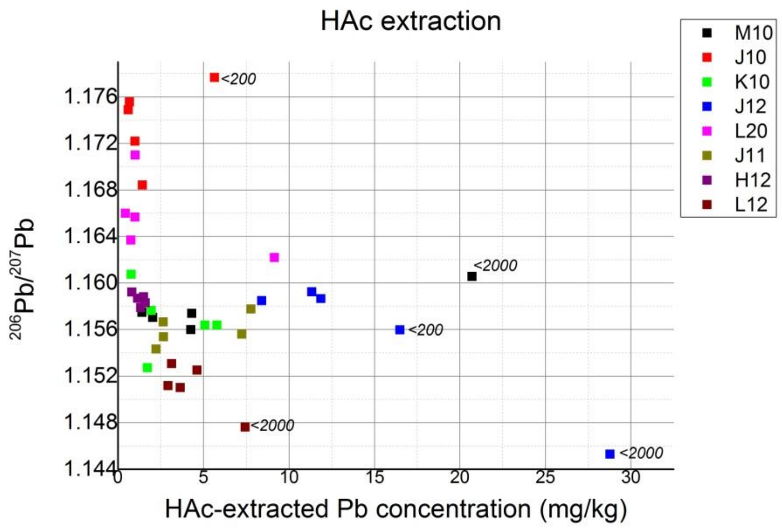


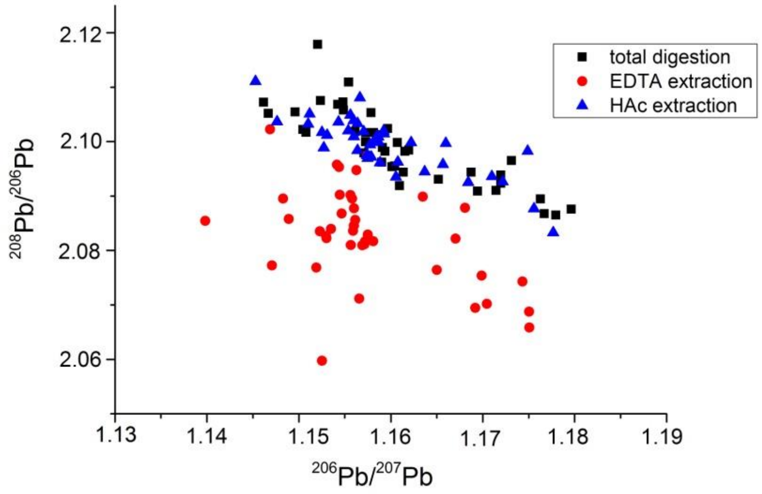




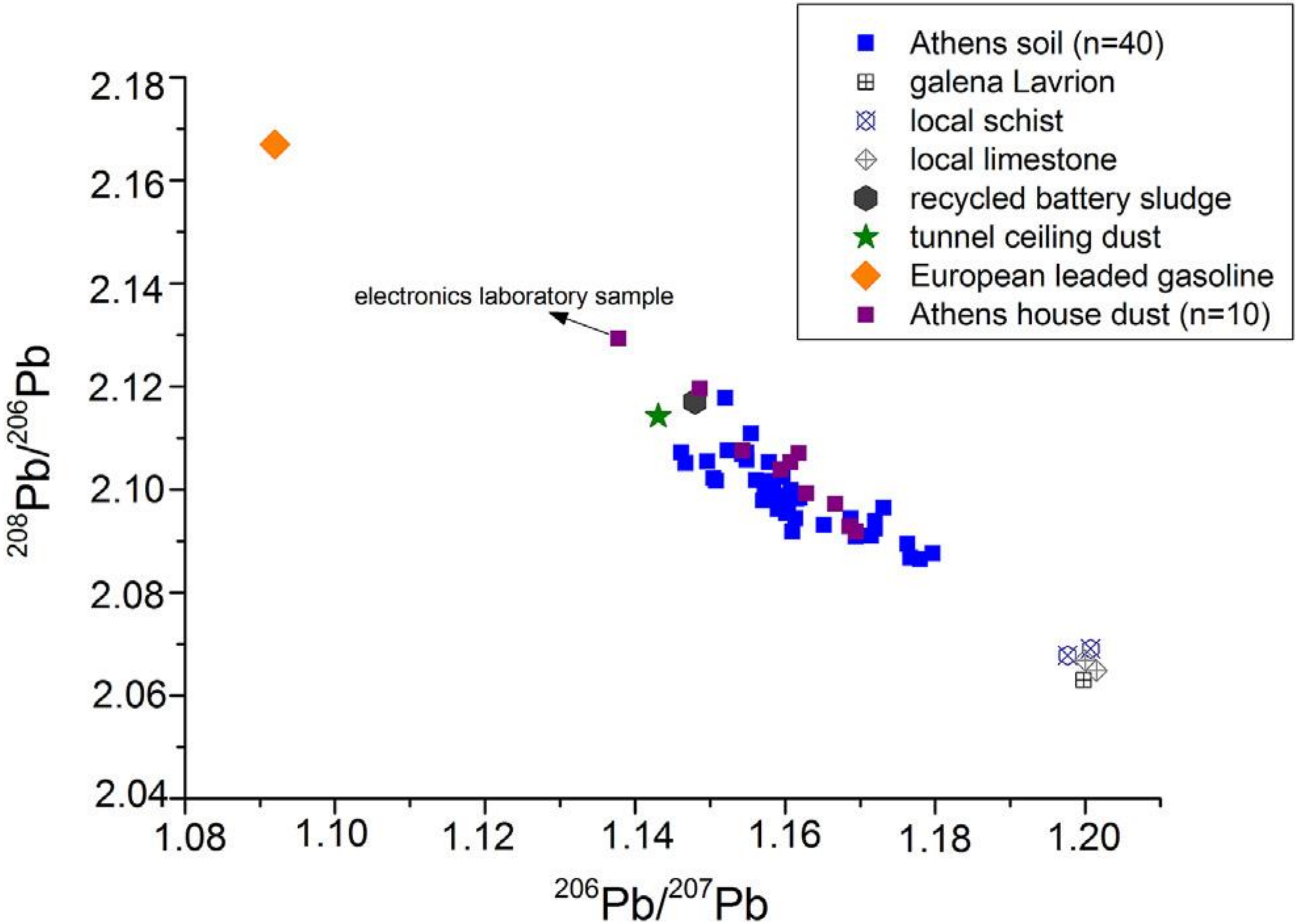
Pb concentrations and Pb isotopic ratios







Source identification of Pb in Athens



Relative contribution (%)

$$X_{sample} = \Big[({}^{206}Pb/{}^{207}Pb)_{sample} - ({}^{206}Pb/{}^{207}Pb)_{background} \Big/ ({}^{206}Pb/{}^{207}Pb)_{anthropogenic\ Pb} - ({}^{206}Pb/{}^{207}Pb)_{background} \Big] \times 100$$