

URBAN GEOCHEMICAL STUDIES IN EUROPE

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Abstract

Urban soil is generally contaminated to a variable degree depending on its proximity to contamination sources. Traffic is one of the main sources of urban contamination; lead (Pb) from the use of leaded petrol, zinc (Zn) and cadmium (Cd) from tyre wear, antimony (Sb) from break pads, and the platinum group elements (PGEs) from the wear of catalytic converters, are some typical elements that often reach high concentrations in the urban environment. Lead was also a key ingredient in white paint, and in towns with a high proportion of white wooden houses very high concentrations were found in soil. Crematoria can or have emitted mercury (Hg). Coal and heavy oil fired municipal power and heating stations emit sulphur (S), silver (Ag), vanadium (V), bromine (Br) and barium (Ba). The use of impregnated wood may have resulted in high concentrations of arsenic (As), especially in kindergartens (nursery schools) and playgrounds. Building materials (plaster and paint) may also contain high concentrations of organic contaminants, especially polychlorinated biphenyls (PCBs), which again end up in urban soil. Coal and wood burning, the use of diesel fuel, and the production of coke, all lead to the emission of polycyclic aromatic hydrocarbons (PAHs). There exist countless other sources of local contamination in towns, and there is thus every reason to be concerned about the quality of the urban environment, and the suitability of soil for sensitive land uses, such as schools, playgrounds, parks and vegetable gardens. Contaminated urban soil may contaminate indoor dust and, therefore, to an increased human exposure to toxic chemicals. Consequently, the distribution of toxic contaminants in urban soil needs to be documented and known by city administration to avoid costly mistakes in land use planning, and further spreading of highly contaminated materials.

The EuroGeoSurveys 'Geochemistry' Expert Group during the compilation of a proposal to the Directors for a European wide urban geochemistry project, using a harmonised sampling and analytical methodology, it discovered that many urban geochemical studies have been performed in Europe by National Geological Surveys, which are not known to the wider geoscientific community. Since, the results of these studies are directly related to our quality of life, the EuroGeoSurveys 'Geo-

chemistry' Expert Group decided to publish at least one case study from each country in a book, which will be available in the second half of 2010. A concise description of some of these studies will be given in this paper.

Key words: urban geochemistry, toxic chemical elements, contamination, soil, dust, Europe.

1. Introduction

The town is a heterogeneous complex structure that has been developed by humans as a necessity for protection, collaboration, trade, *etc.*, and is growing, changing, but also decaying, and its build-up is never completed. Since, urban areas in Europe are growing, the quality of their environment is becoming an important issue in the 21st century, following the serious degradation with the release of many toxic chemical elements and compounds by industrial processes, beginning from the industrial revolution, with a peak after the Second World War, as well as the modern style of living.

Industries were, and still are, variously located within the urban structure of many European towns. Since, the 1970s an attempt is, however, being made in many countries to develop industrial estates outside the urban structure. But, within the urban environment remain brownfield sites, and the enormous effort of their redevelopment in order to reduce the pressure on greenfield sites. However, this does not solve the contamination problem that has been developed over tens or hundreds of years in many urban centres, which may apparently be exacerbated in the not too distant future. At the beginning of the 20th century about 15% of the world's population was living in towns, and recent projections indicate that by the year 2030 the urban population will be two times as large as the rural. This increase will consume an important natural resource, *soil*; part of it will be completely lost through sealing, and the other will most likely lose its multi-functionality, because of contamination and compaction.

In comparison to atmosphere and water bodies, many contaminants are not diluted in soil, but are accumulated over time. In many cases, soil functions as a sink, with both inorganic and organic substances being adsorbed on soil colloids (*e.g.*, humic matter, clay minerals, iron and manganese hydroxides). Often, toxic substances are converted in soil to other, more stable, insoluble forms. Besides soil composition, the types of substances that accumulate in soil are governed by pH, redox conditions, and micro-organisms. A characteristic of urban areas is the wide distribution of fly ash and construction materials with neutral to basic pH values. Such conditions increase the immobilisation of many substances in urban soil. If soil conditions change, however, these substances can be remobilised and may enter ground or surface water.

Due to heterogeneity and continuous change of urban areas, it is important to understand, therefore, the distribution of chemical elements in the various environmental compartments (soil, atmosphere, road dust, house dust, water), and the methods for distinguishing human induced geochemical anomalies, *i.e.*, areas with chemical element concentrations above the natural geochemical baseline variation. The variable character of the natural geochemical baseline of chemical elements is an important concept that should be understood by decision-makers and planners; in simple terms, it means that elevated element concentrations, may be geochemically anomalous in one environment, whilst they can be part of the natural baseline concentrations in another; this continental scale natural geochemical baseline variation is well portrayed in the EuroGeoSurveys' "*Geochemical Atlas of Europe*" (<http://www.gtk/publ/foregsatlas/>). Therefore, geochemical maps of urban areas are needed to display the geographical distribution of chemical elements and compounds, in order to allow reliable recognition of contaminated areas.

Since, many health related problems are linked to the state of the urban environment, the European citizens are entitled to know the quality of not only the land their houses are built on, but also that of schools, parks, playgrounds, recreation areas, and workplaces. Estate agents would like to know the quality of the land they are marketing, and insurance brokers the potential risks on their customers.

2. Geochemical state of urban land

Concentrations of many potentially harmful elements (PHEs) are enhanced in the urban environment as a result of atmospheric and terrestrial contamination and the nature of urban ground, which is often disturbed and in-filled and frequently bears little relation to the residual soil, bedrock and superficial cover of the surrounding rural hinterland. Even in completely undisturbed urban areas, such as parks, many PHEs signatures are elevated in comparison to the rural natural geochemical baseline concentrations, due to atmospheric contamination, littering, urban surface run-off and other factors. Hence, it is necessary to establish the overall urban geochemical signature, so that areas of concern within a town can be highlighted, and detailed site investigation and contamination studies can be assessed in terms of the urban geochemical profile in addition to the rural baseline chemical element variation. It should be noted that systematic urban surveys do not replace the need for site-specific contaminated land investigations, but such data provide the citywide framework and context to more detailed assessments.

Urban soil is generally contaminated to a variable degree depending on its proximity to contamination sources. Traffic is one of the main sources of urban contamination; lead (Pb) from the use of leaded petrol, zinc (Zn) and cadmium (Cd) from tyre wear, antimony (Sb) from break pads, and the platinum group elements (PGEs) from the wear of catalytic converters, are some typical elements that often reach high concentrations in the urban environment. Lead was also a key ingredient in white paint, and in towns with a high proportion of white wooden houses very high concentrations were found in soil. Crematoria can or have emitted mercury (Hg). Coal and heavy oil fired municipal power and heating stations emit sulphur (S), silver (Ag), vanadium (V), bromine (Br) and barium (Ba). The use of impregnated wood may have resulted in high concentrations of arsenic (As), especially in kindergartens (nursery schools) and playgrounds. Building materials (plaster and paint) may also contain high concentrations of organic contaminants, especially polychlorinated biphenyls (PCBs), which again end up in urban soil. Coal and wood burning, the use of diesel fuel, and the production of coke, all lead to the emission of polycyclic aromatic hydrocarbons (PAHs). There exist countless other sources of local contamination in towns, and there is thus every reason to be concerned about the quality of the urban environment, and the suitability of soil for sensitive land uses, such as schools, playgrounds, parks and vegetable gardens. Contaminated urban soil may contaminate indoor dust and, therefore, to an increased human exposure to toxic chemicals. Consequently, the distribution of toxic contaminants in urban soil needs to be documented and known by city administration to avoid costly mistakes in land use planning, and further spreading of highly contaminated materials.

Next to soil, other natural materials could be sampled, as road dust, house dust, and attic dust. The chemical composition of each of these materials reveals a specific aspect of the urban environment. Road dust characterises mainly the current active sources of contamination. House dust is the material that children especially come mostly in contact with, and is characteristic of the narrow local home contamination. Attic dust, although not of direct concern to the quality of the home environment, it preserves a long record of past contaminating sources. Surface and ground water is an additional medium of concern that is closely associated with the quality of life of the population in some urban areas.

Of concern in the home environment are the levels of natural radon, which are based on geological factors, relation to mines and mine tailings, as well as the concentration of radium and radon in water supplies. Radon gas can penetrate houses from many sources and in different ways. In general, high levels of radon are associated with granite, igneous rocks, shale, slate, dirty quartz sedimentary rocks, phosphate deposits and some beach sands, which may contain high levels of radon progenitors, *i.e.*, uranium, or thorium. The most important contributor to indoor radon is the soil from which radon can be drawn through large and small subsurface gaps in the house foundations. A map of radon distribution should be produced to help planners and builders to site houses, or housing estates, on ground with low radon emission, and/or to reduce natural radon penetration in the home environment.

3. National Geological Surveys and urban issues

Soil contamination is becoming a key issue, and urban planning needs soil that is fit for human use, and is a matter that should be tackled efficiently. At European level, an initiative called “*Soil and Land Alliance of European Cities and Towns*” has been founded with the aim to make an active contribution to sustainable use of soil in communities [http://www.soil-alliance.org/e_manifesto.htm]. Production of a high quality compatible database on the geochemistry of urban soil is time consuming and costly, and especially if information down to the property level is required, since such systematic studies demand the use of the same sampling, sample preparation and analytical methodology, as well as data presentation. Existing urban soil geochemical databases from various sources have problems of data comparability, because different approaches to sampling, sample preparation and chemical analysis have been used.

Each European urban area has its own unique development, which is a result of many variables linked to historical, social, economic, cultural, geographical and climatic issues. Differences in living habits, land use practices, and use of building materials, may have resulted in different ways contaminants are stored in the various types of natural soil. Such a European wide comparison of the geochemistry of urban areas, using exactly the same methodology in all the investigation steps, will document the local peculiarities, and possible mistakes that have been made in one region do not need to be “transferred” to another. It is, therefore, strongly believed that there is a lot to be learned by such a well-coordinated European comparison of the geochemical state of the urban environment, and city administrators and planners will have at their disposal a high quality database for efficient urban planning.

Such systematic work in urban areas can only be carried out by national Geological Surveys, because they have the scientific expertise for such studies, and the infrastructure to maintain the required Geographical Information System databases to be accessed by each citizen. Something that has already been demonstrated by the production of the Geochemical Atlas of Europe (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006), and the pending Geochemical Atlas of Agricultural and Grazing land soil, which has started in 2008 (EGS Geochemistry, 2008; Reimann *et al.*, 2009).

4. Methods

4.1 General

Since, it is important to have comparable results across Europe, a field sampling manual for urban geochemical investigations in Europe is under compilation by the EuroGeoSurveys Geochemistry Expert Group, and should be released in 2010. Some of the principles have, however, been agreed,

and are described herein. The average sampling density should be 4 soil samples/km². In order to cover the urban area uniformly, it is proposed to collect soil samples from the central nodes of a 500 x 500 m grid. The sampling density can, however, be varied in sections of the town where contamination is suspected to the central nodes of a 250 x 250 m grid (16 samples/km²), and in the surrounding rural area to the central nodes of a 1000 x 1000 m grid (1 sample/km²).

There was a lively discussion with respect to the thickness of soil to be sampled, and whether single or composite samples should be collected. The different proposals were 0-2 cm, 0-5 cm, 0-10 cm and 0-20 cm. It was finally decided to collect surface soil samples down to a depth of 10 cm, after removal of surface litter, since this will give the best impression of anthropogenic impact. There is still disagreement, however, between single or composite soil samples. Collection of composite soil samples from four to five sub-sites up to a distance of 10 m around the central node is considered that it will give greater reproducibility and representativeness. This could be argued as suitable for natural situations, but in areas where humans have intervened for tens or hundreds of years, as is the case of urban environments, the variation could be enormous even at very short distances, since the principles governing the distribution of elements in the natural environment are no longer applicable. Hence, a composite soil sample may end-up diluting a significant point pollution target. Single spot soil samples have the advantage of representing precisely the site from which they have been collected. Reproducibility may not be good, but this is expected, because there are no rules about the spatial distribution of human induced contamination.

Soil samples should be collected from parks, playgrounds, sport fields and schoolyards, because these are the areas used by children and teenagers alike. Extensively used sites are preferred as, for example, in a grass covered park the most suitable site shall be where the grass has been worn through continuous use.

All field teams shall be provided with the same sampling equipment, purchased from the same source. At each sample site, GPS coordinates and field observations shall be recorded, and digital photographs taken; the recommendation is to take four general landscape photographs of the surrounding environment (North-East-South-West), and a site photograph showing details of soil texture.

Soil samples to be air dried and sieved to <2 mm (the standard fraction used in soil sciences) and pulverised to <0.063 mm prior to laboratory analysis. It is suggested to firstly analyse the samples by an aqua regia digestion. Total element concentrations (XRF or multi-acid-extraction) should be measured as well. A weak extraction would provide valuable information about availability, needed for the toxicological evaluation of the results. Because most weak extractions are quite element specific, it will not be easy to decide which one to use. Probably the Canadian “water extractable” standard, developed for the North-American geochemical mapping programme, is the best choice. All chemical analyses for a particular suite of parameters must be carried out in one laboratory only. All samples need to be randomised, and quality control samples (standards and duplicates) included at regular intervals (one in ten). Finally, all samples shall be submitted to the laboratory as one single batch.

Additional standard information needed for soil samples includes: pH, organic matter (*e.g.*, LOI as a proxy), and grain size analysis.

5. Results

Urban geochemical results are presented concisely from Berlin (Germany), Lavrion (Hellas), Madrid (Spain) and Prague (Czech Republic). There are many other case studies from Naples (Italy), Ljubljana (Slovenia), Trondheim, Bergen and Oslo (Norway), Stassfurt (Germany), and many others that

will be published in a book entitled “*Mapping the chemical environment of urban areas*” (Johnson *et al.*, 2010).

5.1 Berlin, Germany

About 4000 topsoil samples (0-20 cm) were taken in industrial and suburban areas of Berlin at a variable density between 20 and 40 samples/km² in densely populated and industrial parts of the city, and at a lower density (1-2 samples/km²) in the suburbs (Birke & Rauch, 1997, 2000; Birke *et al.*, 2000). The soil samples were air dried, sieved through a 2 mm nylon screen, and milled with an appropriate mill (planetary ball mill with agate grinding jars) to a grain size of <63 μm. The <2 mm fraction was analysed for 11 major elements (Si, Al, Fe, Mg, Ca, Na, K, P, S, total C, TOC) and 41 trace elements (Ag, As, B, Ba, Be, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, F, Ga, Ge, Hg, I, In, La, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr). Electrical conductivity and pH were also determined. Hydrocarbons, aromatics, volatile halogenated compounds and polychlorinated dibenzodioxins and dibenzofurans (PCDD/PCDF) were analysed only in topsoil from the central part of Berlin. For the urban Berlin area the estimated median value is 0.98 ng ITE/kg for PCDD/F's.

The spatial distribution of Al, K, Si, Na, Rb, Zr, Nb, Co, Sc, and Ti is mainly of geogenic origin, *i.e.*, related to the chemical composition of parent material.

Industrial areas tend to be characterised by contamination of top- and sub-soil with respect to Cu, Cd, Zn, Hg, Pb and Sn. Industrial and commercial areas often display considerably elevated values for Mo, Ni, As, Ag, Cr, Sb, Sr, TOC, Fe, Mn, Mg, P and, especially, Pb and Hg.

Wooded areas show no great enrichment, except for Cd and Zn. In the area around Berlin, strong and extensive anomalies occur near iron and steel industries and construction materials industries, as well as in the vicinity of sewage treatment plants. There is local heavy-metal pollution (Hg, Cd, Zn) from the sewage treatment plants north and south of Berlin.

Urban geochemical studies in Berlin, and other German cities, have shown that toxic elements (*e.g.*, Cd, Cu, Cr, Hg, Ni, Pb, Zn and As) are enriched in soil by 1.8 to 8.9 times the natural geogenic concentrations (Table 1).

Especially in the polluted soil of old industrial sites, peak values of 2050 times the geogenic background were measured for Cu, 1780 times for Hg, and 1638 times for Cd. This means that, taking a soil of 1.2 g/cm³ density and the median concentration values from Berlin as an example of a large

Table 1. Topsoil element concentrations in Berlin (in mg/kg; n=3,746)

<i>Element</i>	<i>Arithmetic mean</i>	<i>Highest mode</i>	<i>Element</i>	<i>Arithmetic mean</i>	<i>Highest mode</i>
As	4.4	2.4	F	280	200
B	17.6	13.0	Hg	0.29	0.04
Be	1.14	1.0	Ni	8.1	2.7
Cd	0.65	0.08	Pb	85.8	21.7
Co	1.9	<1.0	Sb	2.92	2.1
Cr	28.7	12.2	Sn	7.6	1.6
Cu	53.1	6.0	Zn	166	19.3

city, the topsoil (0-20 cm depth) contains about 834 tonnes (t) As, 74 t Cd, 5,366 t Cr, 6,660 t Cu, 40.6 t Hg, 1,646 t Ni, 16,377 t Pb and 27,580 t Zn.

5.2 Lavrion, Hellas

Lavrion is a town 55 km to the south-east of Athens. Historically is a unique place, together with its surroundings, in the classical history of Hellas, since the mining of argentiferous galena provided the financial means for the Golden Age of Pericles during the 5th Century B.C. Almost two-and-a-half thousand years later (1865-1989 A.D.) was again a centre for mining and ore-smelting activities. Such a unique place in World history deserved a unique integrated environmental impact study, leading to recommendations for the necessary remediation measures that must be taken in order to make the area safe for habitation (Demetriades *et al.*, 1997; Demetriades, 1999a, b, c, d, e, 2010; N.T.U.A., 1999).

The following sample types were collected from an area of 7 km², covering the urban and suburban parts of Lavrion: (i) parent rocks (n=140), (ii) metallurgical processing residues (n=62), (iii) overburden including residual soil from 0-5 cm (n=224), (iv) house-dust (n=127), (v) metallurgical processing wastes and residual soil for particle-size analysis (n=21), (vi) ground water (n=15), (vii) metallurgical processing wastes for particle characterisation (n=31), and (viii) overburden from drill-hole core and vertical profiles (n=165). In addition, biomedical samples (n=235) collected during the last cross-sectional epidemiological study in March 1988, and soil samples for an agronomy study (n=583) were also utilised.

To begin with, the geochemistry of parent rocks, which depicts the natural levels of elements at the archetype state was studied (Table 2). Subsequently, human intervention followed with the exploitation of the mineral resources of the greater Lavrion area and the Lavreotiki peninsula, which had severe effects on the chemistry of soil. The enormous amount and expanse of metallurgical wastes in the Lavrion urban area contributed, together with other factors (aerial, fluvial, *etc.*), in the contamination of soil by Pb, Zn, As, Sb, Cd, Cu, Hg, *etc.* The geochemical investigation of the soil cover revealed the intensity and extent of contamination (Table 2). House dust is also severely contaminated (Table 2). Use of a sequential extraction method has given information about the geochemical behaviour, leachability, mobility and potential bioaccessibility of chemical elements in soil and house dust. These parameters were significant in the assessment of the effects of environmental contamination on the health of the local population.

Exposure to local environmental pressures is indicated by high Pb concentrations in child blood (5.98-60.49 $\mu\text{g}/100\text{ mL}$, mean 19.43 $\mu\text{g}/100\text{ mL}$, n=235), and deciduous teeth (0.97-153.26 $\mu\text{g}/\text{g}$, mean 9.88 $\mu\text{g}/\text{g}$, n=82), as well as by high As levels in 24 hour urine As (0.53-77.23 $\mu\text{g}/24\text{h}$, mean 8.59 $\mu\text{g}/24\text{h}$, n=261) (Stavrakis *et al.*, 1994), and total As in urine (9.7-1279 $\mu\text{g}/\text{L}$, mean 163.1 $\mu\text{g}/\text{L}$, n=65) (Demetriades *et al.*, 2008). The child blood-Pb levels, together with the geological, geochemical, metallurgical processing wastes and land use variables, were used in the risk assessment and subsequent environmental management scheme for the Lavrion urban area.

The percentage proportion of the Lavrion urban-suburban area with potentially hazardous element concentrations to human health is: (a) 100% for As, Pb, Cd and Zn, (b) 90 to 99% for Ag, V and Sb, (c) 45 to 68.8% for Cu and Mo, and (d) 13.8 to 33% for Ba, Ni and Cr. It is concluded, therefore, that the multi-element contamination of the Lavrion overburden/soil and house dust is extremely high, and presents an unacceptable risk on the quality of life of the local population, and is also potentially hazardous to plants and animals. Hence, it is highly urgent to rehabilitate the whole area by suitable remediation techniques.

Table 2. Statistical parameters of inorganic elements in samples of surface soil, house dust, parent rocks and metallurgical processing wastes, Lavrion, Hellas (values in mg/kg).

Element	Overburden samples, including residual soil (n=224)				House dust (n=127)	Parent rocks (n=140)	Metallurgical processing wastes (n=62)
	Min.	Max.	Mean	Median	Median	Median	Median
Ag**	1.4	204.6	17.8	12.1	4.81	0.5	18.9
As	50	24,000	2,194	1,290	750	15.6	2492
Ba	64	4,555	663.2	479	473	210	243
Be**	0.2	2.7	1.1	1	0.5	0.5	0.5
Cd	4	925	68	38	16.3	0.5	20.6
Co	3	106	17.7	16	8.1	20.5	23.8
Cr	2	1,083	264.2	183	114	20	73.2
Cu	43	4,445	357	186	179	25	630.5
Mo**	1.7	108.9	6.9	4.9	4.1	0.5	3.6
Ni	40	591	141.4	127	84	54.5	38.5
Pb	810	151,579	11,578	7,305	3,091	22	20,750
Sb ^{§**}	<6.8	567	121	121	-	2.5	189
V	26	325	86.1	75	42.5	9	46.3
Zn	591	76,310	10,872	6,668	3,044	57	39,800

[§]Overburden: Sb (n=90); **Rock: Ag, Mo (n=155); Be, Sb (n=48).

5.3 Madrid, Spain

The Madrid investigation was a multi-media urban geochemical study that covered an area of 400 km², *i.e.*, (1) 1730 top soil samples (0-20 cm) were collected at a density of 4 samples/km² from public gardens, buildings sites, *etc.*; the <180 µm fraction was analysed for major and trace elements by ICP-AES following (a) partial extraction by hot HNO₃+HCl acid (leach for 6 hours at 100°C), (b) a hot tetra-acid digestion (nitric, perchloric, fluorhydric, chloridric), and also (c) total contents by INAA (48 elements), (2) 248 soil samples at a density of 0.6 samples/km² were taken for the determination of organic compounds, such as volatile halogens, extractable halogen organic compounds (EOX), PAHs, and PCBs, (3) 302 pavement and sidewalk dust at a density of 0.75 samples/km² were collected by sweeping a surface of 15-20 m², and the <180 µm fraction was analysed for major and trace elements, and (4) 25 leaf samples were collected from plants and after ashing at 550°C total element concentrations were determined for 48 elements by ICP-AES and INAA.

The levels of most organic compounds were always below the detection limits of analytical methods, except EOX that showed some local contamination of small extension and intensity.

Overall the soil geochemical and dust patterns were of lithogenic origin, except locally where they

are disturbed by human factors due to the allochthonous nature of transported materials. The most significant anthropogenic signatures in soil with respect to total element contents were (a) Cu, Pb, Zn, P, Ni, Sb, Ag, (\pm Cd, Co, Cr) patterns that are ascribed to industrial and airport activities and fertilisation with sewage sludge, (b) Br, Organic Matter, Cr, (\pm Sb, Co, Pb, P, Mo) have a strong relationship with traffic and burning of liquid and solid fuels, and (c) Au has its own pattern, as it does not show any correlation with other elements. Geochemical patterns from partial extraction analyses are similar to those from total extraction, although the levels are lower; for some contaminants, however, patterns are more distinct, as is the case of W, which delineates more clearly pollution from the airport and some metal industries. An interesting observation was the distortion of natural geochemical patterns from the waste demolition dumps in the suburban area of Madrid, and the localised contamination by metallic elements.

Settled dust had contamination signatures from traffic, and fuel combustion, but also it delineated some new anomalies of industrial origin at the south-eastern, eastern and northern parts of Madrid.

The conclusion of this study was that Madrid has a similar contamination problem as other large industrial cities, and that the collected information would be useful for the establishment of a monitoring network for the detailed study of local polluted areas.

5.4 Prague, Czech Republic

The soil geochemical survey of Prague covered an area of 550 km² at a density of 1 sample/km² (Duris, 1999; Zimova *et al.*, 2001). The whole study area was divided into 1 km² grid cells, which were subsequently subdivided into 4 quadrants for sampling purposes. From each 1 km² cell a composite sample was made by taking a surface soil sub-sample (0-20 cm) from each quadrant. The soil samples were air dried (\approx 20°C), sieved through a 180 μ m nylon screen, and ground to <75 μ m for analysis. In addition, pavement dust was collected at selected road junctions in 1996 and 1999.

Concentrations of some inorganic and organic pollutants in soil are tabulated in Table 3. The Prague results show that Pb has elevated concentrations over the whole urban area, and the highest levels are in the city centre together with Cu and Hg. Similar patterns are observed with respect to PAHs and PCBs.

Changes of Pt, Pd and Pb concentrations in pavement dust at selected road junctions from 1996 to 1999 are shown in Table 4. It is indeed interesting to observe the drop in Pb, since the introduction of unleaded petrol, but also the rise of Pt and Pd from the use of catalytic converters.

Table 5 shows the concentrations of selected elements in child body tissues. Since, the Prague environment has elevated levels of contaminants in soil, the urban geochemical survey results are being evaluated from the public health risk point of view.

6. Conclusions

These urban geochemical studies have provided a comprehensive geochemical data base that permits differentiation between the natural geochemical background and local anthropogenic contamination.

It is also quite apparent from these studies that toxic element concentrations in topsoil vary considerably in an urban environment. Elevated values primarily reflect land use and the type and volume of industrial production.

The above studies have also shown that different sampling, sample preparation and analytical meth-

Table 3. Statistical parameters of inorganic and organic pollutants in surface soil (0-20 cm), Prague (values in mg/kg, unless otherwise stated).

<i>Element</i>	<i>Minimum</i>	<i>Maximum</i>	<i>Arithmetic mean</i>	<i>Geometric mean</i>	<i>Median</i>
Sb	0.1	8.6	1.3	1.6	0.9
As	7	102	18	16	16
Be	<0.8	3	1.5	1.4	1.4
Sn	<7	60	8	6.6	4
Cr	48	187	83	82	82
Cd	<0.4	9.1	0.5	0.5	0.4
Cu	<7	152	45	39	37
Ni	<7	103	32	29	31
Pb	13	420	74	62	58
Hg	<0.03	2.45	0.33	0.25	0.23
Tl	<0.05	0.89	0.15	0.13	0.14
V	14	89	37	36	35
Zn	41	912	201	173	167
PAHs ($\mu\text{g}/\text{kg}$)	211	95176	8379	3699	3319
PCBs ($\mu\text{g}/\text{kg}$)	3	7527	118	43	39

Table 4. Changes of Pt, Pd and Pb from 1996 to 1999 in pavement dust at selected road junctions in Prague.

<i>Road junction</i>	<i>Pt ($\mu\text{g}/\text{kg}$)</i>		<i>Pd ($\mu\text{g}/\text{kg}$)</i>		<i>Pb (mg/kg)</i>	
	<i>1996</i>	<i>1999</i>	<i>1996</i>	<i>1999</i>	<i>1996</i>	<i>1999</i>
Argentinská, Plynární	103	222	6	91	410	376
Spojovací Konevova	77	317	7	191	360	312
Žitná, Mezibranská	171	502	32	164	690	427
V Botanice, Zborovská	72	44	15	18	344	132
Barr. most (Smíchov)	41	983	5	329	785	335
Vítězné náměstí	25	61	5	17	414	271
Pod mag. U Bulhara	89	362	13	119	335	348

Table 5. Concentrations of Cd, Cu, Hg, Pb and Zn in child body tissues (in $\mu\text{g}/\text{L}$). It is noted that the WHO upper admissible limit for Pb in child blood is 100 $\mu\text{g}/\text{L}$.

<i>Body tissue</i>	<i>Statistics</i>	<i>Cd</i>	<i>Cu</i>	<i>Hg</i>	<i>Pb</i>	<i>Zn</i>
Blood	Median	0.15	1058	0.57	33	5202
	Minimum	0.015	511	0.04	8	2500
	Maximum	3.6	2074	7.8	247	8900
Urine	Median	0.235	10.1	0.25	3.73	547
	Minimum	0.035	0.799	0.01	0.16	54
	Maximum	5.91	460	87.5	36.2	2952

ods have been used, making, therefore, very difficult the comparison of results. Since, it is very important at the European level to have results that are compatible, the EuroGeoSurveys Geochemistry Expert Group, with the approval of Survey Directors, will be carrying out in 2010-11 an urban geochemical survey in at least ten cities with exactly the same methodology of sampling, sample preparation, laboratory analysis and map plotting.

In conclusion, the distribution of toxic contaminants in urban soil needs to be documented and results made known to town authorities for planning purposes in order to avoid costly mistakes in land use planning, and further spreading of highly contaminated materials.

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8. References

- Birke, M. & Rauch, U., 1997. Geochemical investigations in the Berlin metropolitan area. *Zeitschrift für Angewandte Geologie* 43(1), 58-65.
- Birke, M. & Rauch, U., 2000. Urban geochemistry: investigations in the Berlin metropolitan area. *Environmental Geochemistry and Health* 22, 233-248.
- Birke, M., Rauch, U. & Raschka, H., 2000. *Geochemical investigations in urban areas: megacities, mining districts, waste disposals and industrial zones*. Report (0120667), Federal Institute for Geosciences and Natural Resources, Berlin, 66 pp.
- Demetriades, A. (Editor), 1999a. *Geochemical atlas of the Lavrion urban area for environmental protection and planning; Volume 1, Explanatory text*. Project "Soil rehabilitation in the Municipality of Lavrion", EU LIFE programme Contract No.: 93/GR/A14/GR/4576. Institute of Geology and Mineral Exploration, Athens, Hellas, Open File Report E8272, 365 pp.
- Demetriades, A. (Editor), 1999b. *Geochemical atlas of the Lavrion urban area for environmental protection and planning; Volume 1A, Tables and figures*. Project "Soil rehabilitation in the Municipality of Lavrion", EU LIFE programme Contract No.: 93/GR/A14/GR/4576. Institute of Geology and Mineral Exploration, Athens, Hellas, Open File Report E8272, 210 pp.
- Demetriades, A. (Editor), 1999c. *Geochemical atlas of the Lavrion urban area for environmental protection and planning; Volume 1B, Appendix reports*. Project "Soil rehabilitation in the Municipality of Lavrion", EU LIFE programme Contract No.: 93/GR/A14/GR/4576. Institute of Geology and Mineral Exploration, Athens, Hellas, Open File Report E8272, 176 pp.
- Demetriades, A. (Editor), 1999d. *Geochemical atlas of the Lavrion urban area for environmental protection and planning; Volume 2, Geochemical Atlas*. Project "Soil rehabilitation in the Municipality of Lavrion", EU LIFE programme Contract No.: 93/GR/A14/GR/4576. Institute of Geology and Mineral Exploration, Athens, Hellas, Open File Report E8272, 222 pp.
- Demetriades, A. (Editor), 1999e. *Environmental management plan for the rehabilitation of soil in the Lavrion urban area; Volume 4*. Project "Soil rehabilitation in the Municipality of Lavrion", EU LIFE programme Contract No.: 93/GR/A14/GR/4576. Institute of Geology and Mineral Exploration, Athens, Hellas, Open File Report E8272, 155 pp.
- Demetriades, A., 2010. The Lavrion urban geochemical study. In: C.C. Johnson, A. Demetriades, R.T. Ottesen & J. Locutura (Editors), *Mapping the urban chemical environment*. Wiley, London (in preparation).

- Demetriades, A., Stavrakis, P. & Vergou-Vichou, K., 1997. *Exploration geochemistry in environmental impact assessment: examples from Greece*. In: P.G. Marinos, G.C. Koukis, G.C. Tsiambaos & G.C. Stourmaras (Editors), *Engineering Geology and the Environment*. Balkema, Rotterdam, Volume 2, 1757-1762.
- Demetriades, A., Vergou, K. & Vlachoyiannis, N., 2008. *The contamination of Lavreotiki peninsula and the urban environment of Lavrion from the mining-metallurgical wastes and the effects on the health of the local population*. Proceedings of the 9th Scientific Meeting of S.E. Attiki, Lavrion Attiki, 13-16 April 2000. Society of Studies of South-east Attiki, Kalivia Thorikon, Hellas, 573-624 (text in Hellene).
- De Vos W., Tarvainen T. (Chief Editors), Salminen R., Reeder S., De Vivo B., Demetriades A., Pirc S., Batista M.J., Marsina K., Ottesen R.T., O'Connor P.J., Bidovec M., Lima A., Siewers U., Smith B., Taylor H., Shaw R., Salpeteur I., Gregorauskiene V., Halamic J., Slaninka I., Lax K., Gravesen P., Birke M., Breward N., Ander E.L., Jordan G., Duris M., Klein P., Locutura J., Bel-lan A., Pasieczna A., Lis J., Mazreku A., Gilucis A., Heitzmann P., Klaver G. and Petersell V. 2006. *Geochemical Atlas of Europe. Part 2 - Interpretation of Geochemical Maps, Additional Tables, Figures, Maps, and Related Publications*. Geological Survey of Finland, Espoo, 692 pp. Available online at: <http://www.gtk.fi/publ/foregsatlas> (last accessed on 17/1/2010).
- Duris, M., 1999. Geochemical and ecological survey of the Prague agglomeration. In: D.A. Lovejoy (Editor), *Heavy metals in the environment: An integrated approach conference presentations from the 1st international conference "metals in the environment"*. Institute of Geology, Vilna, Lithuania, 134-136.
- EGS Geochemistry, 2008 (EuroGeoSurveys Geochemistry Working Group). *EuroGeoSurveys Geochemical mapping of agricultural and grazing land soil of Europe (GEMAS) - Field manual*. Geological Survey of Norway, Trondheim, NGU Report 2008.038, 46 pp. Available online at: <http://www.ngu.no/en-gb/hm/Publications/Reports/2008/2008-038/> (last accessed on 17/1/2010).
- Johnson, C.C., Demetriades, A., Ottesen, R.T. & Locutura, J., 2010. *Mapping the urban chemical environment*. Wiley, London (in preparation).
- N.T.U.A., 1999. *Environmental characterisation of Lavrion site – Development of remediation techniques*. Volume 3, In: Soil Rehabilitation in the Municipality of Lavrion. Project "Soil rehabilitation in the Municipality of Lavrion", EU LIFE programme Contract No.: 93/GR/A14/GR/4576. National Technical University of Athens, Hellas, 175 pp.
- Reimann, C., Demetriades, A. Eggen, O.A., Filzmoser, P. & the EuroGeoSurveys Geochemistry Expert Group, 2009. *The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) - Evaluation of quality control results of aqua regia extraction analysis*. Geological Survey of Norway, Trondheim, NGU Report 2009.049, 94 pp. Available online at: <http://www.ngu.no/en-gb/hm/Publications/Reports/2009/2009-049/> (last accessed on 17/1/2010).
- Salminen R. (Chief Editor), Batista M.J., Bidovec M., Demetriades A., De Vivo B., De Vos W., Duris M., Gilucis A., Gregorauskiene V., Halamic J., Heitzmann P., Lima A., Jordan G., Klaver G., Klein P., Lis J., Locutura J., Marsina K., Mazreku A., O'Connor P.J., Olsson S.Å., Ottesen R.T., Petersell V., Plant J.A., Reeder S., Salpeteur I., Sandström H., Siewers U., Steenfelt A. and Tarvainen T. 2005. *FOREGS Geochemical Atlas of Europe, Part 1: Background Information, Methodology and Maps*. Geological Survey of Finland, Espoo, 526 pp. Available online at: <http://www.gtk.fi/publ/foregsatlas> (last accessed on 17/1/2010).
- Stavrakis, P., Vergou-Vichou, K., Fosse, G., Makropoulos, V., Demetriades, A. & Vlachoyiannis, N., 1994. A multidisciplinary study on the effects of environmental contamination on the human population of the Lavrion urban area, Hellas. In: S.P. Varnavas (Editor), *Environmental Contamination*. 6th International Conference, Delphi, Greece, CEP Consultants, Edinburgh, 20-22.
- Zimova, M., Duris, M., Spevackova, V., Melichercik, J., Lepsi, P., Tesarova, B., Knotek, P., Kubinova, R. & Ronen, Y., 2001. Health risk of urban soils contaminated by heavy metals. *International Journal of Occupational Medicine and Environmental Health*, 14, 231-234.