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# URBAN GEOCHEMICAL MAPPING MANUAL

## Sampling, Sample preparation, Laboratory analysis, Quality control check, Statistical processing and Map plotting

EuroGeoSurveys
Brussels 2015

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Front cover photograph: Twenty-first century Athens, the capital of Hellas (22nd June 2015).

The hill in the centre of the photograph is Acropolis and on its top is the temple of the goddess Athéna, the Parthenon (5th century BC); at the left foothills of Acropolis is the Odeon of Herodes Atticus (2nd century AD).

The photograph shows a span of 2600 years of the Athens urban history, starting from the 5th century BC (Parthenon) to the 21st century AD (modern buildings).

In Athens, the earliest human presence goes back to the 11th — 7th millennium BC, with continuous urban habitation starting from the 5th — 4th millennium BC, making it, together with Árgos (a town in Pelopónnesus), the two towns in Europe with continuous urban settlement for the past 7,000 years of recorded history.

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## Sampling, Sample preparation, Laboratory analysis, Quality control check, Statistical processing and Map plotting

Alecos Demetriades and Manfred Birke

with contributions by
The EuroGeoSurveys Geochemistry Expert Group

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EuroGeoSurveys,
The Geological Surveys of Europe,
36-38, Rue Joseph II,
1000 Brussels, Belgium.
Tel : +32 2 888 75 53
Fax : +32 2 503 50 25
info@eurogeosurveys.org
http://www.eurogeosurveys.org

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[1] Institute of Geology and Mineral Exploration, Hellas. Home address: P.O.Box 640 47, Zografou, Gr-157 10 Athens, Hellas.
E-mail: alecos.demetriades@gmail.com
[2] Federal Institute for Geosciences and Natural Resources, Stilleweg 2, 30655 Hannover, Germany.
E-mail: Manfred.Birke@bgr.de

# SUMMARY

Given that the quality of the urban environment is a key issue in planning a healthy home, school, work, and recreational facilities, there is an urgent need to know the concentration of chemical elements and compounds, which are currently in our urban environment, and how they differ from the pre-urbanisation stage. Once we have defined the urban geochemical baseline, this will serve as the timeline for monitoring future changes. The produced results should be of high quality and integrity for multipurpose use, and to be legally defensible as they are very sensitive environmental data, because they inform us about the chemical state of our living, work, and recreational environments, which affects our quality of life.

Sampling, is the most important part in urban geochemical mapping, as in any applied geochemical survey, and must be carried out with the utmost care. Any mistakes during this stage are difficult to trace and correct afterwards. Hence, this manual presents urban geochemical methodologies tested and tried around the world. By its nature, recommends what to do in order to standardise the approach to urban geochemical mapping across Europe, and the whole World, and not to keep reinventing the methodology, as this is a waste of time and resources.

The manual describes the procedure of (i) sampling topsoil, subsoil, house dust, attic dust, road dust or sediment, air particulates and bio-indicators, including human tissues, (ii) sample preparation, (iii) laboratory analysis, (iv) quality control, (v) data conditioning, and (vi) data processing and map plotting. It stresses the necessity for the preparation of a reference sample or samples, before the start of the urban geochemical project, and that the collected samples must be prepared in just one laboratory, and analysed for the same suite of determinands in the same laboratory, following a strict quality control procedure.

**Keywords**: Geochemical mapping; Methodology; Systematic survey; Sample media; Sampling; Soil; House dust; Attic dust; Road dust; Road sediment; Air particulates; Bio-indicators; Human tissues; Sample preparation; Chemical analysis; Reference samples; Quality control; Data treatment; Map plotting

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## CHECKLIST FOR URBAN GEOCHEMICAL MAPPING PROJECTS

The following is a checklist of salient points for Urban Geochemical Mapping projects using topsoil/subsoil, house dust, road dust or road sediment, air particulates and bio-indicator plants:

- √ Nominal sample density 4 samples/km$^2$ to obtain an overall view of the quality of the urban and suburban environment; detailed urban geochemical surveys can be of any sample density, even down to the individual household level.
- √ Use 1:5000 topographical map sheets or cadastral plans or orthophotographs.
- √ Superimpose on the maps/plans/photos a 500 x 500 m grid (central part of city) to 1000 x 1000 m grid (suburbs); of course, denser grids can be superimposed depending on the objectives of the survey; this grid is suitable for the sampling of all sample media, except air particulates.

IMPORTANT: All hand jewellery must be removed before sampling. Smoking is strictly prohibited. All sampling tools and containers must be free of contaminants. All sampling tools must be thoroughly cleaned at each sample site before moving to the next one.

- √ Sample site selection:
    - ➢ Select a suitable patch of undisturbed (or least-disturbed) urban soil near to the grid nodes;
    - ➢ The sampling site should be preferably of bare soil (not covered by grass, *etc.*) as this is directly amenable to children, and to deflation (removal of loose dry fine-grained particles (clay and silt sizes) by the turbulent eddy action of wind). If a patch of bare soil cannot be found, then select a site with sparse grass or short grass; the last choice should be grass-covered soil.
    - ➢ Select suitable sites for sampling house dust, and road dust or road sediment near to the grid nodes.
    - ➢ Select suitable sites for sampling air particulates and bio-indicator plants.
    - ➢ Human tissue sampling sites should be planned together with epidemiologists, as a follow-up study to assess the exposure of the population to environmental contaminants.
- √ Sample numbering:
    - ➢ Routine sample number should consist of the town or city code (three letters) and the sample site number (four digits); if different sample types are going to be collected from the same site they should be suitably coded, *e.g.*, topsoil (just number), and subsoil, house dust, attic dust and road dust, should have after the number a suffix code B, H, A and R, respectively.
    - ➢ Duplicate field sample number should be collected at every 20th sample site for projects with a total number >400 samples, and to be given the same sample number as that of the routine sample, but should have at the end the capital letter "D". For projects with a total number of <400 samples, duplicate field samples should be collected at every 10th sample site.
- √ Sample material: Topsoil should be collected from 0 to 10 cm depth; the zero level starts from the surface after removal of living vegetation, fresh litter, and surficial stones. Subsoil is collected from a sampling depth of 50 to 60 cm (*although the optimum depth range should be decided after carrying out an orientation survey*; this is the only orientation survey that is required to be performed in each town or city;
- √ Sampling: Each topsoil (0-10 cm) sample should be collected from a single patch of 50 x 50 cm; similarly, the subsoil sample to be taken from the same patch.
- √ Bagging up all sample types:
    - ➢ Use only strong certified trace element free polymer Rilsan® bags;
    - ➢ Use only black water resistant markers for writing on the bag;
    - ➢ In addition, for safety purposes, write sample number on a small card, which should be placed in a small plastic zip-lock bag, and then inserted in the Rilsan® bag and on top of the sample.
    - ➢ Remove air from the Rilsan® bag, and close it firmly with a self-locking plastic tie strap (plastic cable tie). This firm closing of the sample bag safeguards its accidental opening at any stage before reaching the sample preparation laboratory.
    - ➢ For safety during packing and transportation, the Rilsan® bag should be placed in a larger plastic bag.

  - Place the sample bag in a strong carton box. Note: *Do not put too many sample bags in a single box, because overfull boxes are a significant health and safety hazard, particularly for the staff that will move them alone.*

- √ Field observations and documentation:
  - The Field Observations Sheet must be completed at each sample site (Appendix 5).
  - Coordinates: The global positioning system (GPS) tracker should be tuned to record WGS 84 geographical coordinates in degrees, minutes, and seconds (make sure that your GPS is turned to "WGS84").
  - The sample site and number should be marked on a topographical map.
  - Photographing: At each sample site, the conditions must be recorded with a number of photographs. ALWAYS start by photographing (i) the sample number, (ii) the dug up soil before sampling, and at least (iii) one general landscape photograph. As the photographic documentation is important, it is recommended that four (4) landscape photographs should be taken, North, East, South and West (always in this order). Photographs should be taken of the sites from where samples of (a) road dust or road sediment, (b) house dust, (c) attic dust, (d) bio-indicator plants, and (e) human tissues are taken; again, always start by photographing the sample number, and then take all the other photographs. This is the only safe way to ensure that the set of photographs taken after the sample number belong to that particular sample.

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# 1. INTRODUCTION

Humans ever since their appearance on Earth are trying to improve their living conditions. In this attempt through the ages, they have modified the natural environment, and especially in urbanised areas, with the release of many toxic elements and compounds by industrial processes and style of living. Such has been the impact of the human race on our planet that a new geological epoch, the Anthropocene, has recently been introduced recognising the significant human changes made to ecosystems (Chin *et al.*, 2013). Starting from the industrial revolution, with a peak after the Second World War, the urban environment has been contaminated with many toxic elements and compounds emitted by a wide variety of human activities, and often accumulated in urban soil (Johnson *et al.*, 2011; Lyons and Harmon, 2012). Although the negative long-term effects of certain elements, such as lead, were known in ancient Hellenic times (Conophagos, 1980), no precautions were taken to protect the workers and the environment. Industries were, and often still are, haphazardly distributed within the urban structure. Since, the 1970's a conscious attempt is being made in many countries to develop industrial estates outside the residential, commercial, and recreational parts of cities. Within the urban structure remain, however, the brownfield sites, and the enormous problem of their redevelopment in order to reduce the pressure on greenfield sites.

According to a 2014 United Nations report, 54% of the world's population resides in urban areas, while in 1950 this figure was 30% (UN, 2014). The urban population is expected to reach 60% by 2030 (UN, 2006), and 66% by 2050 (UN, 2014). Presently, Tokyo is the world's largest city with 38 million inhabitants, followed by Delhi with 25 million, Shanghai with 23 million, and Mexico City, Mumbai and São Paulo, each with around 21 million inhabitants (UN, 2014). By 2030, it is projected that the world will have 41 mega-cities each with more than 10 million inhabitants. As it may be appreciated, the quality of the urban environment is becoming an important issue in the 21st century, and systematic applied geochemical surveys should be carried out.

Johnson and Ander (2008, p.522-523) summarise satisfactorily the most common sample media used in urban geochemical studies: "*Soil is the most widely used sample medium, particularly for systematic sampling of complete urban areas. As many targeted studies have been in connection with vehicle pollution, roadside dust is also a frequently reported sample medium. Drainage sediments are not as widely used as in nonurban studies, mainly on account of their artificial and inaccessible nature (e.g., underground water culverts) in built-up environments. Studies that have used drainage sediments (e.g., Fordyce et al., 2004) are better able to consider movement of contaminants between the different urban environmental compartments. Tree bark and attic/house dusts (e.g., Tye et al., 2006) can be used for targeted studies involving atmospheric transport of contaminants. Atmospheric levels of elements and compounds are rarely reported in geochemical journals, and research tends to be done by other disciplines. This point illustrates the need for greater interdisciplinary cooperation, particularly in the study of the movement of chemicals and compounds between the different compartments of the urban environment, which will be represented by different sample media*".

Topsoil is the principal sample type used in urban geochemical studies, since this is the medium that children especially are in direct contact with. Urban topsoil, particularly in the older parts of cities, is a rather complex and heterogeneous mixture of different materials and substances, and its chemical composition depends on the anthropogenic activities that were operating during its historical development. This heterogeneous mixture is known as the '*cultural layer*' (Blume, 1989; Burghart, 1994; Alexandrovskaya1 and Panova, 2003; Rossiter, 2007; Baltakov, 2008). Depending on the urbanisation history and age of the city, the cultural layer varies from a few centimetres to a few metres (Photos 1 & 2).

Urban topsoil is a sink for a city's contaminating activities (Appendix 3) and, whilst current legislation may have substantially reduced these activities, a legacy of contamination can remain in soil for tens, hundreds, or even thousands of years. Thus, with the frequent occurrence of often highly contaminated soil in urban areas, a conscious management of soil excavation, transport, and redistribution within a city is also an important issue that should be tackled.

Since, many health related problems are linked to the state of the urban environment (Thornton and Culbard, 1987; Demetriades, 2011a; Filippelli *et al.*, 2012), each citizen wants to know the geochemistry of the land his/her house is built on. Similarly, it is just as important to know the chemical quality of soil in schoolyards, parks, playgrounds, kindergartens, recreation areas, allotments, gardens, and workplaces. Town planners and estate agents want to know the quality of the land they are planning and marketing, respectively, and insurance brokers the potential risks to their customers. Local politicians need data of high integrity for sound policy decisions. It is important, therefore, to involve in the planning of an urban geochemical mapping project the local authorities and national environmental agency.

Given that soil contamination is a key issue in planning a healthy home, school, work, and recreational environment, there is an urgent need to know "*what chemical elements are in our urban environment, and how this differs from the pre-industrialisation landscape. Once we have defined the urban chemical baseline, then we can monitor it for future changes, understand the sources of contamination and, with epidemiological and human health data, we will have a better understanding of the chemical elements and their compounds that damage our health* (Johnson and Demetriades, 2011, p.7). This statement provides the overall objectives of urban geochemical mapping, and further the need of close collaboration between city environmental authorities, local politicians and scientists from different disciplines. In fact, multidisciplinarity and interdisciplinarity take on a completely new dimension in the tackling of urban environmental problems, caused by contaminating activities, *i.e.*, applied geochemists work alongside public health officers, urban planners, medical doctors, *etc.* Hence, for the production of an urban geochemical database of high quality and integrity for multipurpose use a multidisciplinary team is required.

Production of a high quality database of the geochemistry of urban soil to meet the requirements of national legislation is time consuming and costly, given that information down to the scale of property level is required. Before reaching this level of detail, one should start from mapping the overall or general urban soil geochemistry, especially if a comparison will be made among towns and cities of the European or other continents, or even within a national urban geochemical mapping programme. Such a comparison can only be achieved by a systematic urban geochemical survey of the participating towns or cities using the same sampling, sample preparation and analytical methodology, with samples analysed in the same laboratory, following strict internal and external quality control procedures. These are very important conditions in the development of a quality controlled geochemical database that will represent the urban baseline and timeline against which future human induced changes can be assessed. Furthermore, the results of the overall urban soil geochemical mapping will provide the necessary background information for planning more detailed projects in parts of the towns or cities where there is contamination, in order to delineate precisely the contaminated areas and to reduce, therefore, the remediation costs, if this is deemed necessary.

Systematic work to produce a high quality and legally defensible urban soil geochemical database for multipurpose end-use can only be managed by national or regional Geological Survey organisations, because they have the scientific expertise for such studies, and the infrastructure to maintain the required Geographical Information System (GIS) databases to be accessed by each citizen, researcher, town planner and State authority official. Furthermore, they have the storage facilities to archive safely the collected samples, because these are very important for future research. All sample types will represent the year of their collection, and they will be an invaluable source of information in case of a serious accident that has a health-related impact on the urban environment.

As there is no standard or recommended methodology for mapping the chemical state of the urban environment in the way that there is for continental scale geochemical mapping (Darnley *et al.*, 1995; Salminen, Tarvainen *et al.*, 1998; Lech *et al.*, 2007; EGS, 2008; Smith *et al.*, 2013), this manual attempts to fill the gap. It also compliments the manual that was written for the second URban GEochemistry topsoil mapping project in Europe (URGE II), to be carried out by the EuroGeoSurveys Geochemistry Expert Group in different European towns and cities (Demetriades and Birke, 2015).

The emphasis of this manual is on urban topsoil, which if contaminated is unfit for sensitive land uses, such as playgrounds, parks and vegetable gardens, as observed in many urban areas. Contaminated urban topsoil may lead to contaminated indoor dust and, consequently, to an increased human exposure to toxic chemicals (Thornton and Culbard, 1987; Roberts *et al.*, 1992, 2009; Roberts and Dickey, 1995; Demetriades, 2010, 2011a; Demetriades *et al.*, 2010a, b). In addition, other sampling media, such as subsoil, road dust or sediment, attic dust, air particulates, and bio-indicators, including human tissues, can be collected from urban areas, and the procedures for their collection are described in this manual.

Decision makers, responsible for policy and legislation, are interested, however, in more tangible proof that contamination in urban centres is affecting the health of the population (Kienzl *et al.*, 2003). They are not satisfied with just statements from environmental geochemical studies that urban soil, house dust, attic dust, and road dust are contaminated, and determinand concentrations are above legislative guideline values, and that the human population may be at risk. Bio-indicators, such as organisms (plants and animals), and human tissues, offer an indirect or direct procedure, respectively, to assess the impact of anthropogenic activities on the exposed population. If human tissues (blood, urine, hair, teeth, nails, breast milk) are sampled, then the answer to the crucial question about the risk on the human population can be answered directly. Therefore, for the sake of completeness of this manual, sampling of plants and human tissues are included, and procedures requiring the input of other specialists from a multidisciplinary team.

Finally, it should be pointed out at the outset that the purpose of this manual is to introduce well-tested methods that can be used directly, since it is considered necessary to standardise the approach of urban geochemical mapping, across not only Europe but also the whole World. The only orientation survey that is needed concerns the depth range of subsoil sampling, because the geomorphological conditions and urbanisation history of each town or city are different, and the thickness of soil and/or cultural layer is most likely different.

## 1.1. What constitutes an 'urban area'?

As there is a broad spectrum of definitions of what constitutes an '*urban area*' is essential to define it at the onset of this manual, because it is important to compare like with like when contrasting the geochemical data from different towns and cities across Europe or the World.

The Oxford dictionary definition of '*urban*' is that grammatically is an adjective, and used as an attribute of, *for example*, 'areas', 'population', *etc.*, and means that it is "*situated in or living in a city or town*" (Oxford, 1993).

The National Geographic's (2015) definition of an '*urban area*' is "*the region surrounding a city. Most inhabitants of urban areas have non-agricultural jobs. Urban areas are very developed, meaning there is a density of human structures, such as houses, commercial buildings, roads, bridges, and railways.*" An '*urban area*' can refer to "*towns, cities, and suburbs. An urban area includes the city itself, as well as the surrounding areas. Many urban areas are called metropolitan areas, or 'greater' as in Greater New York or Greater London*".

Hence, an '*urban area*' describes the built-up area that constitutes a town or city, and is not extended to rural settlements, such as villages and hamlets.

There are another two terms that should be defined in order to delineate the limits of urban geochemical surveys, *i.e.*, ‘*suburb*’ and ‘*peri-urban*’.

The Oxford dictionary defines ‘*suburb*’ as “*the district outside the central part of a town or city, e.g., an industrial suburb, a suburb of Naples...*” (Oxford, 1993). Hence, a ‘*suburb*’ is the built-up part around the metropolitan area, and it could be either residential or industrial.

‘*Peri-urban*’ is defined as “*the landscape interface between town and country, or also as the rural-urban transition zone where urban and rural uses mix and often clash. It can thus be viewed as a landscape type in its own right, one forged from an interaction of urban and rural land use*” (Wikipedia, 2015a). ‘*Outskirts*’ and ‘*rurban*’ are synonyms to ‘*peri-urban*’.

Urban geochemical surveys should definitely cover the ‘*central urban or metropolitan area*’ of a town or city, its ‘*suburbs*’, whether residential or industrial, and extend for at lest 500 metres in the ‘*peri-urban area*’, to cover sequentially areas with less human influence.

### 1.2. Composite versus spot sampling

Question: *Should composite or spot soil samples be taken?* This is, indeed, a dilemma. Some applied geochemists prefer to make a composite sample from about five sites (Fordyce *et al.*, 2005; Gosar *et al.*, 2006; Abimbola and Olatunji, 2011; Albanese *et al.*, 2011; Batista *et al.*, 2011; Birke *et al.*, 2011a, b; Bityukova and Birke, 2011; Demetriades, 2011a; Ďuriš, 2011; Flight and Scheib, 2011; Gregorauskienė *et al.*, 2011; Lax and Andersson, 2011; Li, 2011; Locutura and Bel-lan, 2011; Šajn *et al.*, 2011; Tarvainen and Jarva, 2011; Vidojević and Gulan, 2011; Argyraki and Kelepertzis, 2014), and others single site or spot samples (Andersson *et al.*, 2011; Demetriades, 2011b; Jensen *et al.*, 2011; Ottesen *et al.*, 2011; Smith *et al.*, 2011).

A composite soil sample is considered more representative of the site from which it is taken. Such a sampling scheme may be appropriate in natural conditions, but in an urban environment with a multitude of contaminating activities, and the inherent heterogeneity of soil, is not considered suitable, because the distribution of contaminants is usually haphazard. Hence, sub-samples of variable chemical composition are mixed, and contamination will either be enhanced or diluted, depending on the volume of contaminated and uncontaminated soil collected. The strong heterogeneous nature of urban soil, and especially in the inner older parts of cities, can be observed at archaeological sites (Photo 1) or excavations for construction purposes (Photo 2).

In the geochemical mapping of urban topsoil, "*The Solution to Pollution is NOT dilution*" is quite appropriate, because the *objective is to map the chemical composition of soil in the urban environment*. Consequently, with composite topsoil sampling, contaminant concentrations may be either overestimated or underestimated.

Therefore, in the geochemical mapping of urban topsoil, *single spot sampling* is considered more appropriate, because the sample characterises precisely the individual spot from which it is taken, since there is no averaging involved, as with composite sampling. Thus, to avoid such impasses, the collection of topsoil samples from a '*single spot*' is recommended in this manual.

### 1.3. Sampling depth

The second key issue is sampling depth. Johnson and Demetriades (2011) in their review of the case studies in the EuroGeoSurveys textbook "*Mapping the Chemical Environment of Urban Areas*" (published by Wiley-Blackwell), noted that the sampling depth of topsoil is quite variable, namely 0-2 cm, 0-5 cm, 0-10 cm, 0-15 cm, 0-20 cm and 0-25 cm. *For example*,

(i) 0-2 cm (Andersson *et al.*, 2011; Jensen *et al.*, 2011; Ottesen *et al.*, 2011);

(ii) 0-5 cm (Demetriades, 2011a; Šajn *et al.*, 2011);

(iii) 0-10 cm (Gregorauskienė *et al.*, 2011);

(a) (b)

(c) (d)

Photo 1. Archaeological sites portray very well the heterogeneity of urban soil, the so called *'cultural layer'*: (a) 4th century BC to 3rd century AD bath complex, and (b) shows close-up of a soil block left by the archaeologists, Acropolis Museum, Athens, Hellas; (c) 3rd to 4th century AD bath complex, and (d) close-up of 'overburden' (soil and rubble) profile, Athens, Hellas (Source: Demetriades, 2014, Photo 11, p.21).

(a) (b)

Photo 2. Excavations show the strong heterogeneous nature of urban 'soil', the so-called *'cultural layer'* – a mixture of soil and rubble, especially in the old parts of cities: (a) Athens, Hellas, and (b) Oslo, Norway (Source: Demetriades, 2014, Photo 11, p.21).

(iv) 0-15 cm (Albanese *et al.*, 2011; Abimbola and Olatunji, 2011; Li, 2011; Smith *et al.*, 2011);

(v) 0-20 cm (Birke *et al.*, 2011a, b; Batista *et al.*, 2011; Bityukova and Birke, 2011; Ďuriš, 2011; Locutura and Bel-lan, 2011);

(vi) 5-20 cm (Flight and Scheib, 2011; Lax and Andersson, 2011), and

(vii) 0-25 cm (Tarvainen and Jarva, 2011).

Other urban geochemical surveys in Europe used 0-10 cm (Argyraki and Kelepertzis, 2014; Bavec *et al.*, 2015), 0-15 cm (Gosar *et al.*, 2006), 0-20 cm (Pasiecza, 2003), and 5-20 cm (Fordyce *et al.*, 2005).

In some surveys (Batista *et al.*, 2011; Flight and Scheib, 2011; Lax and Andersson, 2011; Bavec *et al.*, 2015), deeper soil samples were collected at the same site for assessing probable contamination of topsoil by comparing top- and sub-soil sample element concentrations, with depths varying from 40-60 cm, 35-50 cm, >80 cm, and 10-20 cm, respectively. According to Johnson and Ander (2008) subsoil samples are generally collected from depths >35 cm for the purpose of establishing a relationship with parent material or using results in the context of a regional baseline geochemical survey.

The choice of topsoil sampling depth is directly related to child health criteria, and the risk of exposure to contaminants in soil, which suggests that the top layer of urban soil is the optimum sampling medium. As the definition of topsoil varies from 0-2 to 0-25 cm, the main criterion used is the maximum depth that any potential contamination is not diluted by geogenic material, and this is the depth range of 0-10 cm. Topsoil collected from greater depth ranges than this thickness will most likely end-up in diluting any potential contamination.

It is important to remember that the objective of an urban geochemical survey, using topsoil as the sampling medium, is to delineate areas with potential contaminated topsoil that directly affects the quality of the living, working and recreational environments, and last but not least human health. Therefore, the depth range of 0-10 cm is the maximum soil thickness to be sampled for mapping the geochemical baseline of an urban area. This will also serve as the timeline against which future human induced changes can be assessed.

Depending, however, on the objectives of the urban geochemical survey, other topsoil depth ranges may be more appropriate. *For example*, if there is an industrial accident and airborne contaminants are dispersed in the environment, and the objective is to assess the environmental impact of this particular event, then it will be more appropriate to collect topsoil samples from the very surface, *i.e.*, down to a depth of 1 cm or 2 cm (maximum). However, because of the difficulties in consistently sampling a small column of soil with a high degree of precision, any procedure for sampling depths of <5 cm is likely to introduce large uncertainties in the results (Johnson and Ander, 2008), which is referred to as the "*depth effect*" by Ramsey and Ellison (2007).

## 1.4. Systematic versus Random sampling

The third key issue is systematic versus random sampling. Systematic sampling refers to the collection of samples in a defined pattern, such as at intersection points (nodes) on a square grid (Fig. 1). Because such a grid can be used to cover evenly a particular area, systematic sampling is the most effective method of collecting samples for the detection, evaluation, and interpretation of spatial patterns of geochemical variation (Open University, 1972; Demetriades, 2014).

Random sampling refers to the independent collection of samples from random geographical locations. Such collection of samples does not usually provide an even coverage of a specific area and it is, therefore, not suitable for urban geochemical mapping where the town or city should be covered in a systematic manner for the development of a database of high integrity, and production of geochemical baseline maps for utilisation by a multitude of end users. *Consequently, systematic soil sampling on a square grid should be used in urban geochemical* *mapping*. The advantage of a square grid is that it can easily be converted to a denser grid in parts of the town or city where it is deemed necessary (Fig. 1).

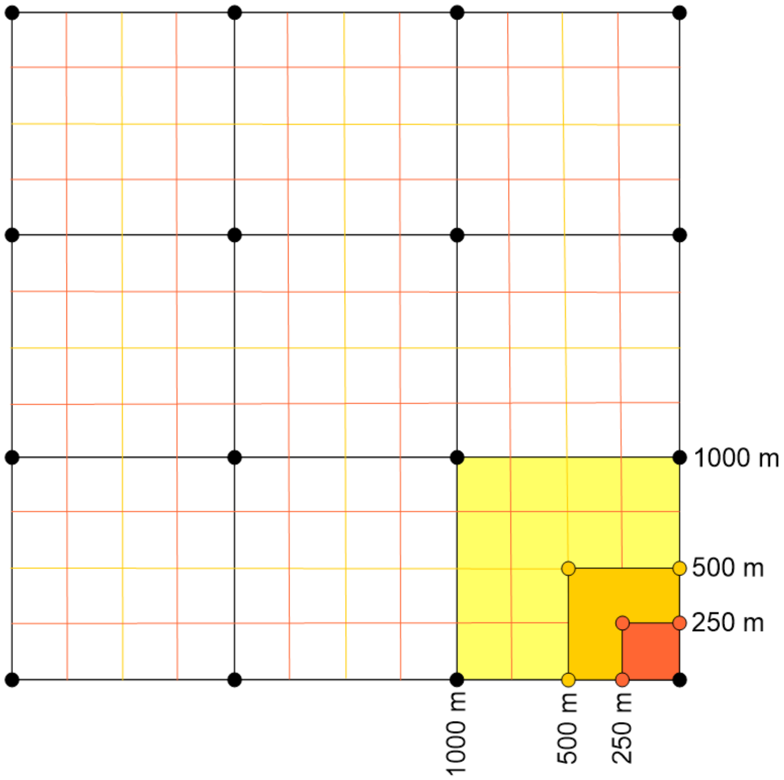


Figure 1. Sampling grid of 1000 x 1000 m. It can easily be converted to a denser grid of 500 x 500 m, 250 x 250 m, *etc.* The different coloured grid lines show the development of denser sampling grids.

### 1.5. Sample density and number of samples

The fourth key issue is sample density, which is directly related to available funds. Funding is a political issue that should be discussed by the officials of each Municipality. The question they must somehow answer is: *What sort of urban environment would they like to live themselves, and more importantly their children?* Considerable funds are invested on the construction and maintenance of a town's infrastructures. Therefore, they should have the wisdom to invest on the development of an urban soil geochemical database of high quality and integrity, as this will provide the necessary information of where there are patches of contaminated soil that require remediation. Furthermore, this database will serve as the baseline and timeline against which any future changes will be compared.

The nominal sample density of the EuroGeoSurveys urban topsoil geochemical project for covering systematically a town or city is 4 samples/km$^2$ (Demetriades and Birke, 2015); it recommends the use of a variable size grid of 500 x 500 m for the central older parts of towns or cities, and 1000 x 1000 m for the newer parts (suburbs; Fig. 1). This density is considered appropriate to obtain a satisfactory overview of the spatial distribution of chemical elements in urban topsoil. It will not provide, however, information at the individual property level (land parcel). Of course, each town or city is free to decide on a denser grid, depending on the objectives of the urban geochemical survey and available funds.

It is important to understand the limitations even of systematic geochemical mapping with respect to the delineation of areas with contaminated topsoil, as this depends directly on sample density. Figure 2 shows the variation in the character of a geochemical response with changes in the sampling point interval. Critical examination of these sketch distribution maps shows how under-sampling can lead to the non-detection of contamination (Fig. 2c).

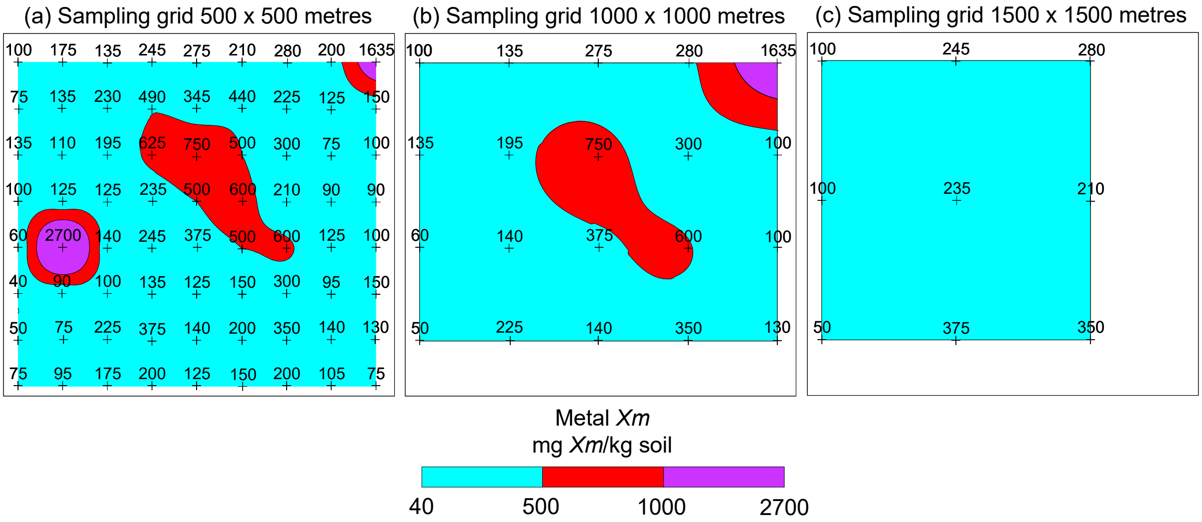


Figure 2. Sketch determinand distribution maps showing the change in size of the contaminated areas with different square grid dimensions (numbers over the crosses represent Metal *Xm* concentration values in mg/kg). The statutory limit for the concentration of the metal *Xm* in urban soil is set at 500 mg/kg. The optimum grid in this case is (a) 500 x 500 m, while (b) 1000 x 1000 m gives a very generalised picture and misses an important 'hot spot' with a concentration of 2700 mg/kg of metal *Xm*, and (c) 1500 x 1500 m finds no contamination, and the city's topsoil is declared as being uncontaminated (Source: Demetriades, 2014, Fig. 5, p.7, slightly modified).

## 1.6. Abbreviations, Acronyms, Glossary and Chemistry of contaminating activities

The Abbreviations and Acronyms, and a Glossary of Terms used in this manual are given in Appendices 1 and 2, respectively. The glossary is by no means exhaustive; it defines only selected terms that were considered necessary. The user of this manual can, of course, consult the World Wide Web for any term that is not defined.

A very useful guide is Appendix 3 where the chemistry of many anthropogenic activities is given with respect to organic and inorganic contaminants.

# 2. FIELD SAMPLING METHODOLOGY

## 2.1. Sampling equipment

The following equipment and materials are required for urban geochemical sampling:

### *2.1.1. Equipment for topsoil sampling*

- Stainless steel digging tool (hand hoe or grub hoe) – Photo 5b;
- Chisel-end geological hammer (Photo 5b);
- Plastic or stainless steel scoop (Photos 5b & h) or trowel (Note: Do not use coloured plastic scoops, because yellow, orange or red colours use pigments containing cadmium sulphides and sulphoselenides, as well as compounds with other metals, *e.g.*, Sn, Ti, Zn; use only white coloured plastic scoops);
- Strong stainless-steel kitchen knife;
- Unpainted steel or stainless steel spade (Note: Do not use painted steel, because the coating may contain a variety of contaminants, *e.g.*, Al, Cu, Zn, polyesters, plastisols, polyurethanes, polyvinylidene fluorides, epoxies);
- Wooden folded 2-m long metre or measure (alternate coloured-sections – Photo 5b);
- Plasticised scale-bar for photographs (0-10 cm marked) – Photos 5c and 6b;
- Geological compass or any type of compass for orientation when taking the general landscape photographs at each site towards North, East, South, and East.

### *2.1.2. Equipment for subsoil sampling*

- Unpainted cutter mattock or pick axe or trenching tool;
- Soil auger;
- Unpainted steel or stainless steel spade;
- Chisel-end geological hammer;
- Plastic or stainless steel scoop or trowel;
- Strong stainless-steel kitchen knife;
- Wooden folded 2-m long metre or measure (alternate coloured-sections) to be used for recording depth, and as a scale for photographs;
- Geological compass or any type of compass for orientation when taking the general landscape photographs at each site towards North, East, South, and East.
- Disposable plastic sheet for placing retrieved soil auger sections (plastic sheet to be used only once).

### *2.1.3. Equipment for house dust sampling*

- High-volume cyclonic vacuum cleaner.

### *2.1.4. Equipment for attic dust sampling*

- High-volume cyclonic vacuum cleaner, or paintbrush and dustpan;
- Dust mask with disposable filters;
- Disposable powder-free vinyl gloves.

### *2.1.5. Equipment for road dust sampling*

- Nylon brush and dustpan, or rechargeable vacuum cleaner.

### *2.1.6. Equipment for air particulates sampling*

- Sequential gravimetric sampler;
- Real-time particulate matter monitor, and
- Filters of 47 or 50 mm (*e.g.*, depth or fibrous filters, membrane filters, or coated fibre filters).

### *2.1.7. Equipment for bio-indicator plant sampling*

- Disposable powder-free vinyl gloves;
- Ceramic knife or pair of scissors;
- Perforated polyethylene (PE) or paper or linen trace-element free sample bags;
- Aluminium foil for samples that will be analysed for organic compounds;
- High speed cutter with a special titanium nitrite coating for tree bark sampling;
- Self-sealable polyethylene sample bags for tree bark sampling, and
- Car refrigerator or cool box.

### *2.1.8. Equipment for human tissue sampling*

- Blood sampling: Disposable powder-free nitrile gloves, sterilised syringes, needles, and test tubes; anticoagulants ethylenediaminetetraacetic acid (EDTA), and heparin.
- Urine sampling: Disposable powder-free nitrile gloves, water for injection, sterilised gauze sponges, 120 ml trace element free polyethylene cup, or 3 litre trace element free polyethylene container.
- Hair sampling: Disposable powder-free nitrile gloves, stainless-steel scissors, ethanol, and self-sealable PE bags.
- Deciduous teeth sampling: Self-sealable PE bags.
- Nail sampling: Stainless steel scissors or nail clippers, ethanol, and self-sealable PE bags.
- Mother's breast milk sampling: Disposable powder-free nitrile gloves, water for injection, sterilised gauze sponges, sterilised 100 ml glass jar, and potassium dichromate pellets.

### *2.1.9. Equipment common for all sample media*

- Rilsan® bags for bagging samples, or any other type of certified trace-element free plastic bags;
- Self-locking plastic tie strap (plastic cable tie) for the secure sealing of the Rilsan® bags;
- Small cards for writing sample number;
- Small self-sealing (zip-lock) plastic bags for the protection of the small cards;
- Outside plastic bag for protection of Rilsan® bags during packing and transportation;
- Topographical maps or cadastral plans or orthophotographs (scale 1:5000 or other suitable scale);
- Global Positioning System (GPS);
- Permanent drawing ink marker (preferably black or blue);
- Bristle brush for cleaning sampling equipment;
- Wire brush for cleaning unpainted steel or stainless steel spade; chisel-end geological hammer, stainless steel scoop or trowel, *etc.*
- White cotton wad for cleaning sampling equipment;
- Strong carton boxes for transporting and storing samples;
- Field Observations Sheets for recording of observations at each sample site (see Appendix 5);
- Digital camera (>7 Megapixels) capable of taking close-up photographs;
- Spare batteries for GPS and digital camera (if the camera has rechargeable lithium batteries, always carry with you an extra fully charged lithium battery);
- Extra memory card for digital camera, and
- Laptop/tablet computer or smart phone for the digital entry of observations in the evening.

Sample bags: The Rilsan® bags can be obtained directly from TUB-EX ApS Industrivej 10, DK-9830 Taars, Denmark, Tel.: +45 9896 1122 / 4701; E-mail: info@tub-ex.com. The website where the bags are displayed is: http://www.tub-ex.com/page38.aspx?recordid38=4&q=Rilsan. It is noted that Rilsan® bags are suitable for storing samples on which semi-volatile organic compounds (PAHs and PCBs) are planned to be determined (Vane *et al.*, 2014).

In case volatile organic compounds (VOCs) are going to be determined, then amber (dark brown) bottles with gas-tight caps should be purchased (Harrison and Reeder, 2011).

**IMPORTANT**

*During sampling, all hand jewellery must be removed.*

*Smoking is strictly prohibited.*

*All sampling tools and containers must be free of contaminants.*

*All sampling tools must be thoroughly cleaned at each sample site before moving to the next one.*

## 2.2. Topsoil sample collection

Topsoil is the most widely used sample medium, particularly for systematic sampling of the whole urban and suburban area. The nominal sample density of the pending second urban geochemistry mapping project of the EuroGeoSurveys Geochemistry Expert Group is 4 samples per square kilometre (Demetriades and Birke, 2015). A spot topsoil sample should be collected at each node of a 500 x 500 metres (inner city) to 1000 x 1000 metres (suburbs) sampling grid. Of course, a denser grid may be planned according to the objectives of the urban geochemical mapping survey. The nodes of the quadrangles of the 1:25000 or 1:10000 or 1:5000 topographical maps or corresponding scale orthophotographs, are used to plan and record the sampling.

It is advisable to pre-number all Rilsan® bags in the evening, and the small cards that are placed in the small plastic zip-lock bag (Photo 7a). Hence, for safety the topsoil samples are numbered twice: one on the outside of the Rilsan® bag, and second on the small card, which is protected by the small plastic zip-lock bag and placed on top of the sample inside the Rilsan® bag. Since the small card will be used as the sample reference during sample preparation, the sample number should be written on both sides.

In the case of a national urban geochemical survey project, each participating town or city should be given a three-letter code, and the routine topsoil sample number to consist of the town or city code (*e.g.*, Athens: code ATH), and the sample number (four or five digits, depending on the total number of samples to be collected from each town or city). If subsoil samples are going to be taken at each site, they should have the same number as that of the topsoil samples, and to add at their end the capital letter "B" (bottom), *e.g.*, the twentieth routine topsoil sample collected in Athens will bear the number ATH0020 (just number without a suffix letter code), and the subsoil sample from the same site the number ATH0020B. In case different sample types from the same location or parcel are going to be collected, use the following coding, *e.g.*,

- topsoil (just number without suffix code) - ATH0020;
- subsoil (suffix code: B) - ATH0020B,
- house dust (suffix code: H) - ATH0020H,
- attic dust (suffix code: A) - ATH0020A, and
- road dust or road sediment (suffix code: R) - ATH0020R.

The sampling design for the collection of air particulates and bio-indicator samples, including human tissues, is completely different, and their coding should be different.

Field duplicate samples should be collected at every 20th sample site for a particular sample type, and bear the same sample number as that of the routine sample, but at the end they should be identified by the capital letter "D". In the case of collecting different duplicate sample types (*e.g.,* topsoil, subsoil, house dust, attic dust, road dust, *etc.*) from the same location or parcel, use the aforementioned suffix code for each sample type and add at the end the letter "D", *e.g.*,

- topsoil - ATH0020D,
- subsoil - ATH0020BD,

- house dust - ATH0020HD,
- attic dust - ATH0020AD, and
- road dust or road sediment - ATH0020RD.

Hence, each sample has a unique sample number consisting of:

"City code + sample site number + sample type (+ Duplicate code)".

Of course, each sample type is characterised by the site coordinates and the number or name of the topographical map sheet, as well as the field observations recorded at each site.

It is noted that the rate of collection of field duplicate samples depends on the planned total number of routine samples. In large projects, exceeding a total number of 400 routine samples, the collection of duplicate field samples at every 20th sample site is satisfactory, but in projects, with a total number of routine samples of <400, duplicate field samples should be collected at every 10th sample site for a particular sample type (*e.g.*, topsoil, subsoil, house dust, attic dust, road dust, *etc.*). The limiting condition for small projects is Ramsey's (1998) specifications of eight (8) duplicated sample sites in a balanced ANOVA design (see Sections §7 & §10.2.8).

To ensure that topsoil (and other samples types: subsoil, house dust, attic dust, road dust or road sediment, and air particulates, *etc.*) are representative, it is necessary for all samples to be taken using a standardised sampling method, as described below.

Select a suitable patch of undisturbed (or least-disturbed) urban topsoil near the grid node, which is typical and representative of the land use type; the patch to be as flat as possible and in an open space (not under trees or bushes). Typical types of land use include domestic gardens, allotments, parks, recreational grounds, cemeteries, roadside verges, agricultural land, and industrial sites.

For geochemical mapping of urban soil, the collection of *spot topsoil samples* (0-10 cm) is recommended, and should be taken from a patch of undisturbed (or least-disturbed) surface soil independent of soil horizon (*i.e.*, even if different horizons are mixed), as the objective of an urban topsoil geochemical survey is the geochemical mapping of the current state of urban topsoil, and the understanding of the distribution and fate of contaminants that may pose a risk to the environment and human health. It is noted that in conventional soil geochemical surveys, soil samples are always collected from the same horizon, because each horizon has its own physico-chemical properties.

<u>IMPORTANT NOTE</u>: If topsoil and subsoil samples are going to be collected at all sample sites, then the two samples should be collected from the same depth ranges. At most sites in the central parts of towns or cities, the *'cultural layer'* is heterogeneous to some depth (Photos 1 & 2), depending on the historical activities and, therefore, it is unlikely to find natural soil with developed soil horizons. However, in the very unlikely case of finding a site with naturally developed soil, then the topsoil should be collected from the same horizon, and the same applies to the collection of the subsoil sample.

Locate in an open space a spot of bare topsoil, *i.e.*, not covered by grass, as this is soil that is directly amenable to children, and to deflation (Photo 3). If a spot of bare topsoil cannot be found, then the next best option is one with either sparse grass or short grass (Photo 4).

Other conditions for the selection of the topsoil sampling spot are to avoid:

- Forest soil, where there is development of humus layers, as these horizons with their high percentage of organic material can compromise the comparability of the samples.

(a) (b)

Photo 3. Select a bare spot in grass-covered areas for soil sampling. If possible, avoid spots under trees in order to minimise the effects of throughfall and stemflow precipitation.

(a) (b)

Photo 4. Select a spot with a sparse grass cover for soil sampling. Again if possible, avoid spots under trees in order to minimise the effects of throughfall and stemflow precipitation.

- Sites with layers of clearly anthropogenic origin; this condition concerns slag, asphalt, gravel, and similar layers of anthropogenic derived material, and
- Sites of recently dug up soil with fresh manure or fertiliser.

Avoid, if possible, sampling during the winter months, and bad weather conditions with pouring rain.

Remember a *single spot topsoil* sample (0-10 cm) should be taken at each sampling site.

If organic compounds, such as polychlorinated biphenyls (PCBs; industrial chemicals, no longer produced but persistent in the environment), and polycyclic aromatic hydrocarbons (PAHs; products of fuel combustion) (Andersson *et al.*, 2011; Harrison and Reeder, 2011; Jensen *et al.*, 2011; Ottesen *et al.*, 2011; Birke *et al.*, 2009, 2011a, b), are going to be determined it may be necessary to collect a second topsoil sample, a subsoil sample, *etc.* (refer to note below - Section §2.2.1).

### *2.2.1. Sampling a bare topsoil spot*

a) Select and mark a 50 x 50 cm a bare topsoil spot using the folded wooden 2-m measure (see Photos 5a & b).
b) Remove by hand any fresh litter and stones from the surface.
c) Mark within the 50 x 50 cm spot, and in its centre, a 25 x 25 cm sub-spot (Photo 5b), and dig a pit down to 10 cm depth with a stainless steel digging tool or other unpainted steel digging tool (Photo 5c).
d) Remove the topsoil down to a depth of 10 cm from the 25 x 25 cm sub-spot, and expose the vertical sides of the shallow pit (see Photo 5c).
e) At this point is time to take all digital Photographs, and always in the following order (Photo 6):
    (i) the sample site number (this helps to locate the set of digital photographs of each sample site – Photo 6a);
    (ii) the dug up topsoil with the plasticised scale-bar placed at a vertical position on the side wall of the pit (Photo 6b), and
    (iii) a general landscape photograph portraying the dominant feature (Photos 6c-f).

   As the photographic documentation is important, it is recommended that four (4) general landscape photographs should be taken (North, East, South, and West - always in this order) - use the compass to orientate yourself (see Photos 6c-f). Record the number of each photograph on the Field Observations Sheet (Appendix 5).
f) Note that the upper level of the bare topsoil section is the zero point (0.00 cm), and the pit is dug down to a depth of 10 cm. In grass-covered patches, first cut or scalp the grass down to its roots with a strong stainless steel kitchen knife or spade, and the zero point starts at the beginning of the grass roots; the pit is then dug down to a depth of 10 cm. When digging and removing the grass roots shake off the loose topsoil from the grass roots. In both cases, the vertical sides of the pit should be studied carefully, and all field observations noted on the Field Observations Sheet (see Appendix 5).
g) Dig down to a depth of 10 cm with a stainless steel digging tool, or other unpainted steel digging tool, the remaining part of the 50 x 50 cm spot (Photos 5d-g).
h) Remove pieces of roots (*ca.* >1 cm) – Photo 7.
i) Remove coarse clastic material (*ca.* >1 cm) – Photo 7.
j) Remove material (*ca.* >1 cm) that is recognisable as of anthropogenic origin, *e.g.*, pieces of bricks, glass, scrap metal.
k) Mix thoroughly the dug up topsoil of the 50 x 50 cm spot with the plastic or stainless steel scoop, break up any lumps, and shape it into a heap (Photo 5h).

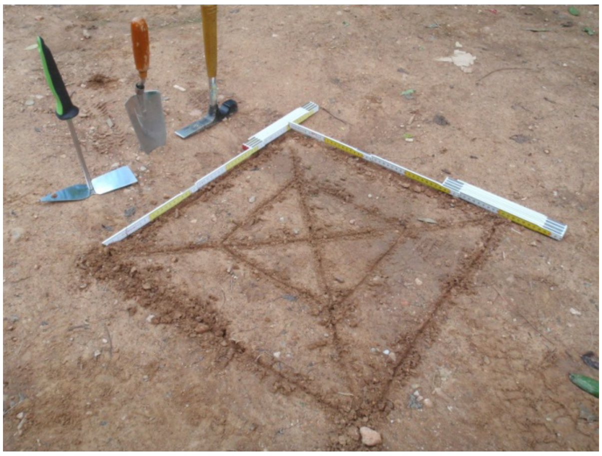
l) Start taking scoops of topsoil from different points of the heap within the 50 x 50 cm spot (Photo 5h), and place the topsoil aliquots into a pre-numbered Rilsan® bag (250×500×0.04 mm, clear with a white field for writing); collect a sample weight of 1 to 1.5 kg.
m) Place the small pre-numbered card, which is protected by the small zip-lock bag, on top of the topsoil sample.
n) Remove air from the Rilsan® bag, and close it firmly with a self-locking plastic tie strap (plastic cable tie) - Photo 7b. This firm closing of the sample bag safeguards its accidental opening at any stage before reaching the sample preparation laboratory.
o) For safety during packing and transportation, the Rilsan® bag should be placed in a larger plastic bag (Photo 7c).
p) Place the sample bag in a strong carton box.
q) Record all observations on the Field Observations Sheet (see Appendix 5), including the GPS geographical coordinates in degrees, minutes and seconds using the WGS 84 system, and finally
r) Mark on the topographical map or cadastral plan or orthophotograph the sample site and number (this is an important step, in case the GPS fails to record correctly the sample site coordinates).
s) All sampling equipment must be thoroughly cleaned at each site before moving to the next sample site. Clean thoroughly all sampling equipment using the bristle brush and white cotton wad. If the sampling equipment cannot be cleaned properly with the bristle brush and white cotton wad, use water and then dry the equipment with the white cotton wad.
t) In the evening, transfer all field observations to the digital database.

**Note for samples intended for the determination of semi-volatile organic compounds (PAHs and PCBs)**: According to USEPA, 2014, Chapter 4, p.1) "*Once the sample has been collected it must be stored and preserved to maintain the chemical and physical properties that it possessed at the time of collection. The sample type, type of containers and their preparation, possible forms of contamination, and preservation methods are all items which must be thoroughly examined in order to maintain the integrity of the samples*". It should be stressed that the preservation and preparation methods described in different national regulations are cumbersome, and lack supporting experimental data that prove beyond any doubt their validity.

***We do not recommend, therefore, any of these methods. Below a number of procedures are presented, as well as some literature on the subject, and the decision is left to the user of this methods manual.***

- To preserve the integrity of the samples the minimum requirements are to bag the samples in either Rilsan® bags or in amber glass containers, and in the field to be stored in a car refrigerator or a cool box at a temperature of ≈4°C, and afterwards to be frozen at a temperature of -18°C.
- Vane *et al.* (2014) for the determination of PAHs and PCBs on topsoil from London (United Kingdom), packed samples in Rilsan® bags, stored them in the field at a temperature of ≈4°C for 1 to 3 hours and then frozen them to -18°C (ISO, 2005).
- Similar field sample preservation is described by Birke *et al.* (2009) and Harrison and Reeder (2011), except that is recommended to store the samples in amber glass or metal containers.
- ISO 14507 recommends chemical drying followed by cryogenic grinding of samples prior to PAH quantification (BSI, 2003; ISO, 2003).
- ISO 13877 recommends air-drying a sample at room temperature, mortar crushing and sieving to <2 mm prior to analysis by High Performance liquid chromatography (HPLC) (ISO, 1998).

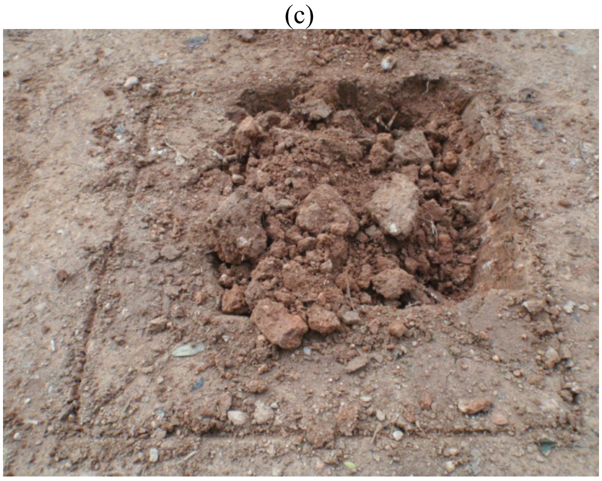
(a)



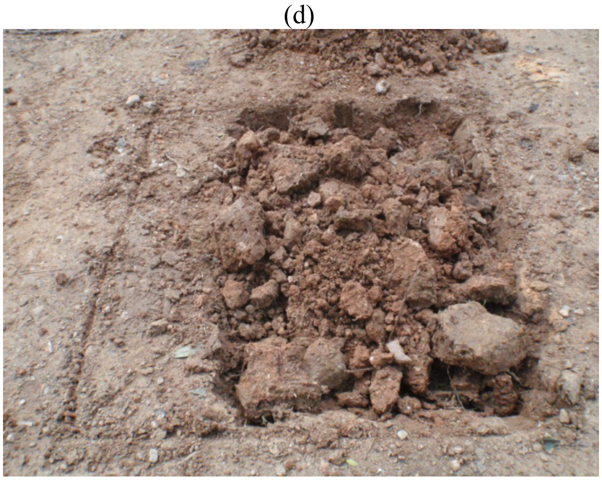
(b)

(c)

(d)



(e)



(f)

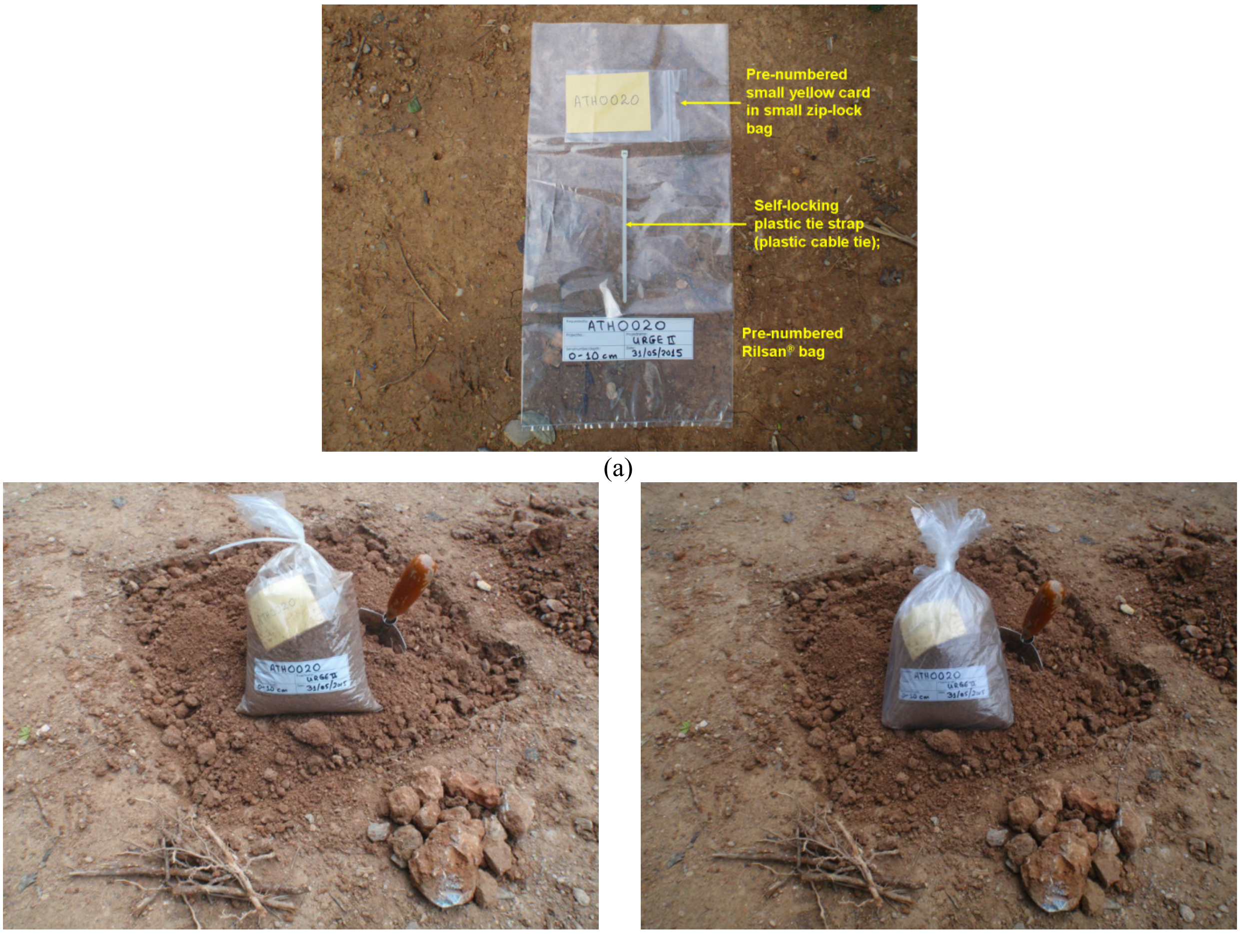
(g)

(h)

◄Photo 5 on page 26. (a) Select a bare topsoil sample site; (b) mark the pit dimensions: outside spot of 50 x 50 cm, and inside sub-spot of 25 x 25 cm; (c) excavate first the 25 x 25 cm sub-plot down to a depth of 10 cm, and take the photograph showing the characteristic features of topsoil; (d) excavate back the 1st side; (e) excavate back the 2nd side; (f) excavate back the 3rd side; (g) excavate back the 4th and final site; (h) break-up lumps of soil with the chisel-end of the geological hammer or stainless scoop and homogenise the dug up soil and prepare it for sampling.

(a) (b) (c) (d) (e) (f)

Photo 6. Photographic documentation of each topsoil sample site by taking a series of photographs in the following order: (a) Sample site number; (b) topsoil sampling site showing the characteristics of the sampled soil layer; (c) North facing photograph; (d) East facing photograph; (e) South facing photograph, and (f) West facing photograph.



(b) (c)

Photo 7. (a) Pre-numbered Rilsan® bag, pre-numbered small yellow card in small zip-lock bag, and self-locking plastic tie strap (plastic cable tie); (b) Topsoil sample in Rilsan® bag, and on the right hand side the stones and plant roots that were removed; (c) Topsoil sample with outside plastic bag for the protection of the Rilsan® bag during transportation..

(a) (b)

Photo 8. (a) Duplicate field sample site at a distance of 3 m to the east of the routine sample site, marked with a red ellipse; (b) Close-up of the bare topsoil spot for collection of duplicate field sample using the same procedure as that of the routine sample (see Photos 5 & 6).

- BS EN 16179:2012 suggests that pre-treatment of samples prior to organic analysis should be subjected to either freeze-drying or chemical drying only (BSI, 2012).
- The Environment Agency for England and Wales recognises that low molecular weight PAHs are '*borderline determinands*', *i.e.*, neither volatile nor non-volatile, placing the onus

on the analyst to select physical treatment methods that are fit-for-purpose, and do not lead to significant losses of analytes (EA, 2006).

- In Germany, the accredited laboratories are analysing PAHs and PCBs after DIN ISO 18287:2006-05 (DIN ISO, 2006; ISO, 2006) and DIN ISO 10382:2003-05 (DIN ISO, 2003; ISO, 2002). Both standards (norms) require the refrigerated storage and transport of samples in suitable containers (<10°C), and the appropriate sample pre-treatment (chemical or freeze-drying). The sample storage until the delivery to the laboratory should not exceed 7 days. A possible solution here could be the storage of samples in a frozen state. In any case, the determination must be carried out on dry matter content on the field fresh sample after ISO 11465 prior to analysis (ISO, 1993).
- In the United Kingdom, laboratories analysing organic compounds in soil for regulatory purposes must be accredited to the Monitoring Certification Scheme (MCERTS) (EA, 2012), and have their methods accredited to the British, European and international standard ISO/IEC 17025 (BSI, 2005).
- In the United States of America, laboratories are required to follow prescribed methods for their regulatory analyses, *e.g.*, methods 3540C and 3550C require a chemical drying step prior to extraction and analysis (USEPA, 2013).

A few studies have shown that the accuracy and precision of semi-volatile organic compounds, such as PAHs, can be affected by the physical sample preparation technique used prior to extraction and analysis (Berset *et al.*, 1999; Shu and Lai, 2001; Thompson and Nathanail, 2003; Belkessam *et al.*, 2005; Khan *et al.*, 2005; Narizzano *et al.*, 2013). However, as noted by Beriro *et al.* (2014), none of them have provided a comprehensive statistical evaluation of their effect. In their research work, they demonstrated that the selection of drying and comminution type has a statistically significant effect, which can influence the outcome of the risk evaluation stage of human health risk assessment (HHRA) for risk-based land management.

As is pointed by Beriro *et al.* (2014) there is at present:

- A wide variety of in-house or prescribed methods that have been devised by analysts, standards committees and state agencies that produce wide divergent results in the quantification of PAHs, and
- No universally agreed method, supported by published data for the physical treatment of soil or sediment samples prior to PAH quantification.

They conclude that a necessary preliminary step, guiding the development of a standardised physical treatment combination, is a robust statistical evaluation of the effect that drying and comminution techniques have on the reliability and repeatability of PAHs concentration data.

### *2.2.2. Sampling a topsoil spot with sparse grass or short grass*

a) Cut or scalp the sparse grass or short grass or grass using either a strong kitchen stainless steel knife or unpainted spade (or stainless steel spade);

Then follow the steps (b) to (t) of the sampling procedure described above (§2.2.1). It is noted that the loose topsoil should be shaken off the grass roots.

## 2.3. Sampling of field duplicates

The field duplicate topsoil sample should be taken at a distance of 2 to 3 metres from the routine sample site, and at every 20th site (Photo 8). For other urban geochemical surveys, where the area of the town or city is small, field duplicates may be collected at every 10th site. Duplicate field samples can be taken, of course, in a random order, with either 10% or 20% duplication. For the collection of the field duplicate topsoil sample, follow the steps described in section *'§2.2.1. Sampling a bare topsoil spot'* (above).

It is noted that the distance of 2 to 3 metres of the duplicate field sample site from the routine sample site is very conservative. According to Michael H. Ramsey (pers. commun., 2015, School of Life Sciences, University of Sussex, Falmer, Brighton, UK) there have been several suggestions in the literature on how to select the distance between routine and duplicate sample sites:-

1. To reflect the typical surveying error.
2. To reflect the ambiguity in the sampling protocol (*e.g.*, if the same sampler, or another person, repeat the surveying procedure, how far away might the actual sampling point be for the same nominal location).
3. To represent a proportion of the grid spacing (*e.g.*, 10%).
4. To select a distance that enables the quantification of the contribution of the '*within-location*' in-situ heterogeneity to the measurement uncertainty arising from sampling.

As pointed out by Michael H. Ramsey, the above suggestions are not mutually exclusive, as fulfilling #2 achieves #4, and #1 is part of #2.

Ideally one could experimentally determine #2 by asking several different samplers (*e.g.*, 8 people) to independently identify the physical location of several (*e.g.*, 8) independent nominal sampling locations (using the specified survey methodology). These locations should preferably have different urban land uses (*e.g.*, park, schoolyard, urban garden), to reflect how the survey methodology, and the user's interpretation, changes between different situations. Then one could measure the typical distance of separation between the replicated locations, and use this as the duplicate separation distance for all locations in the main survey.

Duplicate field samples should be taken for all sample types. As already discussed, field quality control or duplicate samples are usually collected at a rate of 20% in large geochemical surveys, and in small surveys at a rate of 10%. Ramsey (1998) has devised a cost-effective method requiring the collection of duplicate field samples from at least 8 locations in a balanced design to estimate the geochemical, sampling and analytical variance, and measurement uncertainty, using robust analysis of variance, RANOVA (Boon, 2007; Lyn *et al.*, 2007). The experimental design of duplicate field sampling, and duplicate-replicate chemical analysis, in a balanced ANOVA design was originally suggested by Miesch (1964, 1967, 1973, 1976), and subsequently by Garrett (1969, 1973). A detailed description of the method proposed by Ramsey (1998) is given by Demetriades (2011b), Demetriades and Vassiliades (2016) and in Section §10.2.8 of this manual.

## 2.4. Where does one collect urban soil samples in densely populated areas?

This is the question that all people are asking, and will be answered by using Athens, the capital of Hellas, which is one of the most densely populated cities in Europe, with very little green space. As can be observed in Figure 3a there are potential sample sites near to each 500 x 500 m grid node. Even at the most difficult sample sites (E479000 & N4203500; E479000 & N4204500 and E480000 & N4203500), there are within 100 m suitable open green spaces where a topsoil sample can be taken. Therefore, a suitable topsoil sampling spot can be found within 100 m from the grid node. Figure 3b shows the 1000 x 1000 m grid in a northern suburb of Athens, where it can be seen that suitable sites for sampling topsoil can easily be located.

Photos 9A to 9D are a number of photographs showing possible sites for the collection of topsoil samples. It is stressed again that sites under trees and bushes should be avoided, if possible, in order to minimise the effects of throughfall and stemflow precipitation.

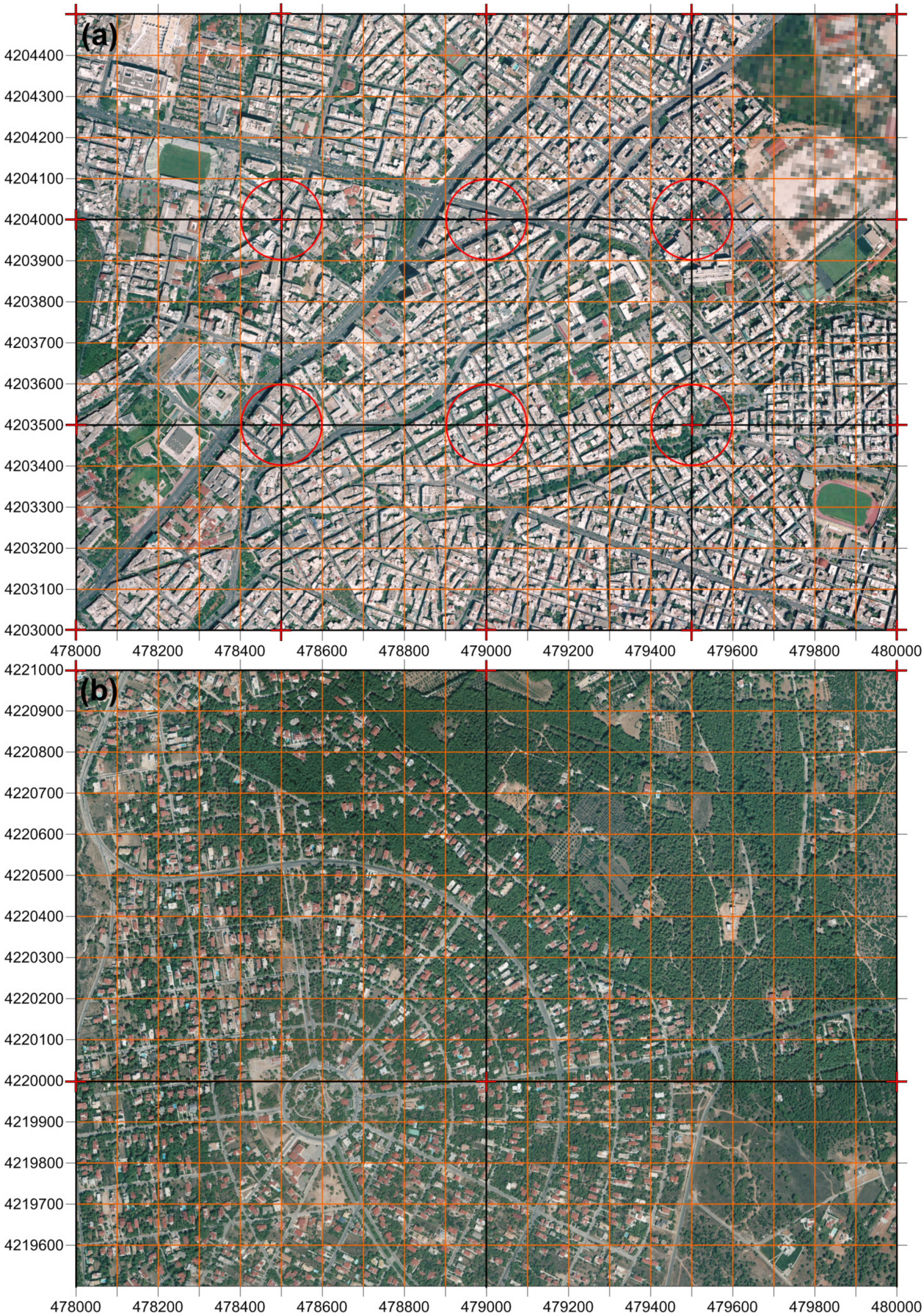


Figure 3. Orthophotographs of Athens, the capital of Hellas: (a) central part of Athens (Ampælókipi-Ghoudí-Ilíssia), and (b) a northern suburb (Thrakomakædónæs). Red crosses indicate the urban soil sample sites using a grid of 500 x 500 m (central part) and 1000 x 1000 m (suburb). The orange colour grid lines mark a grid of 100 x 100 m, and the red circle the maximum radius of the search area about grid nodes to locate a suitable open patch of land for sampling topsoil. Source of orthophotographs: Hellenic Cadastre and Mapping Agency (http://www.okxe.gr/el).

In many municipalities of Athens is impossible to assess the quality of soil at the individual property level, because the non-built parts are covered by concrete. Consequently, the densest sampling grid that can be applied in the central part of Athens is 100 x 100 m. Such restrictions to the planning of future denser urban geochemical surveys should be considered during the planning of the current 500 x 500 m (inner city) to 1000 x 1000 m (suburbs) grid survey, because these will give the maximum search radius about each grid node to locate a suitable site for soil sampling.

(a) Grass-covered area

(b) Tram green spaces

(c) Small grass-covered spot at a road junction.

(d) Small grass-covered spaces in a pedestrian road.

(e) Small green space about a monument (see 9f).

(f) A suitable spot for soil sampling at site shown in Photo 9e can be found, which is not under the tree.

Photo 9A. A number of photographs showing possible topsoil sample sites in a densely populated city, such as Athens, Hellas.

The series of photographs (Photos 9A-D) show possible sites for the collection of topsoil samples, and places that should be avoided. The most suitable sites for sampling are open spaces, and not below trees and bushes in order to minimise the effects of throughfall and stemflow precipitation.

(g) Small green space in a pedestrian street (see 9h).

(h) Possible bare soil spot for sampling (see 9g).

(i) Possible soil sampling at the open space at the back of the trees (avoid sampling below the trees).

(j) Possible soil sampling site outside playground.

(k) Possible soil sampling site in a small neighbourhood park. A spot not under the trees can be found at the front and centre of the small park.

(l) Possible soil sampling site in a small neighbourhood park. At the centre of the park, a spot not under the trees can be found.

Photo 9B. A number of photographs showing possible topsoil sample sites in a densely populated city, such as Athens, Hellas.

(m) Possible soil sampling in a roadside verge (see 9n).

(n) Possible soil sampling site in a roadside verge (see 9m).

(o) Possible soil sampling on the grass covered area away from the flowerbed.

(p) Possible soil sampling site on grass covered area on the left hand side of the flowerbed.

(q) Possible soil sampling site outside sports ground. A spot can be found that is not under trees.

(r) Possible sampling site in a nursery schoolyard. A spot can be found that is not under the trees.

Photo 9C. A number of photographs showing possible soil sampling sites in a densely populated city, such as Athens, Hellas.


(s) Possible sampling site in the grass covered plot on the right hand side. The plot on the left is not an ideal site, because it is under the trees.


(t) Bare topsoil sampling site in a Secondary schoolyard. It is not, however, an ideal spot, because it is under the eucalyptus tree.


(u) Avoid, if possible, sampling below trees and bushes (see 9v).


(v) Bare soil spot, but it is under trees (see 9u). Avoid, if possible, sampling below trees and bushes.


(w) Sampling site at the side of a main road. It is not, however, an ideal site because of the bushy vegetation.


(x) Avoid, if possible, sampling below trees and bushes.

Photo 9D. A number of photographs showing possible soil sampling sites in a densely populated city, such as Athens, Hellas.

## 2.5. Other urban sampling media

Other sampling media used in urban geochemical mapping are

(a) subsoil,
(b) house dust,
(c) attic dust,
(d) road dust or road sediment,
(e) air particulates, and
(f) bio-indicators, including human tissues (*e.g.*, blood, urine, teeth, hair, nails, breast-milk).

Ideally, subsoil should be collected at every topsoil sample site, as this will provide a good comparison of element concentrations between topsoil and subsoil, and an assessment of contamination provided, of course, the subsoil is collected deep enough to give the site geochemical background conditions.

House and attic dust, although they are very good sampling media for assessing contamination in the home environment, are more difficult to plan and execute, because it involves the active participation of the householders.

As many targeted urban geochemical studies are connected with vehicle pollution, roadside dust or sediment is a frequently reported sample medium (Farago *et al.*, 1995, 1998; Ely *et al.*, 2001; Gómeza *et al.*, 2002; Whiteley, 2005; Mathur *et al.*, 2010; Locutura and Bel-lan, 2011; Bavec *et al.*, 2015). Road dust or road sediment is a rather difficult sample medium for it involves the sweeping of pavements or road gutters, and is subject to climatic conditions, *e.g.*, the sampling should be carried out during a prolonged dry period, which means the summer period in almost all climatic zones.

Particle pollution in the air (particulate matter, PM) includes a complex mixture of solids and liquid droplets. This pollution, also known as air particulate matter or air particulates, is made up of a number of components, including acids, metals, organic chemicals, soil or dust particles, and allergens.

Primary PM originates from natural or anthropogenic sources. Natural sources include sea salt, naturally suspended dust, pollen, and volcanic ash (EEA, 2012), and in some Mediterranean countries dust from the Sahara (Muhs *et al.*, 2010a). There is evidence that the African dust reaches Atlantic Islands and Florida in the USA (Muhs *et al.*, 2007, 2010b) and West Indies (Muhs and Budahn, 2009). Anthropogenic sources include fuel combustion in thermal power generation, incineration, domestic heating for households, and fuel combustion from vehicles, as well vehicle wear (tyre and brake), road wear, and other types of anthropogenic dust (*e.g.*, road dust re-suspension, burning of biomass or fossil fuels for domestic heating; EEA, 2014).

Particles less than 10 micrometres (PM10) in diameter pose the greatest problem, because they can reach deep into the lungs, and may even end up into the bloodstream. Small particles of concern include 'fine particles', which are 2.5 micrometres in diameter or less (PM2.5), and 'coarse particles', which have diameters between 2.5 and 10 micrometres. The particles most likely to cause adverse health effects are the ‘fine’ particles PM10 and PM2.5 – particles smaller than 10 and 2.5 µm. They are sampled with either (i) a high volume sampler with a size-selective inlet using special (*e.g.*, quartz) filter, or (ii) a dichotomous sequential sampler that operates at a slower flow rate, separating on a Teflon or cellulose nitrate filter particles smaller than 2.5 µm, and sizes between 2.5 and 10 µm. Particulate matter measurement and sampling should be done only by special technical sampler equipment (Photo 10), according to the European requirements of CEN EN 14907 for the PM2.5 fraction (CEN, 2005) and CEN EN 12341 for the PM10 fraction (CEN, 1998).

(a) (b)

Photo 10. Equipment for sampling air particulates: (a) Leckel SEQ 47/50 Sequential Gravimetric Sampler (Source: http://www.et.co.uk/docs/SEQ47-50%20Product%20Datasheet.pdf; http://www.et.co.uk/products/air-quality-monitoring/particulate-monitoring/seq-4750-sequential-gravimetric-sampler/); (b) Thermo 5030 Synchronised Hybrid Ambient Real-time Particulate Matter Monitor (SHARP 5030) (Source: http://www.socaar.utoronto.ca/fac-inst/instruments.htm; http://www.thermoscientific.com/content/tfs/en/product/5030-sharp-monitor.html#sthash.UGWkTDas.dpuf).

For the characterisation of emissions and the atmospheric transport of contaminants in urban areas, bio-indicators can be used, such as tree barks (outer and inner barks; Hofmann *et al.*, 2001; Birke *et al.*, 2009), ryegrass (*Lolium multiflorum*, tobacco (*Nicotiana tabacum*), bush bean (*Phaseolus vulgaris*), weaves (*e.g.*, *Hypogymnia physodes*), pine needles (*Pinus sylvestris*) earthworms (Meyer *et al.*, 1993), and terrestrial moss (*Hylocomium splendens*) (Reimann *et al.*, 2011c). With these various bio-indicators, an active and passive environmental monitoring survey can be carried out. For assessing heavy metal emission, especially ryegrass, pine needles, earthworms and tree barks are best-suited (Arnt *et al.*, 1987).

As many contaminants can persist in the urban environment for a long time, the most appropriate way to assess exposure of the human population is to obtain biological measurements from blood, urine or other human tissues from cases and controls, because these give a direct assessment of internal dose of the contaminants (Etzel, 2008).

Three sampling media that are not discussed in this manual are roof rain gutter sediment, stream sediment, and overbank or floodplain sediment.

Sediment from roof rain gutters (Urbonas and Doerfer, 2003), although interesting is not widely used in urban geochemical studies. The roof rain gutter sediment, apart from grit particles originating from the composition of roof materials, it consists of leaves and very fine sediments derived from atmospheric fallout, and may even contain particles from meteorites. Hence, roof rain gutter sediment could be considered as similar to road sediment, and its sampling has the same drawbacks as attic dust, because traditional houses with roofs are needed.

Stream sediment is the principal sampling medium used by applied geochemists to conduct systematic regional geochemical surveys. Overbank or floodplain sediment has been introduced in geochemical surveys by Ottesen *et al.* (1989), and is used in regional- (Ottesen *et al.*, 2000, 2010) and continental-scale geochemical mapping (Salminen *et al.*, 2005; De Vos, Tarvainen *et* *al.*, 2006; Wang and CGB Project Team, 2015; Wang *et al.*, 2015). Stream and overbank sediments are, therefore, inappropriate sampling media for use in an urban setting, and thus are not discussed in this manual.

### *2.5.1. Subsoil sample collection*

The heterogeneity *'par excellence*' of urban soil, and especially in the old central part of most European cities, can be observed in sections. Archaeological sites (Photo 1) or excavations for construction purposes (Photo 2) show this feature quite well.

If there is an intention to collect subsoil samples, it is recommended to contact first an orientation survey in order to find solutions to problems that may be encountered during the systematic sampling. An effective way is to carry out a north-south and an east-west transect through the centre of a town or city, and to collect top- and sub-soil samples. These samples to be collected at the nodes of the planned sampling grid. Ideally, subsoil samples should be collected below a depth of 50 cm, and from the same soil horizon in case natural soil horizons can be distinguished. However, in the central parts of most towns or cities, natural soil may not be found even below this depth. It is expected, therefore, that the recommended orientation survey will provide the necessary information about the sampling depth for the collection of subsoil samples.

Subsoil samples can be collected by either digging a pit down to the required depth, or using a soil auger. In the Mediterranean countries of southern Europe, it may be difficult to use a soil auger for subsoil sampling, because of the dry nature of most urban soil. Hence, pitting should be the preferred method. However, digging a soil pit can be time consuming – samplers can collect subsoil samples much more rapidly using a soil auger, if conditions favour this. In any case, the subsoil sampling depth to be used in the systematic urban geochemical survey will be decided on the results of the recommended orientation survey.

Select the sample site from where the topsoil sample will be collected. Collect first the topsoil sample, according to the procedure already described, and then use either the soil auger or dig a pit for the collection of the subsoil sample from a depth range of 50 to 60 cm (Photo 11), or the depth resulting from the orientation survey.

If a soil auger is going to be used, the retrieved successive subsoil sample sections should be placed on a plastic sheet in the order retrieved. It may be necessary to retrieve more than one 'core' for making a sample of about 1.5 kg. The subsoil 'core(s)' should be photographed first prior to sampling; before photographing the 'subsoil core' the folded wooden 2-m measure should be opened and placed next to the 'core'; take at least two photographs, one showing the whole 'core', and a second a close-up of the part that will be sampled. After sampling, all observations should be recorded on the Field Observations Sheet. The instructions given in section *'§2.2.1. Sampling a bare topsoil spot'* from (f) to (t) should be followed.

If pitting is going to be used for the collection of the subsoil sample, again first collect the topsoil sample, and then dig up the pit down to the decided depth. Place at one of the vertical sides of the pit the folded wooden 2-m measure, and take a general photograph of the pit (Photo 11a), and a second a close-up of the section that will be sampled (Photo 11b); if a fill-in flash is used, take two photographs, one under natural conditions and the second with the flash. Again, after sampling, all observations to be recorded on the Field Observations Sheet. The instructions given in section *'§2.2.1. Sampling a bare topsoil spot'* from (f) to (t) should be followed.

In case subsoil samples cannot be taken at each topsoil sample site, it is recommended to collect subsoil samples from a few sites in such way to be representative of the different parts of the town or city. The other alternative is to collect subsoil samples only at sites with anomalous determinand concentrations for differentiating geogenic and anthropogenic sources. If this procedure is followed, the subsoil samples will be collected after the completion and interpretation of the topsoil geochemical results.

**IMPORTANT NOTE**: *After collecting the subsoil sample, and completing the Field Observations Sheet, the soil pit needs to be carefully filled in, and the patch restored to its previous condition without leaving a hole in the ground that could be a potential public hazard.*


(a) (b)

Photo 11. (a) Pit dug down to a depth of 50 cm at the same site as that of the topsoil (see Photos 5 & 6); (b) Digging bottom of pit down to 60 cm, breaking up lumps, and homogenising subsoil for sampling, Athens, Hellas.

### *2.5.2. House dust sample collection*

The following description was abstracted from Demetriades (2014, p.22-23).

"According to USEPA (2008) the predominant pathway for lead exposure of young children is ingestion of indoor surface dust, as a result of hand-to-mouth activity (USEPA, 1986, 2005; Laxen *et al.*, 1987; Lanphear *et al.*, 1998, 2002; Sterling *et al.*, 1998; Succop *et al.*, 1998; ATSDR, 1999; Manton, *et al.*, 2000). It has been shown that lead-contaminated house dust is the strongest predictor of blood-lead levels in children (Roberts and Dickey, 1995; Lanphear *et al.*, 1998, 2002; Succop *et al.*, 1998; Jacobs *et al.*, 2002). Therefore, house dust is the commonest sampling medium used to assess exposure of young children to environmental contaminants. However, there is no universally accepted standard technique for the collection of house dust samples.

Sampling techniques vary from asking the householder (a) to place in a given pre-numbered bag all dust swept with a broom from the floor of the whole house for a period of 15 to 20 days, or (b) to use a new bag, if a commercial vacuum cleaner is available, for collecting the dust for again a period of 15 to 20 days (Photo 12), and at the end of the sampling period to place the vacuum cleaner bag in a given pre-numbered bag (Demetriades, 2011a). The instructions given to the householder are simple, as *for example*, the broom, or vacuum cleaner to be used only for sweeping or vacuuming the indoor house dust. Hence, the quality of sampling of using non-standardised techniques is a serious disadvantage. The best approach is to use a commercial vacuum cleaner to sample house dust in all selected homes, and to cover similar size areas in the home environment, especially rooms used by children, such as bedroom and living room or playroom.

The American Society for Testing and Materials (ASTM) recommends the use of high-volume cyclonic vacuum cleaners for collecting house dust - Photo 13 (ASTM, 2005; USEPA, 2008). These vacuum cleaners are useful for a variety of surfaces, and have documented greater precision and collection efficiency than other sampling methods, and most importantly, the collected sample is substantially unmodified. The procedure covers the collection of dust from carpets and bare tile or wooden floors, and the house dust samples can be analysed for Pb, pesticides, or other chemical compounds and elements, except asbestos fibres.

(a) (b)

Photo 12. House dust sampling: (a) House-dust in vacuum cleaner bag; (b) Close-up of house dust showing its heterogeneous nature (Source: Demetriades, 2014, Photo 13, p.23).

(a)
A European high-volume cyclonic vacuum cleaner for collecting house dust (Source: https://upload.wikimedia.org/wikipedia/commons/5/5e/Dyson_DC07_Vacuum_Cleaner.jpg).

(b)
USGS scientist collecting house dust with a high-volume cyclonic vacuum cleaner (Source: http://www.usgs.gov/envirohealth/geohealth/full_activities_list.html; http://www.usgs.gov/envirohealth/geohealth/images/HouseDustCollectionWithVacum_1.jpg).

Photo 13. High-volume cyclonic vacuum cleaners for collecting house dust.

Houses to be sampled should be selected near to the planned grid node. If garden soil is planned to be collected in the same sampling campaign, it is strongly recommended to sample house dust from these houses as well. Usually, a variable sample density is used by taking more samples from the older inner part of the city, where anthropogenic impact is greater, than from the newer outer part. USEPA (2008) recommends the selection of houses by using a stratified random sampling plan to increase the likelihood of obtaining a representative statistical sample of houses, which should contain ranges of contaminant values that are deemed important, and are consistent with the range of values for the attributes found in the population. Since, this is a specialised sampling design, it is recommended to use the expertise of a statistician. Finally, all house dust samples should be collected within the same period.

All sampling equipment should be thoroughly cleaned after each sample to avoid any cross-contamination."

House dust samples should be collected at each node of a 500 x 500 m grid (central part of city) to 1000 x 1000 m sampling grid (suburbs), giving a nominal density of 4 samples/km$^2$, the same as the urban soil survey. In towns and cities, where most people live in storeys of flats, a decision must be made of collecting house dust from either ground floor or first floor flats.

It is important to record all observations on the Field Observations Sheet, and to take digital photographs of the house dust, and the areas from where the house dust is collected, and general photographs of the exterior conditions of each selected house. In fact, the instructions given in section '*§2.2.1. Sampling a bare topsoil spot*' from (m) to (t) should be followed.

### *2.5.3. Attic dust sample collection*

The following description was abstracted from Demetriades (2014, p.23-24).

"In towns with traditional houses with tiled roofs and attics (Photo 14a), attic dust is a good sample medium to assess urban airborne contamination in the home environment (Šajn, 2003, 2005, 2006; Gosar and Šajn, 2003; Gosar *et al.*, 2006; Hensley *et al.*, 2007; USEPA, 2008). Šajn (2005) defines *attic dust* as "*the dust that accumulates on wooden carpentry of attics*, *where the influence of inhabitants is minimised*" (Photo 13b). Attic dust is a heterogeneous mixture of dust particles, mainly derived from external household sources through aerosol deposition and as a result of soil dusting. Dust settling within the attics is thus often preserved from the time the house is built until its final demolition. Therefore, undisturbed attic dust can provide a historical record of ambient air pollution. It is thus recommended, when planning to use attic dust, to select houses of similar age in order to assess urban contamination over a specific period.

Selection of sampling locations within each attic is done on a site-by-site basis, as each attic has different physical constraints (USEPA, 2008). A composite sample should be made by collecting dust from multiple points within the attic, such as beams, insulation, roof, and rafters, and, especially, from places where the dust is undisturbed, as near eave vents (Photo 14b). In some cases, however, access will be restricted to areas near the attic entry, and this would represent dust that is most likely to be tracked into the living space."


(a) (b)

Photo 14. Attic dust sampling: (a) House with an attic; (b) attic dust (Source: Demetriades, 2014, Photo 14, p.24).

"USEPA (2008) recommends the use of a high-volume cyclone vacuum to sample attic dust. If this is not possible, then a paintbrush with a dustpan, or any other appropriate receptacle, such as a polypropylene scoop, may be used. It is stressed, as in all cases of geochemical sampling, the equipment must be thoroughly cleaned directly after the sample is bagged in order to avoid any cross-contamination. It is strongly recommended to sample attic dust from houses of similar age, and all samples to be collected during the same period."

Ideally, attic dust samples should be collected at each node of a 500 x 500 m grid (central part of city) to 1000 x 1000 metres sampling grid (suburbs), giving a nominal density of 4 samples/km$^2$, the same as the urban soil and house dust surveys, but this depends on the housing situation in each town or city. In Athens (Hellas), an attic dust survey is impossible to carry out, because in the most populated parts of the city there are mostly storeys of flats. Therefore, an attic dust survey depends on the availability of houses with uninhabited attics.

It is important to record all observations on the Field Observations Sheet, and to take digital photographs of the areas from where the attic dust is collected, and general photographs of the exterior conditions of each selected house. In fact, the instructions of Section *"§2.2.1. Sampling a bare topsoil spot'* from (m) to (t) should be followed.

### *2.5.4. Road dust sample collection*

The following description was abstracted from Demetriades (2014, p.24).

"Road dust (or road deposited dust or road deposited sediment or roadside sediment) is a heterogeneous mixture of particles from exhaust fumes, warned tyre debris, brake pad linings, pulverised plant material, and dust from geological sources. Therefore, road dust is a good sampling medium to assess outdoor urban contamination (Farago *et al.*, 1998; Gómeza *et al.*, 2002; Varrica *et al.*, 2004; Whiteley, 2005; Robertson and Taylor, 2007; Guney *et al.*, 2009; Mathur, 2010; Kadıoğlua *et al.*, 2010; Duong and Lee, 2011; Locutura and Bel-lan, 2011; Singh, 2011; Bavec *et al.*, 2015).

Road dust is collected with a nylon brush and a dustpan or a vacuum cleaner from either road gutters or pavements (Photo 15). Samples of road dust are normally collected from road junctions. However, the sampling plan depends on the objectives of the survey. Road dust from each sample site should be collected from an area of similar size, and during the same period. Again all sampling equipment must be thoroughly cleaned after the collection of each sample to avoid cross-contamination."

Road dust or sediment samples should be collected at each node of a 500 x 500 m grid (central part of city) to 1000 x 1000 m sampling grid (suburbs), giving a nominal density of 4 samples/km$^2$, the same as the urban soil and house dust surveys. The nearest road junction to each grid node should be selected. The reasons for selecting road junctions are:

- Vehicles use their brakes to stop, meaning that there is wear and tear of brake pads, and the release into the urban environment of elements, such as Sb, Zn, Mo, Cu and Mn (Uexküll *et al.*, 2005; Iijima *et al.*, 2007; Thorpe and Harrison, 2008; Gieti *et al.*, 2010; Amato *et al.*, 2012), and
- Vehicle idling (when a vehicle stops at a red light or a road junction, and has its engine running), apart from burning fuel unnecessarily, increases emissions that affect the urban environment. With the use of automobile catalytic converters, there is a release of platinum-group elements (PGEs), such as Rh, Pd, and Pt (Farago *et al.*, 1995, 1998; Zereini and Alt, 2000; Ely *et al.*, 2001; Whiteley, 2005; Wichmann *et al.*, 2007; Zereini *et al.*, 2007; Wiseman and Zereini, 2009; Ďuriš, 2011).

It is important to record all observations on the Field Observations Sheet (see Appendix 5), and to take digital photographs of (i) the road dust or road sediment, and general photographs about the sample site. In fact, the instructions of Section *"§2.2.1. Sampling a bare topsoil spot'* from (m) to (t) should be followed.

(a) (b)

(c) (d)

Photo 15. Road dust or road sediment sampling from a junction: (a) road junction near the Temple of Olympian Zeus, Athens, Hellas – the sample was collected from the left gutter, and the road dust sample has been placed on a white piece of paper and is marked by wooden stick with red-white ribbon; (b) close-up of road dust, which is a heterogeneous mixture of dust particles, plant remains, cigarette (bad habit of Hellene drivers to throw the butt-ends of their cigarettes on the road); (c) sampling of road dust from the pavement at the road junction – the pavement within the marked area was swept and pavement dust is on the white sheet of paper; (d) close-up of the road pavement dust, which is again a heterogeneous mixture of dust particles, small stones and plant remains (Source: Demetriades, 2014, Photo 15, p.25).

### *2.5.5. Air particulates sample collection*

The measurement methods for the determination of concentrations of PM2.5 and PM10 emission particles are based on the principle of impaction (VDI, 1999, 2004; DIN EN, 2002). Particulate matter sampling and measurement, as well as the equipment used (Photos 10 & 16) for this purpose must comply with the requirements of the European technical rules by CEN (1998, 2005), and at the international level by ISO (DIN ISO, 1994, 1995; UNEP/WHO, 1994; VDI, 1999, 2004).

Air filtration is the most widely used technique to collect air particle samples, because of its efficiency, ease of handling, and economy (Snedden, 1983). However, it is very important that any filter used should satisfy the following conditions:

- mechanical stability (good weighing properties);
- chemical stability (compatibility to the applicable analytical methods);
- high particle collection efficiency (high particulate separation);
- low flow resistance;
- good retention without clogging, and
- low and consistent blank values and artefacts.

Generally, the filter material available for the particulate matter collection falls into three broad classes: depth or fibrous filters, membrane filters, and coated fibre filters. Depth filters are made from either glass or quartz fibres, and membrane filters from organic material, such as

Teflon (PTFE), polycarbonates and cellulose acetates. Details about the properties of various filter types can be found in Logde (1989), Pall (2000), and Pesch *et al.* (2007).

(a) (b)

Photo 16. Sampling of air particulates in the city of Stassfurt, Germany. The equipment is installed on the roof of a house. (a) Real time particulate matter monitor 'Sharp 5030' (MLU, 2006) on the left and SEQ 47/50 Sequential Gravimetric Sampler on the right (Leckel, 2006); (b) Close-up of SEQ 47/50 Sequential Gravimetric Sampler (Source: Manfred Birke, 2015).

The sequential sampler SEQ47/50 (Photos 10a & 16) is designed for outdoor use at all temperatures and environmental conditions. The magazines for the blank and sample collection filters are able to load 17 filter holders. By enclosing the upper sample collection filter holder, and the superimposition of the other filter holders within the magazine for the sample collection filters, the air volume above each filter is so small that particulate volatile material cannot evaporate into the air. Additionally, the complete sampling system up to the filter is cooled by sheath air. By these measures, after a sampling period of 17 days, a reliable determination of the particle masses collected on the filters is guaranteed. The filter holders are capable to hold filters with diameters of 47 and 50 mm. The airflow's temperature is measured directly behind the filter that is currently sampled. If the temperature falls below the dew point, during winter operation under ambient air conditions, the filter temperature will be increased to avoid icing and soaking of the filter.

The PM2.5 and PM10 particle measurements and sampling are carried out according to CEN EN 14907 (CEN, 2005) and CEN EN 12341 (CEN, 1998). The dimensions of the suction tube (inside diameter of 27 mm), between the inlet and the filters, are such that particle losses at the tube's inner wall cannot occur.

The selection of the sampling site is determined by the objectives of the study, but there are some general rules that should be fulfilled when selecting a site for the installation of the instruments (USEPA, 1975; Ott, 1977):

- It should be easily accessible, secure for personnel, and not prone to vandalism or tampering.
- It should not be located near obstructions, such as trees or tall buildings, which inhibit or enhance the airflow.
- The sampling intake should be high enough to avoid re-entrainment of large particles near the ground, and
- Inlet should be at a height and location that reflects potential exposure.

### *2.5.6. Bio-indicator plant sample collection*

According to Arndt *et al.* (1987), Markert *et al.* (1999, 2008, 2011), Markert (2007) and Fränzle *et al.* (2012), the term bio-indicator is used for organisms or organism associations that respond to pollutant load with changes in vital functions, or which accumulate pollutants. Information about specific biological effects supplements data on air pollution.

*Bio-indicators* are commonly grouped into *accumulation* and *response indicators*. The former group stores pollutants without any evident changes in its metabolism. While the latter group, the *response indicators*, reacts with cell changes or visible symptoms of damage when taking up even small amounts of harmful elements and substances. In addition to microorganisms, fungi, algae, mosses, lichens, ferns and higher plants (Markert *et al.*, 2003), and animals, including human tissues (blood, urine, teeth, hair, *etc.*), can be used as bio-indicators.

When higher plants (*e.g.*, trees) are used for bio-monitoring, it is important to consider the influence of soil. In view of the fact that soil contamination could also be a significant factor, samples are taken, not only from the outer bark layers contaminated by emissions, but also from the inner bark layers, which are protected against the direct impact of air pollution (Hofmann, 1998; Hofmann *et al.*, 1999, 2001).

*Bio-monitoring* is divided into *active* and *passive*. *Active bio-monitoring* includes all methods that insert organisms (*e.g.*, green kale, eye grass, tobacco, beans) under controlled conditions into the site to be monitored (Nobel *et al.*, 2005). While *passive bio-monitoring* uses organisms, organism associations, and parts of organisms (*e.g.*, pine needles, lichen, earthworms, barks), which are a natural component of the ecosystem and appear there spontaneously.

The objectives of collecting bio-indicator samples have to be clearly established, because it will demand different sampling and preparation procedures. *For example*, plant samples for determining pollutant deposition must be analysed in an unwashed condition (Ernst, 1994). In all sample procedures, it is essential to avoid contamination. If possible, a mixed sample of several plants of the same type should be taken. For grass samples, it is not necessary to distinguish between different species of grass. When taking grass samples a cutting height of at least 6-8 cm should be adhered to.

Grass stems and flowers are to be avoided.

For moss monitoring, only samples of the specified moss species should be taken (Herpin *et al.*, 1997; Siewers and Herpin, 1998; Markert *et al.*, 1996). The main moss species sampled in Germany was *Pleurozium schreberi* (Siewers and Herpin, 1998). Samples sent to the laboratory should be cleaned of material adhering to the moss, but not submitted to any further washing. The green to brownish-green parts of moss, representing a growth period of two to three years, are used for analysis.

It is recommended to collect 5-10 subsamples of plant material from each site, on a completely random basis, and finally mix them to make up a single sample. The total weight of the mixed plant sample should be at least 300-500 g.

For plant sampling, ceramic knives or scissors should be used. If possible, always living green and not withered or dead plant material should be sampled. Within a single species, it should be possible to sample plant parts of the same age. The plant parts must be cut from the plants by sample collectors wearing powder-free vinyl gloves, and stored in perforated PE, paper, or linen trace-element free sample bags. Plant samples for the determination of organic compounds should be kept refrigerated in aluminium foil, while samples for the determination of inorganic determinands may be stored and transported at temperatures below 10°C.

For bark sampling, suitable trees (*e.g.*, oaks, linden trees) of sufficient age should be used. It is possible, therefore, to conduct standardised bark sampling for monitoring air quality. Outer bark has to be removed from several trees at each site as circumferential samples from a height of approximately 1.5 m above the ground, with a total circumference of at least 5 m being maintained (Photo 17). The outer bark layer is removed to a defined thickness of 1 mm with a specially developed bark sampler (Hofmann, 1998). A precise description of the method and sampling technique applied by the sampler is provided in Hofmann *et al.* (2001). A high-speed cutter with a special titanium nitrite coating is used, which is tested to ensure the absence of any contamination from the range of substances analysed. The cutter speed is set at 15,000 rpm. The fine-grained bark samples are placed directly into self-sealable PE sample bags (Photo 17 - inset); the bags are sealed immediately after completion of sampling, and then transported to the laboratory for further processing.

Samples of the inner bark layers are taken, using a special cutting tool made of carbon-steel, after careful removal of the outer bark layers in order to avoid contamination at several places. The samples are also placed in self-sealable PE bags, and the bag surface is subsequently incised with a bark cutter in the laboratory in order to avoid contamination.

Photo 17. Sampling of outer bark at location S11 (Industrial Street) in the Stassfurt urban area, Germany (high speed milling cutter with a special titanium nitrite bit, sampling depth: 1 mm, milling speed 15,000 rpm (Source: Birke *et al.*, 2009, Fig. 200, p.327).

### *2.5.7. Human tissue sample collection*

When applied geochemists map contamination in urbanised centres they, with support from members of their multidisciplinary team, should go a step further by investigating whether the elevated determinand concentrations have affected the health of the exposed population. This is a necessary step in order to convince local politicians that the population is at risk.

Exposure of the human population to urban contamination can be tested directly by the collection of human tissues, such as blood, urine, hair (scalp or pubic), deciduous teeth, nails and even mother's breast milk. Such samples cannot be collected, however, by the applied geochemist, as the techniques are specialised and will usually require ethical approval. Sampling of human tissues and the obtaining of ethical approval must be performed by trained medical practitioners. Such public health studies are usually carried out by epidemiologists or other specialist public health staff. *Epidemiology* is defined as "*the study of the distribution and determinants of health-related states or events (including disease), and the application of this study to the control of diseases and other health problems"* (World Health Organisation; http://www.who.int/topics/epidemiology/en/). Various methods can be used to carry out epidemiological investigations: *surveillance* and *descriptive studies* can be used to study distribution; *analytical studies* are used to study determinants. Epidemiology is the cornerstone of public health, and informs policy decisions and evidence-based practice by identifying risk factors for disease and targets for preventive healthcare. Therefore, the applied geochemist should collaborate closely with an epidemiologist or other public health physician in the collection and analysis of human tissue samples.

The medical practitioner will be responsible for the design of any epidemiological study. Such studies may be classified as follows (Alexander G. Stewart, pers. commun., 2015):

| ***Study type*** | ***Description*** | ***Comments*** |
|---|---|---|
| Descriptive | Answers "who, what, when and where" questions about the distribution of disease and/or risk factors in a population. | Cannot attribute causality. Example: case report; case series (patients or situations with a similar disease or outcome). |
| Cross-sectional (prevalence) | Describes status of an individual with respect to a disease and/or exposure at a given point in time. | Gives prevalence and measure of risk, but cannot always distinguish which came first, exposure or disease. |
| Cross-sectional (correlation) | Describes status of a population with respect to a disease and/or exposure at a given point in time. | Often uses routinely collected data (saving time and money). Populations defined in various ways, *e.g.*, geography, time trends, social class, occupation. Cannot draw conclusions about an individual. |
| Analytical (observational) | *Case control*: compares two groups (ill/not ill) by exposure(s) of interest.<br>*Cohort*: follows two or more groups over time (prospective or retrospective), comparing outcomes by exposure. | *Case control*: assesses risk factors; shows association not causation. Useful for rare outcomes or diseases, with large numbers involved, an unknown population at risk, or when only a small proportion of exposed people becomes ill. Can identify multiple exposures.<br>*Cohort*: retrospective cohort study generally used with smaller numbers, who can all be contacted and grouped by exposures. Prospective cohorts expensive and time-consuming. |
| Analytical (interventional / experimental) | Investigates the impact an intervention in a population. | Time-consuming, expensive; best way to evaluate impact of intervention. |

The expertise of the applied geochemist in sampling designs, randomisation of samples, quality control procedures, and plotting of data on topographical maps, can be very valuable in the design of an epidemiological study (Demetriades, 2011a; Schmidt *et al.*, 2011), particularly in ensuring that the health study is closely related to the environmental investigation. Consequently, such collaboration will produce very useful and valuable results about the health status of the urban population, and may identify the human health risks. The local and regional health authorities should be involved in such an epidemiological study. In some countries, this may be a prerequisite, because only health organisations are authorised to carry out such surveys (*e.g.*, Germany).

As the health status of population is influenced by a variety of factors, such as environmental, education level, dietary habits, workplace, lifestyle, *etc.*, these have to be taken into account. Hence, the epidemiologist may need to design a suitable questionnaire, which is completed by each sampled human subject.

#### *2.5.7.1. Blood sampling*

Venous blood (*i.e.*, related to veins) samples are collected by venipuncture from the subject's arm. The correct sampling tube should be used, *e.g.*, polypropylene tubes containing the anticoagulants ethylenediaminetetraacetic acid (EDTA) for lead, and heparin for haemoglobin (WHO, 1994; Kafourou *et al.*, 1997; Dobler *et al.*, 2007a, b; 2008); heparin conflicts with any analysis of proteins. The blood samples are subjected directly afterwards to deep-freezing at -20°C until their analysis.

Sample bottles, syringes, needles, test tubes, reagents, *etc.* should be previously tested to ensure that they are free from contaminants.

#### *2.5.7.2. Urine sampling*

Two different types of urine specimen samples may be collected, namely first morning void urine, and timed urine samples; the latter can either be an 8-hour or 24-hour urine sample (Specimencare, 2015).

First morning void urine is the sample of choice for urine analysis, since the urine is generally more concentrated (due to the length of time the urine is allowed to remain in the bladder) and, therefore, contains relatively higher levels of cellular elements and analytes (Hinwood *et al.*, 2004; Dobler *et al.*, 2007a, b; Figueiredo *et al.*, 2007; Colín-Torres *et al.*, 2014). Abnormal constituents are also likely to be present in higher concentration and, thus, more likely to be detected. It is also a much simpler procedure to follow by the donors and, therefore, less prone to errors.

Timed urine samples may be required for quantitative measurement of certain analytes, including those subject to diurnal variation, such as creatinine, urea, cortisol, citrate, amino acids, catecholamines, metanephrines, vanillylmandelic acid (VMA), 5-hydroxyindoleacetic acid, protein, oxalate, uric acid, 17-ketosteroids, and 17-hydroxysteroids, Ca, Cu, K and Na (Specimencare, 2015). A timed urine sample allows measurement of the excretion of these substances in urine over a specified length of time, usually, but not always, 8 or 24 hours; the latter is normally preferred (Eikmann *et al.*, 1991; Makropoulos *et al.*, 1992). In this collection method, the bladder is emptied prior to beginning the timed urine collection. Then, for the duration of the designated time period, all urine is collected and pooled into a collection container, with the final collection taking place at the very end of the predetermined period. Half-an-hour before the end of the collection period, it is helpful to ask the donor to drink a glass of water, so that the last urine specimen can be obtained. If no specimen is produced, then the total volume and time of collection cannot be determined. It is also important to caution the donor not to lose urine sample to the toilet during defecation. Accurate timing is very important as this information forms a critical part of the calculations performed to determine urine clearance values (*e.g.*, creatinine clearance). Interpretation based on faulty calculations can result in improper diagnoses. Such 24-hour collections are fraught with difficulties, particularly completeness, and should not be undertaken lightly.

In both cases, the donor should wash thoroughly the area of the genitals, then wear powder-free nitrile gloves and rinse the genitals with injection water, which is completely trace element free, and dry by gentle tapping with sterilised gauze sponges.

Each donor collects the first morning void urine in a sterilised leak-proof 120 ml trace element free polyethylene cup, and screws the cap tightly. The time of collection is recorded.

In the case of collection of either an 8- or 24-hour urine sample, each donor collects the urine in a sterilised leak-proof 3-litre trace element free polyethylene container, and screws the cap tightly.

Urine samples should be deep-frozen to $-20^{o}C$ within 12 hours after collection until their analysis.

### *2.5.7.3. Hair sampling*

Hair is a very suitable alternative to both blood and urine, as determinand concentrations are comparatively higher, at least tenfold than those in blood and urine, and hair is biologically a more stable human tissue. It can be stored without deterioration, and, most importantly, hair sampling is a non-invasive technique (Bland, 1983; Gellein *et al.*, 2008). Two different types of human hair are collected, either scalp or pubic hair (Wilhelm *et al.*, 1990; Williams *et al.*, 1998; Hindmarsh *et al.*, 1999). The latter is usually preferred, because it minimises external contamination, although, in many situations, the use of scalp hair is an acceptable alternative. However, there is a minor drawback with pubic hair as in young children it does not grow until puberty; in boys, puberty starts around 12 to 13 years of age; while in girls, it usually starts around 11 years of age.

An evaluation of the relationship between natural hair colour (blonde, black, brown, red, grey) and trace element levels (Al, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Pb, Se, Zn), performed on 3,564 scalp hair samples, showed that there is no significant relationship between hair colour of men and women and trace element levels, and the variation from natural hair colour to hair colour is not important (Bland, 1983); these results have been verified by Chittleborough (1980) in his review of the analysis of human hair for trace elements. Therefore, it can be safely assumed that the chemical composition of human hair is independent of natural hair colour. A drawback, however, is dyeing of hair by women, and nowadays men, as well as hair bleaching and cold waving. McKenzie (1978) has determined that bleaching of the hair and cold waving have an impact upon the concentration of Zn and Cu, but that dyeing, hair sprays, and shampoos, which do not contain trace elements, have little or no impact upon hair element concentrations. However, one has to be wary of Se-bearing anti-dandruff shampoos (Fordyce, 2005). It is, therefore, recommended to record on the questionnaire the type of hair dye and anti-dandruff shampoo used.

The sampler should wear powder-free nitrile gloves, and cut freshly washed scalp or pubic hair with a pair of stainless-steel scissors that has been previously washed with ethanol. The head hair sample is collected from several spots around the nape of the neck, cutting close to the scalp (Revich, 1994; Williams *et al.*, 1998; Hindmarsh *et al.*, 1999). The back of the head is chosen largely for aesthetic reasons when removing such an amount of hair at one time. Similarly, each donor collects pubic hair samples randomly from any specific spots (Williams *et al.*, 1998). At least one gram of hair sample should be collected and placed directly in a self-sealable polyethylene sample bag. The length of the hair from the shaft cut should be noted as this allows comparison between individuals.

#### *2.5.7.4. Deciduous teeth sampling*

Human teeth are often used to monitor human exposure to harmful heavy elements, and especially Pb. Studies use either shed deciduous teeth to monitor the extent of childhood exposure (Fosse and Berg-Justesen, 1977, 1978; Needleman *et al.*, 1979; Paterson *et al.*, 1988; Fergusson *et al.*, 1989; Stavrakis *et al.*, 1994; Fosse *et al.*, 1995; Tsuji *et al.*, 2001), or permanent teeth found at ancient burial sites to investigate the degree of human exposure in past times (Fosse and Wesenberg, 1981; Patterson *et al.*, 1991; Budd *et al.*, 1998, 2000, 2004).

Deciduous teeth sampling requires collaboration with parents and dentists. Parents should be informed about the aim and procedure of the study, and asked to complete a questionnaire.

Normally shed deciduous teeth are collected from children of 5 to 12 years old (Stavrakis *et al.*, 1994; Farmer *et al.*, 2006; Barton, 2011; Khafif *et al.*, 2012; Alomary *et al.*, 2013), and placed directly into self-sealable polyethylene (PE) sample bags.

#### *2.5.7.5. Nail sampling*

Nail sampling is a non-intrusive way of determining contaminant exposure of the human population. Nail samples can be taken from either the hands or feet or both (Wilhelm *et al.*, 1994; Reis *et al.*, 2015). Toe-nails grow more slowly and may have higher levels of contaminants present. The donor should wear powder-free vinyl gloves, and to cut freshly washed hand and foot nails with a pair of stainless-steel scissors or nail clippers that have been previously washed with ethanol.

Varnished nails should not be sampled.

Nail clippings from each hand or foot are placed in self-sealable trace-element free bags; each donor should place the nail clippings of the left hand, right hand, left foot and right foot in different self-sealable PE bags, and label them accordingly. The scissors or nail clippers should be washed with ethanol between each nail set.

#### *2.5.7.6. Mother's breast milk sampling*

Mother's breast milk sampling is a non-intrusive way of determining contaminant exposure of infants and a useful biomonitoring tool (Sharma and Pervez, 2005; UNEP, 2007; UNEP-GEF, 2010; Mandour and Ghanem, 2013). Breast milk sampling has been used to test for persistent organic pollutants (POPs) globally for several decades, and is a good indication of regional intake from diet and environmental pollution.

Breast milk sampling should be conducted at the same time as the blood-sampling programme, and mothers should donate both blood and breast milk samples (UNEP, 2007).

The questionnaire given to mothers should include information on age, number of children and number of children that they have breastfed (including children of relatives, *etc.*).

Breast milk is sampled from mothers between the 2nd and 4th week post-partum (UNEP, 2007). The breasts, prior to sampling, are washed, rinsed with injection water, which is completely trace element free, and then dried with sterilised gauze sponges. The donor should wear powder-free nitrile gloves during the sampling procedure, extract a volume of 100 ml breast milk, and place it directly in a sterilised glass jar, which contains three potassium dichromate pellets to preserve the sample appropriately (UNEP-GEF, 2010). The breast milk sample may be kept in the home refrigerator, at approximately 4°C, for no longer than 72 hours, and then at the laboratory deep-frozen at -20°C until its analysis (UNEP, 2007).

# 3. SAMPLE PREPARATION AND STORAGE

## 3.1. Sample preparation and storage for the determination of inorganic chemical elements

### *3.1.1. Soil sample preparation and storage*

All collected samples should be sent to a central laboratory for sample preparation, homogenisation, and splitting into sub-samples for laboratory analysis, and safe storage for future use. The total number of splits depends on the analytical programme. At least two sample splits should be archived for future use. The following procedure is recommended for the preparation of soil samples on which inorganic elements will be determined:

- Soil (top- and sub-soil) samples for the determination of inorganic trace element analysis are either air-dried at room temperature, or dried in a thermostatically controlled oven at a temperature not exceeding 25°C (it is noted that Hg escapes even at 30°C).
- The small numbered card in the small zip-lock bag accompanies the sample during the sample preparation. It should be placed in a secure position in the drying tray.
- After drying, the samples are carefully disaggregated by a porcelain pestle in a porcelain mortar, taking care not to grind small pebbles.
- Following disaggregation, soil samples are sieved through a nylon screen of 2 mm.
- The whole <2 mm soil fraction is suitably homogenised, and split into sub-samples and placed in trace-element free containers. The process of homogenisation and sample splitting is an art if it is done by hand, *i.e.*, coning and quartering (Schumacher *et al.*, 1990; Gerlach *et al.*, 2002). Therefore, well-trained technicians should be given the task of homogenisation and sample splitting. Of course, there is an easier method by using a riffle splitter (Schumacher *et al.*, 1990). Whatever method is used, the splits or sub-samples should be representative of the whole sample.
- All utensils are carefully cleaned after the preparation of each sample in order to avoid cross-contamination of samples.
- Soil (top- and sub-soil) sample splits for chemical and physico-chemical analyses are sent to the selected laboratory or laboratories, remembering that all samples must be analysed for the same suite of determinands at the same laboratory by the same analytical method.
- The remaining splits of <2 mm soil (top- and sub-soil) should be archived in a dust free storeroom where the ambient temperature does not exceed 30°C. This is the reference collection for future use.

Applied geochemists that are interested in sample preparation and determination of inorganic chemical elements should consult Chapter 3 (p.28-46): *Sample preparation and inorganic analysis for urban geochemical survey soil and sediment samples* by Allen *et al.* (2011) in C.C. Johnson *et al.* (Editors), *Mapping the chemical environment of urban areas* (Published by Wiley-Blackwell, John Wiley & Sons Ltd., Chichester, U.K.).

### *3.1.2. House and attic dust sample preparation and storage*

House and attic dust are, of course, completely different sample media in comparison to topsoil and subsoil, and their particle size is much finer grained. In case comparisons are going to be made among soil, and house and attic dust, the samples should be prepared according to the aforementioned procedure for soil by skipping the disaggregation stage (see Section §3.1.1). If, however, house and attic dust samples are not going to be compared with other media, then they should be sieved to <0.125 mm.

### *3.1.3. Road dust sample preparation and storage*

Similarly, road dust or road sediment is a completely inhomogeneous sample medium, and different from all other media, with a variable particle size. As comparisons will be most likely made between soil, house and attic dust, the samples should be prepared according to the aforementioned procedure for soil by skipping the disaggregation stage (see Section §3.1.1). If, however, road dust samples are not going to be compared with other media, then they should be sieved to <0.125 mm.

### *3.1.4. Air particulate sample preparation and storage*

Before the start of the sampling campaign, different filters should be assessed in order to find the most suitable type for metal analysis. As fibrous filters are not mechanically strong and fibres are lost during handling, only filters of membrane and membrane coated fibre types can be recommended for analysis of metal composition.

For equilibration of the filters, before weighing they should be conditioned in a suitable oven for at least 24 hours at a constant humidity of about 50% and a temperature of about 22°C (DIN EN, 2014). The filters are placed in Petri dishes for better ventilation. For weighing the filters, a laboratory balance (*e.g.*, type micro M3P from Satorius) with a gravimetric resolution of 1 µg (of a total load of 1500 mg) should be used. The nominal precision of the balance should be in the range from 0.1 to 100 mg (about 1%). The balance should be set up in a climatically controlled weighing room, with humidity and air temperature control; thus, the atmosphere is also the conditioning medium for the filter material.

Immediately after determining the empty weight, the filters are placed in the filter holder for the particulate sampling. The prepared filter holders are kept until transportation and installation in a closed aluminium container. For the determination of dust mass concentration in the atmosphere after controlled sampling, the enriched particulate matter masses on the filters are determined gravimetrically. This takes place after returning the filter to the analytical laboratory, where they are kept for at least 24 hours equilibration in an air-conditioned weighing chamber.

The gravimetric determination of particulate matter mass of the collected filter samples is the basis for the calculation of particle concentration in the atmosphere.

The metal content of the particulate matter fractions PM2.5 and PM10 is determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectroscopy (ICP-MS). Certified reference materials (CRMs) should be analysed also to give an indication of typical extraction efficiency. The PM samples have to be dissolved, along with blank samples and CRMs, using an acid microwave digestion method (Birke *et al.*, 2009). The samples are digested using a mixture of hydrochloric and nitric acid, and then heated for 15 minutes at 1000 psi by using an autoclave. The recovered samples are analysed along with mixed standard solutions for the metals of interest.

### *3.1.5. Bio-indicator plant sample preparation and storage*

All plant samples (*e.g.*, grass, leaves, moss, barks, *etc.*) should be air-dried; they can also be freeze-dried. Then the dried plant parts should be pulverised to pass a 0.150 mm (100-mesh) screen in a carbon steel or better agate rotary or ball mill. The samples should be kept under dark and dry conditions in PE sample bags or boxes.

The homogenised samples are then digested in an acid mixture ($HNO_3$ + HF, HCl), and in a microwave oven, using sealed Teflon vessels. All solutions should be analysed by inductively coupled plasma mass spectrometry (ICP-MS) for at least 54 inorganic chemical elements.

### *3.1.6. Human tissue sample preparation and storage*

As the epidemiologists in the multidisciplinary team will be carrying out the human tissue sampling, they will be also responsible for the sample preparation and storage of samples. Since these are completely specialised techniques are not described in this manual.

## 3.2. Sample preparation and storage for the determination of organic chemical compounds

As mentioned in Section §2.2.1 we do not recommend any of the sample preparation methods for samples destined for organic compound analysis. Different methods are presented and the users of this methods manual must make the decision, based on the required criteria of their project. This will include economic as well as scientific criteria.

Samples for the determination of persistent organic pollutants (POPs) should be kept at a temperature of <4°C, and sent directly to the laboratory for sample preparation.

Samples to be analysed for volatile organic compounds (VOCs) are placed directly in the field into amber (dark brown) glass vials with a double-safety cap, stored in a refrigerator at a temperature of <4°C, and despatched directly to the laboratory for analysis without being subjected to any preparation. In the laboratory, the samples should be stored in a refrigerator at a temperature of <4°C, and analysed within 12 days from the day of collection.

Applied geochemists that are interested in sample preparation and determination of organic chemical compounds should consult Chapter 4 (p.47-60): *Organic analysis for urban geochemical survey soil samples* by Harrison and Reeder (2011) in Johnson *et al.* (Editors), *Mapping the chemical environment of urban areas* (Published by Wiley-Blackwell, John Wiley & Sons Ltd., Chichester, U.K.).

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## 4. PROJECT REFERENCE MATERIALS

A large reference sample is being prepared for use by the EuroGeoSurveys Urban Geochemistry Mapping Project at the Geological Survey of Slovakia (State Geological Institute of Dionyz Stur, Spisska Nova Ves) (Demetriades and Birke, 2015). Apart from the homogeneity tests that will be performed by the Geological Survey of Slovakia (Mackových and Lučivjanský, 2014), the project reference sample will undergo a ring test with many participating laboratories in order to be certified (Reimann *et al.*, 2012; Reimann and Kriete, 2014).

It is strongly recommended that other countries or continents planning an urban geochemical mapping project in many cities, they should invest in the preparation of at least one large reference sample.

A large solid blank reference sample should also be prepared. Schermann (1990) recommended such a reference sample of either quartz or kaolin or bentonite to be prepared for the Regional Geochemical Mapping of Europe (Western European Geological Surveys, WEGS, presently EuroGeoSurveys). Aliquots of this sample to be packed in the field, as the normal routine sample, and to undergo the whole procedure of sample preparation (drying, disaggregation, homogenisation, sub-sample splitting, and analysis). This sample will serve to pin point any potential cross-contamination of samples during their preparation and laboratory analysis stages. Of course, the preparation of such a sample should undergo homogeneity and ring testing.

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# 5. ARRANGEMENT OF SAMPLES FOR ANALYSIS

## 5.1. Systematic errors and randomisation of samples

Randomisation of soil samples and, of course all collected sample types, is a necessary procedure in a geochemical survey to locate systematic errors introduced during sample preparation and analysis. Some of these systematic errors are (Plant, 1973; Fletcher, 1981, 1986):

- contamination of uncontaminated soil (house and attic dust, road sediment, *etc.*) samples by contaminated samples during sieving;
- within-batch contamination of soil samples from an external source during grinding and pulverisation, and
- during the analysis of samples in the laboratory, changes in the conditions may occur, namely weighing balance drifting, analytical instrumental drift, interferences, *etc.*, such changes are monitored by the analysis of reference or standard samples introduced in every batch.

The greatest problem is to attempt to interpret data affected by such systematic errors, because of the inherent difficulty to distinguish between false and real geochemical patterns.

Randomisation of samples is the method devised by applied geochemists to remove any systematic relationship between order of analysis and geographical location (Plant, 1973; Plant *et al.*, 1975; Thompson, 1983; Schermann, 1990; Darnley *et al.*, 1995; Reimann *et al.*, 2009, 2011a, 2012; Demetriades *et al.*, 2014; Demetriades and Birke, 2015). By randomisation of samples any systematic between batch variation in analytical level is transformed to increased analytical variability, meaning that any systematic errors are spread randomly over all the samples. This converts data that would be reflected as areas of shifted geochemical background levels, and are artefacts of the lack of accuracy in the chemical analyses, into increased local noise. Care should be taken, therefore, to include a sufficient number of control reference samples, and to monitor their analyses, in order to detect between-batch variation. If such variations are identified, then the affected batches of soil samples should be submitted for re-analysis, and the new analytical results utilised, provided they are satisfactory according to fitness-for-purpose. Furthermore, randomisation of samples has another advantage, because project and international reference samples, and project replicate samples can be hidden in the batches and, thus, not recognised by the laboratory.

After the experience with the EuroGeoSurveys Urban Geochemistry pilot project, it is strongly recommended to have in large projects, where many towns or cities are participating, a very strict field sampling schedule, because it is important to submit to the analytical laboratory all collected urban topsoil samples in one large batch. Otherwise, serious quality control problems will most likely arise, with the production of incompatible analytical results.

### *5.1.1. Randomisation and insertion of control samples*

Randomisation of samples can be done in two different ways:

(1) During the planning of the field survey the total number of routine and duplicate field samples, and their replicated splits, is estimated, as well as the number of reference samples that will be inserted for analysis. Then this number is randomised, and a list made of the random numbers generated. Numbers should be reserved for inclusion of reference and project replicate samples. A digital computer software program can perform the randomisation of sample numbers, and an output produced (Appendix 4). During the field survey, each sample is assigned in turn a random number from the list. In the preparation laboratory, the samples are ordered in ascending numbers during sample preparation, and the project reference samples,

and the routine and field duplicate sample splits, are inserted at the appropriate reserved places using the same coding, and a record kept.

(2) The randomisation of routine urban geochemical samples, and control samples (reference and analytical replicates) is performed in the sample preparation laboratory, and project samples are assigned new numbers; again, quality control samples (reference samples and project replicate splits) are inserted. This procedure has a major disadvantage, because the samples lose, in fact, their identity, as completely new numbers are assigned. Hence, the procedure must be done very carefully, and a good record kept of the project sample numbers, and their corresponding new random numbers, because upon receiving the analytical results the original sample numbers must be given.

## 5.2. Arrangement of samples for analysis

Whichever of the two aforementioned randomisation methods is used, the project samples, together with the quality control samples, should be submitted to the analytical laboratory in a random order and in one large single batch. In order to arrange the project's external quality control samples in each analytical batch, you must ask the analytical laboratory to provide the following information:

(i) the number of samples analysed in each analytical batch;
(ii) the number of blank samples in each analytical batch;
(iii) the number of international and internal reference samples in each analytical batch, and
(iv) the number of replicated splits of project samples.

When you have this information, you will be able to arrange randomly the place to insert:

- one project reference sample per 20 samples;
- the second split of the field routine sample, and
- the two splits of the field duplicate sample.

## 6. LABORATORY ANALYSIS

### 6.1. Analytical laboratory arrangements and obligations

All samples should be sent to a selected laboratory or laboratories for analysis. Each laboratory should analyse all samples for the same suite of elements/determinands in a short time, as this is the only way to produce good quality and comparable results.

For the analysis of all urban geochemical sample types, a reputable accredited laboratory should be selected, and the analytical method agreed, as well as the digital format for reporting the results (Johnson, 2011). The laboratory should:

- reanalyse a second split of the 20th sample of each batch;
- analyse international and internal reference materials;
- analyse standard and blank solutions;
- analyse the samples according to the submitted numerical order, and NOT to randomise the samples, and
- must report all instrument readings (uncensored values) without any rounding or cut-off at the laboratory's pre-determined detection limit, and even sub-zero (negative) measurements should be recorded and submitted. Further, the analytical results should not be truncated at any upper limit.

All the aforementioned results should be made available to the applied geochemist, together with:

- ❖ a concise description of the analytical method used;
- ❖ lower and upper detection limits and limits of quantification of each determinand;
- ❖ recommended values of reference materials, and
- ❖ a report of any problems encountered during the analysis of the samples, and solutions given.

If a large number of samples is being analysed over a long period, it is important to monitor any changes by analysing the same reference materials in each batch of samples. The aim is, however, to analyse all project samples in the shortest possible period.

It is very important for the applied geochemist to have a good communication and cooperation with the laboratory.

*IMPORTANT CONDITION*: In the contract to be signed with the laboratory is important to include a clause stating that payment will be made subject to the acceptance of the analytical results by following the underlying procedure:

- upon receipt of the analytical results from the laboratory, the responsible applied geochemist should carry out an exhaustive statistical analysis of their quality using the internal and external quality control results;
- if analytical problems are located, the analytical batch or batches will be reanalysed by the laboratory without any charge, and
- in case all the analytical results are of poor quality, then the laboratory will be obliged to reanalyse all the samples without any charge, subject again to the same conditions for the verification of their quality (see the quality control about the determination of particle or grain size in Reimann *et al.*, 2011a, p.10-11 and 28-31).

### 6.2. Determination of inorganic elements and other parameters

Ideally, a large suite of elements should be determined on urban geochemical samples by a true 'total' and an aqua regia method, as the latter is normally used in environmental legislation, *e.g.*, Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr (Allen *et al.*, 2011). The aqua regia method should be able to analyse a sample aliquot of 15-gram weight, and the elements determined by an ICP-MS or a combination of ICP-AES and ICP-MS (Reimann *et al.*, 2009; Birke *et al.*, 2014). Commercial laboratories nowadays even have aqua regia methods using 25-gram aliquots. Some laboratories use methods with 0.5 gram aliquots; such methods should not be selected, because of the very small weight, which is not representative of the sample to be analysed.

It is recommended to determine platinum-group elements (PGEs), such as Ru, Rh, Pd, Os, Ir, and Pt, because automobile catalytic converters are dispersing these elements into the environment (Farago *et al.*, 1995, 1998; Zereini and Alt, 2000; Ely *et al.*, 2001; Gómeza *et al.*, 2002; Whiteley, 2005; Wichmann *et al.*, 2007; Zereini *et al.*, 2007; Wiseman and Zereini, 2009; Ďuriš, 2011).

For total concentration, measured by X-ray fluorescence (XRF), the <2.0 mm after sieving is milled to 63 μm for the preparation of fused beads.

Other parameters to be determined are: pH, Loss on Ignition (LOI), grain-size, total nitrogen and total organic carbon.

Applied geochemists that are interested in the determination of inorganic chemical elements should consult Chapter 3 (p.28-46): *Sample preparation and inorganic analysis for urban geochemical survey soil and sediment samples* by Allen *et al.* (2011) in C.C. Johnson *et al.* (Editors), *Mapping the chemical environment of urban areas* (Published by Wiley-Blackwell, John Wiley & Sons Ltd., Chichester, U.K.).

### 6.3. Determination of organic compounds

Organic compounds, such as polychlorinated biphenyls (PCBs; industrial chemicals, no longer produced but persistent in the environment), polycyclic aromatic hydrocarbons (PAHs; products of fuel combustion), polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDDs/PCDFs; industrial process by-products) and benzene, toluene, ethylbenzene, and xylene (BTEX; petroleum fuel hydrocarbons) may also be determined (Birke *et al.*, 2009, 2011b; Harrison and Reeder, 2011; Jensen *et al.*, 2011; Andersson *et al.*, 2011; Ottesen *et al.*, 2011).

Applied geochemists that are interested in the determination of organic chemical compounds should consult Chapter 4 (p.47-60): *Organic analysis for urban geochemical survey soil samples* by Harrison and Reeder (2011) in Johnson *et al.* (Editors), *Mapping the chemical environment of urban areas* (Published by Wiley-Blackwell, John Wiley & Sons Ltd., Chichester, U.K.).

## 7. QUALITY CONTROL PROCEDURES

Urban geochemical surveys produce data that are very sensitive, because they are directly related to the quality of our living, working and recreational environments, and to our health. Consequently, the generated data must be legally defensible. Apart from the estimation of sampling, analytical, and geochemical variance, the installed quality control procedures *must include the calculation of measurement uncertainty* (Ramsey, 1997, 1998; Ramsey and Argyraki, 1997; Ellison *et al.*, 2000; Ramsey and Ellison, 2007; Ellison and Williams, 2007, 2012; Demetriades, 2011b; Majcen *et al.*, 2011).

A balance hierarchical sampling and analytical scheme should be used for the estimation of *geochemical, sampling,* and *analytical variance* and *random components of measurement uncertainty*. Robust analysis of variance (RANOVA) is preferred, because it is suitable for small areas due to the small number of duplicate samples required, *i.e.*, duplicate samples from at least 8 sites or locations, and the use of the scheme illustrated in Figure 4, and because it accommodates outlying values that exceed a certain distance from the mean (usually 1.5 times the standard deviation) by down-weighting them rather than rejecting them (Ramsey, 1998; Lee and Ramsey, 2001; Boon, 2009). The RANOVA method was proposed by Ramsey (1998), and subsequently verified by Lyn *et al.* (2007). In case, for some reason, the routine and duplicate samples from the same location cannot be split into two sub-samples for analysis, then two different aliquots of each routine and duplicate sample should be analysed randomly within the sample suite of the project.

Collection of field duplicate samples is an inherent part of the *field geochemical investigation* itself, because the different types of variation of a parameter in the study area must be known. In fact, the "*sampling & analytical noise*" should be estimated (Ramsey, 1998), *i.e.*,

*Sampling + Analytical variance <20% of the total variance in the study area for each determinand studied.*

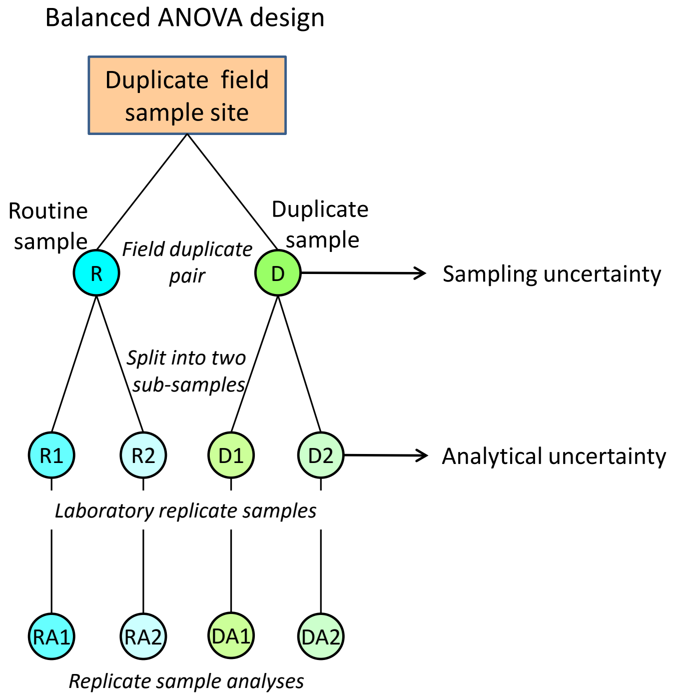

Figure 4. Balance hierarchical geochemical sampling and analytical scheme for the estimation of geochemical, sampling, and analytical variance and random components of measurement uncertainty (Ramsey *et al.*, 1992; Ramsey, 1998) (Source: Demetriades, 2011b, Fig. 6.1, p.78).

This is a requirement in order to be able to map the spatial or geochemical variability of a determinand or variable across the investigated area. In geochemical surveys, 10% to 20% of sites are normally duplicated, depending on the size of the area covered and the total number of samples collected. In small areas, however, with say 100 samples 35-40% of sites should be replicated in order to have a satisfactory statistical number of sites (>30) in order to use reliably single classical statistical analysis of variance schemes. Therefore, if a minimum of say 40 sites is replicated, a total of 80 analytical determinations for each parameter have to be performed (40 sites x 2 samples). Nowadays, with "*robust statistical two way analysis of variance*" (RANOVA), the total number of duplicated sites has been reduced to a minimum of 8, and each routine and duplicate sample is split into two sub-samples for analysis:

(8 routine samples x Analysis of 2 splits) + (8 duplicate samples x Analysis of 2 splits) = 32 analyses.

Therefore, due to the cost-effectiveness of the RANOVA method, even small investigations can afford to include it in order to test the reliability of the geochemical results, and the estimation of measurement uncertainty.

### 7.1. Quality control report

Upon receiving the analytical results from the laboratory the quality and integrity of the data should be verified, using various statistical techniques (Johnson 2011; Demetriades, 2011b), as it has been done in the GEMAS project, and a quality report written (Reimann *et al.*, 2009, 2011a, 2012; Demetriades *et al.*, 2014). See below Chapter 10 'Data checking'.

## 8. SUPPORTING INFORMATION

For the interpretation of urban geochemical data, the following information is required:

- a lithological (parent material) map as well as any lithogeochemical data;
- a geological map;
- a soil map;
- a land use map with the location of all recent potential contaminating activities and petrol stations;
- historical record of past industrial activities, and
- climatic data, *i.e.*, records of rainfall and temperature.

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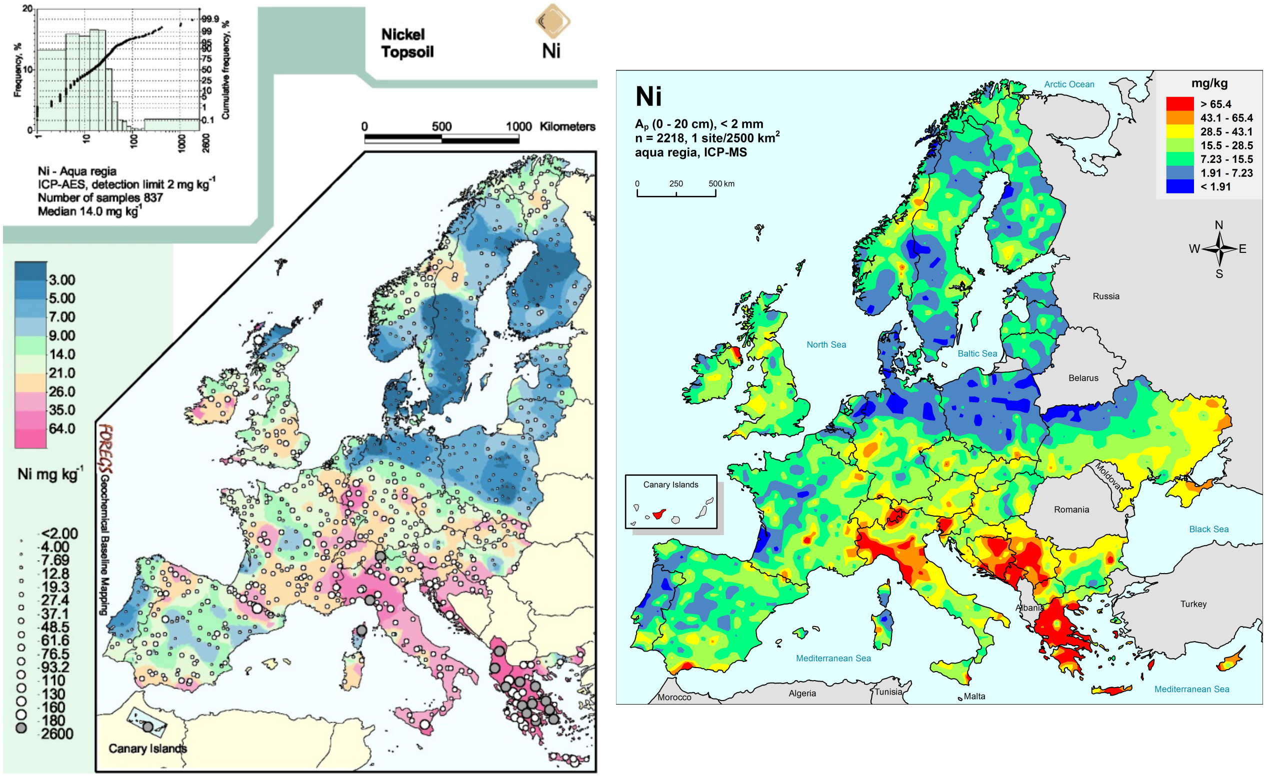
## 9. GUIDELINE VALUES

A *guideline or intervention value* refers to *a legislated contaminant concentration in a sample medium below which no harm to human health will occur*. Of course, there is the reverse definition: *a guideline or intervention value* refers to *a legislated contaminant concentration above which there is a potential unacceptable chronic risk (long term) to human health*. To our knowledge, with respect to the sample types (soil, house dust, attic dust, and road dust or sediment) used in urban geochemical mapping, guideline values exist only for soil, and in some countries for sediment (VROM, 2000).

National *soil guideline values* (SGVs) are normally set for different land use types, *e.g.*, residential, allotments, recreational and work (industrial and commercial). They also take into account human receptors as, *for example*, children who may be more susceptible to some chemicals than adults, and women (especially pregnant women), who may be more susceptible to some chemicals than men.

Most European countries have set their own national soil guideline values (*e.g.*, APAT, 2006; EA, 2009; VROM, 2000; FME, 2002; Carlon, 2007). It is very important to understand that each country derives its SGVs according to different criteria and, therefore, these guideline values cannot be used in other countries. To understand the futility of such attempts two maps of the aqua regia extractable Ni in the <2 mm soil fraction from the FOREGS *'Geochemical Atlas of Europe'* (Salminen *et al.*, 2005) and the EuroGeoSurveys *'Geochemical Mapping of Agricultural and Grazing land'* (GEMAS) in Europe (Reimann *et al.*, 2014) are presented (Fig. 5). As it can be observed, there are distinct differences from northern to southern Europe, with the Balkans having the highest Ni concentrations in topsoil, and the countries north of the Pleistocene glacial limit the lowest.



(a) (b)

Figure 5. Geochemical distribution of aqua regia extractable Ni in Europe (a) topsoil (Salminen *et al.*, 2005, p.360), and (b) agricultural soil (Reimann *et al.*, 2014, Fig. 11.39.5, p.329).

Let us consider the Finnish soil guideline value of Ni, which is set at 50 mg/kg, and determined by an aqua regia extraction (Tarvainen and Jarva, 2011). Nickel values in Finnish soil vary from <2 to 36 mg/kg, with a median of 6 mg/kg. Hence, the aforementioned guideline value of Ni is appropriate for soil in Finland. If we now look at the Hellenic Ni results, these vary from 2 to 1812 mg/kg, with a median of 72 mg/kg; the high Ni values are geogenic and are mainly due to the mafic-ultramafic (ophiolite) complexes, and their erosion products. Therefore, if someone attempts to use in Hellas the Finnish soil guideline value of Ni, these naturally elevated values will be considered hazardous. This is, of course, absurd, but it could have happened twelve years ago, during the Technical Working Group discussions, established under the European Commission's Thematic Strategy for Soil Protection in 2003-4 (Van-Camp, 2004), as some were considering of proposing a single soil guideline for the whole of Europe. Fortunately, the results of the FOREGS *'Geochemical Atlas of Europe'* (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006) averted this proposal, as there was sound evidence about the variable natural chemical variation in Europe.

The question posed is the following: *Are national guideline soil values valid for the whole country?* Taking into consideration the variable lithology of each country and, hence, the inherent variable chemical composition, the answer is emphatically *'No'*. Lax and Andersson (2011) in their discussion of geochemical baseline levels in Sweden, they finally suggest that local or site-specific guideline values in each urban area should be established. Similar conclusions have been reached in Hellas (Demetriades, 2011c), Finland (Tarvainen and Jarva, 2011) and the United Kingdom (Flight and Scheib, 2011; Ander *et al.*, 2013). Therefore, for the assessment of potential urban soil contamination, local guideline values for each determinand must be established. A good example in English of how soil guideline values (SGVs) are derived is given by the United Kingdom's Environmental Agency (EA, 2009), and should be consulted.

# 10. DATA CHECKING

## 10.1. Obligations of applied geochemist

At the present time, most commercial laboratories are accredited. It is very important to understand the accreditation process. It is a process of certifying that a laboratory is competent in the application of specific documented laboratory methods and standard operating procedures. Accreditation mandates to keep a record of all the procedures that a batch of samples undergoes in the laboratory. Hence, any errors can be located by backtracking. Accreditation requires that quality control and quality assurance programmes be in place for all aspects of the laboratory operations. All facilities and equipment are tightly scrutinised to assure adequacy for intended applications, and the laboratory must be participating in a proficiency analytical testing programme. To put it simply, an accredited laboratory has the right procedures in place to analyse samples. *It is, therefore, the professional responsibility of the applied geochemist to install his/her own external quality control procedures to ensure that results received are of a good standard and fit for the purposes of the project.*

Checking the quality and integrity of analytical results is the first obligation of the professional applied geochemist. It is important to remember that the analytical results of urban geochemical mapping projects must be legally defensible, because they are related to the quality of our living and working environments, as their quality affects our health. Therefore, the applied geochemist must not rely on the '*element concentration numbers*' given by the laboratory. He/she must ensure that these '*numbers*' are meaningful, and are substantiated by independent external quality control results. Consequently, the professional applied geochemist, upon receipt of results, must check them thoroughly to verify their quality.

To begin with, the applied geochemist studies the analytical report of the laboratory, before proceeding to check the quality of analytical data. Then proceeds in the arduous task of verification of the quality of the analytical data, using his/her external quality control results, and the laboratory internal quality control results. If the applied geochemist is not satisfied with the quality of analytical results, then the laboratory is obliged to reanalyse the problematic batch of samples, or even the whole sample suite. Verifying the quality of the generated analytical results is an important condition that should be included in the contract with the laboratory.

When satisfied with the quality of the analytical results, then and only then the applied geochemist should proceed to the second step, which is the estimation of geochemical, sampling and analytical variation, as well as measurement uncertainty, by using the robust statistical method proposed by Ramsey (1998; Lee and Ramsey, 2001; Lyn *et al.*, 2007, Boon, 2009; Demetriades, 2011b). These statistical results show the contribution that arises from the processes of primary sampling and chemical analysis. In urban geochemical mapping surveys, the estimation of measurement uncertainty of the analytical results of each determinand is of paramount importance, because the results must be legally defensible. It is surprising that courts ask to be informed about the measurement uncertainty. Some laboratories nowadays report measurement uncertainty, but it is prudent for the applied geochemist to estimate measurement uncertainty using his/her own independent quality control results.

As urban geochemical data can be used in legal cases where health related issues are involved, it is important to write a detailed quality control report. Hence, the statement that *the generated urban geochemical data must be legally defensible*. In fact, *the first and foremost obligation of the professional applied geochemist is the delivery of good quality geochemical data for multipurpose use*. Finally, when the applied geochemist is satisfied that the quality and integrity of survey results is up to the standard required for the investigation (fitness-for-purpose), only then should proceed with data processing and map plotting.

For more information, the quality control reports of the EuroGeoSurveys project '*Geochemical Mapping of Agricultural and Grazing land soil*' GEMAS project should be consulted (Reimann *et al.*, 2009, 2011a, 2012; Demetriades *et al.*, 2014), and the procedures discussed by Johnson (2011) and Demetriades (2011b).

## 10.2. Checking of raw analytical data

Johnson (2011) has written an excellent chapter "*Understanding the Quality of Chemical Data from the Urban Environment − Part 1: Quality Control Procedures*" in the textbook "*Mapping the Chemical Environment of Urban Areas*", which should be consulted. The procedure for checking the raw analytical data upon receipt from the laboratory has been abstracted and is given below (p.67-71):

"An initial assessment of data quality will consist of simple and obvious procedures that involve looking at the data, as they are received from the laboratory. This needs to be done in a systematic way, directly after the results are received, so any quality issues can be dealt with promptly. A series of questions should be addressed:

1. Are all the elements specified in the contract reported?
2. Is the number of samples reported the same as the number of samples submitted?
3. Are the results reported with the correct concentration units?
4. Have results outside detection limits and/or missing data been reported correctly?
5. Does the range of element values for each element look reasonable for the survey area?
6. Can any systematic trends (analytical drift or cross sample contamination) be identified in samples reported in the order they were analysed?

Answers to the above questions will give an immediate impression of the quality of the data, and it is at this stage where the most obvious problems with the data can be identified. At this point, something should also be done with respect to missing, semi-quantitative and unreliable data (see Johnson *et al.*, 2008), as such data will affect the data analysis process (see Reimann *et al.*, 2008, Chapter 2, p.13-28).

An archive of the original data file, as received from the laboratory, should always be saved before any changes are made."

A work analytical data file should be prepared. If the project samples have been given new random numbers, then the first task is to associate them with those in the original field database, where all control samples are characterised. For extracting all control sample analytical results, such as those of duplicates, replicates, project reference materials, and project blanks, it is recommended that the samples should be suitably coded in the original database that is submitted to the laboratory, *i.e.*:

- field duplicate samples: DUPA and DUPB;
- field replicate samples: REPA and REPB;
- project reference sample(s): REF1 and REF2 (in case more than one project reference sample has been prepared), and
- project blank sample: BLK

Upon preparing different files of the quality control data, the applied geochemist can proceed to check the quality of analytical results by a variety of statistical techniques, which are described below. Most of these descriptions have been abstracted from Johnson (2011) and Demetriades (2011b). Other open file quality control reports that should be consulted are by Reimann *et al.* (2009, 2011a, 2012).

### *10.2.1. Blank solution*

First check the analytical results of the blank solutions, which should all be below the laboratory's detection limit for all determined elements. The primary purpose of blank solutions is to trace sources of artificially introduced contamination in the laboratory. Therefore, if elevated values are observed for any element, then laboratory contamination is suspected, and it should be checked by reanalysis of the sample batches analysed during that particular date. Once satisfied with this particular visual test, you can proceed in the verification of the quality of the analytical results.

### *10.2.2. Control chart*

The following description is abstracted from Johnson (2011, p.67-71), except where indicated, and the Figure numbers changed according to the numerical order of this manual.

"The results for reference materials can be plotted on a control chart (also referred to as a Shewhart plot or X-Chart), which is a time sequenced graph with fixed defining limits (Miller and Miller, 2005). An example of such a chart is given in Figure 6. The x-axis shows the date of analysis or the laboratory batch, if batch numbers are assigned sequentially. The y-axis shows the element concentration and the accepted value (AV) for the reference material, a value calculated from previous repeated analyses of the reference material. The AV will depend on the method of chemical extraction and analysis - a partial method of extraction will yield a lower AV than a total extraction method. It is impossible to know what the 'true' value is, but the AV should be a good approximation of it. Defining limits are also plotted on the chart; in Figure 6, these are calculated as the AV ± 2 and 3 standard deviations (SD). The AV ± 2SD threshold is normally used as an alert to possible analytical problems, and exceeding the AV ± 3SD requires an explanation, and a possible indication that the batch of samples needs reanalysis, particularly if this is a trend, observed for more than one element. This process of plotting a control chart is something that is usually done by the laboratory itself with its own reference materials. Using the standard reference materials (SRMs) inserted in each sample batch, the geochemists can check accuracy for themselves by visual inspection of these plots. *Accuracy* is a measurement of how close to a 'true' or 'accepted' value a result is. A scattering of results about the AV line is to be expected, though a consistent trend to a higher or lower value would be referred to as *analytical bias*.

Control charts are invaluable in detecting analytical shifts that can occur over time, as, *for example*, after the installation of a new X-ray tube in X-ray fluorescence spectrometry (XRFS). This can be used to identify levelling factors, required to level chemical results collected over a long period of time (Johnson *et al.*, 2008)."

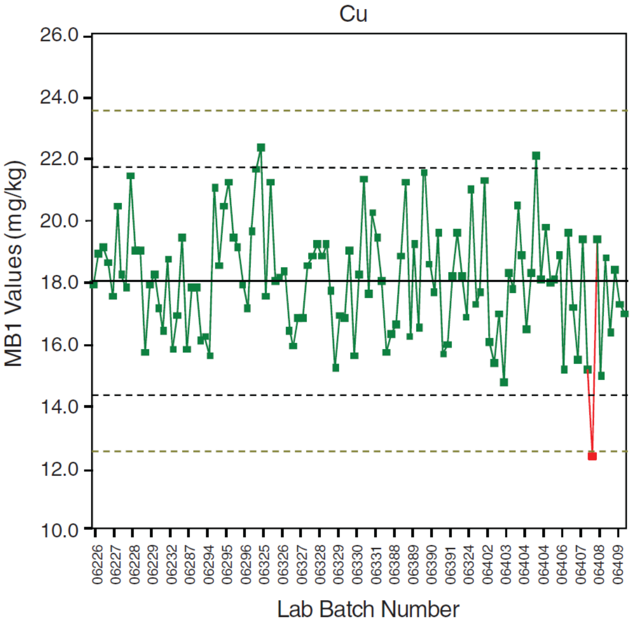


Figure 6. Example of a control chart plot using QI Analyst software for the BGS Moroccan secondary reference material MB1 (after Johnson *et al.*, 2001, Fig. 2.4, p.10). Central solid line represents accepted value (AV); outer dashed lines are at AV ± 2SD and AV ± 3SD. Symbol plotted in red represents a batch that fails QC criteria (Source: Johnson, 2011, Fig. 5.4, p.68).

The second example is a control chart of a project reference sample (Fig. 7), which does not show the expected random variation of the individual sub-sample results about the mean. It has many outliers, and even time trends. Such data cannot be accepted when the objective is to compare the analytical results among different cities. There are even problems between two batches of one city.

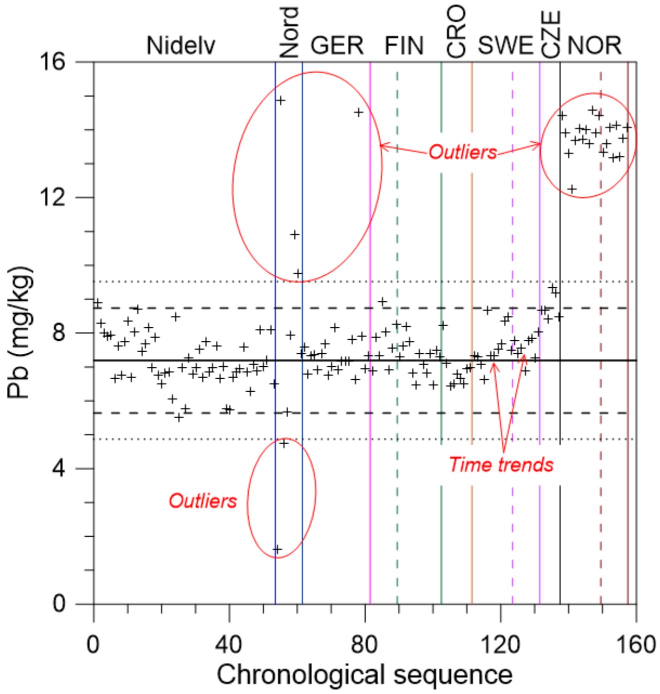


Figure 7. Example of a control chart plot using Golden Software's Grapher v.11 for a secondary reference sample used in the URGE I project. Central solid line represents the mean value; outer dashed lines are at mean ±2SD and stippled lines at mean ±3SD. The secondary reference sample was used in the urban geochemical mapping projects in different European cities, the results of which are separated by solid coloured lines. In some cases, the city samples were analysed in two different batches and at different time, and dashed lines separate the two batches.

### *10.2.3. Precision*

Analytical precision can be calculated by different statistical methods, which are described below. The underlying method is abstracted from Johnson (2011, p.68).

"*Precision* is a measurement of how closely the analytical results can be reproduced, and is independent of the true value (*i.e.*, results can all show close agreement, but they may be a long way from the accepted value, AV). A visual impression of precision can be gained from the control chart (Fig. 6), since data will plot in a much narrower band if the method has good precision. Similar visual impressions of precision can be given by the x-y plots (Fig. 8) and Thompson and Howarth plots (Figs. 9 & 10), which are described below. Overall precision at the 95% confidence level can be also expressed quantitatively, based on the mean (m) and standard deviation (SD) expressed as a percentage:

$$\text{Precision, P (\%)} = \frac{1.96 * \text{SD}}{\text{m}} * 100 \qquad (1)$$

$$\text{Coefficient of variation, CV (\%)} = \frac{\text{SD}}{\text{m}} * 100 \qquad (2)$$

Substituting CV in Equation 1:

$$P(\%) = 1.96 * CV \quad (3)$$

Precision varies with concentration (Thompson and Howarth, 1976; Fletcher, 1981, 1986; Demetriades, 2011b). At low concentrations, near to the detection limit precision is poor, and normally improves with increasing concentration."

### *10.2.4. Duplicate-Replicate x-y plot*

The following description is abstracted from Johnson (2011, p.69-70).

"A simple x-y plot of duplicate-replicate pair results for an element gives an immediate visual appreciation of the laboratory precision for that particular element (Fig. 8). If in these plots the cluster of points does not follow closely the line of gradient 1, but instead forms a dispersed scatter of points, then data for that element should either be rejected or used with caution. A random scatter would indicate that variability in the results is most likely generated in the laboratory (for replicate samples) or includes significant within-site variability (if seen in the duplicate plots). Figure 8 displays some example plots from the BGS G-BASE soil samples for East Midlands urban samples. The Cu plot shows that the sampling and analytical variances are low, so there is confidence that Cu results reflect actual between site variability. The Ni plot exhibits a number of outlying DUPA versus DUPB points, indicating that when a site is sampled for a second time there are occasional significant within-site variations, a feature displayed for the same duplicate pairs by other elements (*e.g.*, Fe, V, Cr and Co - not illustrated herein). This is to be expected in urban areas, where there is greater inhomogeneity in soil over short distances due to anthropogenic contamination."

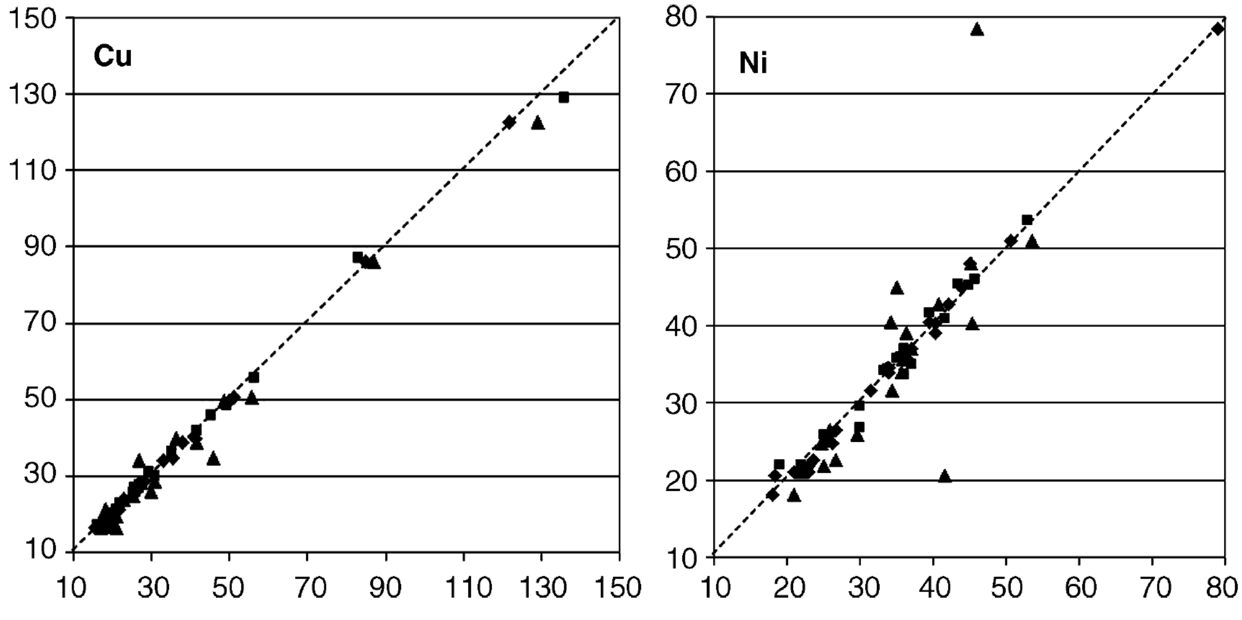


Figure 8. Duplicate-replicate plots for Cu and Ni for G-BASE urban soil (35-50 cm) from UK East Midlands. Axis units in mg/kg. Triangle = DUPA versus DUPB; Square= REPA versus DUPA; and Diamond = REPB versus DUPB (all x-axis versus y-axis) (Source: Johnson, 2011, Fig. 5.6, p.69).

"This method is only applicable if there is a sufficient number of duplicate-replicate pairs with a range of element concentrations that can produce a meaningful plot. When only single or a small number of duplicate-replicate pairs are available the Thompson-Howarth plots (Thompson and Howarth, 1976, 1978; Thompson, 1983; AMC, 2002) described below, can be used.

A quantitative measure of variability can be determined from the duplicate and replicate pairs for each element:

$$\text{Variability (Var)} = \frac{\sum(X_{DUPA}-X_{DUPB})^2}{n} \qquad (4)$$

where X is an element concentration and n the number of sample pairs. Standard deviation (SD) is estimated by:

$$\text{Standard deviation (SD)} = \sqrt{}\text{Var} \qquad (5)$$

Substituting SD in equation 2 with the terms of equation 5 gives the:

$$\text{Coefficient of Variation (CV) \%} = \frac{\sqrt{}\text{Var}}{m} * 100 \qquad (6)$$

Substituting CV in equation 6 with the terms of equation 3 gives the:

$$\text{Precision, P (\%)} = 1.96 * \frac{\sqrt{}\text{Var}}{m} * 100 \qquad (7)$$

Software for x-y plots is readily available and MS Excel or R routines provide adequate graphs (Reimann *et al.*, 2008). The G-BASE project uses the macro facility of MS Excel rapidly to plot duplicate-replicate graphs for some 50 elements simultaneously. Charts of interest can be subsequently extracted and formatted in a suitable manner for publication."

### *10.2.5. Practical detection limit and analytical precision*

The following description is abstracted from Demetriades (2011b, p.81-83).

"The practical detection limit and analytical precision can be estimated by using the method proposed by Howarth and Thompson (1976) and Thompson and Howarth (1976, 1978), with modifications made by Demetriades and Karamanos (2003; Demetriades, 2009) at a particular step of the procedure. Replicated analyses are performed on at least 50 (or better 55) randomly selected samples. The steps followed are:

1. Calculate the mean values of the 50 pairs [$(X_1+X_2)/2$]. According to Thompson and Howarth (1978), this mean value is an estimate of true concentration of an element for the particular analytical method used.

2. Calculate the absolute differences between each pair $|X_1-X_2|$. The absolute difference is an estimate of the standard deviation, $\sigma_c$, at that particular concentration. $|X_1-X_2|$ is normally distributed and relates to the parent population, with a standard deviation $\sigma_c$, such that:

$$\sigma_d = \sqrt{2 * \sigma_c} \qquad (8)$$

where $\sigma_d$ is the standard deviation of the difference $|X_1-X_2|$;

$$d = 1.128 * \sigma_c \qquad (9)$$

where d is the mean value for the difference; and

$$M_d = 0.954 * \sigma_c \qquad (10)$$

where $M_d$ is the median value for the difference. The statistic $\sigma_c$ can be obtained from each of these relationships, but the median ($M_d$) is the most convenient estimator, because it is (i) relatively little affected by wild or extreme values; (ii) readily estimated graphically, and (iii) corresponds very closely to $\sigma_c$ without further calculation (Fletcher, 1981).

3. Arrange list in increasing order of concentration means.

4. From the first 11 results, calculate the mean concentration (*Group mean*) and the median difference (*Group median*).

5. Repeat step 4 for each successive group of 11 samples, ignoring any remainder less than 11. *Hence, the reason for suggesting that replicated analyses should be performed on at least 55 randomly selected samples, which gives 5 groups of 11 samples.*

6. Calculate the linear regression of the median difference (*y-axis, dependent variable*) on the means (*x-axis, independent variable*). At this point, the first author has introduced a modification. In classical regression, ($Y = a + bX$), a linear relationship is quantified by fulfilling the following requirements of (a) dependency and (b) knowing one variable without error. Thompson and Howarth (1978) assumed that the group means are the independent variable or predictor ($X$), by which the group median difference ($Y$) is estimated. The question posed is the following: *which is really the dependent variable?* Since, both variables are derived from the grouping of the same analytical data set, they are subject to errors of the same order of magnitude. It is concluded, therefore, that the requirements of classical regression cannot be met. To overcome this situation Kermack and Haldane (1950) developed the reduced major axis line, which is the line of best-fit between a set of points (Fig. 9; Till, 1974). Essentially, is the best-fit line between the two regression lines of ($Y = a + bX$) and ($X = a + bY$). Hence, errors of estimation are minimised;

7. Obtain from the major axis regression line of the group median differences, $|X_1\text{-}X_2|$, on the group means, $(X_1+X_2)/2$, the intercept, $a$, and coefficient, $b$.

8. Multiply by 1.048 (*i.e.*, 1/0.954) the intercept, $a$, and coefficient, $b$, to obtain $\sigma_o$ and $k$, respectively; from the regression $\sigma_c = \sigma_o + kc$, so that the precision, $P_c$, is given by

$$P_c = \frac{1.96 * \sigma_o}{X_{ci}} + 1.96 * k \tag{11}$$

   which is the variation at approximately the two standard deviation (95%) confidence level.

9. Calculate the percentage precision $P_c\%$ by using the equation:

$$P_c\% = \left( \frac{1.96 * \sigma_o}{X_{ci}} + 1.96 * k \right) * 100 \tag{12}$$

$$= \frac{196 * \sigma_o}{X_{ci}} + 196 * k \tag{13}$$

   where $X_{ci}$ is the element concentration determined on individual samples. Hence, it is possible to estimate, by this method, the precision for every determination.

10. Calculate the detection limit. Detection limit is normally defined as the concentration that gives rise to a signal equal to twice the standard deviation of blank fluctuations, *i.e.*, at a value of $P_c = 100\%$ and $X_{ci} = 1.96\sigma_o$. At concentrations higher than the detection limit, precision falls asymptotically towards the value of 1.96k as defined in the

expression $P_c = (1.96\sigma_o / X_{ci}) + 1.96k$ (Equation 11). For further information, and the implications involved in the estimation of these quality control parameters, Thompson and Howarth (1976) should be consulted."

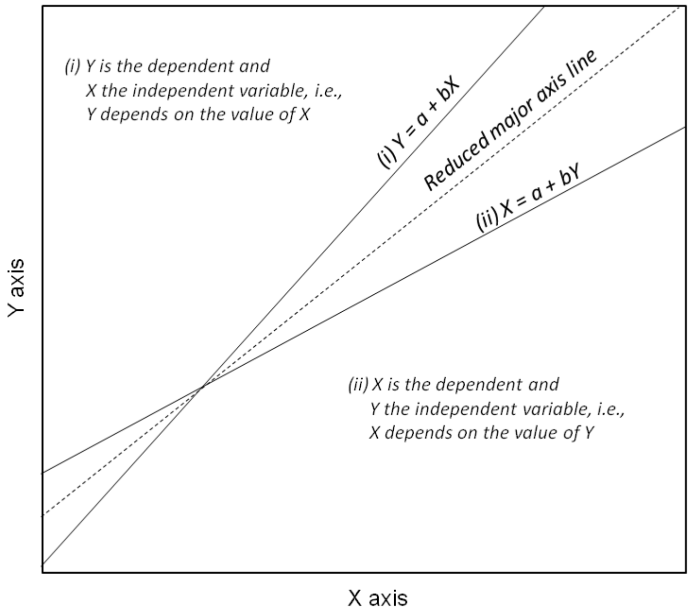


Figure 9. The reduced major axis line is the best fit line of Y on X and X on Y (Source: Demetriades, 2011b, Fig. 6.2, p.82).

"It is important to understand the asymptotic nature of precision, and that it is wrong to quote a single value for precision, *i.e.*, at concentrations higher than the detection limit, precision falls asymptotically towards the value of 1.962k or 196k in the above expressions (refer to Fletcher, 1981, Figure 2-5, p.32; see Fig. 10 below). On the geochemical distribution maps the relative precision equation should be given, so that the reader can estimate precision at any specific concentration.

Practical detection limits determined by this method are subject to the variation of element concentrations in the selected random samples. In case the samples have a good distribution of element concentrations, approaching a normal Gaussian distribution, the practical detection limits of these elements are either the same or very close to instrument detection limits. Elements that have a non-Gaussian distribution, their practical detection limits are normally very different from those quoted by the analysts.

Ideally, the samples selected for replicate measurements should include very low, low, moderate, high and very high concentrations of the determinands studied. However, this selection can only be made upon completion of the routine site investigation, and evaluation of analytical results. Therefore, the duplicate samples are selected in a completely random manner across the project area, and in such a case, the most dominant features are replicated.

For the estimation of precision by the above method, an Excel Workbook is available from the first author.

Further, Lee and Ramsey (2001) modelled measurement uncertainty as a function of concentration and they estimate analytical precision and detection limit, among other things."

The asymptotic nature of precision is shown in Figure 10, using the Be duplicate-replicate results from the aqua regia GEMAS grazing land soil data set. In this case, the laboratory provided uncensored data, and even sub-zero (negative) values. Using the procedure described above, two different estimations were made, with and without the negative values. The precision in both cases falls asymptotically towards the value of 1.962k or 196k in the above expressions. Beyond this limit, the curve reaches a plateau, and this is considered to be the overall precision.

The practical detection limit (PDL), as already mentioned above, is defined as the concentration that gives rise to a signal equal to twice the standard deviation of blank fluctuations, *i.e.*, at a value of $P_c = 100\%$ and $X_{ci} = 1.96\sigma_o$. On the graph, it is the tangent to the curve leading to $P_c = 100\%$. As expected, there are differences in the estimation, even by removing a single pair of negative values:-

(a) PDL = 0.072 mg Be/kg, and an overall precision of 18.4% at the 95% confidence level, and a precision equation:

$$P_c\,\% = \frac{5.858}{X_{ci}} + 18.385 \qquad (14)$$

(b) PDL = 0.046 mg Be/kg, and an overall precision of 24.5% at the 95% confidence level, and a precision equation:

$$P_c\,\% = \frac{3.439}{X_{ci}} + 24.543 \qquad (15)$$

where $X_{ci}$ in both cases is anyone concentration of Be that one is interested to know its precision at the 95% confidence level. *For example*, a Be concentration of 50 mg/kg has a precision of 18.5% and 24.6% for (a) and (b), respectively.

The laboratory's lower detection limit is 0.1 mg Be/kg, which is higher than the values estimated for the practical detection limit, i.e., 0.072 and 0.046 mg Be/kg (see Fig. 10). For elements, such as Be, where most of the values are very low, and near to the method's detection limit, it is an advantage to estimate the practical detection limit, using actual project data. Otherwise, if the laboratory provided censored analytical data at the laboratory's detection limit of 0.1 mg Be/kg, all values below this limit would have been given half the value of the detection limit, *i.e.*, 0.05 mg Be/kg. Thus, losing many actual values.

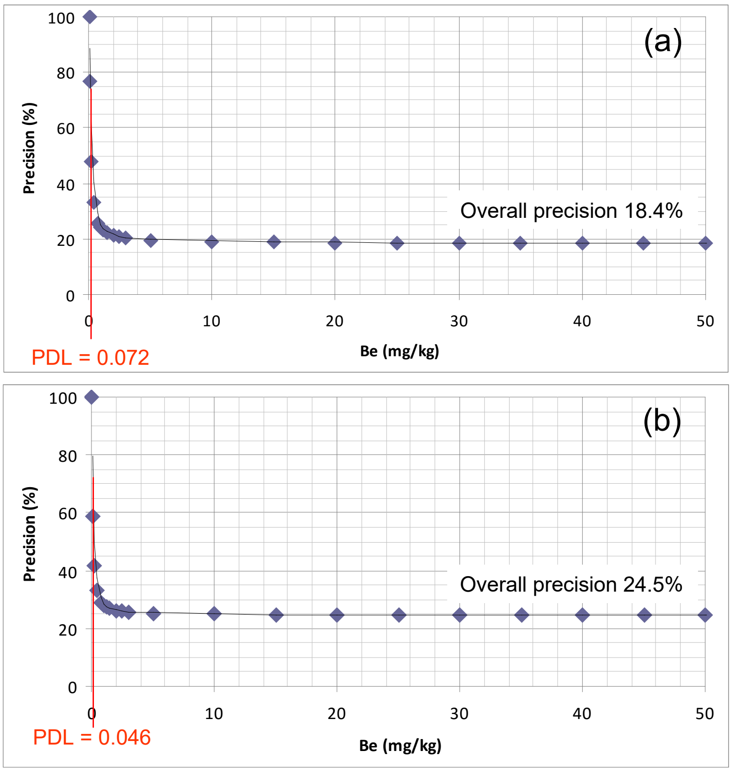


Figure 10. Variation of precision with concentration. Two examples of Be from the aqua regia GEMAS grazing land soil data set (Reimann *et al.*, 2014) plotted with Microsoft® Excel: (a) with negative values (n=94 pairs), and (b) with negative values removed (n=93 pairs). The former gives an overall precision of 18.4% at the 95% confidence level, and the latter an overall precision of 24.5% at concentrations beyond 50 mg Be/kg.

### *10.2.6. Cumulative probability plot*

The following description is abstracted from Johnson (2011, p.68-69).

"Replacing the below detection limit (DL) value with an arbitrary value (usually half the cited detection limit) will introduce a distortion in the data distribution at low concentrations, and this will have an impact on both descriptive and multivariate statistics. Analysts tend to be conservative with their DLs and, furthermore, many results reported as below detection have recordable useful values that show structure in the data distribution below the laboratory's cited DL. This is illustrated in Figure 11 by a cumulative probability plot, where the flattening of the graph indicates a more realistic limit of detection, which is much lower than that cited by the analyst. Cumulative probability plots have long been used by geochemists to partition results into a combination of different populations (Tennant and White, 1959; Lepeltier, 1969; Sinclair, 1976, 1983, 1986), and their usefulness in establishing more realistic detection limits is shown herein. A procedure for estimating practical detection limits for chemical elements determined on project samples is described by Thompson and Howarth (1978).

Reporting of values below the cited DL, as a single value should be discouraged (AMC, 2001) in favour of delivering the values as measured by the analytical instrument. Users of the data can then better utilise values at the lower end of the data distribution without degrading the quality of the data. A single below detection value applied to many samples will distort statistically estimated parameters that may be significant in determining at which side of a guideline value a result will fall."

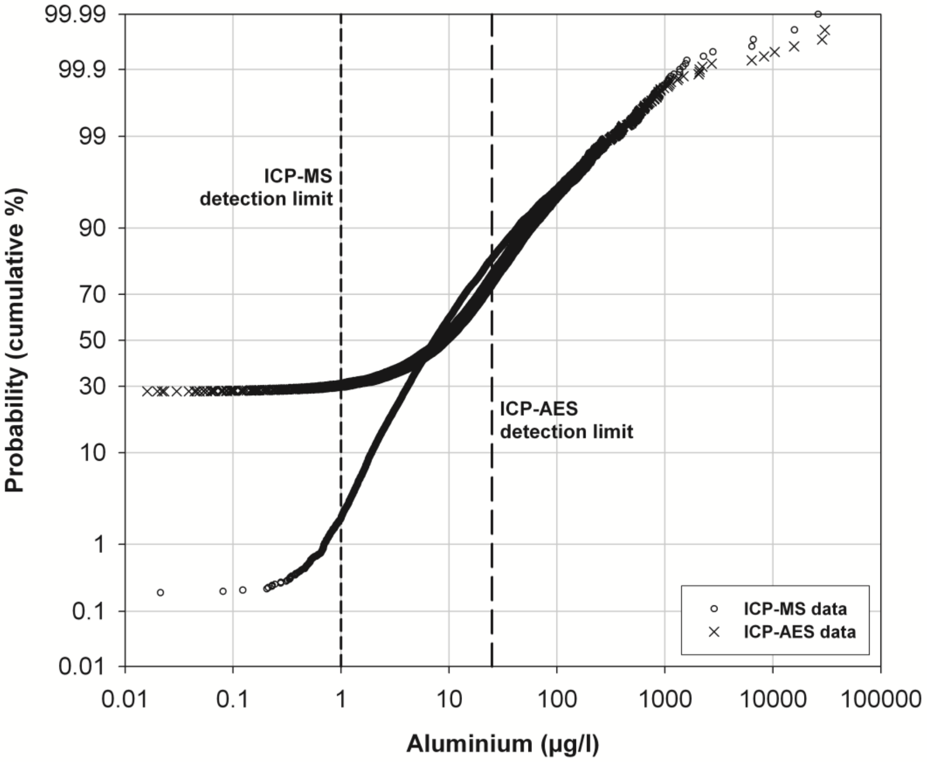


Figure 11. Cumulative probability plot indicating true detection limits for water samples determined by two different analytical methods (after Johnson *et al.*, 2008, Fig. 5.5, p.103). This was plotted using SigmaPlot v.10 software by E.L. Ander (BGS). (Source: Johnson, 2011, Fig. 5.5, p.69).

Another example of cumulative frequency is displayed in Figure 12, using the uncensored Be and Bi analytical results from the EuroGeoSurveys project of Geochemical Mapping of Agricultural and grazing land soil of Europe (GEMAS). It is quite evident that the detection limit of Be and Bi is lower than that given by the laboratory.

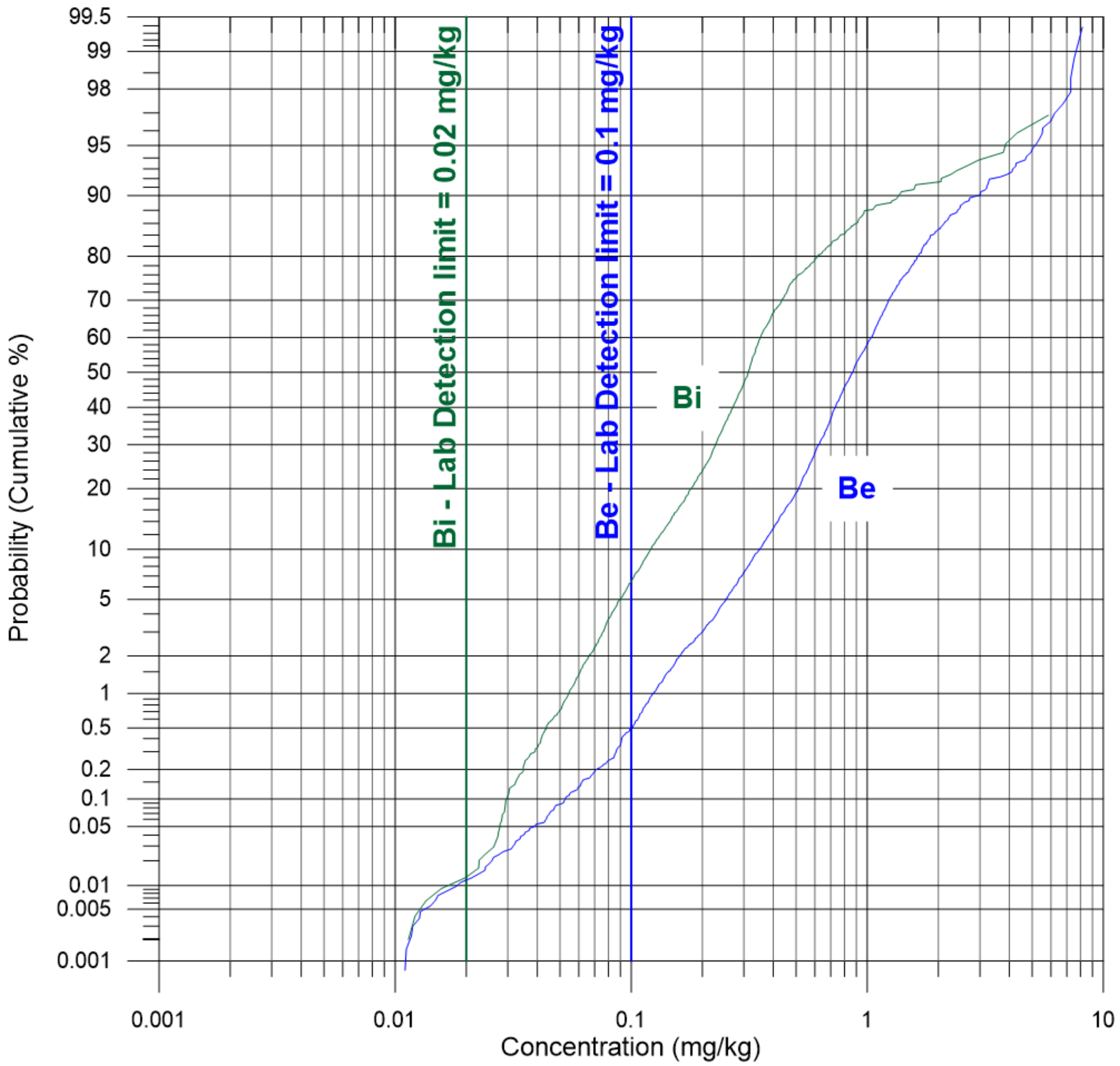


Figure 12. Cumulative probability plot indicating true detection limits of Be and Bi for the grazing land soil samples of the EuroGeoSurveys project of Geochemical Mapping of Agricultural and grazing land Soil (GEMAS) of Europe, using uncensored data (Reimann *et al.*, 2014). This was plotted using Golden Software's Grapher v.11.

### *10.2.7. Thompson-Howarth plot*

The following description is abstracted from Johnson (2011, p.70).

"Thompson and Howarth (1978) and Thompson (1983) describe a method of estimating analytical precision using duplicate-replicate sample pairs. This is a graphical method, which can be used even for a single replicate pair that gives an immediate visual impression of the precision of the analytical method (see Fig. 13). The absolute difference between the two replicate analyses is plotted against the mean of the replicate results. On the graph, the fit-for-purpose criteria are defined by the detection limit (herein 0.2 µg/L As) and 99, 90, and 50 percentile lines. In Figure 13, precision is generally good with only a small percentage of duplicate-replicate pairs plotting above the 90th percentile line. The example graph shown here was plotted using SigmaPlot software. Reimann *et al.* (2008) give examples of Thompson-Howarth plots generated using R."

The second Thompson and Howarth plot (Fig. 14) is a variant using normal linear axes. In this case, the 10% precision at the 95% confidence level is generally good at the 99th percentile, as only 4 duplicate-replicate pairs plot above the 99th percentile line.

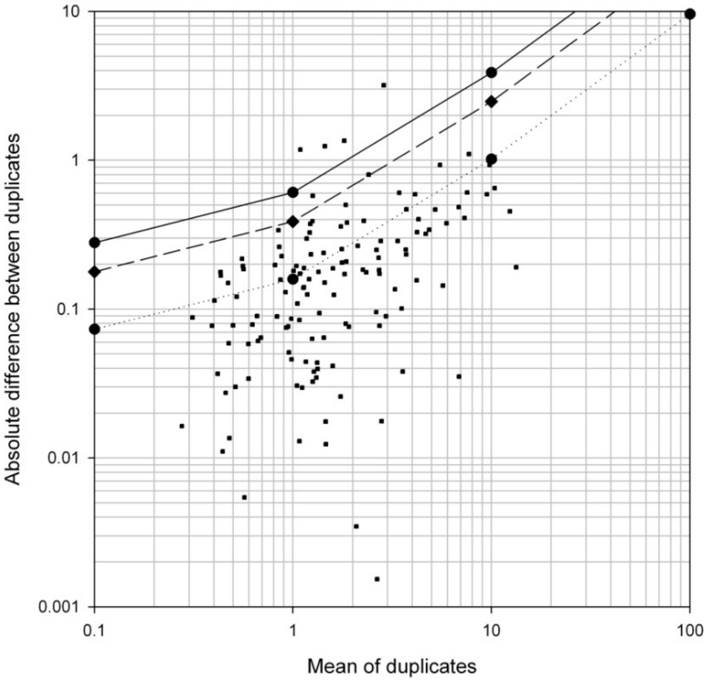
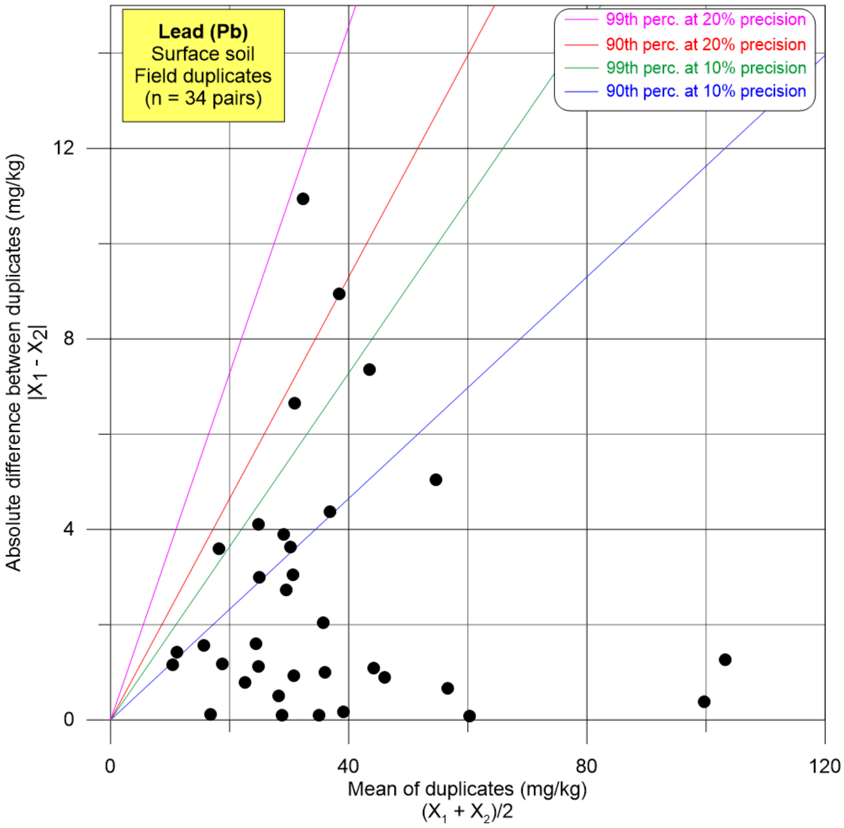


Figure 13. A logarithmic scale Thompson-Howarth plot used for visualising analytical precision. This is a plot of G-BASE stream water duplicates for As with probabilities calculated at 0.2 µg/l detection limit using SigmaPlot v.10 software by E.L. Ander (BGS). See AMC (2002) for rationale behind the Thompson-Howarth plot. Solid, dashed and dotted lines represent 99, 90, and 50 per cent confidence levels (Source: Johnson, 2011, Fig. 5.7, p.71).



Precision control chart for P = +/-10% and 20% at the 95% confidence level

Control lines at the 90th and 99th percentiles

Figure 14. A normal linear scale Thompson and Howarth plot used for visualising the precision of Pb. This is a plot from the results of the Hellenic Institute of Geology and Mineral Exploration's urban soil geochemistry project at Thrakomakædónæs, a suburb of Athens. It was plotted with Golden Software's Grapher v.11. Colour lines represent 10% and 20% precision at the 95% confidence level, and at the 90th and 99th percentiles.

### *10.2.8. Robust ANOVA and estimation of uncertainty due to sampling and analysis*

Geochemical, sampling and analytical variance is normally estimated by classical analysis of variance (ANOVA), which is a statistical method strongly affected by a few outlying values, and also is based on three assumptions, *i.e.*, (i) the variances should be independent, (ii) each level of variance should be homogenous, meaning that it should not vary systematically within one level, and (iii) the distribution of errors within each level of variance should be approximately Gaussian (Ramsey, 1998). These problems are largely overcome by using robust analysis of variance (RANOVA), as already mentioned.

The RANOVA method proposed by Ramsey (1998), apart from estimating the geochemical, sampling and analytical variance, it calculates measurement uncertainty, which is an essentially parameter for the qualification of the urban geochemical data set, and its legal defensibility.

The underlying description was abstracted from Demetriades (2011b, p.79-81).

"For the estimation of measurement, uncertainty two different methods have been proposed, *i.e.*, (a) the 'bottom up' (or 'modelling', 'theoretical', 'predictive'), and (b) the 'top down' (or 'empirical', 'experimental', 'retrospective') approaches (Ramsey, 1998; Ramsey and Ellison, 2007).

The '*bottom-up*' approach is comparatively simple, practical, and cost-effective for a project, because the random error from each individual component of a method is quantified separately as a standard deviation $s$. Then the overall uncertainty is estimated by summing up the individual errors by their variances $s^2$ (Ramsey, 1998; Ellison *et al.*, 2000; Ellison and Williams, 2012). Its limitation is the requirement to identify all sources of uncertainty. However, it is relatively easy to consider the obvious sources of error, which are explicit parts of a method, *e.g.*, weighing, volumetric additions.

The '*top-down*' approach is more difficult to use, comparatively impractical and somewhat costly for a project, because for the estimation of the total uncertainty of a measurement inter-laboratory trials must be carried out, such as proficiency tests or collaborative trials (Argyraki *et al.*, 1995). Thus, in this case many laboratories (n>8) are involved in the analysis of the same sample, by using exactly the same analytical method. The scatter of measurements reported by all laboratories is then used to derive an overall estimate of uncertainty.

Whichever approach is followed, the general objective is to obtain a sufficiently reliable estimate of the overall uncertainty of measurement. It does not require all the individual sources of uncertainty to be quantified, but only the combined effect to be assessed. If, however, the overall level of uncertainty is found to be unacceptable, according to the requirements of the project, *i.e.*, the measurements are not 'fit-for-purpose', and then actions should be taken to reduce the uncertainty. Alternatively, the estimated measurement uncertainty may be unnecessarily small, in such a case there may be justification for increasing the analytical uncertainty, and thereby decreasing the cost of analysis.

As pointed out by Ramsey (1998) two of the component variances can be classed as *measurement uncertainty*, and these are the *sampling* $s^2_{samp}$ and *analytical variance* $s^2_{anal}$. The third component is the between location variance, due to real variation of the determinand across the investigated site. This is called the *geochemical variance* $s^2_{geoch}$, in this particular case of a geochemical investigation.

*Sampling uncertainty*, or *within-location variance*, is partially due to small scale geochemical variation within the location, and represents the uncertainty in all samples that can be collected from that particular 'location', as specified by the investigation, *e.g.*, one or two metre radius, depending, however, on the distance of grid nodes.

All three variances of a particular determinand in a material, such as soil, can be summed up to give the *total variance* $s^2_{total}$ of a survey. This figure would be estimated when calculating the variance of all analyses, and can be expressed by:

$$s^2_{total} = s^2_{geoch} + s^2_{samp} + s^2_{anal} \tag{16}$$

Ramsey *et al.* (1992) proposed initially the term *technical variance* $s^2_{tech}$ for the sum of the *sampling* $s^2_{samp}$ and *analytical* $s^2_{anal}$ *variance* of a particular determinand in a material. It has been replaced since then by the term *measurement variance* $s^2_{meas}$ (Ramsey and Argyraki, 1997; Ramsey, 1998), *i.e.*,

$$s^2_{meas} = s^2_{samp} + s^2_{anal} \tag{17}$$

Hence, the *total variance* ($s^2_{total}$) of a particular determinand in a material becomes:

$$s^2_{total} = s^2_{geoch} + s^2_{meas} \tag{18}$$

The *measurement uncertainty u* can be estimated using this *bottom-up* approach, from the combination of sampling and analytical variance:

$$\textit{measurement uncertainty, } u = s_{meas} = \sqrt{(s^2_{samp} + s^2_{anal})} \tag{19}$$

It is a normal statistical procedure to increase the confidence interval of the uncertainty by multiplying by a *coverage factor k* 1.96 (for the 95% confidence level) to give the *expanded or extended uncertainty U*:

$$\textit{expanded measurement uncertainty, } U = k * u = 1.96 * s_{meas} \tag{20}$$

Ramsey (1998) uses 2 as the coverage factor, but this represents a confidence level at 95.44%. Since, computers perform nowadays all calculations, it is recommended to use the coverage factor of 1.96, representing the 95% confidence level.

The *expanded or extended uncertainty U* expressed as a percentage in relation to the mean concentration of a particular determinand gives the *relative measurement uncertainty U%*:

$$\textit{relative measurement uncertainty, } U\% = \frac{196 * s_{meas}}{m} \tag{21}$$

where:

$m$ is the estimated mean concentration of a determinand at the investigated site.

The calculated value of the uncertainty is applied to measurements on single samples taken during the investigation. According to Ramsey (1998), if $n$ multiple samples are collected at any individual location within the investigated site, the uncertainty on the average for that location is the value given by Equation 21 divided by $\sqrt{n}$; this is equal to the standard error on the mean value ($s_{total} / \sqrt{n}$); *for example*, the estimated relative uncertainty at a location, where four measurements (1A, 1B, 2A, 2B) have been made, would be half ($1 / \sqrt{4}$) of the value as given by equation (21). However, after due consideration, Ramsey and Ellison (2007) have proposed that the uncertainty at a duplicated site should not be divided by the square root of 4 ($\sqrt{4}$), but by the square root of 2 ($\sqrt{2} = 1.414$), because the sampling uncertainty is the limiting factor. Therefore, it is duplicated field sampling (x2) that reduces the confidence interval on the uncertainty estimate. Thus, the value as given by Equation 21 should be divided by the square root of 2 ($\sqrt{2}$), as is shown below:

$$\textit{relative expanded measurement uncertainty, } U\% = \left(\frac{196 * s_{meas}}{m}\right) \div \sqrt{2} \tag{22}$$

The *upper limit of relative expanded measurement uncertainty U%* at the 95% confidence level is estimated by the equation:

$$C + U = C \left( 1 + \frac{U\%}{100} \right) \tag{23}$$

and the *lower limit of relative expanded measurement uncertainty* is calculated by the equation:

$$C - U = C \left( 1 - \frac{U\%}{100} \right) \tag{24}$$

where:

$C$ = the concentration of the determinand in the sample medium

$U$ = the expanded measurement uncertainty at the 95% confidence level

$U\%$ = the relative expanded measurement uncertainty at the 95% confidence level.

The above Equations 23 and 24 may be refined if the *analytical bias* $B_a$ is estimated by the use of certified reference samples (Ramsey and Argyraki, 1997; Ramsey, 1998), which is a procedure employed by conventional accredited laboratories. According to Ramsey and Argyraki (1997), the uncertainty interval of any concentration $C$ becomes asymmetric. The *upper limit of expanded measurement uncertainty U* at the 95% confidence level is estimated by:

$$C + U = C \left( 1 + \frac{U\%}{100} \right) \left( 1 - \frac{B_a}{100} \right) \tag{25}$$

and the lower limit by:

$$C - U = C \left( 1 - \frac{U\%}{100} \right) \left( 1 - \frac{B_a}{100} \right) \tag{26}$$

where:

$C$ = the concentration of the determinand in the sample medium

$U$ = the expanded measurement uncertainty at the 95% confidence level

$U\%$ = the relative expanded measurement uncertainty at the 95% confidence level

$B_a$ = the analytical bias estimated as a percentage by regression

Ramsey and Argyraki (1997) point out that the interpretation of *relative uncertainty* in the measurements of a particular determinand in soil assumes that it does not vary with concentration. Such a case has been observed in determinands, the analytical precision of which is considerably higher than the detection limit (Thompson and Howarth, 1976, 1978). Since the *relative analytical precision* $P_c\%$ varies according to the concentration of the determinand, the above equations 23 and 24 may be improved, by incorporating precision, estimated on survey samples (Ramsey 1997, 1998; Ramsey and Argyraki, 1997). The *upper limit of expanded measurement uncertainty U* at the 95% confidence level can be calculated, therefore, by:

$$C + U = C \left( 1 + \frac{U\%}{100} \right) \left( 1 - \frac{P_c\%}{100} \right) \tag{27}$$

and the lower limit of expanded measurement uncertainty is calculated by the equation:

$$C - U = C \left( 1 - \frac{U\%}{100} \right) \left( 1 - \frac{P_c\%}{100} \right) \tag{28}$$

where:

$C$ = the concentration of the determinand in the sample medium

$U$ = the expanded measurement uncertainty at the 95% confidence level

$U\%$ = the relative expanded measurement uncertainty at the 95% confidence level

$P_c\%$ = the analytical precision at the 95% confidence level

The practical detection limit, and analytical precision, can easily be estimated using the method described above" (see *Section §10.2.5*).

# 11. PRESENTATION OF URBAN GEOCHEMICAL MAPPING RESULTS

## 11.1. Graphical plots

There are many univariate plots that can be used to display the statistical distribution of determinand values (Fig. 15), *e.g.*, histogram, frequency plot, cumulative frequency plot, log-probability plot, quantile plot, boxplot, notched box-and-whisker plot, one-dimensional scatterplot, *etc.* Good statistical books to consult are by Till (1974) and Reimann *et al.* (2008), as well chapters in other books by Reimann *et al.* (2011b) and Filzmoser *et al.* (2014).

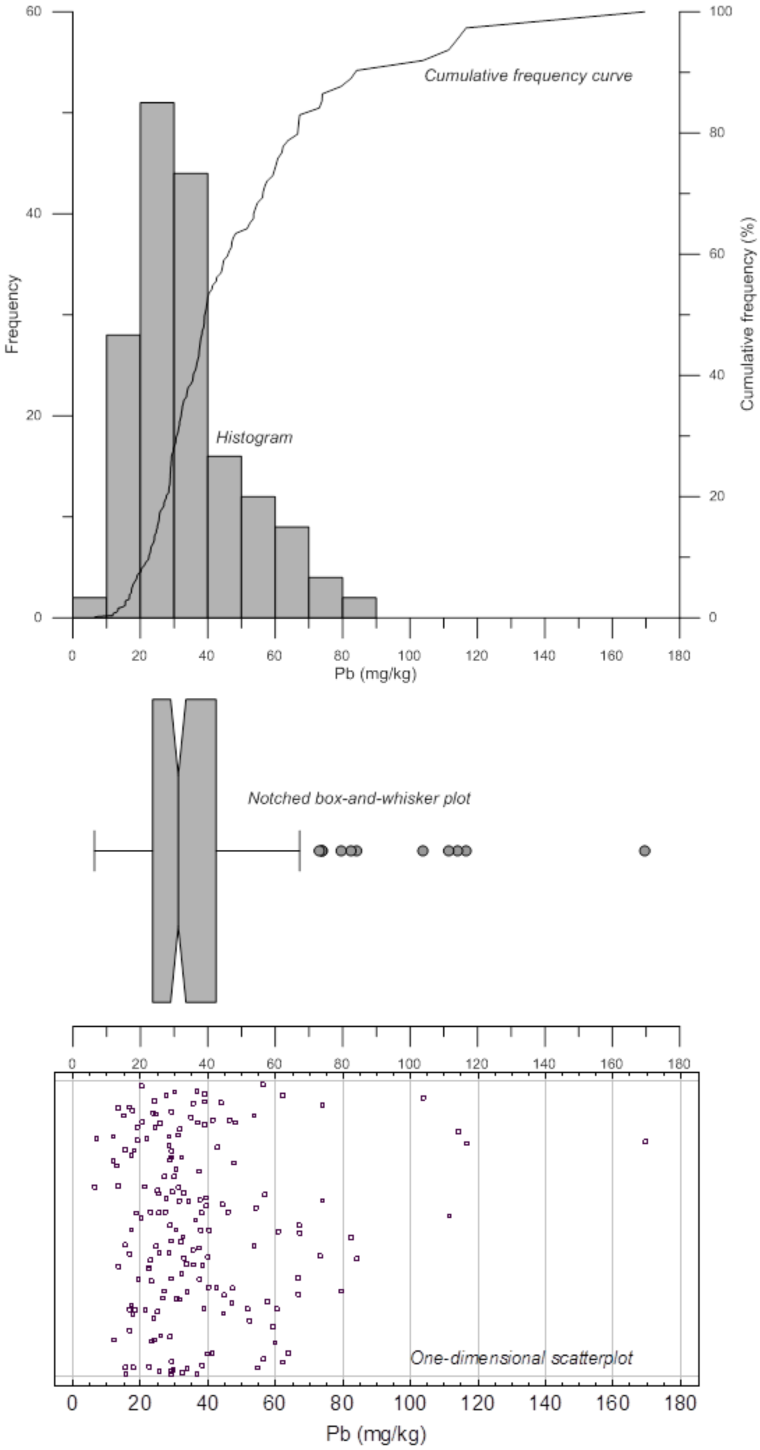


Figure 15. A composite univariate plot of the statistical distribution of Pb, Thrakomakædónæs, Athens, Hellas (N=173): (a) cumulative frequency curve, (b) histogram, (c) notched box-and-whisker plot and (d) one-dimensional scatterplot. The graphical plots (a) to (c) were plotted with Golden Software's Grapher v.11, and (d) with Statpoint's Statgraphics Centurion v.15 (Source of data: Vassialiades, 2008; Tassiou, 2009).

Figure 15 shows a number of univariate plots. The different plots assist in the study of the statistical distribution of a determinand.

The *histogram* groups the data into classes and gives the frequency of each class as the bar height, the spread of the data, skewness, presence of multiple modes, and occurrence of outliners.

The *cumulative frequency curve* is useful in distinguishing different populations, and the percentage of samples above or below a specific value.

The *boxplot*, and especially the *notched box-and-whisker plot* is a powerful graphical tool that provides information about the spread of the data (minimum and maximum values), median, 95% confidence interval on the median, mean, 25th and 75th percentiles, and outliers (Kürzl, 1988).

The *one-dimensional scatterplot* provides a quick visual representation of the spread of data values, and identifies outliers.

### 11.2. Map plotting

There is a tendency to present urban geochemical data as interpolated colour gridded maps (Albanese *et al.*, 2011; Birke *et al.*, 2011a, b; Ďuriš, 2011; Gregorauskienė *et al.*, 2011; Li, 2011; Locutura and Bel-Ian, 2011; Šajn *et al.*, 2011; Bavec *et al.*, 2015). Reimann *et al.* (2011b) caution that colours have different meanings in different cultures, and some individuals are blind to certain colours. Flight and Scheib (2011; see Fig. 16) and Smith *et al.* (2011; see Fig. 17) refer to the problems associated with over-interpolating in urban areas, something that can blight property prices and cause local inhabitants much anxiety, and may even lead to legal actions for health-related damages. The preference in urban areas should be to use point symbol maps, *e.g.*, graduated symbols (growing or variable-size dots), and exploratory data analysis (EDA) symbols. Therefore, if the urban geochemical survey does not have information down to the individual property level (parcel), which means a high sample density survey, it is prudent not to plot interpolated colour gridded maps. In the case of wide-space sampling projects, with a density of 1 sample/4 km$^2$, it is strongly recommended to use point symbol maps.

If, however, wide-space geochemical data are going to be presented as coloured surface maps, it is recommended to superimpose a layer with graduated point symbols (Fig. 18). This particular Pb distribution map from the Lavrion urban area (Hellas) is selected also to show the problems of extrapolating the colour surface into unsampled space (Demetriades, 1999; Demetriades, 2011a). The optimum spatial statistical methodology for estimating values in unsampled space is geostatistics (Matheron, 1963; Marshall, 1972; Journel and Huijbreghts, 1978; Rendu, 1978; Clark, 1979; Isaaks and Srivastava, 1990; Oliver and Webster, 1990; Clark and Harper, 2007a, 2007b, 2008). Kriging is the name given to the technique used in geostatistics to estimate values in unsampled space. It computes the Best Linear Unbiased Estimator (BLUE) in such a way that it matches the correct expected value of the population (unbiased), and minimises the kriging variance of the determinand concentrations (Best estimate). It is a cumbersome method, because it involves a number of steps, starting from the variogram, which should be plotted in different directions in order to understand the spatial structure of the data (Fig. 19), and from which the necessary parameters to validate the interpolation are extracted. To obtain the optimum kriging model for a determinand, it could take a whole day. Geostatistical routines that are included in all-purpose software, such as ESRI's ArcGIS (http://www.esri.com/software/arcgis/), should be used with the utmost care. Geostatitistics is a technique that can be used, therefore, only by people that have a good working knowledge of the principles, and steps that should be followed.

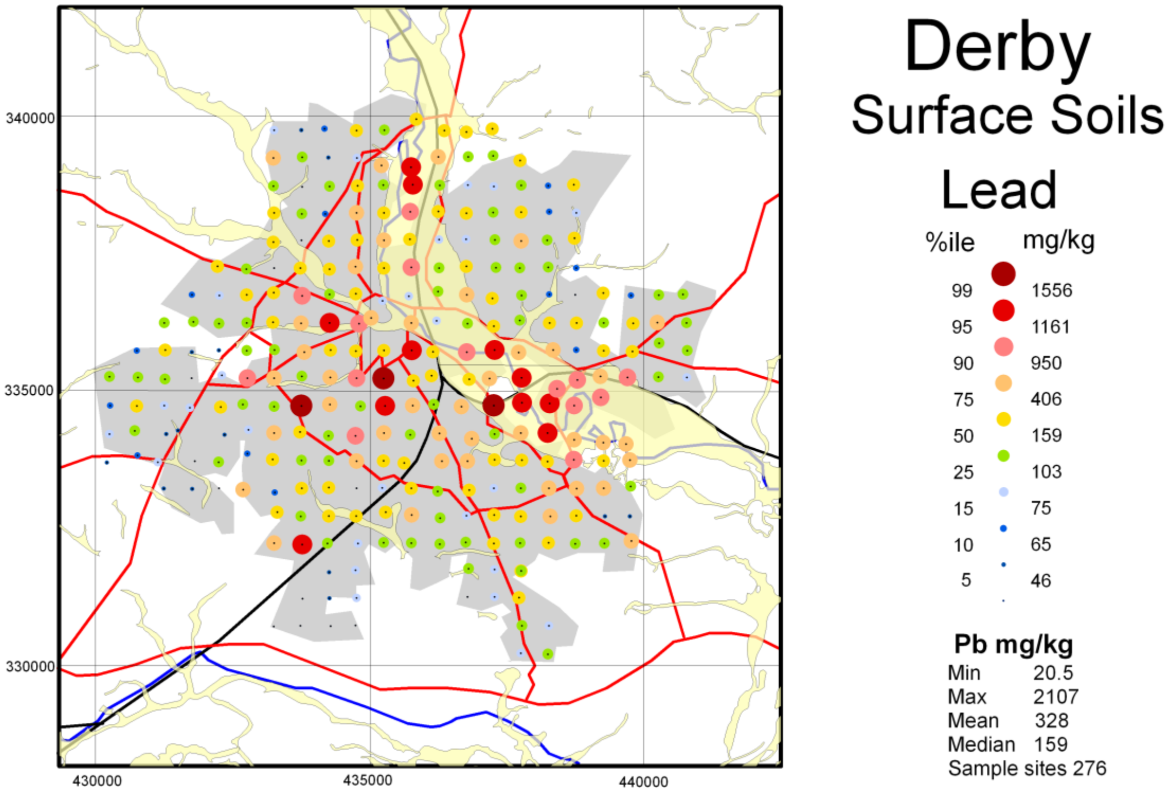


Figure 16. Graduated coloured symbol map of total Pb in the < 2 mm surface soil fraction collected from 5-20 cm, Derby, United Kingdom. Yellow shaded area represents alluvium (Source: Flight and Scheib, 2011, Fig. 13.7, p.200).

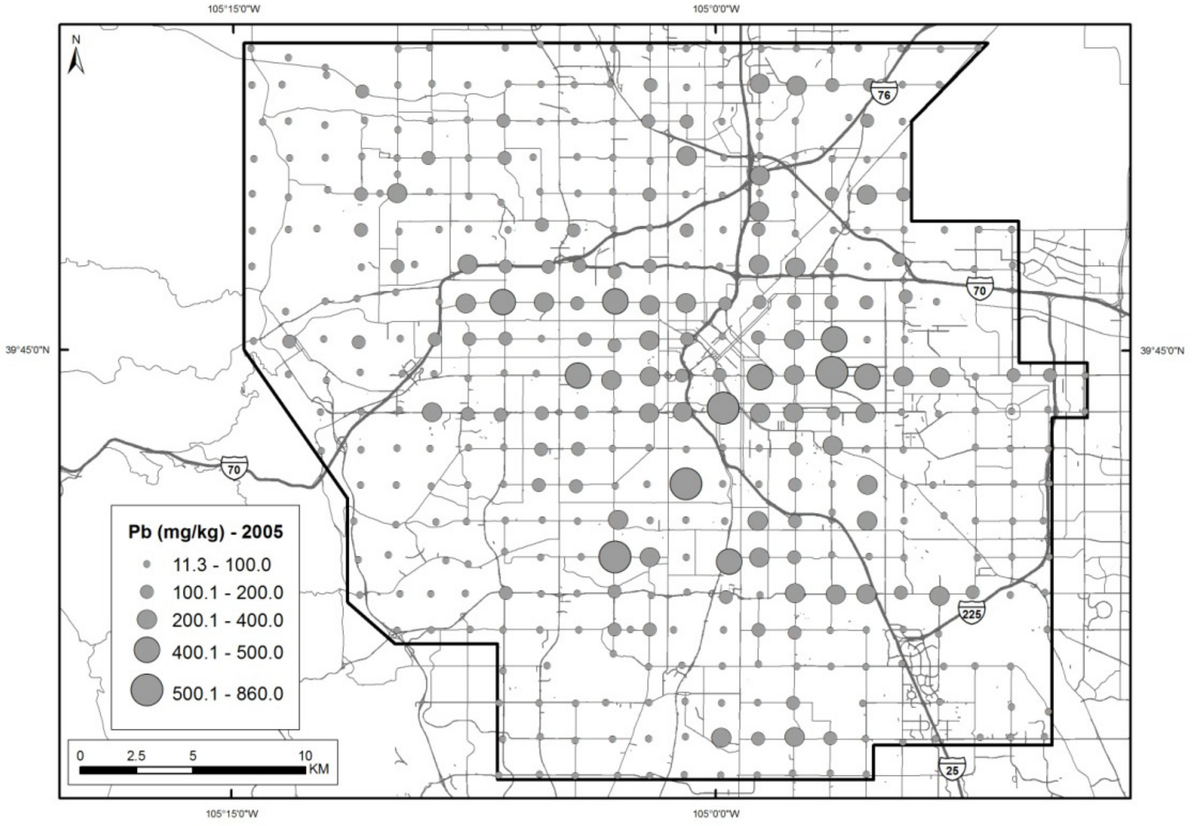


Figure 17. Graduated symbol map of Pb distribution in the <0.250 mm soil fraction collected from 0-15 cm depth (N = 493), Denver area, United States of America (Source: Smith *et al.*, 2011, Fig. 30.5 (b), p.531).

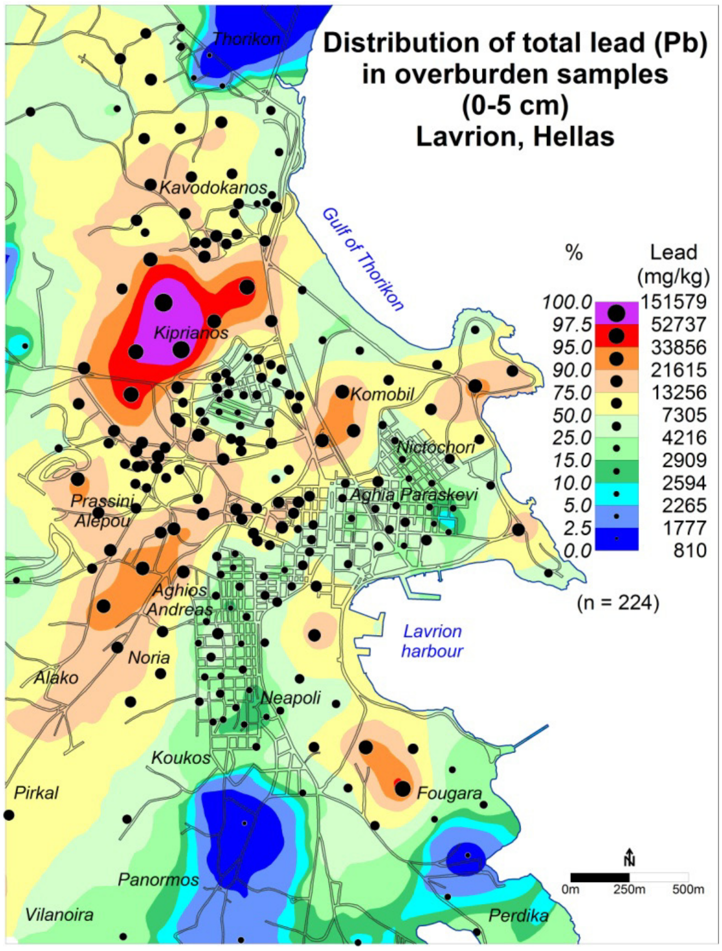
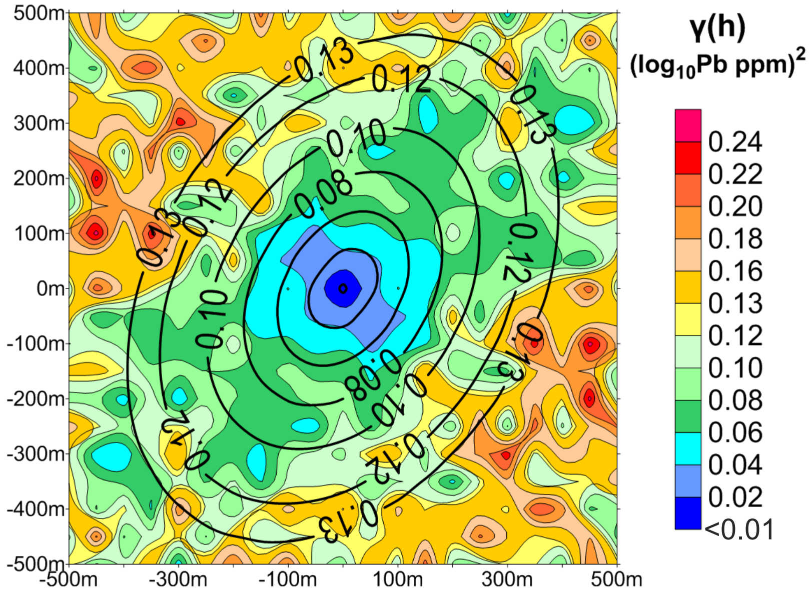


Figure 18. Geochemical distribution of total Pb in the <0.177 mm fraction of overburden samples collected from 0-5 cm depth, Lavrion urban and suburban area, Hellas, using a combined colour gridded map with superimposed graduated symbols (Source: Demetriades, 2011a, Fig. 25.8, p.444). The map was plotted with Golden Software's Surfer v.12.



Range of influence - Major axis: 630 m, 032°
- Minor axis: 435 m, 122°

Figure 19. Experimental and modelled variogram surface of $\log_{10}$ Pb in overburden samples (0-5 cm), Lavrion urban area, Hellas (Source: Demetriades, 1999, Map 3.4, p.3.4). The major trend is NE-SW, but there appears to be minor geochemical structures with a NW-SE orientation (see map in Fig. 18). The geostatistical structural analysis was performed with Variowin (Pennatier, 1996), and plotted with Golden Sofware's Surfer v.12.

As most likely interpolated colour gridded maps will be plotted, it is considered necessary to discuss below the limitations of a geochemical data set.

### *11.2.1. Limitations of a geochemical data set: quality and reliability*

The following description is abstracted from Demetriades (2011b, p.83-84).

"The *combined sampling and analytical variance* (*i.e.*, *measurement variance*), according to Ramsey *et al.* (1992) and Ramsey (1993, 1998), should not exceed the upper limit of 20% of the *total variance*. An upper limit for analytical variance is set at 4% of the total variance. Hence, the sampling variance should not exceed the upper limit of 16% of the total variance. It is significant, as pointed out by all researchers in this field, for the greatest part of the variance to be ascribed to the *geochemical data variance* or *geochemical (spatial) variation*; otherwise, an interpolated contoured geochemical distribution map cannot be produced (Garrett, 1969; Howarth, 1983; Sharp, 1987). In case the geochemical data show no spatial persistence, element concentrations may be plotted at the sample sites as variable-size dots (Bølviken *et al.*, 1986; Björklund and Gustavsson, 1987; Lahermo *et al.*, 1990), symbols (De Vos *et al.*, 1996), Exploratory Data Analysis symbols (Englund and Sparks, 1988; O'Connor *et al.*, 1988; Demetriades, 1990), or recording on maps the sample site analytical data (Van der Sluys *et al.*, 1997). However, final decisions about geochemical distribution map plotting may be decided upon following a thorough geostatistical structural analysis of the data (Journel and Huijbregts, 1978; Rendu, 1978; Clark, 1979; Isaaks and Srivastava, 1989; Clark and Harper, 2007a, 2007b, 2008). According to Sharp (1987, p.11), to construct a valid interpolated geochemical contour map from point data, two very specific rules should be satisfied:

- Rule 1: Point data must show spatial persistence (autocorrelation) up to the second nearest neighbours. The rule insists that point data show sufficient continuity that a minimum determination of both the slope, and its general curvature, can be obtained for any interpolation.
- Rule 2: The contour interval should be selected so that the probable error of any point does not exceed one-half of a contour interval. This rule insists that any new point randomly selected between the drawn contour lines has at least an even chance of being valid.

Ramsey *et al.* (1992) and Ramsey (1993) stressed that, application of ANOVA and Robust ANOVA techniques to environmental surveys, is particularly appropriate due to the high degree of heterogeneity often associated with anthropogenic contamination of the environment (Ramsey *et al.*, 2013). They suggested the graphical display of data quality parameters in the form of a pie chart (Fig. 20). Visual representation of variance on all element distribution maps, gives the reader direct access to significant information about the quality and reliability of geochemical data.

Apart from the estimation of sampling, analytical, and geochemical variability, it is possible to estimate the practical detection limit and analytical precision for each element or determinand for each survey area, as has already been described. However, for the purposes of some project areas this may not be possible, due to the minimum number of random duplicate-replicate analyses that must be made, *i.e.*, a minimum of at least 50 duplicate-replicate analyses. In the case of large surveys, it is advisable to use this procedure.

The following example (Table 1) and pie charts (Fig. 20) show some of the limitations that may be encountered in a geochemical survey.

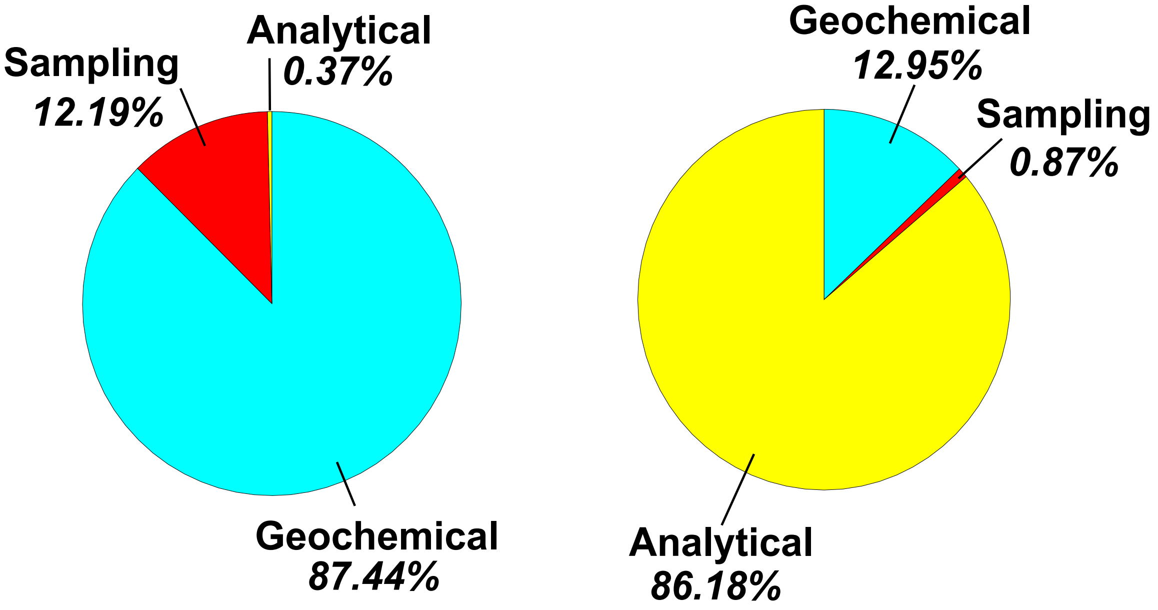
It is quite apparent from the quality control results tabulated in Table 1 that:

- the only elements with combined sampling and analytical variance of <20% of the total are As and Zn; Hg is slightly above this limit.
- Cr and Ni have a very high analytical variance, suggesting that the portable-XRF is not suitable for their determination in this particular area; the reason most likely lies in the mode of occurrence of these elements in soil, probably in disseminated pyritiferous particles.

Table 1. Summary table of sampling, analytical and geochemical variance, and relative expanded or extended measurement uncertainty at the 95% confidence level, all calculated by robust statistics from portable-XRF data (Massa, Avenza-Carrara, Italy). Ideally, the combined sampling and analytical variance should be <20% of the total variance at the 95% confidence level; the sampling variance to be <16%, and the analytical <4% of the total variance (Source: Demetriades, 2011b, Table 6.1, p.85).

| *Variance* | *As* | *Cr* | *Cu* | *Hg* | *Mn* | *Ni* | *Pb* | *Zn* |
|---|---|---|---|---|---|---|---|---|
| Geochemical (%) | 87.44 | 3.12 | 33.88 | 78.07 | 55.72 | 12.95 | 34.77 | 83.35 |
| Sampling (%) | **12.19** | 28.84 | **48.44** | **18.66** | **43.99** | 0.87 | **64.21** | **13.11** |
| Analytical (%) | 0.37 | **68.04** | 17.68 | 3.27 | 0.29 | **86.18** | 1.02 | 3.54 |
| Combined sampling and analytical or measurement variance (%) | 12.56 | **96.88** | **66.12** | **21.93** | **44.28** | **87.05** | **65.23** | 16.65 |
| *Relative expanded measurement uncertainty (+/-U%) at the 95% confidence level* | *49.37* | *36.50* | *30.97* | *27.41* | *73.51* | *75.86* | *96.99* | *45.10* |

| Notation of colour scheme: | Yellow highlighted elements (Cr, Cu, Mn, Ni, Pb) have an unacceptably high combined sampling and analytical or measurement variance (>20% of the total). |
|---|---|
| | Bold black numbers show the variance contributing the greatest proportion to the measurement uncertainty. |
| | Bold red colour numbers indicate combined sampling and analytical or measurement variance >20% of the total. |



(a) (b)

Figure 20. Diagrammatic representation of the relative contributions of variance introduced by primary sampling and geochemical analysis of (a) As and (b) Ni by portable-XRF to the total variance, Massa soil test investigation data, Avenza-Carrara, Italy (Source: Karamanos and Demetriades, 2004, Figure 11, p.16; Demetriades, 2011b, Fig. 6.3, p.84). The pie diagrams were plotted with Golden Software's Grapher v.11.

- Cu, Mn and Pb have a high sampling variance, which is ascribed to site heterogeneity, and
- Cr, Cu, Mn, Ni and Pb have unacceptably high combined sampling and analytical variance (>20% of total variance), and may impair the delineation of contamination *hot spots* or *neoanomalies* (Note: The term *hot spot* used to describe geochemical anomalies produced by human activities is somehow confusing, because it is employed by other disciplines. *Neoanomalies* is a better term, which was proposed by the Russian soil scientist and geochemist V.A. Kovda (1974), and introduced in the Western World by Davies (1980)."

The estimation of sampling, analytical and geochemical variance, and measurement uncertainty is, therefore, very significant for the validation and legal defensibility of analytical results.

### *11.2.2. Effects of measurement uncertainty and probability risk assessment maps*

The following description is abstracted from Demetriades (2011b, p.84-86).

"In order to address the uncertainty of measurements, a probabilistic classification of samples is used to produce probabilistic hazard or risk assessment maps (Ramsey and Argyraki, 1997). The probabilistic hazard or risk assessment maps address decision rule uncertainty by considering the uncertainty as being on the statutory threshold or trigger or guideline value used to determine the decision rule. The classification defines four categories based on the extent of overlap of uncertainty with a single threshold value (Table 2):

(1) Uncontaminated,
(2) Possibly contaminated,
(3) Probably contaminated, and
(4) Contaminated.

Table 2. Probabilistic classification of contaminated soil with measured concentration (C) and uncertainty (U), based on the probability that the contaminant concentration is greater than a particular threshold or trigger or guideline value (T) (Source: Ramsey and Argyraki, 1997, Table 3, p. 251; Demetriades, 2011b, Table 6.2, p.85).

| *Classification* | *Concentration range with uncertainty on C* | *Concentration range with uncertainty on T* | *Probability of C > T, i.e., C being over the threshold T* |
|---|---|---|---|
| (1) | (2) | (3) | (4) |
| Uncontaminated | $C + U < T$ | $C < T - U$ | <0.025 |
| Possibly contaminated | $C < T < C + U$ | $T - U < C < T$ | 0.025-0.500 |
| Probably contaminated | $C - U < T < C$ | $T < C < T + U$ | 0.500-0.975 |
| Contaminated | $T < C - U$ | $C > T + U$ | >0.975 |

*NOTE: The effect of uncertainty on the concentration estimate is evaluated (column 2), but a rapid intermediate calculation can consider the uncertainty as being on the threshold or guideline value (column 3). Uncertainty values are stated at the 95% confidence level, but could be recalculated for whatever confidence interval is considered appropriate for the site investigation.*

"For the category "*uncontaminated*", *for example*, the entire range of uncertainty is lower than the regulatory threshold or guideline value (T). The probability of this site being contaminated, because the element concentration lies over the statutory threshold is, therefore, <0.025 (*i.e.*, 2.5%). This computational device can be used to classify soil samples directly, without the need to calculate uncertainty values for each measurement.

The use of field duplicate samples, as has been shown above, is one method that has been proposed for the estimation of measurement uncertainty (Ramsey and Argyraki, 1997). These authors also mention that there is evidence of uncertainty changes with concentration. The upper limit of uncertainty for each single concentration measurement is given by:

$$C + U = C\left(1 + \frac{U\%}{100}\right) \quad (29)$$

where:

$C$ is the concentration of a determinand in soil or any other sampling medium;
$U$ is the expanded measurement uncertainty, and
$U\%$ is the expanded uncertainty relative to the mean concentration.

The *lower limit of measurement uncertainty* is similarly given by:

$$C - U = C \left( 1 - \frac{U\%}{100} \right) \qquad (30)$$

A '*short cut*' can be used by classifying geochemical samples directly, without calculating uncertainties for each measurement, *i.e.*, the uncertainty values for the particular measurements made are calculated for the concentration equal to the statutory threshold value (*T*). When the '*short cut*' method is used, with the measurement uncertainty expressed on the threshold value, Equations 29 and 30 are modified accordingly by replacing *C* by *T*, and the upper and lower limits are correspondingly given by:

*Upper limit:* $T + U = T(1 + U\% / 100)$ (31)

*Lower limit:* $T - U = T(1 - U\% / 100)$ (32)

The probabilistic classification limits can then be calculated using these equations, *i.e.*,

*Uncontaminated:* $C = T - U\%C$ or $C + U\%C = T$ (33)

*Contaminated:* $C = T + U\%C$ or $C - U\%C = T$ (34)”

### *11.2.3. Worked example*

The following example is from the urban geochemical mapping project carried out by the Hellenic Institute of Geology and Mineral Exploration at Thrakomakædónæs and western part of Varympompi, two northern suburbs of Athens, Hellas (Vassiliades, 2008; Tassiou, 2009).

#### *11.2.3.1. Geochemical map using percentiles*

The first map (Fig. 21) is a normal colour surface map produced by kriging, with superimposed graduated dots and Pb concentrations at each sample site. The class limit intervals are at 2.5, 5, 10, 15, 25, 50, 75, 90, 95, 97.5 percentiles. There are four anomalous patterns of Pb:

- The anomaly in the western border of the map from Korakofoliá to Mt. Párnitha is over limestone, dolomitic limestone, and dolomite of Mid-Triassic to Lower Triassic age, and is considered to be of geogenic origin.
- The anomalous pattern directly to the western part of Thrakomakædónæs housing estate (and to the south-east from Mt. Párnitha) is over Pleistocene stream and scree conglomeratic deposits, consisting of limestone, dolomitic limestone and dolomite cemented by sandy-marl. As it is over deposits derived from the Mt. Párnitha carbonate rocks is considered to be of geogenic origin, too, and
- The two anomalies at the Dekǽlia Railway Station and Tatói Airport are ascribed to an anthropogenic origin, because elevated values of S, Sb, Sn, Zn, and Cd are also observed.

This detailed interpretation is required, because it is important to distinguish between elevated values due to geogenic and anthropogenic sources. The prudent applied geochemist does not jump directly to the conclusion that elevated determinand values are caused by anthropogenic activities. The professional applied geochemist should investigate each anomaly like a detective, and find the cause. Always search first for geogenic sources to explain the geochemical anomalies. An unexplained geochemical anomaly in an urban environment, does not mean that it is caused by anthropogenic activities. To ascribe the cause of a geochemical anomaly to an anthropogenic source, there must be sound evidence, otherwise it is better to state that there is no explanation for the cause of the anomaly, and a more detailed investigation is required to find the source.

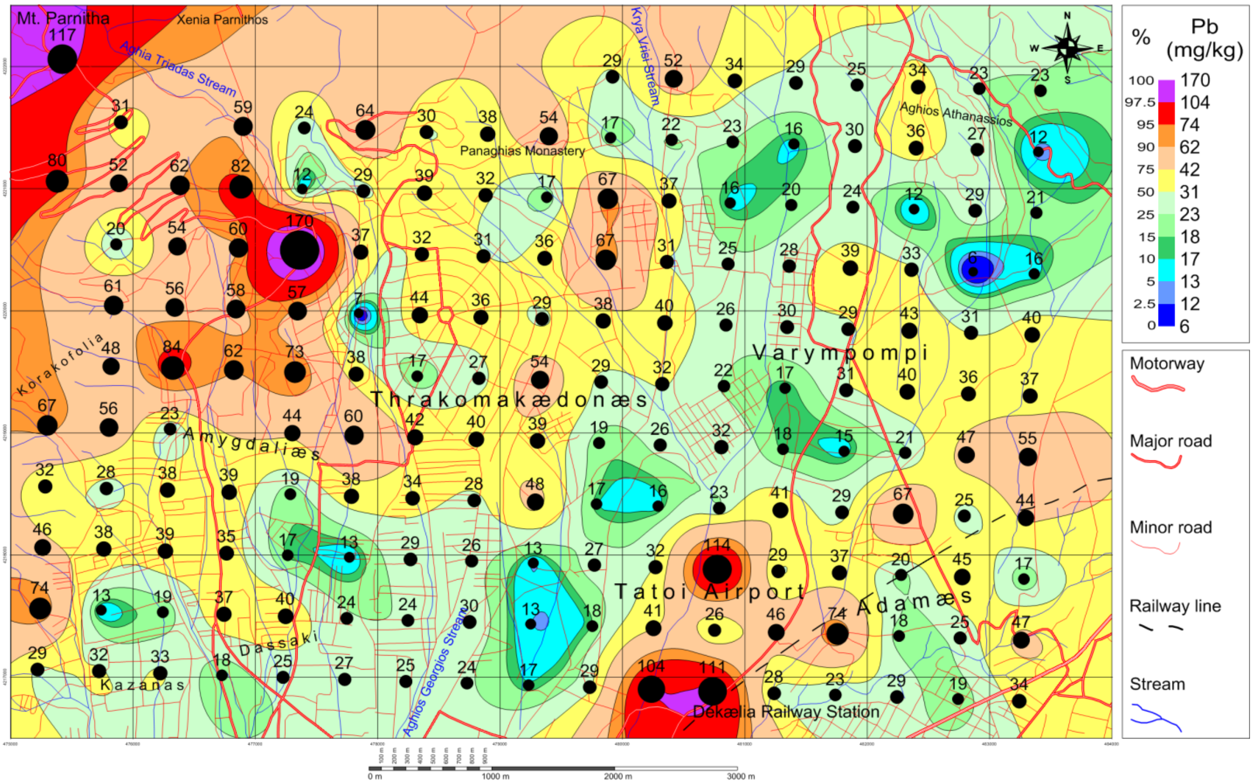


Figure 21. Geochemical distribution of aqua regia extractable Pb in the <2 mm fraction of topsoil samples collected from 0-10 cm depth, Thrakomakædónæs, Athens, Hellas, using a combined colour gridded map with superimposed graduated symbols and site concentration values. The map was plotted with Golden Software's Surfer v.12 (Source: Vassiliades, 2008, Map 30, slightly modified by the addition of the variable-size dots).

### *11.2.3.1. Deterministic risk assessment map*

The second Pb distribution map is a deterministic risk assessment map (Fig. 22). As there are no national hellenic or site-specific guideline values, a *theoretical guideline or threshold value of 60 mg Pb/kg soil* is used to classify the mapped area into two classes:

- Uncontaminated (<60 mg Pb/kg), and
- Contaminated (>60 mg Pb/kg),

or better

- Concentrations of Pb below the *(theoretical) guideline value of 60 mg/kg*, and
- Concentrations of Pb exceeding the *(theoretical guideline) value of 60 mg/kg* (or simply Pb anomalies).

The reason for preferring the latter classification, as has already been pointed out, is that one has to be very careful in jumping into the conclusion that soil is contaminated by human activities without sound evidence about the source or sources of the elevated element concentrations.

As it can be observed on the map, the Pb anomalies are quite extensive, especially in the western part of the map from Amygdaliǽs to Mt. Párnitha, and as it has already been explained above, these anomalous patterns are of geogenic origin; the small N-S elongated anomaly to the south-east of Panaghías Monastery is also of geogenic origin. Whereas, the anomalies at Tatói Airport, Adámæs and Dekǽlia Railway Station are caused by anthropogenic activities.

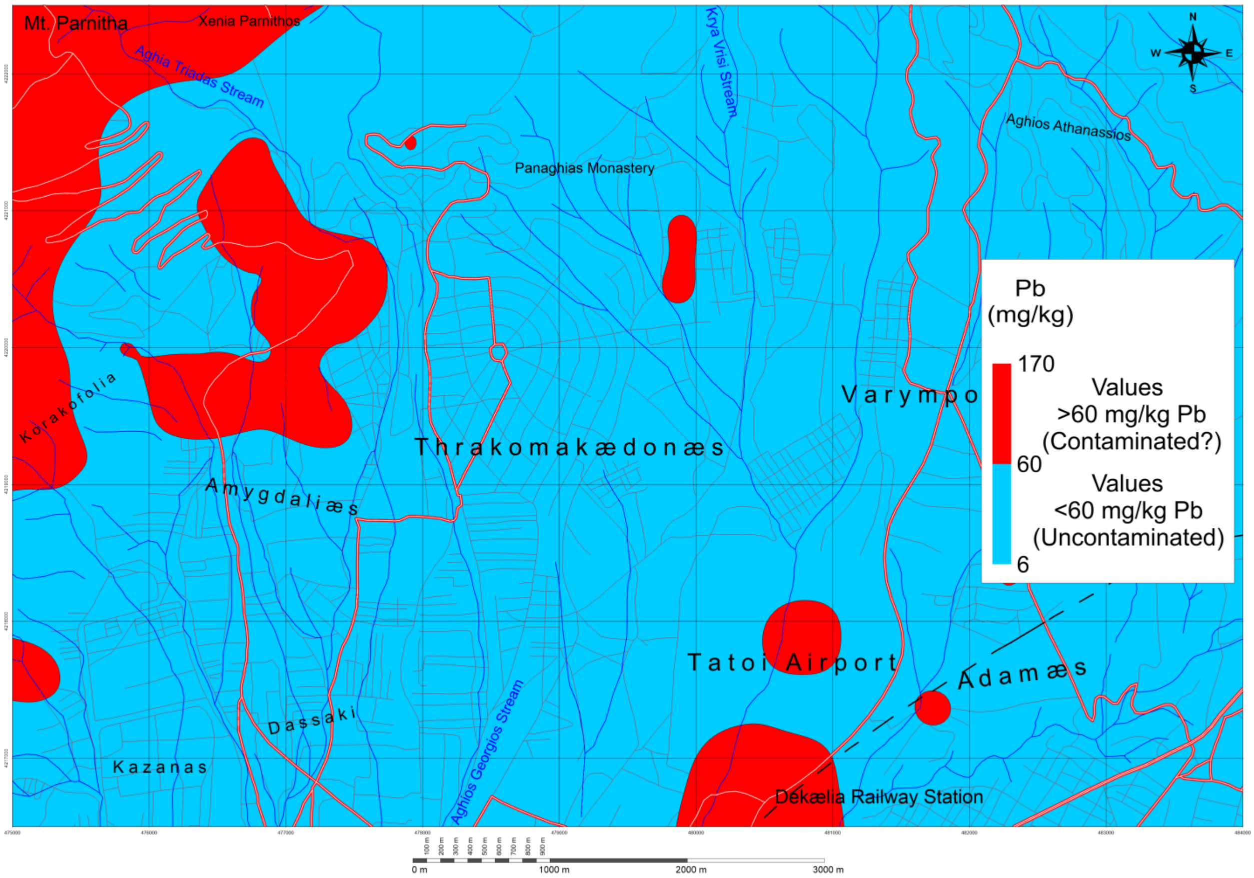


Figure 22. Deterministic risk assessment map of Pb showing how the results of the balanced RANOVA quality control design of duplicate field sampling are used to estimate measurement uncertainty, and to classify the results into (a) uncontaminated and (b) contaminated, using a *theoretical* guideline value of 60 mg Pb/kg of soil, Thrakomakedónæs, Athens, Hellas (Source of data: Vassiliades, 2008; Tassiou, 2009). The map was plotted with Golden Software's Surfer v.12.

### *11.2.3.2. Probabilistic risk assessment map*

The third Pb distribution map is a probabilistic risk assessment map (Fig. 23). It again uses the same *theoretical guideline or threshold value of 60 mg Pb/kg soil* in combination with the estimated relative expanded measurement uncertainty (U%) of 16.53% at the 95% confidence level. Table 3 shows the duplicate-replicate analytical results of Pb, and the robust analysis of variance output from the modified ROBCOOP4 software (Ramsey, 1998; Demetriades and Vassiliades, 2016). Below the grey bar in Table 3 are the calculations for the classification of the urban geochemical mapping results into hazard or risk categories:

- Uncontaminated,
- Possibly contaminated,
- Probably contaminated, and
- Contaminated soil

using the Equations 33 and 34 of the *'short-cut'* method. However, until the verification of the source of elevated Pb concentrations, it is better to use the following classification:

- Definitely below the site-specific guideline value,
- Possibly exceeding the site-specific guideline value,
- Probably exceeding the site-specific guideline value, and
- Definitely exceeding the site-specific guideline value.

Table 3. (a) Duplicate-replicate analytical results of Pb (mg/kg) on routine and duplicate sub-samples; (b) robust analysis of variance (RANOVA) results and apportionment of total variance into Geochemical, Sampling and Analytical variance; (c) values of measurement uncertainty and relative expanded measurement uncertainty (%) at the 95% confidence level according to the method proposed by Ramsey (1998), and (d) probabilistic classification of Urban Geochemical Mapping results, using the *'short-cut'* method into hazard or risk categories by taking into account the relative expanded measurement uncertainty on a theoretical guideline or threshold (T) value of 60 mg Pb/kg (Source of data: Vassiliades, 2008; Tassiou, 2009).

| *Routine sub-samples* | | *Duplicate sub-samples* | | *Pb_1A* | *Pb_1B* | *Pb_2A* | *Pb_2B* |
|---|---|---|---|---|---|---|---|
| TH-C5 | TH-C5A | TH-C5D | TH-C5DB | 56.3 | 56.9 | 45.6 | 46.5 |
| TH-C8 | TH-C8A | TH-C8D | TH-C8DB | 37.8 | 26.8 | 35.1 | 35.0 |
| TH-D4 | TH-A4A | TH-D4D | TH-D4DB | 60.3 | 60.2 | 57.2 | 52.2 |
| TH-H3 | TH-H3A | TH-H3D | TH-H3DB | 39.0 | 34.6 | 22.3 | 23.0 |
| TH-I3 | TH-I3A | TH-I3D | TH-I3DB | 16.8 | 16.9 | 16.5 | 20.1 |
| TH-K10 | TH-K10A | TH-K10D | TH-K10DB | 18.1 | 19.3 | 16.4 | 14.8 |
| TH-KS4 | TH-KS4A | TH-KS4D | TH-KS4DB | 39.0 | 39.2 | 43.6 | 44.7 |
| TH-L11 | TH-L11A | TH-L11D | TH-L11DB | 103.8 | 102.6 | 99.4 | 99.8 |
| TH-L4 | TH-L4A | TH-L4D | TH-L4DB | 31.3 | 30.3 | 24.3 | 25.4 |
| TH-M1 | TH-M1A | TH-M1D | TH-M1DB | 34.2 | 27.5 | 27.2 | 31.1 |
| TH-N11 | TH-N11A | TH-N11D | TH-N11DB | 28.4 | 32.0 | 28.7 | 28.8 |
| TH-R10 | TH-R10A | TH-R10D | TH-R10DB | 47.1 | 39.8 | 36.5 | 35.5 |
| TH-R2 | TH-R2A | TH-R2D | TH-R2DB | 11.8 | 10.4 | 9.8 | 11.0 |
| TH-R6 | TH-R6A | TH-R6D | TH-R6DB | 36.7 | 34.7 | 33.9 | 42.9 |
| TH-TH8 | TH-TH8 | TH-TH8D | TH-TH8DB | 28.5 | 28.0 | 28.2 | 30.9 |
| TH-Z11 | TH-Z11A | TH-Z11D | TH-Z11DB | 26.5 | 23.5 | 25.2 | 23.6 |
| TH-Z3 | TH-Z3A | TH-Z3D | TH-Z3DB | 29.1 | 32.1 | 22.8 | 26.9 |

***Robust analysis of variance results***

| ***Statistical parameters*** | ***Geochemical*** | ***Sampling*** | ***Analytical*** |
|---|---|---|---|
| Variance | 176.17 | 11.02 | 4.09 |
| Standard deviation (+/-) | 13.27 | 3.32 | 2.02 |
| Variance (%) | 92.10 | 5.76 | 2.14 |
| Mean value | 32.59 | | |
| Total standard deviation (+/-) | 13.83 | | |
| *Measurement uncertainty, u, for one sample* | 3.89 | $u = s_{meas}$<br>$u = SQRT(s^2_{samp} + s^2_{anal})$ | |
| *Expanded measurement uncertainty, $u_e$, for one sample at the 95% confidence level* | 7.62 | $u_e = k*u = 1.96*s_{meas}$ | |
| *Relative expanded uncertainty, $u_e$%, for one sample at the 95% confidence level* | 23.38 | $u_e\% = (1.96*100)*s_{meas}$ / Mean | |
| *Uncertainty, U, at a duplicated sample site* | 2.75 | $U = s_{meas}$ / SQRT of 2 (see Note) | |
| ***Relative expanded measurement uncertainty, U%, at the 95% confidence level*** | 16.53 | U% = (1.96*100)*U / Mean | |

*Uncontaminated or below the guideline value of 60 mg/kg by taking into account the relative expanded measurement uncertainty, U%, at the 95% confidence level:*

$$C + U\%*C = T$$
$$C + (16.53/100)*C = 60 \text{ mg/kg Pb}$$
$$C + 0.1653*C = 60 \text{ mg/kg Pb}$$
$$1.1653*C = 60 \text{ mg/kg Pb}$$
$$C = 60/1.1653 \text{ mg/kg Pb}$$
$$C = 51.48 \text{ mg/kg Pb}$$

*Contaminated or above the guideline value of 60 mg/kg by taking into account the relative expanded measurement uncertainty, U%, at the 95% confidence level:*

$$C - U\%*C = T$$
$$C - (16.53/100)*C = 60 \text{ mg/kg Pb}$$
$$C - 0.1653*C = 60 \text{ mg/kg Pb}$$
$$0.8347*C = 60 \text{ mg/kg Pb}$$
$$C = 60/0.8347 \text{ mg/kg Pb}$$
$$C = 71.88 \text{ mg/kg Pb}$$

*Classification of Urban Geochemical Mapping results into hazard or risk categories:-*

| | |
|---|---|
| *Uncontaminated or Definitely below the guideline value:* | *<51.48 mg Pb/kg soil* |
| *Possibly contaminated or Possibly exceeding the guideline value:* | *51.48 < C < 60 mg Pb/kg soil* |
| *Probably contaminated or Probably exceeding the guideline value:* | *60 < C < 71.88 mg Pb/kg soil* |
| *Contaminated or Definitely exceeding the guideline value* | *>71.88 mg Pb/kg soil* |

Note: Ramsey and Ellison (2007) have proposed that the uncertainty at a duplicated site should not be divided by the square root of 4 (√4 = 2), but by the square root of 2 (√2 = 1.414), because the sampling uncertainty is the limiting factor.

In this particular case, only the three patterns at Tatói Airport, Adámæs and Dekǽlia Railway Station are of anthropogenic origin and, thus, the topsoil can be classified as contaminated.

The probabilistic classification (Fig. 23), as it can be observed by comparison with the deterministic map (Fig. 22), reduces the size of the anthropogenic anomalies. In these three areas is important to delineate precisely the contamination by carrying out a more detailed survey in order to reduce the cost of remediation, if this is deemed necessary.

Measurement uncertainty in the interpretation of environmental sensitive urban geochemical investigations does have fundamental effects on the pragmatic assessment of the extent of anthropogenic induced contamination, because it reduces '*misclassification*' of samples. It safeguards the prudent investigator in reaching wrong conclusions and making financial risky recommendations to remediate land, which may be, in fact, uncontaminated, and even worse, parts of it could be regarded as uncontaminated but are truly contaminated. Such decisions, apart from financial implications, may have legal and health extensions. The recommended robust statistical technique separates the different components of variance (sampling, analytical, geochemical), and indicates which ones are unacceptably high, and may need improvement. Further, the compilation of probabilistic hazard or risk assessment maps for each determinand addresses decision rule uncertainty by considering the uncertainty as being on the statutory threshold or guideline value, used to determine the decision rule.

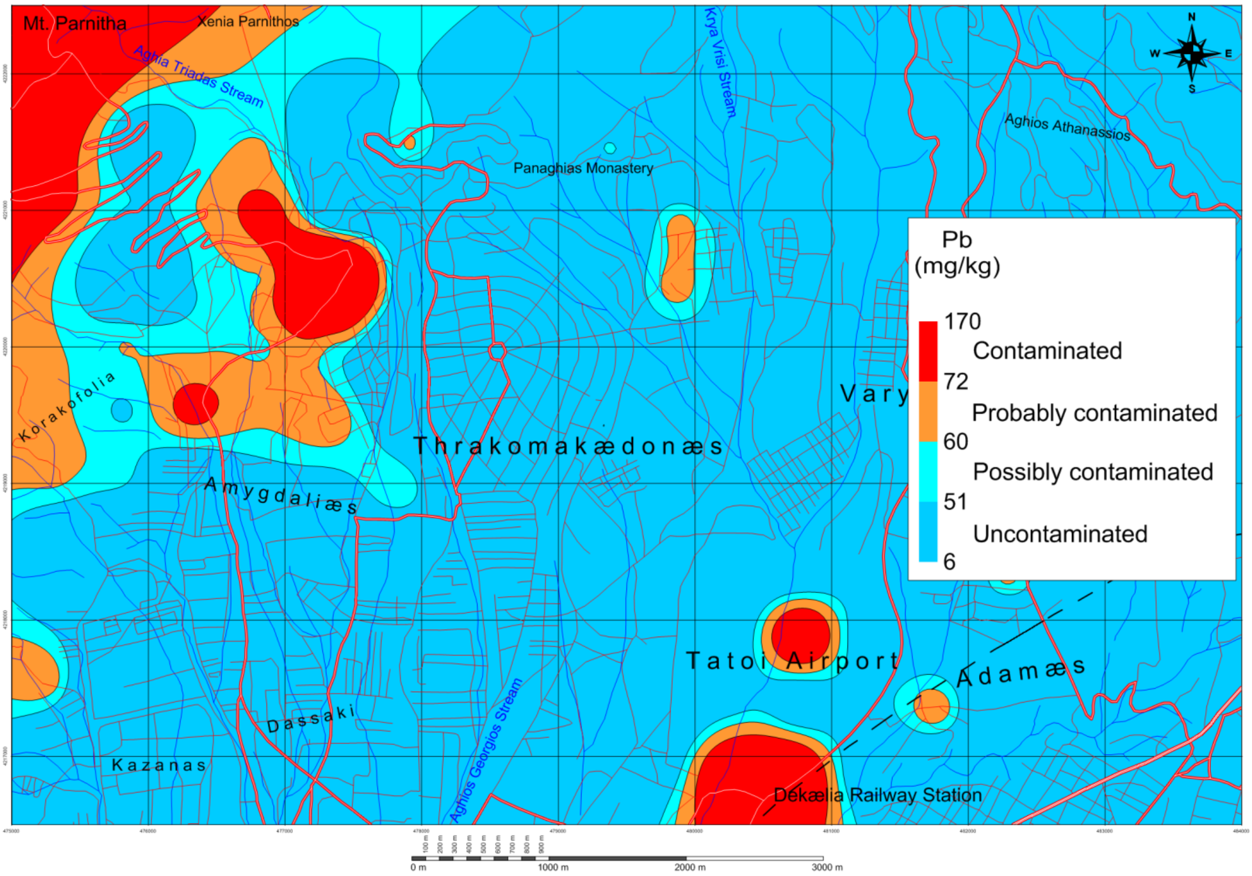


Figure 23. Probabilistic risk assessment map showing how the results of the balanced quality control design of duplicate field sampling are used to estimate measurement uncertainty, and to classify the results, using a theoretical site-specific guideline value of 60 mg Pb/kg of soil into (a) uncontaminated or *definitely below the (theoretical) site-specific guideline value*, (b) possibly contaminated or possibly *exceeding the (theoretical) site-specific guideline value*, (c) probably contaminated or *probably exceeding the (theoretical) site-specific guideline value*, and (d) contaminated or *definitely exceeding the (theoretical) site-specific guideline value*, Thrakomakedónæs, Athens, Hellas (Source of data: Vassiliades, 2008; Tassiou, 2009). The map was plotted with Golden Software's Surfer v.12.

## 12. SUMMARY OF STAGES OF URBAN GEOCHEMICAL MAPPING PROJECTS

The following are the stages of an efficient design of an urban geochemical mapping project:

- ❑ *Design of optimum sample layout for obtaining reliable information*: A square sampling grid is recommended. The grid dimensions depend on project objectives. It is recommended to start from a wide-spaced grid (*e.g.*, 500 x 500 m for the inner city to 1000 x 1000 m for the suburbs), and then carry out detailed surveys in areas that are potential hazardous in order to delineate with a high degree of confidence the contaminated parts.
- ❑ *Randomisation of samples to reduce systematic errors*. Randomised numbers can be either used during the field sampling, or assigned to the samples after sample preparation; the latter means re-numbering the samples, a procedure that must be carried out very carefully and a record kept. Whichever sample randomisation procedure is used, it is important to remember to reserve numbers for inclusion of reference and project replicate samples. The laboratory must be informed not to randomise the samples.
- ❑ *Sampling*:
  - ➢ Samples should be collected by the applied geochemist or well-trained field staff. (Human tissue samples should be collected by trained medical practitioners).
  - ➢ Field duplicates are taken to assess sample site representativeness and variability, and to estimate reliably measurement uncertainty.
  - ➢ Samples are securely packed in the field in certified trace-element free bags (Rilsan®) for the determination of inorganic elements and organic compounds (POPs), and in amber (dark brown) glass containers for determination of volatile organic compounds (VOCs). Samples for the determination of VOCs should be kept at a temperature <4°C or frozen.
  - ➢ Cross-contamination of soil samples, and other sample types, in the field must be avoided, by using a good sampling procedure, and thorough cleaning of all equipment at each sample site before moving to the next one.
  - ➢ Each sample should be described and documented properly by completing the appropriate Field Observations Sheet, marking the sample site on a suitable scale map, recording of coordinates by GPS, and documenting the sample site with a number of site and general landscape photographs. (Human tissue samples should be documented by a questionnaire that is completed by each donor).
  - ➢ Blank samples, such as a kaolin, bentonite, or pure quartz of known composition should be prepared and packed in the field, as the routine and duplicate samples and, taken through the whole process of sample preparation and analysis; this blank sample will assess laboratory contamination.
- ❑ *Sample preparation*:- Samples should be dried at ambient temperature or in a thermostatically controlled oven at a temperature not exceeding 25°C. Samples that need disaggregation, this should be performed by a porcelain pestle in a porcelain mortar, taking care not to grind small pebbles. Following disaggregation, soil samples are sieved through a nylon screen of 2 mm. The whole <2 mm soil fraction is suitably homogenised, and split into sub-samples and placed in trace-element free containers. All sample preparation apparatus should be thoroughly cleaned after each sample. (House dust, road dust or sediment and attic dust samples in the case that they will be compared with topsoil should be sieved to the <2 mm fraction; if such a comparison will not be made then should be sieved to the <0.125 mm fraction).
- ❑ *Archive sample collection*: Enough material should be archived in a dust free storeroom where the ambient temperature does not exceed 30°C. This is the reference collection for future use.
- ❑ *Arrangement of samples for laboratory analysis*: Randomisation of samples, if not already collected in a random order, and insertion of blank, duplicate and project reference/standard samples in the analytical batches:

    - Blank samples assess laboratory contamination;
    - Duplicate-replicate samples analytical precision, and
    - Reference/standard samples analytical accuracy.
- *Analysis of samples in an accredited laboratory*: Analytical methodology should be agreed, as well as the laboratory's quality control procedure, and uncensored analytical results to be reported.
- *Data check*: Thorough checking of analytical results to validate their quality.
- *Quality control problems*: In case, quality control problems are located, the laboratory is obliged to provide explanations, and to reanalyse the problematic batches. If the analytical results are not of the required quality, then the laboratory will be obliged to re-analyse all samples. These quality control issues about the analytical data should be included in the contract with the laboratory.
- *Quality control report*: A quality control report should be written, as this is important as a proof about the quality of the analytical data. In the case of legal proceedings, questions about the quality of the data will be required by the court. Hence, the generated analytical results must be legally defensible beyond any reasonable doubt.
- *Data processing and map plotting*: Data processing begins after the applied geochemist is satisfied about the quality and integrity of analytical results. A variety of statistical graphical diagrams, and geochemical distribution maps can be plotted.
- *Guideline values*: Use local or site-specific guideline values, as each town or city has its own variable natural geochemical background, and the anthropogenic influences are superimposed on this.
- *Data interpretation*: For a good interpretation all supporting information should be used, *i.e.*, lithological map, lithogeochemical data (if available), land use map with potential contaminating activities, climatic data and, of course, the field documentation (observations and photographs). Do not jump to the conclusion that an area with element concentrations exceeding the site-specific guideline value is contaminated. You must have sound evidence to support such a conclusion. Always look first for a geogenic explanation for areas with high determinand concentrations, and if it cannot be found, then begin to consider other plausible sources by using all available current and historical land use information.
- *Report writing*: The report must include a detailed description of all stages of the urban geochemical mapping survey, summary of the quality control results (reference to the QC report), data processing procedures, statistical graphical diagrams, determinand distribution maps, and sound interpretation with conclusions and recommendations.

## 13. FURTHER READING

An attempt has been made to a produce a detailed manual for the geochemical mapping of urban areas. Nevertheless, it is strongly recommended to study all references cited, but also to have copies of the following reference books, reports, and book chapters:

(1) The textbook "*Mapping the chemical environment of urban areas*" edited by C. Johnson, A. Demetriades, J. Locutura & R.T. Ottesen, published in 2011 by Wiley-Blackwell, John Wiley & Sons Ltd., Chichester, U.K. (616 pp.), is strongly recommended (http://eu.wiley.com/WileyCDA/WileyTitle/productCd-0470747242.html). The first part of the book, comprising 12 chapters, covers general aspects of urban geochemical mapping with an overview of current practice, and reviews of different aspects of the component methodologies from sampling, sample preparation, laboratory analysis of inorganic and organic chemical compounds, quality control procedures, and data analysis, including hazard and exposure assessment. The second part includes 21 case histories from different urban areas around Europe, United States of America, Africa, and China.

(2) Demetriades, A., 2014. *Basic considerations: Sampling, the key for a successful applied geochemical survey for mineral exploration and environmental purposes*. Chapter 15.1 In: McDonough, W.F. (volume Editor), *Analytical geochemistry/Inorganic instrument analysis*. Volume 15 In: Holland, H.D. & Turekian, K.K. (Executive Editors), *Treatise on Geochemistry*. Elsevier, Oxford, 1-31. This is a chapter that describes sampling of all sample media (*i.e.*, stream sediment, overbank or floodplain sediment, soil, stream- and ground-water, rock, house dust, attic dust, road dust), and emphasises the significance of good sampling techniques for the successful delineation of natural and human-induced geochemical anomalies.

(3) The textbook "*Statistical data analysis explained: Applied environmental statistics with R*" by C. Reimann, P. Filzmoser, R.G. Garret & R. Dutter, published in 2008 by John Wiley & Sons, Ltd., Chichester, U.K. (343 pp.), is a good introduction in statistical analysis of geochemical data that can be easily understood by non-statisticians (http://eu.wiley.com/WileyCDA/WileyTitle/productCd-047098581X.html).

(4) The three open access quality control reports of the EuroGeoSurveys project "*Geochemical Mapping of Agricultural and Grazing land soil*", known with the acronym GEMAS, are worth studying for they provide good information on the quality control procedure that should be followed, including a bad case example:

    (i) Reimann, C., Demetriades, A., Eggen, O.A., Filzmoser, P. and 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., http://www.ngu.no/upload/Publikasjoner/Rapporter/2009/2009_049.pdf.

    (ii) Reimann, C., Demetriades, A., Eggen, O.A., Filzmoser, P. and the EuroGeoSurveys Geochemistry expert group, 2011. *The EuroGeoSurveys Geochemical Mapping of Agricultural and grazing land Soils (GEMAS) – Evaluation of quality control results of total C and S, total organic carbon (TOC), cation exchange capacity (CEC), XRF, pH, and particle size distribution (PSD) analysis*. Geological Survey of Norway, Trondheim, NGU Report 2011.043, 92 pp., http://www.ngu.no/upload/Publikasjoner/Rapporter/2011/2011_043.pdf.

    (iii) Reimann, C., Demetriades, A., Birke, M., Eggen, O. A., Filzmoser, P., Kriete, C. & EuroGeoSurveys Geochemistry Expert Group, 2012. *The EuroGeoSurveys Geochemical Mapping of Agricultural and grazing land Soils project (GEMAS) – Evaluation of quality control results of particle size estimation by MIR prediction, Pb-isotope and MMI® extraction analyses and results of the GEMAS ring test for the standards Ap and Gr*. Geological Survey of Norway, Trondheim, NGU

Report 2012.051, 136 pp., http://www.ngu.no/upload/Publikasjoner/Rapporter/2012/2012_051.pdf.

A good urban soil geochemical study was carried out in Dublin, and should be consulted (http://www.gsi.ie/Surge.htm):

(5) Glennon, M., Scanlon, R.P., O'Connor, P.J., Finne, T.E., Andersson, M., Eggen, O., Jensen, H.K.B. & Ottesen, R.T., 2012. *Dublin SURGE Project: Geochemical baseline for heavy metals and organic pollutants in topsoils in the greater Dublin area*. Technical Report, Geological Survey of Ireland, Dublin, 198 pp., http://www.gsi.ie/NR/rdonlyres/1F23753A-D662-44D3-AE78-5029700472AE/41993/DublinSoilUrbanGeochemistry.pdf.

(6) *Dublin historic industry database*: http://www.gsi.ie/NR/rdonlyres/EBE7C28D-FAD2-42EA-92BD-8CC2CFA0809F/0/DublinHistoricIndustryDatabaseReport.pdf.

Concerning the availability of geochemical baseline data, outside the urban areas, it is strongly recommended to consult national geochemical atlases, published by the Geological Survey of each country. Furthermore, since 2005 continental scale geochemical atlases have been published in Europe, Australia and the United States of America, and these contain useful freely available information and geochemical baseline data, namely:

(7) Salminen, R., 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. & Tarvainen, T., 2005. *FOREGS Geochemical Atlas of Europe, Part 1: Background Information, Methodology and Maps*. Geological Survey of Finland, Espoo, 526 pp., 36 figures, 362 maps, http://weppi.gtk.fi/publ/foregsatlas/.

(8) 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. & 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, Finland, 692 pp., http://weppi.gtk.fi/publ/foregsatlas/.

(9) Caritat, P. de & Cooper, M., 2011. *National Geochemical Survey of Australia: The Geochemical Atlas of Australia*. Geoscience Australia, Record 2011/20 (2 Volumes), 557 pp., http://www.ga.gov.au/about/what-we-do/projects/minerals/concluded/national-geochemical-survey/atlas; http://www.ga.gov.au/metadata-gateway/metadata/record/gcat_71973; http://www.ga.gov.au/corporate_data/71973/Rec2011_020_Vol1.pdf; http://www.ga.gov.au/corporate_data/71973/Rec2011_020_Vol2.pdf.

(10) Reimann, C., Birke, M., Demetriades, A., Filzmoser, P. & O'Connor, P. (Editors), 2014. *Chemistry of Europe's agricultural soils – Part A: Methodology and interpretation of the GEMAS data set*. Geologisches Jahrbuch (Reihe B 102), Schweizerbarth, Hannover, 528 pp., http://www.schweizerbart.de/publications/detail/isbn/9783510968466.

(11) Reimann, C., Birke, M., Demetriades, A., Filzmoser, P. & O'Connor, P. (Editors), 2014. *Chemistry of Europe's agricultural soils – Part B: General background information and further analysis of the GEMAS data set*. Geologisches Jahrbuch (Reihe B 103), Schweizerbarth, Hannover, 352 pp.,

http://www.schweizerbart.de/publications/detail/isbn/9783510968473/Geologisches_Jahrbuch_Reihe_B_Heft_B103_Chemistry; Parts A & B: http://www.schweizerbart.de/publications/list/series/geoljbb.

(12) Smith, D.B., Cannon, W.F., Woodruff, L.G., Federico, S., Kilburn, J.E., and Fey, D.L., 2013, Geochemical and mineralogical data for soils of the conterminous United States: U.S. Geological Survey Data Series 801, 19 p., http://pubs.usgs.gov/ds/801/; http://pubs.usgs.gov/ds/801/downloads/; http://pubs.usgs.gov/ds/801/pdf/ds801.pdf.

(13) Smith, D.B., Cannon, W.F., Woodruff, L.G., Federico, S. and Ellefsen, K.J., 2014. Geochemical and mineralogical maps for soils of the conterminous United States. U.S. Geological Survey Open-File Report 2014–1082, 386 pp., http://dx.doi.org/10.3133/ofr20141082; http://pubs.usgs.gov/of/2014/1082/pdf/ofr2014-1082.pdf.

The Analytical Methods Committee (AMC) of the Royal Society of Chemistry has published many useful AMC Technical briefs, which are freely available at: http://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/TechnicalBriefs.asp.

In addition, free of charge software is available at: http://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/index.asp:

- A Minitab local macro to calculate robust mean and standard deviation. This macro calculates Huber's 'H15' estimators for robust mean and standard deviation.

- MS EXCEL Add-in for Robust Statistics, which is written for Excel 97 and later versions.

- ROBAN: A stand-alone program, running in Windows, to execute robust analysis of variance with nested balanced data.

- RANOVA: A stand-alone program, running in Windows, to execute robust analysis of variance with nested data.

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## APPENDIX 1: Abbreviations and Acronyms

**AD**: *Anno Domini*, meaning after the birth of Jesus Christ
**AMC**: Analytical Methods Committee (Royal Society of Chemistry, London)
**ANOVA**: analysis of variance
**AOX:** adsorbable organically bound halogen
**ASTM**: American Society for Testing and Materials
**ATSDR**: Agency for Toxic Substances and Disease Registry (USA)
**AV**: accepted value

**BC**: Before Christ
**BGS**: British Geological Survey
**BLK**: project blank sample
**BS**: shorter abbreviation of the British Standards Institute (BSI)
**BSI**: British Standards Institute
**BLUE**: Best Linear Unbiased Estimator
**BTEX**: Benzene, Toluene, Ethylbenzene, and Xylene

**C**: temperature in degrees Celsius
***ca***: *circa*; from Latin, meaning "around, about or approximately"
**CEN**: Comité Européen de Normalisation (European Committee for Standardisation)
**cm**: centimetre; $1\times10^{-2}$ of a metre
**CRMs**: Certified Reference Materials
**CV**: Coefficient of Variation

**DIN**: Deutsches Institut für Normung e.V. (German Institute for Standardisation)
**DL**: detection limit
**DUPA**: first sample of duplicate pair
**DUPB**: second sample of duplicate pair

**E**: east
**EDA**: Exploratory Data Analysis
**EDTA**: EthyleneDiamineTetraacetic Acid
***e.g.***: Latin *exempli gratia*; for example
**EGS**: EuroGeoSurveys
***et al.***: Latin *et alii*, *et alia*; and others
***etc.***: Latin *et cetera*; and the rest; and similar things; and so on
**EuroGeoSurveys**: Association of the Geological Surveys of Europe

**FOREGS**: Forum of European Geological Surveys (now EuroGeoSurveys)

**g**: gram; $1\times10^{-3}$ kg

**G-BASE**: Geochemical Baseline Survey of the Environment (UK Geochemical Mapping programme)

**GEMAS**: acronym of the EuroGeoSurveys Geochemistry Expert Group's project *'Geochemical Mapping of Agricultural and Grazing land soil'* (http://gemas.geolba.ac.at/)

**GIS**: Geographical Information System

**GPS**: Global Positioning System

**HHRA**: Human Health Risk Assessment

**HPLC**: High Performance Liquid Chromatography

**ICP-AES**: Inductively Coupled Plasma Atomic Emission Spectrometry

**ICP-MS**: Inductively Coupled Plasma atomic Mass Spectrometry

***i.e.***: Latin *id est*; that is to say

**IEC**: International Electrotechnical Commission

**ISO**: International Organisation for Standardisation

**kg**: kilogram or kilogramme, a common metric unit of mass, equivalent to 1000 grams

**km**: kilometre

**l**: litre

**LOI**: Loss On Ignition

**m:** metre (notation after a number)

**m**: mean - average value

**ml**: millilitre; $1\times10^{-6}$ of a litre

**µm:** micrometre; $1\times10^{-6}$ of a metre

**mg**: milligram; $1\times10^{-6}$ of a kilogram

**mm**: millimetre; $1\times10^{-3}$ of a metre

**MCERTS**: Monitoring Certification Scheme

**N**: north

**NW**: north-west

**P**: precision

**PAHs**: Polycyclic Aromatic Hydrocarbons, *e.g.*, anthracene, phenanthrene, tetracene, chrysene, triphenylene, pyrene, pentacene, benzo(a)pyrene, corannulene, benzo(g,h,i)perylene, coronene, and ovalene.

**PCBs**: PolyChlorinated Biphenyls are persistent organic pollutants (POPs)

**PCDDs**: PolyChlorinated DibenzoDioxins

**PCDFs**: PolyChlorinated DibenzeFurans

**PDL**: practical detection limit

**PE**: polyethylene

**pers. commun.**: personal communication
**PGEs**: Platinum Group Elements; also abbreviated as PGMs (Platinum Group Metals) – iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh), and ruthenium (Ru)
**pH**: German ‘potenz’ meaning ‘power’ plus the symbol for hydrogen (H); a logarithm of the reciprocal of the hydrogen ion concentration in moles per litre of a solution, giving a measure of its acidity or alkalinity
**PM**: Particulate Matter
**PM2.5**: particulate matter of 2.5 micrometres
**PM10**: particulate matter of 10 micrometres
**POPs**: Persistent Organic Pollutants
**psi**: pounds per square inch
**PTFE**: PolyTetraFluoroEthylene (Teflon)

**QC**: Quality Control

**RANOVA**: robust analysis of variance
**REF**: reference sample
**REPA**: first replicate sample
**REPB**: second replicate sample
**rpm**: revolutions per minute

**SD**: standard deviation
**SE**: south-east
**SGVs**: Soil Guideline Values
**SRMs**: Standard Reference Materials

**UK**: United Kingdom
**UN**: United Nations
**URGE**: acronym of the Urban Geochemistry project of the EuroGeoSurveys Geochemistry Expert Group
**USEPA**: United States Environmental Protection Agency
**USGS**: United States Geological Survey
**UTM**: Universal Transverse Mercator

**Var**: variability
**VMA**: VanillylMandelic Acid
**VOCs**: Volatile Organic Compounds

**WGS84**: World Geodetic System is a standard for use in cartography, geodesy, and navigation (dating from 1984 and last revised in 2004)
**WHO**: World Health Organisation

**XRF**: X-ray fluorescence

**XRFS**: X-ray fluorescence spectrometry

## APPENDIX 2: Glossary

**Accredited laboratory**: see Accreditation

**Accreditation**: Formal recognition that a laboratory is competent to carry out specific tests or calibrations or types of tests or calibrations.

**Accuracy**: Accuracy expresses a measure of how close an analytical result is to a ‘true’ or an ‘accepted’ value.

**Allergen** is a type of *antigen* that produces an abnormally vigorous immune response in which the immune system fights off a perceived threat that would otherwise be harmless to the body (Source: https://en.wikipedia.org/wiki/Allergen). An ***antigen*** is any structural substance that serves as a target for the receptors of an adaptive immune response (Source: https://en.wikipedia.org/wiki/Antigen).

**Analytical bias** is a quantitative term describing the difference between the average of measurements made on the same sample and its true value. In particular, for a measurement laboratory, *bias* is the difference (generally unknown) between a laboratory's average value (over time) for a test item and the average that would be achieved by the reference laboratory if it undertook the same measurements on the same test item (Source: http://chemwiki.ucdavis.edu/Analytical_Chemistry/Data_Analysis/Bias_and_Accuracy).

**Anomaly** (see Geochemical anomaly)

**Anticoagulants** are a class of drugs that work to prevent the coagulation (clotting) of blood (Source: https://en.wikipedia.org/wiki/Anticoagulant).

**Anthropocene**: “It is a term widely used since its coining by Paul Crutzen and Eugene Stoermer in 2000 to denote the present time interval, in which many geologically significant conditions and processes are profoundly altered by human activities. These include changes in: erosion and sediment transport associated with a variety of anthropogenic processes, including colonisation, agriculture, urbanisation and global warming; the chemical composition of the atmosphere, ocean and soil, with significant anthropogenic perturbations of the cycles of elements, such as carbon, nitrogen, phosphorus and various metals; environmental conditions generated by these perturbations, which include global warming, ocean acidification and spreading oceanic 'dead zones'; the biosphere both on land and in the sea, as a result of habitat loss, predation, species invasions and the physical and chemical changes noted above” (Source: http://quaternary.stratigraphy.org/workinggroups/anthropocene/).

**Attic dust** is the dust that accumulates on wooden carpentry of attics, where the influence of inhabitants is minimised (Šajn, 2005).

**Background** (see Geochemical background)

**Baseline** (see Geochemical baseline)

**Bias** (see Analytical bias)

**Bio-indicator**: A bio-indicator is a living organism that gives us an idea of the health of an ecosystem. Some organisms are very sensitive to pollution in their environment, so if pollutants are present, the organism may change its morphology, physiology or behaviour, or it could even die (Source: http://sciencelearn.org.nz/Contexts/Enviro-imprints/Science-Ideas-and-Concepts/Bioindicators).

**Blank sample** (Johnson, 2011, p.63-64): "There are three types of blank samples used to identify laboratory-introduced contamination: (a) a ‘*solid*’ blank control sample is one that contains very low levels of all the chemical elements being determined; for soil or sediments, a pure silica sand is often used; (b) a ‘*reagent*’ blank is made up of the same acids (plus de-ionised water) which are added to solid samples for bringing into solution chemical elements..... A *reagent blank*, is introduced during the addition of reagents to solid samples and, apart from checking the purity of reagents used, it monitors potential contamination during the whole laboratory procedure. A solid *blank sample* is introduced prior to the sample preparation and analysis phase to show up any introduced contamination during all laboratory processes, from sample preparation to laboratory analysis."

**Brownfield**: "It is a term used in urban planning to describe land previously used for industrial purposes or some commercial uses. Such land may have been contaminated with hazardous waste or pollution or is feared to be so. Once cleaned up, such an area can become host to a business development, such as a retail park. Land that is more severely contaminated, and has high concentrations of hazardous waste or pollution, such as a *Superfund site* (see entry), does not fall under the brownfield classification" (Source: https://en.wikipedia.org/wiki/Brownfield_land).

**Censored data**: Determinand concentration values that are reported as being below the laboratory's detection limit, *e.g.*, <0.01 mg/kg Be, with the consequent loss of information.

**Comminution** is the physical reduction in particle size of a sample and is typically achieved by milling or sieving**.**

**Contamination** is the presence of an unwanted constituent, *contaminant* or impurity in a material, physical body, natural environment, workplace, *etc.* (Source: https://en.wikipedia.org/wiki/Contamination).

**Contaminant**: (a) Any physical, chemical, biological, or radiological substance or matter that has an adverse effect on air, water, or rocks. (b) An undesirable substance in water, air, or rocks that is either not normally present or is an unusually high concentration of a naturally occurring substance (Neuendorf *et al.*, 2011). Soil should be, of course, included in these definitions.

**Control samples** (see Quality control samples)

**Control chart** (see Shewhart chart)

**Cross-sectional epidemiological study** is "an observational study in which exposure and disease are determined at the same point in time in a given population; the temporal relationship, however, between exposure and disease cannot be determined; it assesses the prevalence of exposures and/or of diseases in the population, and provides clues for further research into the aetiology of diseases" (Kanchanaraksa, 2008).

**Cryogenic grinding**: also known as *freezer milling*, *freezer grinding*, and *cryomilling*, is the act of cooling or chilling a material and then reducing it into a small particle size (Source: https://en.wikipedia.org/wiki/Cryogenic_grinding)

**Cultural layer**: It is a layer of earth on sites of human habitation containing traces or remains of human activities. The thickness of a cultural layer varies from several centimetres to 30–35 m and depends mainly on the length and intensiveness of human activity at the given site. Cultural layers are excavated to study the remains of human activities and to reconstruct the history of a given settlement (Source: http://encyclopedia2.thefreedictionary.com/Cultural+Layer).

**Data conditioning** (Johnson, 2011, p.61): "The methods used to render the data fit for the purpose for which they are to be used."

**Defecation** is the final act of digestion, by which organisms eliminate solid, semisolid, and/or liquid waste material from the digestive tract via the anus or urethra (Source: https://en.wikipedia.org/wiki/Defecation).

**Deflation**: "The sorting out, lifting, and removal of loose dry fine-grained particles (clay and silt sizes) by the turbulent eddy action of the wind, as along a sand-dune coast or in a desert" (Neuendorf *et al.*, 2011).

**Determinand**: Any chemical or physico-chemical parameter determined on a physical sample, *e.g.*, major and trace elements, pH, *etc.*

**Determinant** (with respect to epidemiological studies – see Determinants of health)

**Determinants of health**: "Many factors combine together to affect the health of individuals and communities. Whether people are healthy or not, is determined by their circumstances and environment. To a large extent, factors such as where we live, the state of our environment, genetics, our income and education level, and our relationships with friends and family all have considerable impacts on health, whereas the more commonly considered factors such as access and use of health care services often have less of an impact. The *determinants of health* include:

- the social and economic environment,
- the physical environment, and
- the person's individual characteristics and behaviours.

The context of people's lives determine their health, and so blaming individuals for having poor health or crediting them for good health is inappropriate. Individuals are unlikely to be able to directly control many of the *determinants of health*. These *determinants*—or things that make people healthy or not—include the above factors, and many others:

- Income and social status - higher income and social status are linked to better health. The greater the gap between the richest and poorest people, the greater the differences in health.
- Education – low education levels are linked with poor health, more stress and lower self-confidence.
- Physical environment – safe water and clean air, healthy workplaces, safe houses, communities and roads all contribute to good health. Employment and working conditions – people in employment are healthier, particularly those who have more control over their working conditions.
- Social support networks – greater support from families, friends and communities is linked to better health. Culture - customs and traditions, and the beliefs of the family and community all affect health.
- Genetics - inheritance plays a part in determining lifespan, healthiness and the likelihood of developing certain illnesses. Personal behaviour and coping skills – balanced eating, keeping active, smoking, drinking, and how we deal with life's stresses and challenges all affect health.
- Health services - access and use of services that prevent and treat disease influences health,
- Gender - Men and women suffer from different types of diseases at different ages".

(Source: WHO, Health Impact Assessment; http://www.who.int/hia/evidence/doh/en/).

**Donor**: a person that provides human tissue samples, namely blood, urine, hair, teeth, nails, and breast-milk.

**Duplicate sample** (Johnson, 2011, p.64): "A '*duplicate sample*' is collected from the same site as another sample in a manner defined by the sampling procedures manual (see Fig. 4). This control sample, along with the '*routine sample*', collected from the same site, form a duplicate pair, and give an indication of 'within site' variability, *i.e.*, sampling variance. As it is collected during fieldwork it is often also referred to as a *field duplicate*."

**Epidemiology** is the science that studies the patterns, causes, and effects of health and disease conditions in defined populations; it is the cornerstone of public health, and informs policy decisions and evidence-based practice by identifying risk factors for disease and targets for preventive healthcare (Source: https://en.wikipedia.org/wiki/Epidemiology). – See Cross-sectional epidemiological study

**Exposure** (see Human exposure)

**Geochemical background** (Johnson and Demetriades, 2011, p.19): "In the context of the urban environment, the geochemical background can be defined as: "*A relative measure to distinguish between natural element or compound concentrations and anthropogenically-influenced concentrations in real sample collectives*" (Matschullat *et al.*, 2000). This can be expressed as a simple equation:

URBAN BASELINE = **BACKGROUND** + Anthropogenic Contribution

This is a fundamental equation in the interpretation and modelling of urban geochemical data. In the absence of any or negligible anthropogenic contribution the urban baseline will be equivalent to the background, and many chapters in this volume use the principle that outside of urban areas we can define the 'natural' baseline (Flight and Scheib, 2011; Tarvainen and Jarva, 2011). The caveat being that the 'natural' geochemical baseline around urban areas needs to have similar soil types and underlying parent material, as those upon which the urban area has been developed. In the equation above, if the 'natural' geochemical baseline replaces the term background, then the anthropogenic contribution in an urban area can be estimated by subtracting the 'natural' baseline from the urban baseline. In reality, this is a more complex estimation, because the background may be made up of many contributing geochemical populations (caused by variations in underlying parent material, *for example*), and the anthropogenic contribution is likely to be from multiple sources. Statistical methods for distinguishing baselines and backgrounds are discussed by Lima (2008) and Albanese *et al.* (2008)."

**Geochemical anomaly** (Govett, 1983, p.30): "An abnormally high or low content of an element or element combination, or an abnormal spatial distribution of an element or element combination in a particular sample type in a particular environment as measured by a particular analytical technique".

**Geochemical baseline** (Johnson and Demetriades, 2011, p.18-19): "The following definition of a *geochemical baseline* is based on that used by the Forum of European Geological Surveys (FOREGS) Geochemical Baseline Mapping Group:

"***A geochemical baseline is the concentration at a specific point in time of a chemical parameter (element, species or compound) in a sample of geological material. It is a fluctuating surface rather than a given value***".

The *geochemical baseline* of element/compound X can be defined as a function of the methodology used to determine it:

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

for 1 to n samples from different locations at a specified point in time, where

A = a defined medium type,

B = a documented sampling method,

C = a documented sample preparation protocol, and

D = a documented analytical method.

A *geochemical baseline* simply reports the chemical state of the surface environment, exactly as it is, with no interpretation or partitioning of the data. The *geochemical baseline* is defined at a specific point in time.

Defining the *geochemical baseline* as a function in this way emphasises the fact that different methodologies will give different baselines. Hence, the need for standardised methodologies, if *geochemical baselines* between different projects and areas are to be compared.

When geochemical mapping in areas of little anthropogenic activity, with the exception of catastrophic events, such as volcanic eruptions or extensive flooding, the *geochemical baseline* changes slowly in response to natural changes in an order of magnitude of decades or centuries. Changes to the urban *geochemical baseline*, as a result of constant anthropogenic activity, would be anticipated as being more rapid, so the time component is a more important factor (Johnson and Ander, 2008)".

**Greenfield**: "Greenfield land is undeveloped land in a city or rural area either used for agriculture, landscape design, or left to evolve naturally. These areas of land are usually agricultural or amenity properties being considered for urban development. Greenfield land can be unfenced open fields, urban lots or restricted closed properties, kept off limits to the general public by a private or government entity" (Source: https://en.wikipedia.org/wiki/Greenfield_land).

**Guideline or Intervention values** (Johnson and Demetriades, 2011, p.19): "These values, often enshrined in legislation, are determined after lengthy consultations by multi-disciplinary teams to which applied geochemists make an important contribution. A good example of how soil guideline values (SGVs) are derived is given by the UK Environment Agency (EA, 2009)".

**Heterogeneity** (noun): "the quality or state of being *heterogeneous* (adjective), meaning made up of different" (Oxford, 1993), *i.e.*, the soil is composed of widely dissimilar constituents.

**Heterogeneous** (see Heterogeneity)

**Homogenise**: the process by which a sample is churned up by physical or mechanical means in such a way that it finally has a uniform composition independent of which sub-sample is taken.

**Hot spot** (see neoanomaly)

**Human exposure**: Exposure occurs when there are complete pathways between a chemical or physical agent and humans.

**Interdisciplinarity**: See Multidisciplinarity

**Intervention value** (see Guideline)

**Milling** is the process of crushing or pulverising the sample to a fine powder, usually <250 µm.

**Multidisciplinarity** "draws on knowledge from different disciplines but stays within their boundaries. *Interdisciplinarity* analyses, synthesises and harmonises links between disciplines into a coordinated and coherent whole. *Transdisciplinarity* integrates the natural, social and health sciences in a humanities context, and transcends their traditional boundaries. The objectives of multiple disciplinary approaches are to resolve real world or complex problems, to provide different perspectives on problems, to develop comprehensive research questions and guidelines, and to provide comprehensive health services. Multiple disciplinary teamwork has both benefits and drawbacks" (Choi and Pak, 2006).

**Neoanomaly**: A *geochemical anomaly* caused by industrial and urban development. This is a term introduced by the Russian geochemist V.A. Kovda (1974), and introduced in the Western world by Davies (1980). This is a far better term than *'hot spot*', but for some peculiar reason is not used (Demetriades, 2011b).

**Persistent organic pollutants (POPs)** "are chemical substances that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment. With the evidence of long-range transport of these substances to regions where they have never been used or produced and the consequent threats they pose to the environment of the whole globe, the international community has now, at several occasions called for urgent global actions to reduce and eliminate releases of these chemicals" (Source: http://www.chem.unep.ch/pops/). This group of priority pollutants consists of pesticides (such as DDT), industrial chemicals (such as polychlorinated biphenyls, PCBs) and unintentional by-products of industrial processes (such as dioxins and furans).

**Plasticise** is the process of adding a plasticiser on a card or sheet of paper to make it impervious to moisture and water. In this particular case, the small 10-cm card, used as a scale for taking photographs, was plasticised.

**Pollutant** is a substance or energy introduced into the environment that has undesired effects, or adversely affects the usefulness of a resource. A pollutant may cause long- or short-term damage by changing the growth rate of plant or animal species, or by interfering with human amenities, comfort, health, or property values (Source: https://en.wikipedia.org/wiki/Pollutant).

**Pollution**: The introduction into the natural environment of a substance that has harmful or poisonous effects or causes adverse changes (Source: https://en.wikipedia.org/wiki/Pollution).

**Precision** (Johnson, 2011, p.68): "*Precision* is a measurement of how closely the analytical results can be reproduced, and is independent of the true value."

**Primary reference material** (see Reference material)

**Quality control samples**: *Quality control samples* are the samples that are used to validate the generated analytical results. These include *Primary* and *Secondary reference samples* (see Reference material), replicate splits of the field routine and duplicate samples and blank solid samples.

**Raw results**: The analytical data as received from the laboratory.

**Reference material** (Johnson, 2011, p.64-65): "*Reference materials* are samples that have been collected, prepared and analysed according to documented procedures, and analysed repeatedly, to give what become accepted '*true*' values. *Primary reference materials* (PRMs) are internationally certified standards with recognised and accepted elemental concentrations. *Secondary reference materials* (SRMs) are generally in-house reference samples developed for internal use by projects, and are kept 'blind' to the analyst. They are cheaper than PRMs, and are submitted at more frequent intervals in the analytical batch. *Reference materials* can be used to indicate the accuracy and precision of the analytical method, and are particularly important for levelling results generated over a long period of time, often by different laboratories or analytical methods. There are not that many PRMs and these thus have the disadvantage that the lab may have used the same PRM to calibrate the instrument(s). Furthermore, PRMs are usually quite expensive and too valuable to be used in large quantities for routine QC. In addition, they are more easily detected in a submission than a SRM – strong reasons to use SRMs for routine quality control."

**Replicate sample** (Johnson, 2011, p.64): "This is made at the field base or laboratory by dividing a collected sample, according to a well-defined protocol. The replicate pair can be used to identify laboratory error. If *replicates* are made from the pair of duplicate samples described above (see Fig. 4), then ANOVA (analysis of variance) can be used to attribute sources of element variability between sites (geochemical or natural variance), within sites (sampling variance) and within the laboratory (analytical variance), and estimate measurement uncertainty (see Demetriades, 2011b). Such samples are also referred to as laboratory duplicates or subsamples – herein the use of '*replicate*' is preferred, since it gives a clear distinction from the field duplicate control sample."

**Road dust**: "is earthen material or dirt that becomes airborne, primarily by the friction of tires moving on unpaved dirt roads and dust-covered paved roads. It consists mainly of coarse particles, which in some cases may be contaminated with human-made and naturally-occurring pollutants, such as asbestos, mining by-products, animal and human waste, snow and ice control applications (salts) and engine oil" (USEPA, 2012). Synonyms: *Road sediment* and *roadside sediment*.

**Road sediment**: see Road dust

**Roadside sediment:** see Road dust

**Routine sample**: It is the sample collected from all the planned sample sites of a geochemical project.

**Secondary reference material** (see Reference material)

**Sheath air** "is clean filtered air that surrounds the aerosol stream to prevent particulates from circulating or depositing within the optic chamber" (Source: http://www.sensidyne.com/dust-particulate-monitor-nephelometer-aerosol-monitor/sheath-air-dust-monitor.php).

**Stemflow**: "Water from precipitation that reaches the ground by running down the trunks of trees or plant stems" (Neuendorf *et al.*, 2011).

**Shewhart chart** or *control chart* or *X-chart* or *process-behaviour chart* in statistical process control is a tool used to determine if an analytical process is in a state of statistical control. It is a time sequenced graph with fixed defining limits (Miller and Miller, 2005; Johnson, 2011). The x-axis shows the date of analysis or the laboratory batch, if batch numbers are assigned sequentially. The y-axis shows the element concentration and the accepted value (AV) for the reference material, a value calculated from previous repeated analyses of the reference material. The AV will depend on the method of chemical extraction and analysis - a partial method of extraction will yield a lower AV than a total extraction method. If the study of the control chart indicates that the analytical process is currently under control (*i.e.*, is stable, with variation only coming from sources common to the process), then no corrections or changes to the analytical process control parameters are needed or desired. If the chart indicates that the monitored analytical process is not in control, the study of the chart can help determine the sources of variation, as this will result in degraded process performance. A process that is stable, but operating outside of desired (specification) limits needs to be improved through a deliberate effort to understand the causes of current performance and fundamentally improve the process (Source: https://en.wikipedia.org/wiki/Control_chart; slightly modified for checking of analytical results. The Shewhart chart is named after Walter Andrew Shewhart (see https://en.wikipedia.org/wiki/Walter_A._Shewhart).

**Superfund site**: "Superfund or Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) is a United States federal law designed to clean up sites contaminated with hazardous substances as well as broadly defined "pollutants or contaminants". Superfund also gives authority to federal natural resource agencies, states and Native American tribes to recover natural resource damages caused by releases of hazardous substances, and it developed the Agency for Toxic Substances and Disease Registry (ATSDR)" – (Source: https://en.wikipedia.org/wiki/Superfund).

**Toxic element**: An elements that is toxic to the human body, as it interferes with its functioning and undermines health, *e.g.*, mercury, lead, cadmium, aluminum, and arsenic. These toxic metals have no known physiological functions.

**Transdisciplinarity**: See Multidisciplinarity

**Throughfall**: "Water from precipitation that falls through the plant cover directly onto the ground or that drips onto the ground from branches and leaves" (Neuendorf *et al.*, 2011).

**Truncated data**: Determinand concentration values that are not reported if the value exceeds some upper limit.

**Uncensored data**: Determinand concentration values reported as measured by the analytical instrument.

**Variogram**: "In spatial statistics, the theoretical variogram $2\gamma(x,y)$ is a function describing the degree of spatial dependence of a spatial random variable or stochastic process $Z(x)$. For instance in geochemistry, a variogram will give a measure of how much two samples taken from the project area will vary in gold percentage depending on the distance between those samples. Samples taken far apart will vary more than samples taken close to each other" (Source: https://en.wikipedia.org/wiki/Variogram; slightly modified).

**Venipuncture** or "*venopuncture* or *venepuncture* is the process of obtaining intravenous access for the purpose of blood sampling of venous (vein) blood. This procedure is performed by trained medical practitioners" (Source: https://en.wikipedia.org/wiki/Venipuncture).

**Venous blood** is "deoxygenated blood which travels from the peripheral vessels, through the venous system into the right atrium of the heart" (Source: https://en.wikipedia.org/wiki/Venous_blood).

**Volatile Organic Pollutants (VOCs)**: "are organic chemicals that have a high vapor pressure at ordinary room temperature. Their high vapour pressure results from a low boiling point, which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air. For example, formaldehyde, which evaporates from paint, has a boiling point of only –19°C (Source: https://en.wikipedia.org/wiki/Volatile_organic_compound; for other definitions consult the USGS Environmental Health – Toxic Substances web page on volatile organic compounds: http://toxics.usgs.gov/definitions/vocs.html).

**X-chart** (see Shewhart chart)

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# APPENDIX 3:  Chemical characteristics of contaminating activities

Table of contaminating activities and their probable organic and inorganic contaminants.  The classification is according to the European Classification of Economic Activities, NACE (EuroStat, 2008), which has been simplified for the purposes of this manual.  Note:  At the end of the Table, there is a list of all abbreviations.

| ***Activity:  Industry, Enterprise*** | ***Organic contaminants*** | ***Inorganic contaminants*** |
|---|---|---|
| Agriculture (including chemical & livestock fertilisers) | Pesticides, Herbicides, Insecticides | As, B, Ba, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, Sb, Se, Zn, $NH_3$, nitrates, nitrites, sulphates, CN, $Cl^-$, $F^-$ |
| Airport | BTEX, PCBs, TPH, VHH, MOHC, Phosphate ester | As, Br, Cd, Hg, Pb, $SO_2$, $CO_2$, CO, $NO_x$, $N_2O$, $NH_3$ |
| Automobile repair and painting | BTEX, MTBE, PAHs, PCBs, TPH, VHH, aliphatic hydrocarbons, Chlorinated hydrocarbons, Organolead compounds, AOX, Phenol index | Cd, $Cl^-$, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, Ti, Zn, Sulphate |
| Battery | PCBs, PAHs, Hydrocarbons | Be, Cd, Cu, Fe, Hg, K, Mg, Mn, Ni, Pb, Se, Zn, Sulphate |
| Beverages manufacture | BTEX, PAHs, PCBs | Cu, Cr, Pb, Zn, $SO_x$, Nitrates, Phosphates |
| Brick making industries | BTEX, TPH, PAHs, PCBs, Aliphatic hydrocarbons | Al, B, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn |
| Cartridges manufacture and Shooting ranges | PCBs, Nitroaromatics | Ba, $Cl^-$, Cu, Ni, P, Pb, Sn, Sr, Zn and inorganic compounds |
| Cast iron smelting | BTEX, PAHs, PCBs, TPH, Hydrocarbons, Phenol index | B, $Cl^-$, CN, Fe, Mn, P, Sulphate |
| Cement manufacture | BTEX, HFCs, TPH, PAHs, PCBs, Aliphatic hydrocarbons, Dioxins, Furans | Al, As, Be, Cd, Cl, Co, Cr, Cu, F, Fe, Hg, Mn, Ni, Pb, Sb, Tl, V, Zn, $NH_3$, $NO_x$, $SO_x$, Sulphate |
| Chemical fertilisers manufacture, including phosphate fertilisers | PAHs, TPH, Hydrocarbons, Pesticides | As, Cd, Cr, Cu, Hg, Mn, Ni, P, Pb, Sb, Se, V, Zn and inorganic compounds |
| Chromite smelting | BTEX, PAHs, PCBs, TPH | Cr, Ni, Fe, V |
| Copper smelting and production | BTEX, PAHs, PCBs, TPH, Hydrocarbons, AOX, Hexachlorbenzol | Al, Ag, As, Au, B, Ba, Cd, Co, Cr, Cu, $F^-$, Fe, Ni, P, Pb, Pd, Pt, Sb, Se, Sn, Te, U, V, Zn, Nitrate, Nitrite, Sulphate, Sulphide, Sulphite, CN |
| Cosmetics, Toiletries & Disinfectants manufacture | BTEX, PAHs, PAE, PCBs, VHH, Phenols, Chlorophenols, Dioxins, Furans, Chlorinated aromatic hydrocarbons | As, B, Ba, Cr, Cu, Hg, Ni, Pb, Zn |
| Dockyards (including shipbuilding) | BTEX, PAHs, PCBs, TPH, VHH, Biocides, Pesticides, Phenols, Chlorophenols, Aliphatic hydrocarbons, Organotin compounds | As, Cd, Cr, Cu, $F^-$, Fe, Hg, Mg, Mn, Ni, Pb, Sn, Zn and inorganic compounds (CN) |
| Electric power plant & distribution station | PAHs, PCBs, BTEX, Hydrocarbons | As, B, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, V, Zn, Sulphate |
| Farming of animals (including pig, cow, sheep, goat & poultry) | Pesticides, Phenol index, Hydrocarbons | As, B, Cd, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, Sb, Se, Zn, $NH_3$, nitrates, nitrites, sulphates, $Cl^-$ |
| Food products and beverages manufacture (including all types of food manufacturing, *e.g.*, dairy products, canned fruit, juice & vegetable) | Acetaldehyde, Acetone, Ethylene glycol, Methanol, Pesticides, HFCs, $CH_4$, BTEX, PAHs, Pesticides, Volatile hydrocarbons | Ba, Cd, Cu, Hg, Ni, P, Zn, Ammonia, Ammonium sulphate (solution), Phosphoric acid, Sulphuric acid, Nitric acid, Chlorine, $NH_3$, $NO_x$, nitrates, nitrites |
| Footwear manufacture | PAHs, Toluene, Methyl ethyl ketone, Acetone, Glycol ethers, Xylene, Methyl isobutyl ketone | Al, As, B, Ca, Cd, Cr, $F^-$, Fe, Hg, Mg, Mn, Na, P, Ti, Sr, $NH_3$, Ammonium sulphate, Nitrate, Nitrite |
| Funeral and related activities (including Cemeteries) | Formaldehyde, various organic pollutants (Furans, Dioxins, Hydrocarbons, Phenols) | As, Cu, Fe, Hg, Pb, Zn, Phosphates, Ammonium, Nitrates |

| ***Activity: Industry, Enterprise*** | ***Organic contaminants*** | ***Inorganic contaminants*** |
|---|---|---|
| Furniture manufacture | BTEX, PAHs, Phenols, Phenol index, Total chlorophenols, Pesticides, Aliphatic hydrocarbons, Organotin compounds | As, B, Cu, Cr, $F^-$, Hg, Ni, Pb, Zn, $NH_3$ |
| Glass manufacture | BTEX, HFCs, PAHs, TPH, VHH, Aliphatic hydrocarbons, Dioxins, Furans, Phenol index | Ag, As, B, Ba, Bi, Cd, Cl, Co, Cr, Cu, $F^-$, Fe, Hg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Ti, Tl, Zn, Zr, $NH_3$, $NO_x$, $SO_x$, and inorganic compounds (Nitrate, Sulphate, Sulphide) |
| Hospital activities | BTEX, PCBs, TPH, PAHs, Phenol index, Phenols, Hydrocarbons, Organic acids, Pesticides | Ag, Al, As, B, Ba, Be, Bi, Cd, $Cl^-$, Co, Cr, Cu, Fe, $F^-$, Ge, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sn, Ti, Pt, Zn, Zr, CN |
| Leather clothes manufacture | PAHs, Toluene, Methyl ethyl ketone, Acetone, Glycol ethers, Xylene, Methyl isobutyl ketone, Phenol index, Hydrocarbons | As, B, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, CN, Ammonium sulphate, Nitrates, Nitrites, $NH_3$ |
| Machinery including electrical | BTEX, PAHs, PCBs, TPH, VHH, Phenols, Chlorophenols, Dioxins, Furans, Aliphatic hydrocarbons, 1,1,1-Trichloroethane, Freon 113, Trichloroethylene, Methyl ethyl ketone, Dichloromethane, Hydrocarbons | As, B, Cd, $Cl^-$, Cr, Cu, Fe, Hg, Ni, P, Pb, Sn, Zn and inorganic compounds (Sulphuric acid, Nitric acid, Nitrite, Ammonium sulphate, Sulphate) |
| Metal plating & aluminium anodising including galvanised pipes | NMVOC, PAHs, PFCs, $SF_6$, Cyanide, Benzene, 1,1,1-Trichloroethane, Dioxins, Furans, BTEX, Hydrocarbons, AOX, Organic acids | Al, As, B, Cd, $Cl^-$, Co, Cr, Cu, F, Fe, Hg, Mg, Mo, Ni, P, Pb, Sb, Sn, V, Zn, Sulphuric acid, Hydrochloric acid, $NH_3$, $NO_x$, $SO_x$, Sulphate, CN |
| Metal smelting, Metal treatment & Metal Works | BTEX, PAHs, PCBs, HCB, TPH, Phenols, Dioxins, Furans | Al, As, Ca, Cd, $Cl^-$, Cr, Cu, $F^-$, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sn, V, Zn, Zr, and inorganic compounds (HCN, CN, Sulphate) |
| Military installations, including explosives | BTEX, NMVOC, PAHs, PCBs, TPH, Hydrocarbons, Nitroaromatics | As, Ba, B, Ca, Cd, $Cl^-$, Cr, Cu, Hg, K, Mg, Na, Ni, P, Pb, Sn, Sr, Zn, $NH_3$, $NO_x$, Asbestos, Nitrate, Nitrite, Sulphate |
| Mining of non-ferrous metal ores, except uranium and thorium ores | BTEX, PAHs, PCBs, TPH | As, B, Cd, Cr, Cu, Hg, Ni, Zn, $Cl^-$, sulphates |
| Mining: Asbestos | BTEX, PAHs, PCBs, TPH | Co, Cr, Ni, asbestos fibres |
| Mining: Chromite | BTEX, PAHs, PCBs, TPH | As, Cr, Ni, Fe, V, Zn |
| Mining: Copper | BTEX, PAHs, PCBs, TPH | As, Ba, Cd, Co, Cr, Cu, Fe, Ni, Pb, U, V, Zn |
| Mining: Pyrite | BTEX, PAHs, PCBs, TPH | As, Ba, Cd, Co, Cr, Cu, Fe, Ni, Pb, U, V, Zn |
| Non-metallic industries (including brick makers, stone makers & plaster) | BTEX, TPH, PAHs, PCBs, Aliphatic hydrocarbons | Al, B, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn |
| Paint and lacquer manufacture | BTEX, PAHs, PCBs, VHH, Phenols, Organotin compounds | Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Ti, Zn, Sulphide |
| Pesticides/ herbicides/ Insecticides manufacture | BTEX, PAHs, TPH, VHH, Chlorophenols, Dioxins, Furans, Aliphatic hydrocarbons, Organotin compounds | As, Ca, Cd, Co, Cr, Cu, $F^-$, Hg, K, Mg, Na, Ni, Pb, REE, Sb, U, Zn and inorganic compounds (sulphate) |
| Petrol station | BTEX, MTBE, TPH, Aliphatic hydrocarbons, Organolead compounds, Trichloroethylene, AOX | Ba, $Cl^-$, Cu, Cd, Fe, Mn, Pb, Ni, Zn, Sulphate |
| Petroleum bulk storage | BTEX, MTBE, NWVOC, PAHs, PCBs, TPH, Phenols, Aliphatic hydrocarbons, Organolead compounds, AOX | As, Cd, $Cl^-$, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, V, Zn, CN, $NH_3$, $SO_x$, Ammonium sulphate, Sulphate |
| Petroleum refinery & Bulk storage (Manufacture of coke, refined petroleum products and nuclear fuel) | BTEX, MTBE, NWVOC, PAHs, PCBs, TPH, Phenols, Aliphatic hydrocarbons, Organolead compounds, Pesticides (screening) | As, Cd, Cl, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, V, Zn, CN, $NH_3$, $SO_x$, Ammonium sulphate |

| ***Activity: Industry, Enterprise*** | ***Organic contaminants*** | ***Inorganic contaminants*** |
|---|---|---|
| Pharmaceuticals | BTEX, DCM, NMVOC, PAHs, PER, TCM, TRI, VHH, Chlorophenols, Phenol index, Aliphatic hydrocarbons, Chlorinated aromatic hydrocarbons, Organic acids | As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Sn, V, Zn and inorganic compounds ($NH_3$, $NO_x$, $SO_x$), CN |
| Photographic processing | BTEX, VHH, Phenol index, Aromatic amines, Organic acids | Ag, As, B, Br, Ca, Cd, Cr, Cu, Hg, K, Mg, Na, Pb, Sb, Zn and inorganic compounds (CN, Ammonium, Sulphate, Sulphite, Sulphide) |
| Plaster making industries | BTEX, TPH, PAHs, PCBs, Aliphatic hydrocarbons | Al, B, Cd, $Cl^-$, Cr, Cu, $F^-$, Fe, Hg, Mn, Ni, P, Pb, Ti, Zn |
| Plastic products | BTEX, PCBs, Acetone, Dichloromethane, Methyl ethyl ketone, Methanol, 1,1,1-Trichloroethane, Styrene, Phenols, Pesticides (screening), Hydrocarbons, Organic P, Phenol index, AOX, Tetrahydrofuran, Dimethylformamide | Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Hg, Pb, Sb, Sn, Sr, Ti, Zn, CN, Carbon disulphide, Nitrite, Sulphate, Sulphite, Sulphide |
| Pottery/Ceramics | BTEX, HFCs, PAHs, PCBs, TPH, Aliphatic hydrocarbons, Dioxins, Furans | As, B, Be, Cd, Cl, Co, Cr, Cu, F, Hg, Ni, Pb, Se, Sn, Ti, Tl, Zn, Zr, $NH_3$, $NO_x$, $SO_x$, and inorganic compounds |
| Prepared feeds manufacture for farm animals | BTEX, PAHs, VHH, Pesticides, Phenols | As, Cd, Cr, P |
| Prepared pet foods manufacture | BTEX, PAHs, VHH, Pesticides, Phenols | As, Cd, Cr, P |
| Processing and preserving of meat and meat products | BTEX, HFCs, PAHs, VHH, Pesticides, Phenols | As, Cd, Cr, $NH_3$, $NO_x$ |
| Publishing, printing and reproduction of recorded media | BTEX, PAHs, PCBs, VHH, Phenols, Organotin compounds | B, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Ti, Zn |
| Pulp, paper and paperboard manufacture | PAHs, PCBs, NMVOC, TPH, VHH, Pesticides, Phenols, Chlorophenols, Dioxins, Furans, Aliphatic hydrocarbons, Phenol index, Derivatives chlorinated benzene | Al, As, Ba, Cd, Cr, Cu, Hg, Mn, Na, Ni, P, Pb, Sb, Ti, Zn, Hydrochloric acid, Sulphuric acid, $NO_x$, $SO_x$, Ammonium sulphate, Chlorine, Chlorine dioxide |
| Rubber products | BTEX, PAHs, TPH, VHH, Phenols, Chlorophenols, Aliphatic hydrocarbons, Chlorinated aromatic hydrocarbons, Phenol index | Al, As, Ba, Ca, Cd, $Cl^-$, Cr, Cu, Fe, K, Mn, Mg, Na, Ni, Pb, S, Sb, Se, Te, Ti, Zn, and inorganic compounds (Thiocarbonate, Sulphuric acid, Hydrochloric acid, Sulphate, Sulphide) |
| Sawmilling and planing of wood; impregnation of wood | BTEX, PAHs, PCBs, Phenols, Total chlorophenols, Phenols, Pesticides, Aliphatic hydrocarbons, Organotin compounds, Nitroaromatics | As, B, Ba, Ca, $Cl^-$, Cu, Cr, $F^-$, Hg, Mg, Na, Ni, P, Pb, Zn, $NH_3$, Nitrate, Nitrite, Sulphate |
| Sewage and refuse disposal, sanitation and similar activities (including household wastes) | BTEX, MTBE, PAHs, PCBs, HFCs, PFCs, TCE, TCM, TPH, VHH, Pesticides, Phenols, Chlorophenols, Dioxins, Furans, Aliphatic hydrocarbons, $CH_4$, Chlorinated aromatic hydrocarbons, Organolead and Organotin compounds | As, B, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Zn and inorganic compounds ($NO_x$, $SO_x$, Hydrochloride, *etc.*) |
| Shipbuilding | BTEX, PAHs, PCBs, TPH, VHH, Biocides, Pesticides, Phenols, Chlorophenols, Aliphatic hydrocarbons, Organotin compounds | As, Cd, Cr, Cu, $F^-$, Fe, Hg, Mg, Mn, Ni, Pb, Sn, Zn and inorganic compounds (CN, Sulphate) |
| Slaughterhouses | BTEX, HFCs, PAHs, VHH, Pesticides, Phenols | As, Cd, Cr, $NH_3$, $NO_x$ |
| Stone making industries | BTEX, TPH, PAHs, PCBs, Aliphatic hydrocarbons | B, Cd, Cr, Cu, Hg, Ni, Pb, Zn |

| ***Activity: Industry, Enterprise*** | ***Organic contaminants*** | ***Inorganic contaminants*** |
|---|---|---|
| Tanning and dressing of leather | BTEX, MTBE, VHH, Aliphatic hydrocarbons, phenols | $Cr^{3+}$, $Cr^{6+}$, Cd, Pb and inorganic compounds ($NO_x$, Hydrochloric acid, Chlorides, Sulphides) |
| Textile finishing (*e.g.*, Textile bleaching & dyeing) | BTEX, NMVOC, PAHs, TPH, PCPs, Pesticides, Phenols, Chlorophenols, Hydrocarbons | Al, B, Ba, Cd, Cr, Cu, Hg, P, Sn, Ti, Zn, Sulphates, Sulphuric acid, Caustic soda, Sodium hypochlorite, Ammonium sulphate, Ammonia, Phosphoric acid, $NO_x$, $SO_x$, $Cl^-$, $F^-$ |
| Tobacco products manufacture | Propylene, Toluene, Acetone, Styrene, 2-Ethoxyethanol, Dibutyl phthalate, Methanol | Al, As, Ba, Be, Br, Cd, Co, F, Fe, Ge, Hg, Mn, Pb, Sb, Sr, Ti, Zn, Zr, $NH_3$, Chlorine compounds, |
| Umber, Bentonite & Gypsum manufacture | BTEX, HFCs, TPH, PAHs, PCBs, Aliphatic hydrocarbons, Dioxins, Furans | Al, As, B, Be, Cd, Cl, Co, Cr, Cu, F, Fe, Hg, Mn, Ni, P, Pb, Sb, Sr, Ti, Tl, V, Zn, $NH_3$, $NO_x$, $SO_x$, Sulphate, Sulphide |
| Vegetable and animal oils and fats manufacture | Pectins, Tannins, Phenols and Organic acids, Volatile hydrocarbons | Ba, Cu, Fe, Mn, Ni, S, P, Zn, Chlorine & N compounds, |
| Washing and dry-cleaning of textile and fur products | BTEX, TPH, VHH, Aliphatic hydrocarbons | B, Ca, Fe, K, Mg, Mn, Na, P, Ammonium, Sulphate, Sulphide |
| Waste treatment plant | BTEX, MTBE, PAHs, PCBs, PCPs, TPH, VHH, Pesticides, Phenols, Chlorophenols, Dioxins, Furans, Aliphatic hydrocarbons, Chlorinated aromatic hydrocarbons, Organolead and Organotin compounds | Al, As, B, Ba, Ca, Cd, $Cl^-$, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, Sb, Se, Zn, Ammonium, Nitrate, Nitrite, Sulphate, Sulphide |
| Wearing apparel and accessories manufacture | 1,1,1-Trichloroethane, Methyl ethyl ketone, Toluene, Dichlorome-thane, Acetone, Xylene, Tetrachloroethylene, Pesticides (screening) | As, B, Cr, Cu, Mn, Sb, Zn, Sulphuric acid, Chlorine |
| Wines manufacture | BTEX, PAHs, PCBs | Cu, Cr, Pb, Zn, $SO_x$, Nitrates, Phosphates |

AOX: Adsorbable organically bound halogen

DCM: Dichloromethane

HCB: Hexachlorobenzene

HFCs: Total mass of hydrogen fluorocarbons, *i.e.*, sum of HFC23, HFC32, HFC41, HFC4310mee, HFC125, HFC134, HFC134a, HFC152a, HFC143, HFC143a, HFC227ea, HFC236fa, HFC245ca

MOHC: Metal Organic Heat Carrier

MTBE: Methyl-Tertiary-Butyl Ether

NMVOC: Total mass of Volatile Organic Compounds

PAE: Phthalatic Acid Esters (phthalates)

PAHs: Polycyclic aromatic hydrocarbons

PCBs: PolyChlorinated Biphenyls

PCPs: 1-(1-Phencyclohexyl) piperidine

PER: Tetrachloroethylene

PFCs: Total mass of perfluorocarbons, *i.e.*, sum of CF4, C2F6, C3F8, C4F10, c-C4F8, C5F12, C6F14

SF6: Total mass of sulphur hexafluoride

TCE: Trichloroethane-1,1,1

TCM: Tetrachloromethane

TPH: Total Petroleum Hydrocarbons

TRI: Trichloroethylene

VHH: Volatile Halogenated Hydrocarbons (Trichloromethane, *etc.*)

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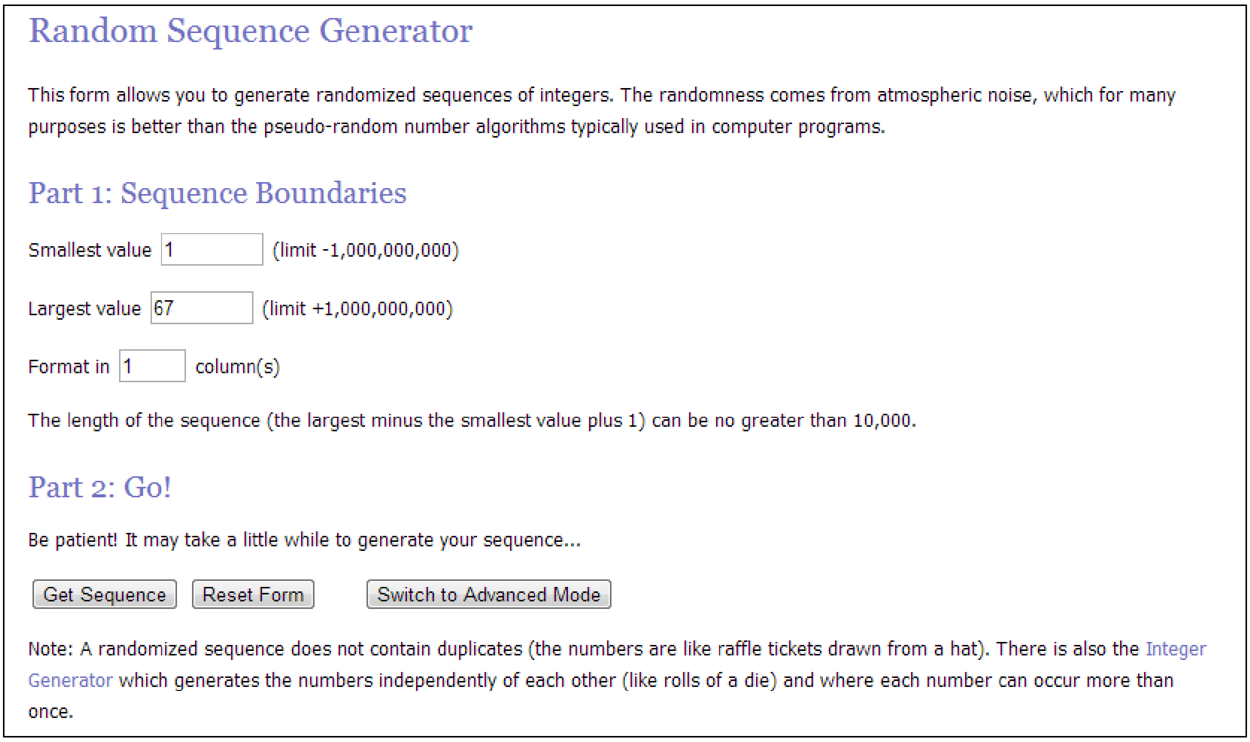
NOTE: This table was first compiled for use in the European Commission co-financed project NORISC (Network Oriented Risk assessment by In-situ Screening of Contaminated sites, EVKT-CT-2000-0026), which was completed in 2004 (http://ec.europa.eu/research/environment/print.cfm?file=/comm/research/environment/newsanddoc/article_1442_en.htm).

It was subsequently developed for use in the recording of potential contaminating activities in Hellas (Demetriades and Kaminari, 2005), and finally updated in 2015 for inclusion in this manual, with additions from Gihr *et al.* (1990) and Birke *et al.* (2009).

## APPENDIX 4:  Generation of random sample numbers

Random numbers can be generated quite easily using tools from the Web, as *for example*, the facility provided by the Random Organisation.  Since, most random number functions usually generate duplicates the ‘*Random Sequence Generator*’ should be used at http://www.random.org/sequences/, because it generates a sequence of unique numbers.  The case of Ajka (Hungary) is used as an example (see Figures A4.1 and A4.2):

(1) Enter the URL http://www.random.org/sequences/ in your web browser.
(2) Enter Smallest value:  1
(3) Enter Largest value:  67
(4) Format in:  1 (to give you the output in a single column)
(5) Click on ‘Get Sequence’
(6) Output is displayed in a window
(7) Use the ‘Copy & Paste’ command to copy the output into an Excel Worksheet.
(8) Place your samples according to the generated random number sequence, and
(9) Order your samples in a consecutive number sequence



Random Sequence Generator

This form allows you to generate randomized sequences of integers. The randomness comes from atmospheric noise, which for many purposes is better than the pseudo-random number algorithms typically used in computer programs.

Part 1: Sequence Boundaries

Smallest value 1 (limit -1,000,000,000)

Largest value 67 (limit +1,000,000,000)

Format in 1 column(s)

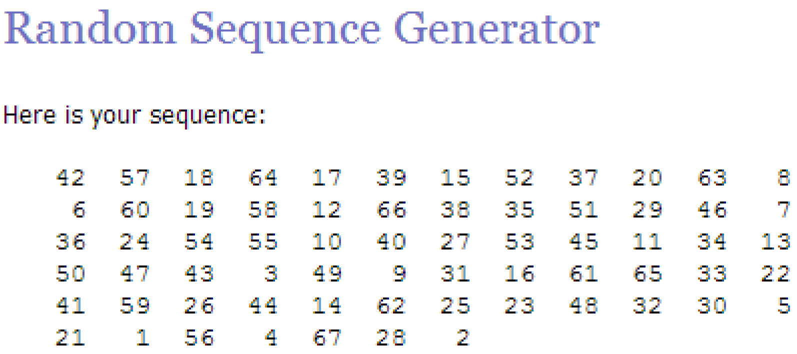
The length of the sequence (the largest minus the smallest value plus 1) can be no greater than 10,000.

Part 2: Go!

Be patient! It may take a little while to generate your sequence...

Note: A randomized sequence does not contain duplicates (the numbers are like raffle tickets drawn from a hat). There is also the Integer Generator which generates the numbers independently of each other (like rolls of a die) and where each number can occur more than once.

Figure A4.1.  Random number sequence generator input page from 1 to 67 (http://www.random.org/sequences/).



Random Sequence Generator

Here is your sequence:

```
42  57  18  64  17  39  15  52  37  20  63   8
 6  60  19  58  12  66  38  35  51  29  46   7
36  24  54  55  10  40  27  53  45  11  34  13
50  47  43   3  49   9  31  16  61  65  33  22
41  59  26  44  14  62  25  23  48  32  30   5
21   1  56   4  67  28   2
```

Figure A4.2.  Output of random number sequence from 1 to 67.  In the above case, the random numbers were output into twelve columns to include in this figure.

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# APPENDIX 5:  Field Observations Sheets

## Urban Soil Field Observations Sheet

## House Dust or Attic Dust Field Observations Sheet

## Road Dust or Road Sediment Field Observations Sheet

## Soil Sampling Protocol for Detailed Urban Soil Geochemical Mapping Surveys

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# URBAN TOPSOIL FIELD OBSERVATIONS SHEET

**SAMPLE ID:** ……………… **Date:** ………………... **Sampler ID:** ……………………………....

**SAMPLE SITE LOCATION**

**CITY:** …………………………………………………….. **MAP SHEET:** …………………………….

**COORDINATES** (in Degrees, Minutes and Seconds)**:**

Projection: Universal Transverse Mercator Zone: 36N (+30 to +36) Datum: WGS 1984

**Degrees:** **Longitude:** ……..°/……..'/……...'' **Latitude:** ……..°/……..'/……...''

**National:** **X-coordinate:** ……………….................. **Y-coordinate:** …………………………...

**SITE DESCRIPTION**

Landscape/Topography: ………………………........................... Altitude (m): ………………………...

Land use:

☐ Garden (specify plants): ........................................................................................................................

☐ Playground ☐ Kindergarten ☐ Schoolyard

☐ Grass-covered plot ☐ Park: Deciduous trees ☐ Park: Coniferous trees ☐ Park: Mixed trees

☐ Unused land ☐ Wetland ☐ Industrial (Specify): ...............................................

☐ Other (Specify): .....................................................................................................................................

Bedrock lithology: ……………………………... Outcrops: ☐ Yes, specify: …………………….........

Formation: ……………………………... ☐ No outcrops

Number of visible soil horizons: ........................................................................................................................

TOPSOIL sampling interval (0-10 cm); if other please state: …………......... cm ☐ Natural soil ☐ Anthropogenic modified soil

**ABUNDANCE OF SOIL CLASTS % (>2mm):**

0: ☐ 0-2: ☐ 2-5: ☐ 5-15: ☐ 15-40: ☐ 40-80: ☐ >80: ☐

**TEXTURE:**

Sandy: ☐ Sandy-loam: ☐ Loamy: ☐ Clayey-loam: ☐ Clayey: ☐ Clay: ☐

**SAMPLE HUMIDITY:** Dry: ☐ Moist: ☐ Wet: ☐

**ORGANIC CONTENT:** Low: ☐ Medium: ☐ High: ☐

**POSSIBLE SOURCES OF CONTAMINATION** (specify): ...................................................................................................

...................................................................................................

**REMARKS**: ........................................................................................................................................

........................................................................................................................................

........................................................................................................................................

........................................................................................................................................

........................................................................................................................................

........................................................................................................................................

Sample number: ............................................................ Sample site photograph: ..................................................

North facing photograph: ............................................... East facing photograph: ....................................................

South facing photograph: ............................................... West facing photograph: ..................................................

Additional photograph: .................................................. Additional photograph: ....................................................

# HOUSE or ATTIC DUST FIELD OBSERVATIONS SHEET

**SAMPLE ID:** ……………… **Date:** ………………... **Sampler ID:** …………………………….....

**SAMPLE SITE LOCATION**

**REGION:** …………………………………………………….. **MAP SHEET:** ……………………………

**COORDINATES** (in Degrees, Minutes and Seconds)**:**

Projection: Universal Transverse Mercator Zone: 36N (+30 to +36) Datum: WGS 1984

**Degrees:** **Longitude:** ……..°/……..'/……...'' **Latitude:** ……..°/……..'/……...''

**National:** **X-coordinate:** ……………….................. **Y-coordinate:** …………………………...

**SITE DESCRIPTION**

Landscape/Topography: ………………………… Altitude (m): ………………………...

Land use in the immediate vicinity of house/flat:

☐ Garden (specify plants): ..........................................................................................................................

☐ Playground ☐ Kindergarten ☐ Schoolyard

☐ Grass-covered plot ☐ Park: Deciduous trees ☐ Park: Coniferous trees ☐ Park: Mixed trees

☐ Unused land ☐ Wetland ☐ Industrial (Specify): ..............................................

☐ Other (Specify): ...........................................................................................................................

Bedrock lithology: …………………………… Outcrops: ☐ Yes, specify: ……………………..........

Formation: …………………………… ☐ No outcrops

Type of overburden: ………………………………………………………………………………

**SAMPLE TYPE:**

House dust ☐ Specify part of house (whole/room): ..................................................................

If in storey of flats, specify floor: ........................................................................

Attic dust ☐

**POSSIBLE SOURCES OF CONTAMINATION** (specify): ………………………………………………....................

..........................................................................................

**REMARKS**: .............................................................................................................................................

.....................................................................................................................................................

.....................................................................................................................................................

…………………………………………………………………………………………………………

General photograph Site photograph

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# ROAD DUST or ROAD SEDIMENT FIELD OBSERVATIONS SHEET

**SAMPLE ID:** ……………… **Date:** ………………... **Sampler ID:** ……………………………....

**SAMPLE SITE LOCATION**

**REGION:** …………………………………………………….. **MAP SHEET:** ……………………………

**COORDINATES** (in Degrees, Minutes and Seconds)**:**

Projection: Universal Transverse Mercator Zone: 36N (+30 to +36) Datum: WGS 1984

**Degrees:** **Longitude:** ……..°/……..'/……...'' **Latitude:** ……..°/……..'/……...''

**National:** **X-coordinate:** ……………….................. **Y-coordinate:** …………………………...

**SITE DESCRIPTION**

Landscape/Topography: ………………………… Altitude (m): ………………………...

Land use in the immediate vicinity of sampling site:

☐ Garden (specify plants): ....................................................................................................................................

| | | |
|---|---|---|
| ☐ Playground | ☐ Kindergarten | ☐ Schoolyard |
| ☐ Grass-covered plot | ☐ Park: Deciduous trees | ☐ Park: Coniferous trees ☐ Park: Mixed trees |
| ☐ Unused land | ☐ Wetland | ☐ Industrial (Specify): ............................................... |

☐ Other (Specify): ....................................................................................................................................

Bedrock lithology: …………………………… Outcrops: ☐ Yes, specify: …………………….........
Formation: …………………………… ☐ No outcrops

Type of overburden: ……………………………………………………………………………………

**SAMPLE TYPE:**

Road dust ☐

Road sediment ☐

**POSSIBLE SOURCES OF CONTAMINATION** (specify): ……………………………………………….......................
..................................................................................................

**REMARKS**: ...................................................................................................................................................

......................................................................................................................................................................

......................................................................................................................................................................

……………………………………………………………………………………………………………

| General photograph | Site photograph |
|---|---|
| | |

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## Appendix 5: Instructions of how to complete the Soil Sampling Protocol for Detailed Urban Soil Geochemical Mapping Surveys

The soil sampling protocol facilitates the systematic recording of observations that should be made at each topsoil/subsoil sample site in a detailed urban geochemical mapping survey, and their electronic storage for subsequent computerised data treatment. As field observations are important in the interpretation of geochemical data, it is absolutely necessary to provide all the information requested in the Field Observation Protocol. Exceptions and further information are given in the following description of the protocol form. To ensure that the sample descriptions of the different sample collectors can be compared, the form for the data recorded in the field should be completed as precisely as possible.

In general, the following should be noted:

The sample number is already printed on the Soil Sampling Protocol. Ensure that the sample number is the same:

- On all four pages of the form, and
- On the outside of the Rilsan® sample bag, and on both sides of the small card.
- Each town or city should be given a three letter code, and the routine sample number shall consist of the town or city code, and the sample number (four digits).
- The topsoil sample collected at each site bears the town or city code and just the sample site number.
- The subsoil sample collected at the same site as the topsoil sample bears the same sample number as the topsoil, and at the end of the number the capital letter "B" is added.
- Field duplicate samples should be collected at every 20th sample site, and bear the same sample number as that of the routine sample, but at the end they will have a capital letter "D". The topsoil sample number has at the end just the letter "D", and the subsoil sample number the letters "BD".

- In general, all of the parts of the form are to be completed. Exceptions are given in the following description of the individual parts of the form.
- The squares at the top and the right (❐) should not be completed by the sample collector. They will be used for respective characteristics and provide a control of the protocol for logical errors and missing data.
- Simple lines (___) are provided for writing alphanumeric data.
- The squares shaded at the bottom and the right (❑) should be used for numbers or letters, depending on the information requested (write only one number or letter per square).
- Circles (○) will be used for the various possibilities of a specific characteristic, *e.g.*, grain size. Tick only one circle for each characteristic. Multiple ticks cannot be coded, and thus invalidate the recorded information. *Hence, the importance that each evening all field observations are checked to ensure that the recorded information is correct.*
- Circles containing a number (①②) are for complex characteristics (*e.g.*, colour) or for two characteristics with the same code (*e.g.*, regional land use or regional sub-land use). Each number for a characteristic is to be ticked only once, *i.e.*, 1x①, 1x②, 1x③. Multiple ticks for a number are invalid.
- Numbers in a white or black circle (①➊) are for characteristics for different soil horizons (*e.g.*, colour). The numbers in a white circle are for the topsoil horizon; the numbers in a black circle are for the lower subsoil horizon; if there is only one horizon, only the field for the topsoil horizon should be ticked.

### 1. Sampling Date

Enter the date the sample is collected: day (01 to 31); month (01 to 12); year (20☐☐)

### 2. Sample Collector

Enter the name of the person collecting and describing the sample material.

### 3. Topographical Map Sheet

Give the number of the topographical map sheet 1:25000, 1:10000 or 1:5000 of the area from which the sample is taken. Write the name of the map on the line, and its national reference number in the boxes.

### 4./5. Northing/Easting

The fields for Northing and Easting are to be completed in the field. National and Universal Transverse Mercator (WGS 1984) should be recorded.

The location at which the sample is taken should be marked with a cross as exactly as possible on the topographical map, together with the last three or four digits of the sample number, *for example*:

- sample ATH0321 should be marked on the map as 321, and
- sample ATH1765 should be marked as 1765.

The recording of the sample location on the topographical map should be done in the field, just in case the GPS fails to record correctly the coordinates.

### 6. Sampling Depth

The upper and lower depth levels (in centimetres) should be entered in the respective boxes. The lower level should be at 10 cm except in the case of a vertical soil profile. The upper level should be at 0.00 cm where possible. In case, of grass or humus horizons, the zero level starts at the base of the grass roots, and the bottom of the humus horizon, respectively.

### 7. Geology/Soil

This section should not be completed in the field.

### 8. Slope gradient

Try to select a flat patch of land for sampling. If this is not possible, then the slope gradient is to be classified according to the following table:

| Classification of slope gradient | Description |
|---|---|
| Not sloped | <0.5°gradient <1° |
| Very slightly sloped | 1° ≤ gradient <2° |
| Slightly sloped | 2° ≤ gradient <3° |
| Medium slightly sloped | 3° ≤ gradient <5° |
| Medium sloped | 5° ≤ gradient <7° |
| Medium strong sloped | 7° ≤ gradient <10° |
| Strong sloped | 10° ≤ gradient <15° |
| Very strong sloped | 15° ≤ gradient <20° |
| Steep | 20° ≤ gradient <30° |
| Very steep | ≥30° |

## 9. Soil moisture

The moisture content of the sample is to be classified according to the following table:

| Classification | Criteria |
|---|---|
| dry | • Soil feels dry, powdery<br>• becomes distinctly darker when moistened |
| slightly moist | • Soil feels cool, does not break down into a powder<br>• does not become significantly darker when moistened |
| moist | • Soil feels distinctly moist<br>• in contact with paper, the paper becomes moist<br>• can be shaped into lumps<br>• does not drain any water |
| wet | • When squeezed, the hand becomes moist<br>• soil is saturated and drops of water drain from it |
| very wet | • Water seeps from the soil |

## 10. Colour of the sample

Typically, the soil colour is classified according to the Munsell colour chart. The colour, however, can also be characterised by older norms or state-owned colour tables.

Hence, each colour description consists of three parts:

- the hue (basic colour) (field b, number 3 - ③❸),
- the value (field b, number 2 - ②❷), and
- the chroma (intensity) (field a, number 1 - ①❶).

The hue (basic colour) and the chroma (intensity) should always be recorded. If the colour is unambiguously described by basic colour and intensity, then value and hue (basic colour) are identical.

For example, if the colour is dark brownish grey:

- a) Colour intensity: ①❶ a cross is to be marked at number 4, dark
- b) Colour: ②❷ a cross is to be marked at number 5, brown
- b) Colour: ③❸ a cross is to be marked at number 1, grey.

If the colour is dark brown:

- a) Colour intensity: ①❶ a cross is to be marked at number 4, dark
- b) Colour: ②❷ a cross is to be marked at number 5, brown
- b) Colour: ③❸ a cross is to be marked at number 5, brown.
-

The colour of the upper horizon is to be entered at ①, ②, and ③ in the field for the topsoil horizon and at ❶, ❷ and ❸ for the lower (subsoil) horizon. If there is only one horizon, then only the field for the upper horizon is used.

On the Munsell colour chart, the colours are defined by a combination of symbols of letters and numbers, where the hue (colour), the value (brightness/grey scale), and chroma (intensity) are considered.

## 11. Grain size

The grain size is classified according to the following table:

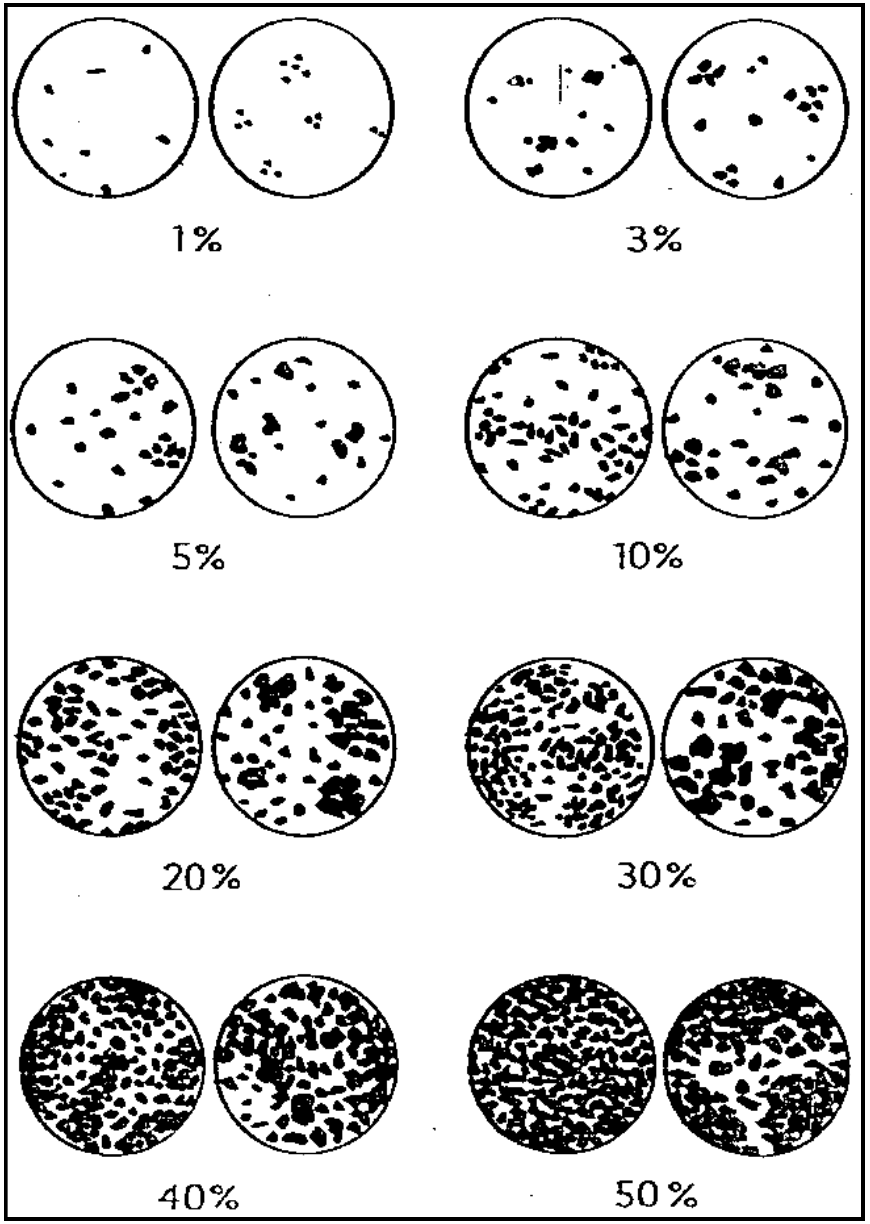
| Grain size | Characteristic |
|---|---|
| clay | • sticky, soapy, shiny<br>• can be shaped into a roll with a diameter <1 mm<br>• easily pliable<br>• grain size <0.002 mm |
| silt | • like flour, not sticky, not slimy<br>• cannot be shaped into a roll<br>• no visible grains<br>• grain size 0.002 - <0.063 mm |
| silty to fine sand | • aggregates easily fall apart; dusty when dry<br>• cannot be shaped into a roll<br>• *ca.* 30-70% of the sample with visible grains<br>• grain size of the sand 0.063 - <0.2 mm |
| fine sand | • not cohesive, not like flour, hardly dirties the hands<br>• grain size 0.063 - <0.2 mm |
| fine to medium-grained sand | • not cohesive, does not dirty the hands<br>• grain size 0.063 - <0.63 mm |
| medium-grained sand | • not cohesive, does not dirty the hands<br>• grain size 0.2 - <0.63 mm; grains like coarse powder |
| medium- to coarse-grained sand | • no aggregate formation even when moist<br>• grain size 0.2 - <2 mm; grains like coarse sugar |
| coarse-grained sand to gravel | • no aggregate formation even when moist<br>• grain size 0.63 - <6.3 mm |
| fine gravel | • grain size 2 - <6.3 mm |
| medium-sized gravel | • grain size 6.3 - <20 mm |
| coarse gravel | • grain size 20 - <63 mm |
| cobbles | • grain size ≥ 63 mm |

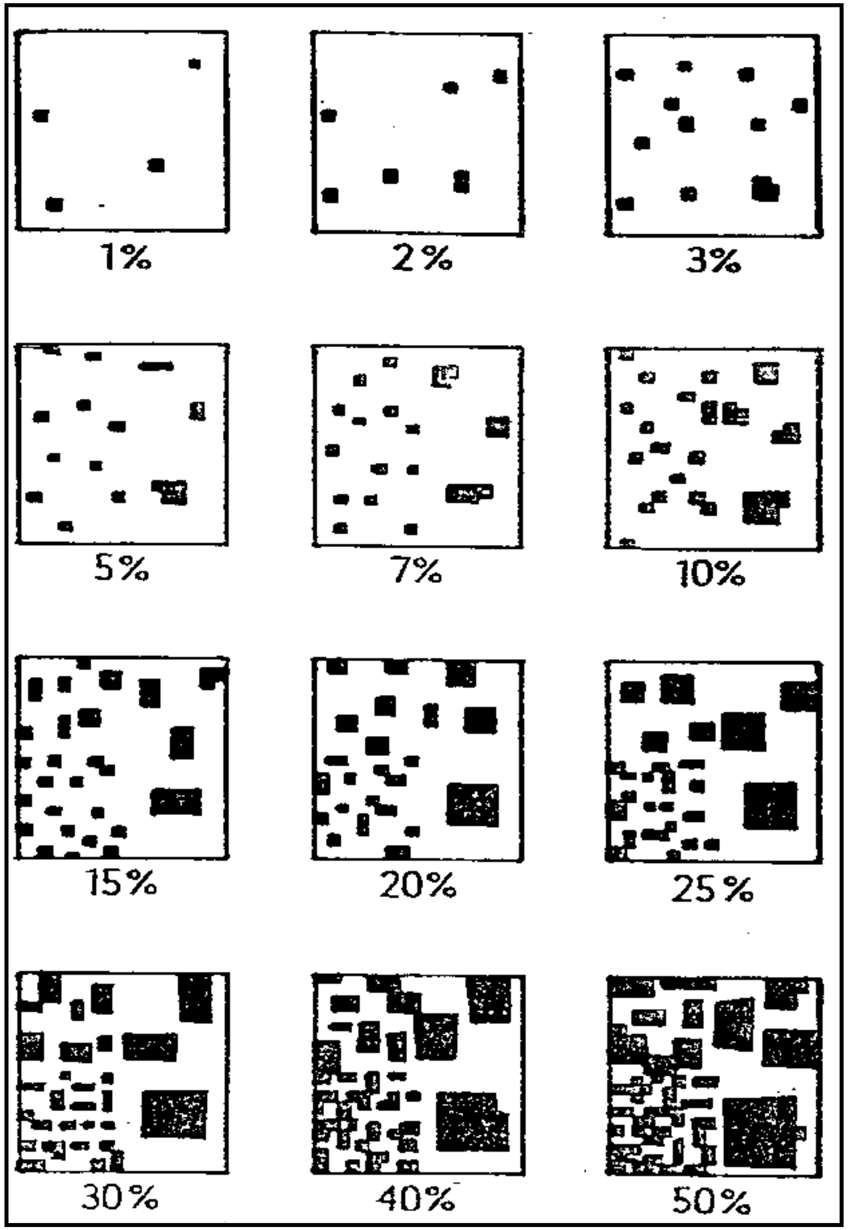
Only the dominant grain size of the soil sample should be recorded. A smaller grain size of up to 10% of the sample is considered as normal. Larger proportions of smaller, and especially of larger grain size, are to be accounted for under Section "12. Skeleton grains".

## 12. Stoniness

This entry has two parts: the grain size and the percentage of grains. In the Soil Sampling Protocol only the sampled horizon should be described.

The percentage of grains to be estimated by using the schematics on the next page and entered at (a). The grain size to be entered at (b).


1%
3%
5%
10%
20%
30%
40%
50 %


1%
2 %
3%
5%
7%
10%
15%
20%
25 %
30 %
40%
50%

The following definitions are to be used:

☐ | ☐

↙ ↘

| ☐ percentage | | ☐ stone grain size | | |
|---|---|---|---|---|
| entry number | % proportion | entry number | description | grain size |
| 1 | ≤ 5% | 1 | sand | 0.063 to 2 mm |
| 2 | 5 - 25% | 2 | gravel | 2 to 63 mm |
| 3 | > 25% | 3 | cobbles | >63 mm |

### 13. Content of organic material / humus

The proportion of organic material is estimated semi-quantitatively, and requires much experience. There are no unambiguous field methods for describing this property. The following table can serve as a guide, whereby there are problems with the application.

| Description | Proportion (%) |
|---|---|
| none | 0 |
| very slightly humic | <1 |
| slightly humic | 1 - <2 |
| medium humic | 2 - <4 |
| considerable humic | 4 - <8 |
| very considerable humic | 8 - <15 |
| extremely considerable humic, half-boggy | 15 - <30 |
| organic, peaty | ≥30 |

### 14. Root penetration

The amount of root penetration is also estimated semi-quantitatively. The following table can serve as a guide:

| Amount of root penetration | Number of fine roots per decimetre square (dm$^2$) |
|---|---|
| none | none |
| very slight | 1 – 2 |
| slight | 3 - 5 |
| medium | 6 - 10 |
| considerable | 11 - 20 |
| very considerable | 21 - 50 |
| extreme considerable to root mat/system | >50 |

### 15. Morphological features

This entry has two parts: the type of morphological feature and the material of that feature. A distinction is made among the following types of features:

| | |
|---|---|
| veins: | Veins are fungus mycelium-like network that generally occurs as a lining of the pore system of soil. |
| bands: | Bands are strips of material with a different colour or grain size within an otherwise uniform horizon. Bands with a thickness of more than 5–10 cm are to be considered as a separate horizon. |
| coatings: | Coatings are visible on the fabric structures. Coatings have different features (*for example*, a different colour or grain size) than the fabric of the sample. |
| spots: | Spots have a different colour than the horizon as a whole; they are generally irregularly distributed and of different sizes. |
| concretions: | Concretions, in contrast to spots, are hard material in the soil. |
| nests: | Nests (also called lenses or impurities) are accumulations of nest or lens-like material with a different grain size, texture or colour within the horizon. |
| Tubes/channels: | Tubes and channels are relatively perpendicular, usually filled structures. |

The following specifications are possible for the materials of the morphological features:

| Specification | Specification | Specification |
|---|---|---|
| bleaching- | gravel- | silt- |
| iron/manganese- | siliceous powder- | detritus/rubble- |
| mica- | coal- | cobble- |
| grit- | loam- | clay- |
| humus- | pyrite- | worm- |
| humic clay- | rust- | root- |
| lime/calc- | sand- | slag- |

Up to two morphological characteristics can be entered in the protocol for a horizon. If there are more than two characteristics, then the two most important are to be entered, and the others to be noted in the Remarks (number 23 in the protocol).

## 16. Soil Association

This characteristic refers to whether the soil at the sampling site is natural or it has been anthropogenically modified, *for example*, by dumping of material from elsewhere.

Note: Farmland (agricultural land) is considered natural, unless it is clearly a result of dumping of material from elsewhere.

## 17. Horizon description

The description of the soil horizon(s) has three parts:

a) *Enter whether the profile was recorded at the sampling site?*
If a vertical profile at the sampling site is recorded, as extending significantly deeper than the bottom level of the subsoil sample, the answer here is "Yes". The horizons of the whole profile are not a part of the protocol and they have to be described separately.

b) *In the detailed urban geochemical mapping project, single soil horizons should be sampled.*
Enter the number of visible horizons in the dug-up section. A horizon below the sample is not to be included nor is any layer, such a humus of foliage layer.

c) *Soil horizon*
The alphanumeric symbol for the type of horizon is to be entered here. The number of symbols must correspond to the number of horizons given at (b).

| Symbol | Horizon description |
|---|---|
| A | Mineral soil horizon<br>topsoil horizon up to 30% organic matter |
| $A_h$ | Humic mineral soil horizon<br>a topsoil horizon with a higher proportion of humus (≤30% organic matter) than the underlying horizon |
| $A_p$ | Arable soil horizon<br>an agricultural soil horizon formed by cultivation, or similar kinds of disturbance |
| $A_{gr}$ | Pasture soil horizon<br>a grazing land soil horizon formed by grazing; horizon under grassland and fallow land |
| Ya | Anthropogenic material of soil formation<br>a horizon containing particulate precipitation (mostly fly ash) |
| Yb | Anthropogenic material of soil formation<br>a horizon containing rubble material (*e.g.*, cultural layer) |
| $A_l$ | Transition horizon<br>a loess like A-horizon with clay depletion; lighter coloured horizon with little clay and sesquioxides; caused by washing out of lower horizons; occurs in haplic luvisol (parabrown earth) and haplic albeluvisol |
| $A_e$ | Transition horizon<br>an A-horizon, acid bleached, podsolised, mostly formed over an illuvial horizon |
| $A_{el}$ | Transition horizon<br>an $A_l$-horizon, characterised by a considerable clay and humus depletion; acid bleached horizon; lighter coloured horizon with little clay and sesquioxides and humus, caused by washing out to lower horizons |
| $A_{he}$ | Transition horizon<br>an $A_e$-horizon, horizon with clay depletion and horizontal uneven humus; pale horizon with a little humus and scattered bleached spots |
| $S_w$ | Mineral subsoil with influence of stagnating water<br>a pale hydromorphic S-horizon caused by water logging of soil; very poorly drained horizon; temporary stagnant water leading to a horizon with wet bleached (spots) and oxidation (rust spots, concretions) features |
| $S_d$ | a water stagnant S-horizon, usually between 50% and 70% rust and bleached spots |
| B | Mineral subsoil; weathering, enriched, and restructured fabric horizon |
| $B_v$ | Brown horizon<br>a brown or yellow weathering horizon without significant washing out of clay; sesquioxides or humus; usually acidic soil |
| $B_s$ | Illuvial horizon<br>a B-horizon with sesquioxides; a hardened or cemented horizon formed by enrichment of sesquioxides; not recognisable enrichment of humus |
| $B_t$ | Illuvial horizon<br>a B-horizon; a clay-enriched horizon with clay coating on the fabric grains and clay fill-in cavities; enriched by washing in of clay |
| $B_{ht}$ | Transition horizon<br>a $B_t$-horizon with recognisable humus enrichment; clay and/or humus enriched horizon characterised by humic clay coatings on the fabric grains and clay / humus fill in cavities, *e.g.*, parabrown (luvisol) and black earth (chernozem) |
| G | Mineral soil horizon with ground water influence |
| $G_o$ | a G-horizon in waterlogged soil with varying enrichment of Fe and Mn oxides, ≥5% of the area with rust spots |

| Symbol | Horizon description |
|---|---|
| $G_r$ | a G-horizon in waterlogged soil with reducing conditions and prevalent grey, greenish, and bluish basic colours or spots, <5% of the area with rust spots |
| C | Mineral soil subgrade, parent material |
| $C_c$ | Carbonate C-horizon<br>horizon enriched with $CaCO_3$ (2-75%) as pore filling, bands, concretions, coatings, *etc.*. |
| H | Organic horizon (peat horizon)<br>horizon containing ≥30 % organic matter |
| $H_v$ | Earthy horizon<br>an earthy horizon (topsoil) in which the high organic matter content has been aerobically decomposed, clumpy |
| $H_m$ | Transition horizon<br>a topsoil horizon of intensive drainaged bogs in which the high organic matter content has been aerobically decomposed; high resistance to wetting; grainy to powdery when dry |
| $H_a$ | Subsoil H-horizon<br>a subsoil horizon in which the high organic matter content has been anaerobically decomposed, resulting in shrinkage; friable lumpy peat horizon |
| $H_t$ | Peat shrinkage horizon<br>an H-horizon in which the high organic matter content has been anaerobically decomposed, resulting in shrinkage, prismatic structure |
| M | Mineral soil horizon, (displacement horizon)<br>horizon of dislocated soil usually containing allochthonous or synsedimentary humus |
| aM | aM-horizon formed by alluvial sediments in the Holocene; organic matter content as in $A_h$-horizon; colour significantly brown (chroma ≥3); typically in floodplain and colluvial soil; horizon with restructured fabric, but with only little material changes, some rusty or pale spots from slope water |

### 18. Hydrological conditions

The predominant hydrological conditions are to be entered here (see sampling protocol).

### 19. Contamination and abandoned waste

At (a) is to be entered whether the sampling site, and immediate area, has surface contamination. Because this is not always unambiguously recognisable, there are four possible entries.

At (b) is to be entered the presence of contamination, which is not recognisable at the surface; *for example*, dumped material in the subsurface.

### 20. Land use

A distinction is made between regional, area (local), and site land use. The area land use can be subdivided into a primary and a secondary use.

The predominant land use within 500 – 10,000 m of the sampling site that significantly influences the geochemical conditions is to be entered as the *regional land use.*

The predominant land use within 500 – 2000 m around the sampling site that significantly influences the geochemical conditions is to be entered as the *local land use*. If there are large differences in land use in this area, the land use that has the larger influence at the sampling site is to be entered as the *primary local land use*, and the one with less influence is to be entered as the *secondary local land use*.

The land use within 50 m of the sampling site is to be entered as the *land use at the site*.

*Example*: A topsoil sample is taken from a small unmowed grass area near an animal barn of a farm with cropland. Next to the barn is a workshop/garage for farm machinery.

The following entries would then be made:

regional land use: agriculture
primary local land use: agricultural buildings
secondary local land use: machine workshop
land use at sampling site: meadow, grass, lawn

### 21. Were samples taken for analysis of organic contaminants?

The field has to be completed and ticked by the sample collector if a second additional sample for organic compound analysis is taken or not.

### 22. Land user

The user of the site at which the topsoil sample is taken should be entered here (name of company, *etc.*.).

### 23. Remarks

Any information about the sample and the sampling site and surrounding area that seems significant, and cannot be documented elsewhere in the protocol can be written here.

- **PHOTOGRAPHING**: At each sample site, the conditions must be recorded with a number of photographs. ALWAYS start by photographing (i) the sample number, (ii) the dug up soil before sampling, and at least (iii) one general landscape photograph. As the photographic documentation is important, it is recommended that four (4) landscape photographs should be taken, North, East, South and West (always in this order). Photographs should be taken of the sites from where samples of (a) road dust or road sediment, (b) house dust, (c) attic dust, (d) bio-indicator plants, and (e) human tissues are taken; again, always start by photographing the sample number, and then take all the other photographs.

**NOTE**: This very detailed sampling protocol was used in the urban geochemical study of Berlin (Birke et al., 2011a).

# Soil Sampling Protocol

**Sample number**: ❑❑❑❑❑❑❑❑❑

**1. Sampling date:** ❑❑.❑❑.20❑❑ **2. Sample collector:** ____________❑❑

**3. Topographical map sheet:**____________________________N-❑❑-❑❑❑-❑-❑-❑

**4. Northing:** ❑❑❑❑❑❑❑ **Easting:** ❑❑❑❑❑❑❑

**5. Northing (DD MM SS):** ❑❑°❑❑'❑❑" **Easting:** ❑❑°❑❑'❑❑"

**6. Sample depth:** upper level in cm: ❑❑❑.❑❑

lower level in cm: ❑❑❑.❑❑

**7. Geology / Soil:** ❑❑

**8. Slope gradient:** ❑❑ **Note:**

| | | |
|---|---|---|
| 1 ○ not sloped | 2 ○ very slightly sloped | 3 ○ slightly sloped |
| 4 ○ medium slightly sloped | 5 ○ medium sloped | 6 ○ medium strong sloped |
| 7 ○ strong sloped | 8 ○ very strong sloped | 9 ○ steep 10 ○ very steep |

**9. Moisture content:** ❑❑

| | | |
|---|---|---|
| 1 ○ dry | 2 ○ slightly moist | 3 ○ moist |
| 4 ○ wet | 5 ○ very wet | |

**10. Colour of the sample:** **1. Upper horizon - ①②③** ❑❑❑ **2. Lower horizon - ❶❷❸** ❑❑❑

| | | | |
|---|---|---|---|
| **a) Colour intensity: (①❶)** | 1 ①❶ white | 2 ①❶ bright | 3 ①❶ medium |
| | 4 ①❶ dark | 5 ①❶ black | |

**b) Colour:** ☞ **give the hue (②❷) and the basic colour (③❸)**

| | | | |
|---|---|---|---|
| 1 ②③ ❷❸ grey | 2 ②③ ❷❸ olive | 3 ②③ ❷❸ yellow | 4 ②③ ❷❸ ochre |
| 5 ②③ ❷❸ brown | 6 ②③ ❷❸ orange | 7 ②③ ❷❸ red | 8 ②③ ❷❸ violet |
| 9 ②③ ❷❸ blue | 0 ②③ ❷❸ green | | |

**11. Grain size:** ❑❑

| | | | |
|---|---|---|---|
| 1 ○ clay | 2 ○ silt | 3 ○ silty to fine sand | 4 ○ fine sand |
| 5 ○ fine to medium sand | 6 ○ medium sand | 7 ○ medium to coarse sand | 8 ○ coarse sand to gravel |
| 9 ○ fine gravel | 10 ○ medium gravel | 11 ○ coarse gravel | 12 ○ cobbles |

**12. Stoniness:** ❑❑

| | | | |
|---|---|---|---|
| **a) Percentage of stones:** | 1 ○ ≤5% | 2 ○ 5 - 25% | 3 ○ >25% |
| **b) Stone grain size:** | 1 ○ sand | 2 ○ gravel | 3 ○ cobbles |

**13. Content of organic material / humus:** ❑❑

| | | | |
|---|---|---|---|
| 1 ○ none | 2 ○ very slightly humic | 3 ○ slightly humic | 4 ○ medium humic |
| 5 ○ considerably humic | 6 ○ very considerably | 7 ○ extremely, semi-boggy | 8 ○ organic, peaty |

**14. Root penetration:** ❑❑

| | | | |
|---|---|---|---|
| 1 ○ none | 2 ○ very slight | 3 ○ slight | 4 ○ medium |
| 5 ○ considerable | 6 ○ very considerable | 7 ○ extreme to root system | |

**Explanations of the symbols used in the soil sampling protocol:**

| | | |
|---|---|---|
| ❑❒ | ☞ | field to be completed by the sample collector (❑) or later when the protocol is enterd into the digital database (❒) with numbers or letters |
| ○ | ☞ | field to be ticked by the sample collector when appropriate |
| ①②③ | ☞ | field for a complex features(*e.g.*, colour) or for two features with the same coding number (*e.g.*, regional and local land use), to be ticked by sample collector |
| ①❶ | ☞ | field for a feature related to a specific horizon (*e.g.*, colour) to be ticked by the sample collector |
| _____ | ☞ | text field to be completed when needed by the sample collector |

# Soil Sampling Protocol

**Sample number**: ☐☐☐☐☐☐☐☐☐

## 15. Morphological characteristics:

**1. upper horizon** (①②) a) ☐☐ b) ☐☐

**2. lower horizon** (❶❷) a) ☐☐ b) ☐☐

**a) The type of morphological features:**

| | | | |
|---|---|---|---|
| 1 ①❶ veins | 2 ①❶ bands | 3 ①❶ coatings | 4 ①❶ spots |
| 5 ①❶ concretions | 6 ①❶ nests | 7 ①❶ tubes / channels | ? ①❶ ____________ |

**b) The specification of morphological features:**

| | | | |
|---|---|---|---|
| **1** ②❷ bleaching | **2** ②❷ iron/manganese | **3** ②❷ mica | **4** ②❷ grit |
| **5** ②❷ humus | **6** ②❷ humic clay | **7** ②❷ lime/chalk | **8** ②❷ gravel |
| **9** ②❷ siliceous powder | **10** ②❷ coal/charcoal | **11** ②❷ loam | **12** ②❷ pyrite |
| **13** ②❷ rust | **14** ②❷ sand | **15** ②❷ silt | **16** ②❷ rubble |
| **17** ②❷ cobble | **18** ②❷ clay | **19** ②❷ worm | **20** ②❷ root |
| **21** ②❷ slag | ? ②❷ ____________ | | |

## 16. Soil association: ☐☐

| | |
|---|---|
| **1** ○ natural soil | **2** ○ anthropogenically modified |

## 17. Horizon description: a) ☐☐ b) ☐☐ c) “☐☐☐“ “☐☐☐“

**a) Was the profile recorded at the sampling site?** **1** ○ yes **0** ○ no

**b) Number of horizons collected in the sample:** ☐

**c) Soil horizons:** ☞ **1. Horizon (above - ①), 2. Horizon (under 1 - ②), 3. Horizon (under 2 - ③)**

| | | | | | | |
|---|---|---|---|---|---|---|
| ① A | ②③ $A_l$ | ②③ B | ②③ G | ②③ C | ①②③ H | ①②③ M |
| ① $A_h$ | ②③ $A_e$ | ②③ $B_v$ | ②③ $G_o$ | ②③ $C_c$ | ①②③ $H_v$ | ①②③ aM |
| ① $A_p$ | ②③ $A_{el}$ | ②③ $B_s$ | ②③ $G_r$ | | ①②③ $H_m$ | |
| ① $A_{gr}$ | ②③ $A_{he}$ | ②③ $B_t$ | | | ①②③ $H_a$ | |
| ① Ya | | ②③ $B_{ht}$ | | | ①②③ $H_t$ | |
| ① Yb | | ②③ $S_w$ | | | | |
| | | ②③ $S_d$ | | | | |

## 18. Hydrological conditions: ☐☐

| | |
|---|---|
| **1** ○ surface runoff | **2** ○ slope water |
| **3** ○ stagnating water | **4** ○ ground water |

## 19. Contamination and abandoned waste: ☐☐

| | | |
|---|---|---|
| **a) The sampling site and immediate area have surface contamination** | **0** ○ none<br>**2** ○ probable | **1** ○ possible<br>**3** ○ certain |
| **b) The sampling site and immediate area have abandoned waste** | **0** ○ none<br>**2** ○ probable | **1** ○ possible<br>**3** ○ certain |

## 20. Land use:

**a) regional land use:** ☐☐☐☐

**0100** ○ **residential**

| | |
|---|---|
| **0101** ○ high density, city centre | **0103** ○ low density, village |
| **0102** ○ medium density, city periphery, suburb | **0104** ○ high proportion of green areas |

**0200** ○ **industial and/or commercial area**
**0300** ○ **agriculture**
**0400** ○ **forestry**
**0500** ○ **uncultivated, fallow**
**0600** ○ **utilities (water, electricity, gas, waste disposal)**
**0700** ○ **military**
**0800** ○ **park or sport area**
**??00** ○ **not classifiable:** ________________________________________

# Soil Sampling Protocol

**Sample number**: ☐☐☐☐☐☐☐☐☐☐

**b) primary local land use** (①): ☐☐☐☐☐☐☐☐

**secondary local land use** (②): ☐☐☐☐☐☐☐☐

**01000000 ① ② residential**

01010000 ① ② no commercial use
**01010100 ① ② core area**
**01010200 ① ② recent building area**
**01010300 ① ② old building area**
**01010400 ① ② residential highrise area**
**01010500 ① ② row houses**
**01010600 ① ② detached houses, villas**

01020000 ① ② some commercial use
**01020100 ① ② core area**
**01020200 ① ② recent building area**
**01020300 ① ② old building area**
**01020400 ① ② residential highrise area**
**01020500 ① ② row houses**
**01020600 ① ② detached houses, villas**

**02000000 ① ② industrial and / or commercial area**

02010000 ① ② commercial area
**02010100 ① ② trading and / or business area**
**02010300 ① ② warehouses**
**02010500 ① ② workshops (autos, machinery, *etc.*)**
**02010200 ① ② petrol stations**
**02010400 ① ② radio / tv and telephone towers**
**0201??00 ① ②** ________________________________

02020000 ① ② industrial area
**02020100 ① ② refining**
02020101 ① ② iron refining
02020102 ① ② nonferrous refining
**02020200 ① ② metal work industry**
**02020300 ① ② machinery construction**
**02020400 ① ② eletrolytic plants**
**02020500 ① ② electronic and electric production**
**02020600 ① ② battery production**
**02020700 ① ② chemical industry**
02020701 ① ② paint and dye industry
02020703 ① ② plastics production and processing
02020705 ① ② rubber production
02020707 ① ② pharmaceutical industry
02020702 ① ② photochemical industry
02020704 ① ② asphalt production
02020706 ① ② petroleum processing
020207?? ① ② ______________________________
**02020800 ① ② wood working (saw mill, cabinet making, *etc.*)**
**02020900 ① ② leather industry**
**02021000 ① ② textile industry**
**02021100 ① ② food processing**
**02021200 ① ② gas works, coking plants**
**02021300 ① ② construction and construction material industry**
**02021400 ① ②** ______________________________

02030000 ① ② agricultural buildings

02040000 ① ② mining
**02040100 ① ② open pit**
020401?? ① ② ______________________________
**02040200 ① ② underground**
020402?? ① ② ______________________________

**03000000 ① ② agriculture**

03010000 ① ② agriculture area
**03010100 ① ② pasture**
**03010200 ① ② crop land**

03020000 ① ② market garden / nursery
**03020100 ① ② open land**
**03020200 ① ② greenhouses**

03030000 ① ② fruit and vegetable farms

03040000 ① ② fruit grove, nursery
**03040100 ① ② fruit grove**
**03040200 ① ② nursery**

03050000 ① ② vineyards

03??0000 ① ② ________________

**04000000 ① ② forest**

04010000 ① ② dense forest
**04010100 ① ② coniferous forest**
**04010200 ① ② deciduous forest**
**04010300 ① ② mixed forest**

04020000 ① ② open forest
**04020100 ① ② coniferous forest**
**04020200 ① ② deciduous forest**
**04020300 ① ② mixed forest**

**05000000 ① ② unused areas**

05010000 ① ② fallow land with herbaceous vegetation and / or bushes
05020000 ① ② grassland, meadow
05030000 ① ② barren land
05040000 ① ② marsh, bog
05??0000 ① ② ________________________________

# Soil Sampling Protocol

**Sample number**: ☐☐☐☐☐☐☐☐☐

**06000000 ① ② utilities, waste disposal**
06010000 ① ② utilities (water, electricity, gas)
**06010100 ① ② power plant, substation**
**06010200 ① ② waterworks, water conservation facilities**
**06010400 ① ② underground reservoir**
**0601??00 ① ②** ______________________________
**06010300 ① ② medical facilities (hospital, nursing home, old people's home)**
06020000 ① ② waste disposal facility
**06020100 ① ② sewage facility**
06020101 ① ② sewage farm, composting
06020102 ① ② sewage plant
**06020200 ① ② waste incinerator, crematorium**
**06020300 ① ② landfill**
06020301 ① ② building rubble
06020302 ① ② household waste landfill
06020303 ① ② hazardous waste depot
06020304 ① ② mixed waste landfill
**06020400 ① ② recycling, junkyard, *etc.***
**06020500 ① ② waste heap, landfill**
**06020600 ① ② fill area**

**07000000 ① ② leisure and recreation areas**
07010000 ① ② city forest
07020000 ① ② park
07030000 ① ② green land
07040000 ① ② sport field, playground
07050000 ① ② weekend and vacation houses
07060000 ① ② allotment garden
07070000 ① ② zoo
07080000 ① ② camping sites
07090000 ① ② cemetery
07??0000 ① ② ______________________________

**08000000 ① ② transportation area**
08010000 ① ② street, road
**08010100 ① ② motorway, freeway**
**08010200 ① ② street / road, verge, associated vegetation**
**08010300 ① ② parking area**
08020000 ① ② railroad land
**08020100 ① ② tram area**
**08020200 ① ② railroad / tram yard**
08030000 ① ② airport
08040000 ① ② port facilities

**09000000 ① ② military**
09010000 ① ② military exercise area, firing range
09020000 ① ② barracks
09030000 ① ② airport
09040000 ① ② military depot
09050000 ① ② border land

**c) land use at the site:** ☐☐☐☐

**0100 ○ forest / woods**
**0200 ○ agriculture**
**0300 ○ fallow land with herbaceous vegetation, heath**
**0400 ○ meadow, grass, lawn**
**0500 ○ pasture, grassland**
**0600 ○ bushes, ornamental plants**
**0700 ○ barren land**
**0800 ○ sediment above or below sealed surface**
**0900 ○ vegetation along roads**
**1000 ○ waste**
1001 ○ domestic waste, bulky refuse, waste from street cleaning
1002 ○ slag
1003 ○ ash
1004 ○ rubble
1005 ○ sewage sludge
1006 ○ industrial sludge
**1100 ○ horticultural used soil**
**1200 ○ recent fill**

## 21. Were samples taken for analysis of organic contaminants? ☐☐

1 ○ yes
2 ○ no

## 22. Land user:

______________________________

## 23. Remarks: (continue on the back side if needed.)

______________________________

Back cover photograph: Twenty-first century Athens, the capital of Hellas (22nd June 2015).

In the western part of the central green patch is the Temple of Olympian Zeus; its foundations were laid down by the popular tyrant Peisístratos in 515 BC, and upon his death in 510 BC the construction stopped; it restarted in the 3rd century BC during the reign of Antiochus IV Epiphanes, and it again stopped upon his death in 164 BC; it was finally completed in 129 AD during the reign of the Roman emperor Publius Aelius Hadrianus (known as Hadrian or Andrianós).

The central part is modern 21st century Athens, and on the right hand side is Lycabettós Hill with the 19th century chapel of Saint George.

Thus, in this photograph we see the Athens urban history from the 6th BC to the present time.

# URBAN GEOCHEMICAL MAPPING MANUAL
## Sampling, Sample preparation, Laboratory analysis, Quality control check, Statistical processing and Map plotting

Alecos Demetriades and Manfred Birke

**EuroGeoSurveys - The Geological Surveys of Europe**
36-38, Rue Joseph II - 1000 Brussels, Belgium
Tel +32 2 888 75 53
E-mail info@eurogeosurveys.org
www.eurogeosurveys.org

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