EuroGeoSurveys
European Geoscience for Society
The Geological Surveys of Europe

GLOBAL SOIL PARTNERSHIP

2015
International Year of Soils

# Urban Topsoil Geochemical Mapping Manual

# URGE II

EuroGeoSurveys
Brussels 2015

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

The hill on the right hand side 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 hill on the left hand side of the photograph was known in ancient times as Moússæs Hill and on its top is the monument of Gaius Julius Antiochus Epiphanes Philopappos (2nd century AD); nowadays, because of the monument, is known as Philópappos hill.

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.

# URBAN TOPSOIL GEOCHEMICAL MAPPING MANUAL
# (URGE II)

Alecos Demetriades and Manfred Birke

with contributions by
The EuroGeoSurveys Geochemistry Expert Group

EuroGeoSurveys
Brussels 2015

Published in 2015 by
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

Global Soil Partnership
http://www.fao.org/globalsoilpartnership/en/

International Year of Soils 2015
http://www.fao.org/globalsoilpartnership/iys-2015/en/

First edition published in 2015

*ISBN:* 9789082254716 Adobe Portable Document format (.pdf)
*EAN*: 9789082254716

ISBN 978-90-822547-1-6

9 789082 254716 >

Citation: Demetriades, A.[1] and Birke, M.[2], 2015. *Urban Topsoil Geochemical Mapping Manual (URGE II)*. EuroGeoSurveys, Brussels, 52 pp.

[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

The second EuroGeoSurveys' Urban Geochemistry Project (URGE II) aims to provide harmonised geochemical data about the current state of the quality of urban and suburban surface soil in European Union countries for multipurpose use. The results produced from such a survey should be of high quality and integrity, and to be legally defensible as they are very sensitive environmental health related data, because they inform us about the chemical state of our home, school, work and recreational environments, which affects our quality of life.

The other objective of the URGE II project is to compare the geochemical results of the participating European cities. Such a comparison, can be made if all participating cities follow the same sampling, sample preparation, and laboratory analysis procedures. Hence, all topsoil samples will be collected according to an agreed field protocol, which is presented in this report. Subsequently, the samples will be prepared in just one central laboratory, and all topsoil samples will be analysed for the same suite of determinands in the same laboratory, following a strict quality control procedure.

**Keywords**: Geochemical mapping; Methodology; Systematic survey; Topsoil; Sampling; Sample preparation; Chemical analysis; Reference sample; Quality control; Data treatment

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## CHECKLIST FOR URBAN TOPSOIL GEOCHEMICAL MAPPING

The following is a checklist of salient points for the EuroGeoSurveys **Ur**ban Soil **Ge**ochemical Mapping project (URGE II):

- √ Nominal sample density 4 samples/km$^2$.
- √ Total number of topsoil samples to be collected from each participating town or city should be between 400 and 500.
- √ Size of town or city participating in the URGE II project should be between 100 and 125 km$^2$.
- √ Use 1:5000 topographical map sheets or cadastral plans, or topographical maps of suitable scale, or orthophotographs.
- √ Superimpose on the maps/plans/photos a 500 x 500 to 1000 x 1000 metres grid.

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 urban topsoil near to the grid nodes; the topsoil should be undisturbed (or least disturbed).
  - ➢ 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.
- √ Sample numbering:
  - ➢ Routine topsoil sample number should consist of the town or city code (three letters) and the sample number (four digits);
  - ➢ Duplicate field topsoil sample number to be collected at every 20th sample site, and to be given the same sample number as that of the routine sample, but to add at the end the capital letter "D".
- √ Sample material: Topsoil from 0 to 10 cm depth; the zero level starts from the surface after removal of living vegetation, fresh litter and surficial stones.
- √ Sampling: Each topsoil (0-10 cm) sample to be collected from a patch of 50 x 50 cm.
- √ Bagging up a topsoil sample:
  - ➢ 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 both sides of a small card, which is placed in a small plastic zip-lock bag that is inserted in the Rilsan® bag and on top of the topsoil 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.
- √ Field observations and documentation:
  - ➢ The Field Observations Sheet must be completed at each sample site (Appendix 1).
  - ➢ Coordinates: The GPS should be tuned to record WGS 84 geographical coordinates in degrees, minutes, seconds (make sure that your GPS is turned to "WGS84").
  - ➢ Before leaving the sample site, mark its position on the topographical map.
  - ➢ Photographing: At each sample site, the field conditions must be recorded with a number of photographs. ALWAYS start by photographing (i) the sample number, (ii) the vertical side of the dug up pit, showing the nature of the topsoil horizon, 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).

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# 1. INTRODUCTION

Given the fact that by 2050 more than 80% of the European population will be living in cities (United Nations, 2014), the quality of the urban environment is becoming an important issue in the 21st century. 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 from 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 1970s 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.

Urban soil, especially 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). Depending on the urbanisation history and age of the city, the cultural layer varies from a few centimetres to a few metres.

Since many health related problems are linked to the state of the urban environment (Thornton and Culbard, 1987; Filippelli *et al.*, 2012), the European citizens want to know the geochemistry of the land their houses are built on. It is as important that the chemical quality of soil in schoolyards, parks, playgrounds, kindergartens, recreation areas, allotments and workplaces is known. Estate agents want to know the quality of the land they are marketing, and insurance brokers the potential risks to their customers.

As an example, the case in Portsmouth (U.K.) is mentioned, where in the 1990s the Lumsden Road housing estate at Eastney was found that it was built on extremely contaminated land (Walton and Higgins, 1998). The whole estate was declared as unfit for family habitation, because of significant quantities of asbestos (10-1000 mg/kg), and high concentrations of arsenic (<3-700 mg As/kg), cadmium (<1-17 mg Cd/kg), copper (<6-10,000 mg Cu/kg), lead (<20-96,000 mg Pb/kg), mercury (<1-590 mg Hg/kg), zinc (11-11,000 mg Zn/kg), and PAHs (10-1000 mg PAHs/kg). The City Council rehoused all families elsewhere, and the soil of the estate rehabilitated.

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.

Urban soil is generally contaminated to a variable degree, depending on its location in relation to a pollution source. Most common contaminants in the urban environment are:

- Polyaromatic hydrocarbons (PAHs), derived from coal tar, crude oil, creosote, roofing tar, dyes, paints, plastics, and pesticides, as well as the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat (Albanese and Breward, 2011; Andersson *et al.*, 2011; Birke *et al.*, 2011a; Ďuris, 2011; Jensen *et al.*, 2011; Ottesen *et al.*, 2011; Plumlee *et al.*, 2012; Beriro *et al.*, 2014; Glennon *et al.*, 2012, 2014; Vane *et al.*, 2014);
- Polychlorinated biphenyls (PCBs) from transformers, capacitors, plasticisers, paints, paper coatings, and certain packaging materials (Orlinskii, 2001; Albanese and Breward, 2011; Andersson *et al.*, 2011; Birke *et al.*, 2011a; Ďuris, 2011; Jartun, 2011; Milke *et al.*, 2011; Ottesen *et al.*, 2011; Plumlee *et al.*, 2012; Glennon *et al.*, 2012, 2014; Vane *et al.*, 2014);
- Lead (Pb) from the former use of leaded petrol and lead-based paints, electronics, and lead industry (Thornton and Culbard, 1987; Cicchella *et al.*, 2008a; Albanese and Breward, 2011;

- ❑ Copper (Cu) and zinc (Zn) from power lines and masts, roofing materials, and metal industry (Albanese and Breward, 2011; Albanese and Cicchella, 2012);
- ❑ Cadmium (Cd), *e.g.*, from transport (wear of tires), electronics, and metal industry (Albanese and Breward, 2011; Ottesen *et al.*, 2011; Albanese and Cicchella, 2012);
- ❑ Arsenic (As) from its use in chromated copper arsenate (CCA) treated wood, often even on playgrounds, and in herbicides, *e.g.*, along railway lines (Albanese and Breward, 2011; Andersson *et al.*, 2001; Milke *et al.*, 2011; Ottesen *et al.*, 2011; Tarvainen, 2011), and
- ❑ Platinum group elements (PGE's, *e.g.*, ruthenium, rhodium, palladium, osmium, iridium, and platinum), as a relatively new threat due to their use in automobile catalytic converters (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; Cicchella *et al.*, 2008b; Wiseman and Zereini, 2009; Mathur *et al.*, 2010; Ďuriš, 2011).

Consequently, urban soil is often unfit for sensitive land uses, such as playgrounds, parks and vegetable gardens, as observed in many urban areas. Contaminated urban soil may lead to contaminated indoor dust and, therefore, 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.*, 2010).

Knowledge about soil contamination, geochemical background concentrations, and detailed spatial element distribution is thus becoming a key issue in urban planning. Hence, the interest is to map the current chemical status of topsoil, and to define potential risks to human health. This knowledge helps to complete a still missing and comparable geochemical data set about urban ecosystems. Additionally, significant information will be provided to decision-makers and town administrations for finding innovative and practical solutions to the concept of sustainable urban development and human health. In fact, multidisciplinarity takes on a whole new dimension in the tackling of urban problems, caused by contaminating activities, *i.e.*, applied geochemists work alongside public health officers, urban planners, medical doctors, *etc.* Hence, the need for the production of an urban geochemical database of high quality and integrity for multipurpose use.

The Geological Surveys of Europe have a long lasting experience in geochemical mapping projects in urban areas. They were among the very first organisations in the world that organised such surveys. This experience is well documented in a EuroGeoSurveys sponsored reference book on urban geochemistry (Johnson *et al.*, 2011). One of the results of this book was that though many investigations have been undertaken in Europe, the European overview, the comparability between investigations and results from different European cities, is missing. Hence, the aim of the second Urban Soil Geochemistry project is to build a directly comparable database for a number of European reference cities (N=10-25).

Such a comparison can only be achieved by a systematic and harmonised urban topsoil geochemical survey of the participating towns or cities using the same sampling, sample preparation and analytical methodology, meaning that all collected samples are analysed in the same laboratory for the same suite of elements and compounds, following strict internal and external quality control procedures.

These are very important conditions in the development of a quality controlled and legally defensible topsoil geochemical database that will represent the baseline, as well as the timeline, against which future human induced changes can be assessed. Moreover, the results of the overall urban topsoil geochemical mapping will provide the necessary background information for planning more detailed projects in parts of the towns or cities where there is proven contamination. These follow-up surveys will delineate precisely the contaminated areas and, thus, reduce the cost of remediation, if such an action is deemed necessary. The URGE II project aims at advising the city administration how such studies should be carried out, and how the data are best stored, presented, evaluated and used.

This manual is specifically written for the URGE II project. The emphasis is on urban topsoil, as this is the most widely used sample medium, and its proper and harmonised collection is an absolute requirement to produce precise analytical results and, thus, an effective assessment of the site being investigated. Errors made during sample collection cannot be recognised in the laboratory and, hence, cannot be corrected afterwards. Consequently, all participating countries must follow exactly the described sampling procedure.

Another more detailed urban geochemistry methods manual is in the process of publication, which apart from topsoil includes instructions for sampling other media, such as subsoil, house dust, attic dust, road dust or road sediment, and air particulates (Demetriades and Birke, 2015).

### 1.1. Sampling depth

The definition of topsoil in urban geochemical surveys reviewed by Johnson and Demetriades (2011) varies from 0-2 to 0-25 cm. In the URGE I project, the choice of sampling depth was directly related to child health criteria, and the risk of exposure to contaminants in soil; hence, the surface layer of urban soil was selected as the optimum sampling medium. *As the URGE I project used the topsoil depth range of 0-10 cm, this will be used for the URGE II project.* It is noted that the URGE I was a pilot project in which a number of European cities participated (Tarvainen 2011; Šorša and Halamić, 2011; Uhlbäck *et al*., 2014; Birke *et al*., in preparation); the results showed that the sampling design and sampling depth are applicable, but there is a need for harmonisation of sample preparation, analytical methods and external quality control, which are in place in the URGE II project.

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. Therefore, the depth range of 0-10 cm is the maximum soil thickness to be sampled, as this is assumed to be the maximum possible where any potential contamination is not diluted by geogenic material. Soil depth ranges greater than this depth will most likely end-up in diluting any potential contamination.

### 1.2. Sample density and number of samples

The nominal sample density of the URGE II project for covering systematically the inner town or city is 4 samples/km$^2$, *i.e.*, a sampling grid of 500 x 500 m, expanding to 1000 x 1000 m in the suburbs (Fig. 1). This variable sample density is considered appropriate to obtain a satisfactory overview of the spatial distribution of chemical elements and organic pollutants in the urban topsoil. It will not provide, however, information at the individual property level (land parcel). Of course, the participating towns or cities are free to decide on a denser grid, but the comparison among the European cities will be performed on the aforementioned nominal sample density of 4 samples/km$^2$, collected at the nodes of a 500 x 500 m grid (inner city) and 1000 x 1000 m grid (outer city - suburbs).

The total number of samples that should be collected from each participating town or city in the URGE II project is set to a minimum of 400 to 500 topsoil samples. Although the total number of samples depends on the area of the town or city, in the URGE II project the selected town or city, including its suburbs, should have a minimum area between 100 to 125 km$^2$.

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 (sample density). Critical examination of these sketch distribution maps shows how under-sampling can lead to the non-detection of contamination (Fig. 2c).

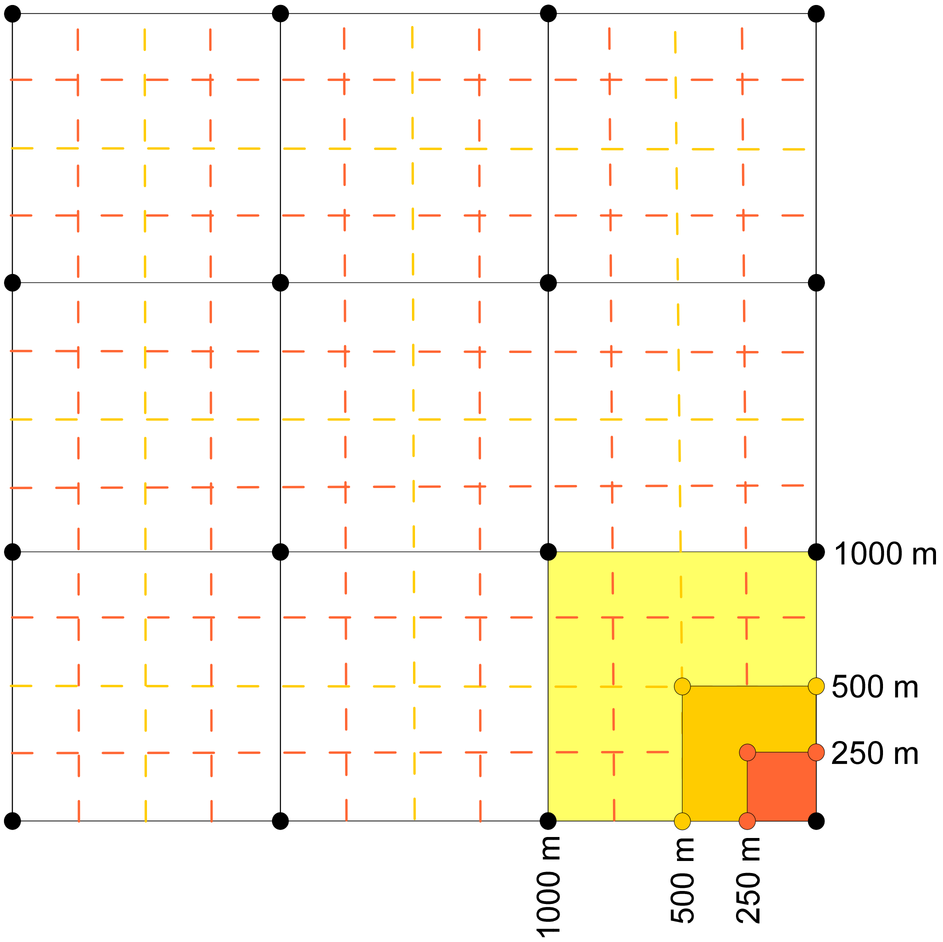


Figure 1. Sampling grid of 1000 x 1000 m, which can easily be converted to a denser grid of 500 x 500 m, 250 x 250 m, *etc.* The different coloured grid lines show the development of denser sampling grids.

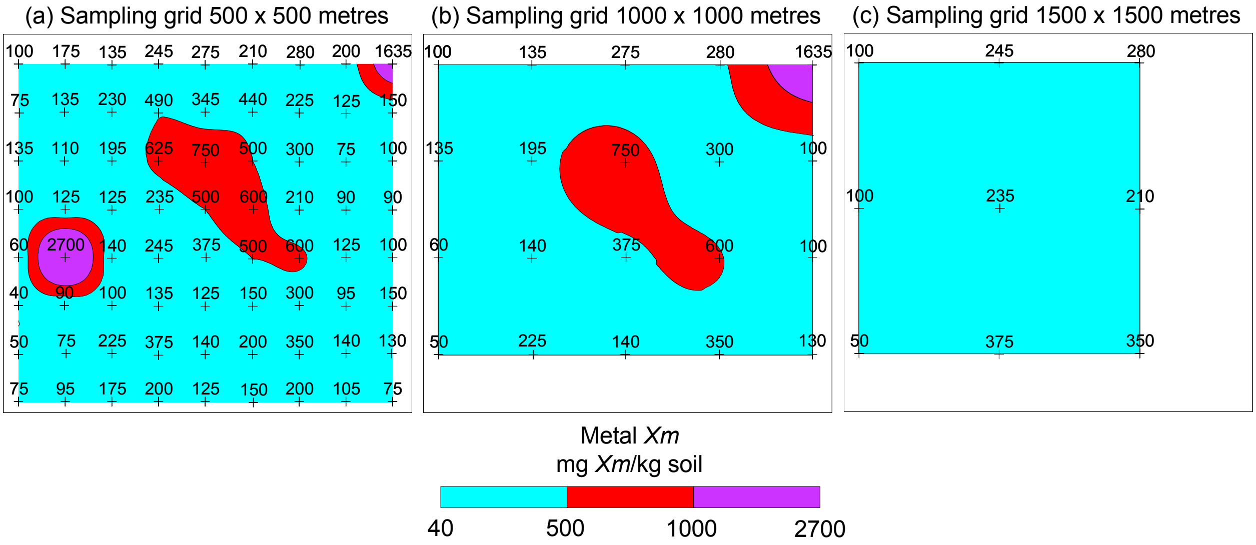


Figure 2. Sketch determinand distribution maps showing the change in size of the contaminated areas with different square grid dimensions (numbers over the crosses represent Metal *Xm* concentration values in mg/kg). The statutory limit for the concentration of the metal *Xm* in urban soil is set at 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 'anomaly' 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).

# 2. FIELD SAMPLING METHODOLOGY

## 2.1. Sampling equipment

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

- Stainless steel digging tool (hand hoe or grub hoe);
- Chisel-end geological hammer;
- Plastic or stainless steel scoop or trowel (Do not use coloured plastic scoops, because yellow, orange or red colours are made with 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 (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 (alternate coloured-sections);
- *Plasticised scale-bar for photographs (0-10 cm marked) - will be provided;*
- *Rilsan® bags (250×500×0.04 mm) for bagging topsoil samples - will be provided;*
- *Self-locking plastic tie strap (plastic cable tie) for the secure sealing of the Rilsan® bags - will be provided;*
- *Small cards for writing sample number - will be provided;*
- *Small self-sealing (zip-lock) plastic bags for the protection of the small cards - will be provided;*
- *Permanent drawing ink marker (preferably black or blue) - will be provided;*
- Outside plastic bag for protection of Rilsan® bags during packing and transportation;
- Topographical maps or cadastral plans or orthophotographs (scale 1:5000), or any other suitable scale topographical maps;
- Geological compass or any type of compass for orientation when taking the general landscape photographs at each site towards North, East, South and East;
- Global Positioning System (GPS);
- Bristle brush for cleaning equipment;
- White cotton wad for cleaning sampling equipment;
- Strong boxes for storing and sending samples;
- Field Observations Sheets for recording of observations at each sample site (see Appendix 1);
- Digital camera (>7 Megapixels) capable of taking close-up photographs;
- 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;
- Laptop computer for the digital entry of observations in the evening, and
- In case funds are available for the determination of semi-volatile organic compounds (PAHs and PCBs), additional instructions about necessary equipment will be given.

The equipment in *italics* will be purchased or prepared centrally and sent to all EuroGeoSurveys URGE II project participating towns or cities.

**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 (Johnson *et al*., 2011). A spot topsoil sample will be collected at each node of the 500 x 500 metres to 1000 x 1000 metres sampling grid; this grid provides the URGE II nominal density of 4 samples/km$^2$. 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. Hence, for safety the topsoil samples are numbered two times: 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.

Each participating town or city will be given a three-letter code, and the routine sample number to consist of the town or city code, and the sample number (four digits).

Field duplicate samples will 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".

To ensure that the topsoil samples 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, even if different layers are mixed, as the objective of the URGE II project 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.

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 1). If a spot of bare topsoil cannot be found, then the next best option is one with either sparse grass or short grass (Photo 2).

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.
- 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) will be taken at each sampling site.

If adequate funds are available, it may be possible to determine 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). In such a case, it may be necessary to collect a second topsoil sample (0-10 cm); additional instructions will be given in due course.

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

a) Mark a 50 x 50 cm single spot using the folded wooden metre (see Photo 3).
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 and dig a pit down to 10 cm depth with a stainless steel digging tool or other unpainted steel digging tool (Photo 3b).
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 3c).
e) At this point is time to take all digital Photographs, and always in the following order (Photo 4):
    (i) the sample number (this helps to locate the digital photographs of each sample site);
    (ii) the dug up topsoil with the plasticised scale-bar placed at a vertical position on the side wall of the pit, and
    (iii) a general landscape photograph portraying the dominant feature.

   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; see Photo 4) - use the compass to orientate yourself. Record the number of each photograph on the Field Observations Sheet (Appendix 1).
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 kitchen knife or spade, and the zero point starts at the beginning of the grass roots, and the pit is 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.
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 3b-g).
h) Remove pieces of roots (*ca*. >1 cm).
i) Remove coarse clastic material (*ca*. >1 cm).
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 3h).
l) Start taking scoops of topsoil from different points of the heap within the 50 x 50 cm spot (Photo 3h), 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 5a. 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 5b).
p) Place the sample bag in a strong carton box.

q) Record all observations on the Field Observations Sheet (see Appendix 1), 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**: In case, semi-volatile organic compounds, such as PAHs or PCBs, are going to be determined, additional instructions will be given, as we are of the opinion that the existing specifications for the preservation of samples are too cautious, and cause a considerable problem to the quality control procedure.

### *2.2.2. Sampling a topsoil spot with sparse grass or short grass or 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 for the URGE II project should be taken at a distance of 2 to 3 metres from the routine sample site, and at every 20th site (Photo 6). For the collection of the field duplicate sample, follow the steps described in section *'2.2.1. Sampling a bare topsoil spot'* (above).

Field quality control or duplicate topsoil 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 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 (2015) and Demetriades and Birke (2015).

(a) (b)

Photo 1. 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)

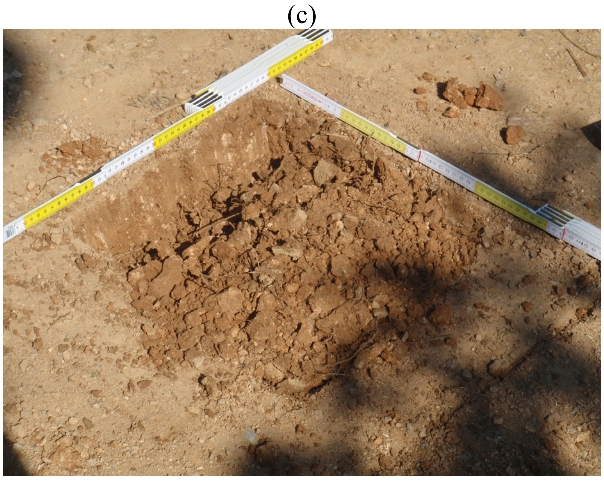
Photo 2. Select a spot with a sparse grass cover for soil sampling. Again if possible, avoid spots under trees in order to minimise the effects of throughfall and stemflow precipitation.

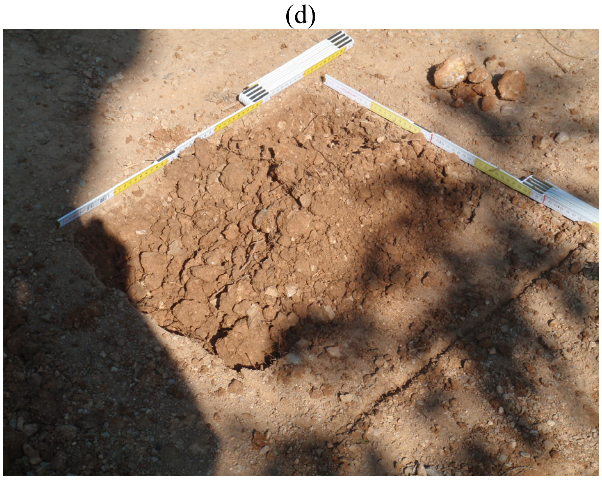

(a)


(b)


(c)


(d)


(e)


(f)


(g)


(h)

◄Photo 3 on page 18. (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 4. Photographic documentation of each topsoil sample site by taking a series of photographs in the following order: (a) Sample number; (b) topsoil sampling site showing the characteristics of the sampled soil horizon; (c) North facing photograph; (d) East facing photograph; (e) South facing photograph, and (f) West facing photograph.

(a) (b)

Photo 5. (a) Topsoil sample in Rilsan® bag, and on the right hand side the stones and plant roots that were removed; (b) Topsoil sample with outside plastic bag for the protection of the Rilsan® bag during transportation.

(a) (b)

Photo 6. (a) Duplicate field sample site at 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 3 & 4).

## 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 & N4205500; 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 7A to 7D 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.

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.

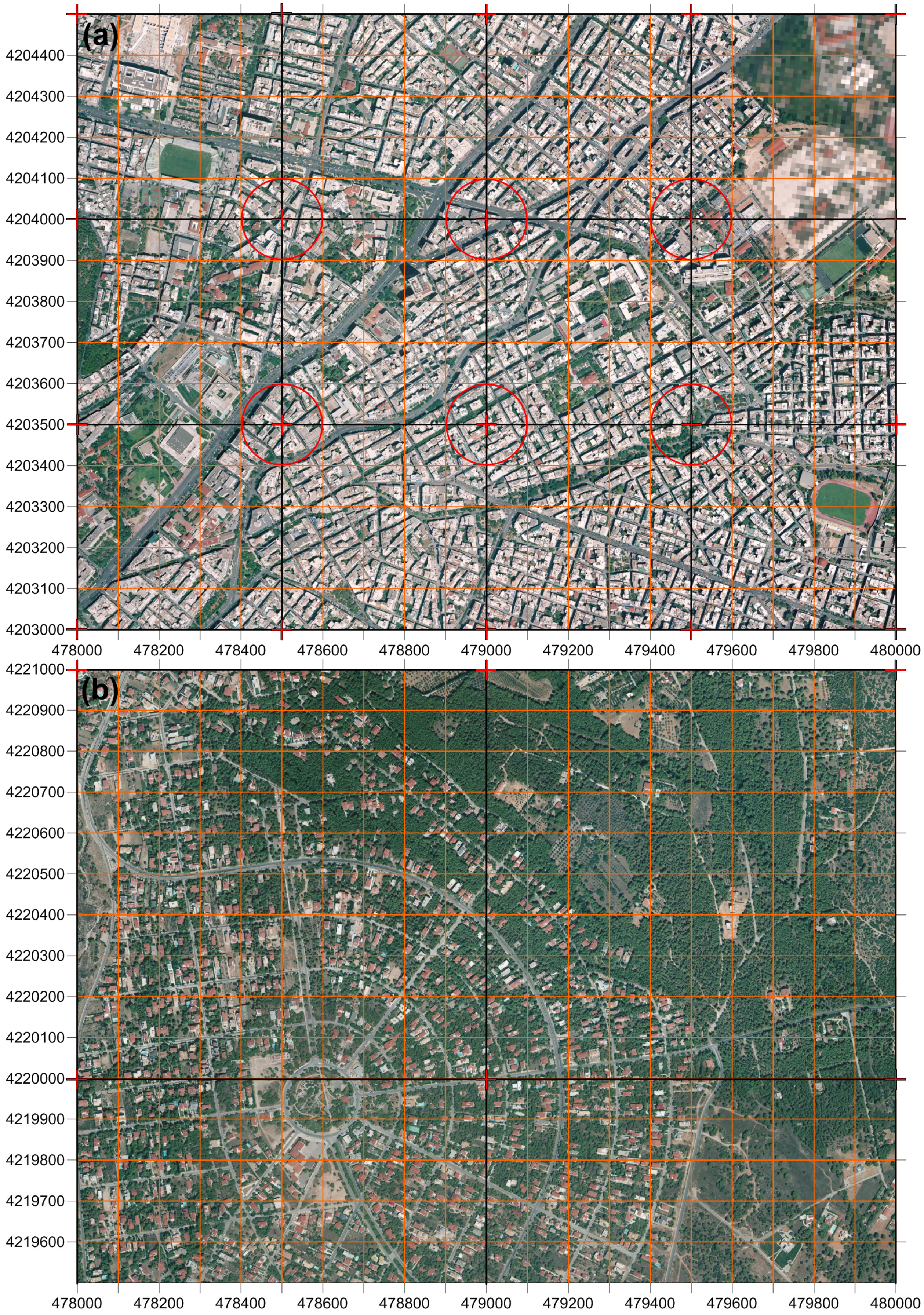


Figure 3. Orthophotographs of Athens, the capital of Hellas: (a) central part of Athens (Ampælókipi-Ghoudí-Ilíssia), and (b) a northern suburb (Thrakomakædónæs). Red crosses indicate the urban soil sample sites using a grid of 500 x 500 m (central part) and 1000 x 1000 m (suburb). The orange colour grid 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).

The following series of photographs show possible sites for the collection of topsoil samples (Photos 7A-D), 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.

(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 7f).

(f) A suitable spot for soil sampling at site shown in Photo 7e can be found, which is not under the tree.

Photo 7A. A number of photographs showing possible topsoil sample sites in a densely populated city, such as Athens, Hellas.

(g) Small green space in a pedestrian street (see 7h).

(h) Possible bare soil spot for sampling (see 7g).

(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 7B. 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 7n).

(n) Possible soil sampling site in a roadside verge (see 7m).

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

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

(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 7C. 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 7v) .

(v) Bare soil spot, but it is under trees (see 7u). 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 7D. A number of photographs showing possible soil sampling sites in a densely populated city, such as Athens, Hellas.

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## 3. SAMPLE PREPARATION AND STORAGE

The preparation of 14,000 to 15,000 topsoil samples over a short period of time at a central laboratory is difficult. Hence, it is suggested that each country, participating in the URGE II project, undertakes to either air-dry at room temperature, or in a thermostatically controlled oven at a temperature not exceeding 25°C, the collected topsoil samples in its own facilities, and to remove only visible stones and plant material (it is noted that Hg escapes even at 30°C). Each participating town or city should follow the underlying procedure for the preparation of its topsoil samples on which inorganic elements will be determined:

- Open the Rilsan® bag in a contamination free environment.
- Remove the small numbered card in the small zip-lock bag.
- Transfer the topsoil sample into a drying tray.
- Place in a secure position in the drying tray the small numbered card in the small zip-lock bag.
- After drying, transfer the dried topsoil sample into a new pre-numbered Rilsan® bag.
- Place on top of the sample the small numbered card in the small zip-lock bag.
- Remove air from the Rilsan® bag, and close it firmly with a self-locking plastic tie strap (plastic cable tie).
- For safety during transportation, the Rilsan® bag should be placed in a larger plastic bag.
- Pack the samples in strong carton boxes, and send them to the selected central laboratory for preparation.

**Note**: Samples for the determination of organic compounds will be sent directly to the selected laboratory for sample preparation and analysis. Additional instructions will be provided.

At the selected central preparation laboratory, the topsoil samples will be carefully disaggregated by a porcelain pestle in a porcelain mortar, taking care not to grind small pebbles. Following disaggregation, soil samples will be sieved through a nylon screen of 2 mm. The whole <2 mm topsoil fraction must be suitably homogenised, and split into eight sub-samples and placed in trace-element free containers.

All utensils should be cleaned very carefully after the preparation of each sample in order to avoid cross-contamination of samples.

Topsoil sample splits for chemical and physico-chemical analyses should be sent to the selected laboratory or laboratories, remembering that all samples must be analysed for the same suite of determinands at the same laboratory. Three topsoil sample splits will be sent to different laboratories for the following determinations:

- aqua regia extractable inorganic chemical elements; Pb isotopes, and PGEs;
- pH and conductivity, and
- total nitrogen, total carbon and total organic carbon.

The remaining five splits of <2 mm topsoil will be archived at the sample storage facilities of the Geological Survey of Sweden where the ambient temperature does not exceed 30°C. Three splits may be used for particle-size analysis, total element determinations and mineralogical analysis, provided funds are available. The remaining two sample splits will be archived, as these will be the reference collection for future use.

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## 4. PROJECT REFERENCE MATERIALS

A large reference sample is being prepared for use by the EuroGeoSurveys URGE II project at the Geological Survey of Slovakia (State Geological Institute of Dionyz Stur, Geoanalytical Laboratories, Spisska Nova Ves). Apart from the homogeneity tests, which 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).

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# 5. ARRANGEMENT OF SAMPLES FOR ANALYSIS

## 5.1. Systematic errors and randomisation of samples

Randomisation of topsoil samples 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 topsoil samples by contaminated samples during sieving;
- within-batch contamination of topsoil samples from an external source during grinding and pulverisation;
- during the analysis of samples in the laboratory, changes in the conditions may occur, such as 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, 2011, 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 topsoil 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 URGE I, it is strongly recommended in large projects, where many towns or cities are participating, to have a very strict field sampling schedule, because it is important to submit to the analytical laboratory all collected urban topsoil samples in one large randomised 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 routine urban topsoil samples of all URGE II project participating towns or cities, and inserted control samples (reference and analytical replicates), will be performed in the sample preparation laboratory, and project topsoil, reference and field duplicate samples will be assigned new numbers. This procedure has a major disadvantage, because the samples lose their identity, as completely new numbers are assigned. Hence, the procedure must be performed 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 field sample numbers must be re-assigned.

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# 6. LABORATORY ANALYSIS

## 6.1. Analytical laboratory arrangements and obligations

All topsoil samples of the EuroGeoSurveys URGE II project will be sent to a selected laboratory or laboratories for analysis. Each laboratory will analyse all URGE II topsoil samples for the same suite of elements and/or parameters in a short time, as this is the only way to produce good quality and comparable analytical results.

For the analysis of all urban topsoil samples, 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, 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.

*IMPORTANT CONDITION*: In the contract to be signed with the laboratory, it 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 an exhaustive statistical analysis of their quality using the internal and external quality control results will be performed;
- if analytical problems are located, the analytical batch or batches will be reanalysed by the analytical laboratory without any charge, and
- in case all analytical results are of poor quality, then the analytical 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 reports about the determination of particle or grain size in Reimann *et al.*, 2011, 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 topsoil 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. Commercial laboratories nowadays even have an aqua regia method using q 25 g aliquot. 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; Mathur *et al.*, 2010; Ďuriš, 2011).

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

### 6.3. Determination of organic compounds

Additional instructions will be given, with respect to randomisation of samples, if funds are available for the determination of PAHs and PCBs.

## 7. QUALITY CONTROL PROCEDURES

Urban topsoil 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. The installed quality control procedures *must include the calculation of measurement uncertainty* (Ramsey, 1997, 1998; Ellison *et al*., 2000; Ramsey and Ellison, 2007; Ellison and Williams, 2007, 2012; Majcen *et al*., 2011), apart from the estimation of sampling, analytical and geochemical variance.

A balance hierarchical sampling and analytical scheme is 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 method was proposed by Ramsey (1998), and subsequently verified by Lyn *et al.* (2007).

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.*

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 duplicated in order to have a satisfactory statistical number of sites (>30), and to use reliably single classical statistical analysis of variance schemes. Therefore, if a minimum of say 40 sites is duplicated, 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 field sites has been reduced to a minimum of 8, and each routine and duplicate field 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. It is important to remember that urban topsoil geochemical surveys are very sensitive, because they are concerned with the quality of our living, working and recreational environments, and extend to issues concerned with our health. Consequently, the objective is to produce legally defensible urban topsoil geochemical mapping results for multipurpose use.

### 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, as it has been done in the GEMAS project, and a quality report written (Reimann *et al*., 2009, 2011, 2012; Demetriades *et al*., 2014).

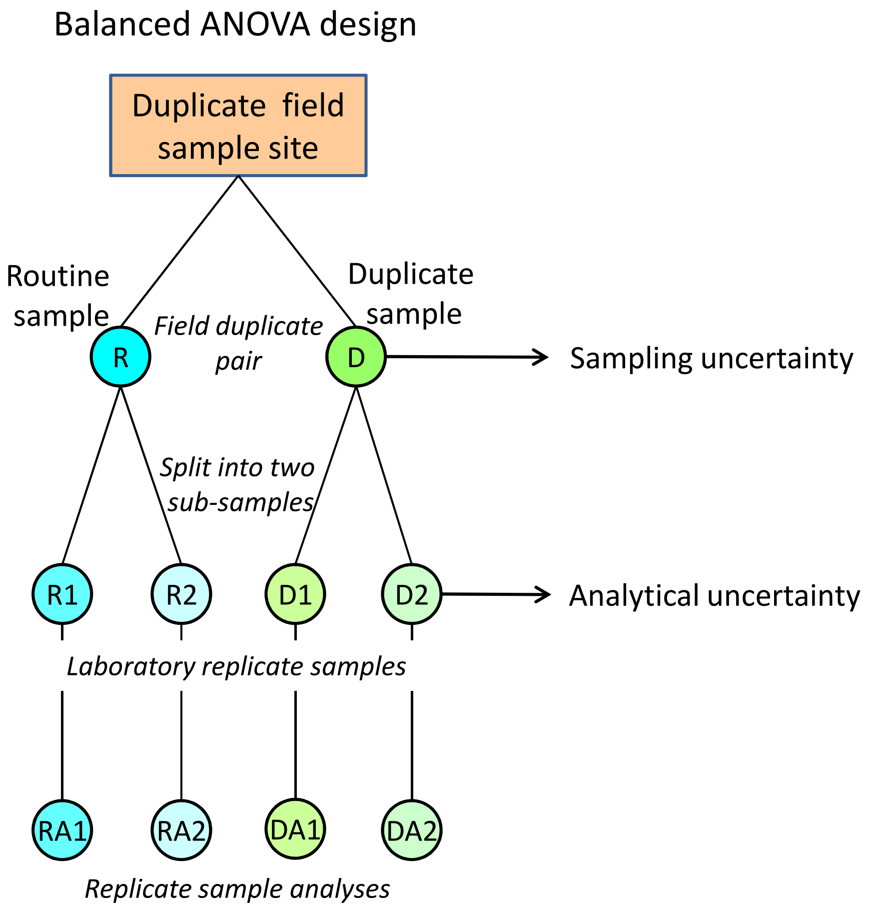

Figure 4. Balanced hierarchical geochemical sampling and analytical scheme for the estimation of geochemical, sampling and analytical variance and random components of measurement uncertainty (Ramsey *et al.*, 1992; Ramsey, 1998) (Source: Demetriades, 2011b, Fig. 6.1, p.78).

## 8. SUPPORTING INFORMATION

For the interpretation of the urban topsoil 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 industrial 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. SUMMARY OF STAGES OF URGE II PROJECT

The following are the stages of the URGE II mapping project:

- ❑ *Sampling grid*: A square sampling grid of variable dimensions from 500 x 500 m (inner city) to 1000 x 1000 m (suburbs) will be used, giving an approximate sample density of 4 samples/km$^2$.
- ❑ *Sampling*:
  - ➢ Topsoil samples should be collected from flat land bare soil spots (if possible) by the responsible applied geochemist or well-trained field staff.
  - ➢ Field duplicates are taken at every 20th site 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.
  - ➢ Cross-contamination of topsoil samples 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 topsoil sample should be described and documented properly by (a) completing the appropriate Field Observations Sheet (Appendix 1), (b) marking the sample site on a suitable scale topographical map, (c) recording of coordinates by GPS, and (d) documenting the sample site with a number of site and general landscape photographs.
- ❑ *Sample preparation*: Collected topsoil samples from each participating town/city are either air dried at room temperature or in a thermostatically controlled oven at a temperature not exceeding 25°C in a clean sample preparation laboratory of each participating Geological Survey. Visible stones and plant material are removed, and the dried topsoil sample is packed in a new Rilsan® bag, and the small numbered card in the small zip-lock bag is placed on top of the sample; air is removed and the bag securely sealed. Samples are packed in strong carton boxes and sent to the central preparation laboratory. Dried topsoil samples are disaggregated by a porcelain pestle in a porcelain mortar, taking care not to grind small pebbles. Following disaggregation, topsoil samples are sieved through a nylon screen of 2 mm. The whole <2 mm topsoil fraction is suitably homogenised, and split into eight (8) sub-samples and placed in trace-element free containers. All sample preparation apparatus should be thoroughly cleaned after each sample.
- ❑ *Archive sample collection*: At least two topsoil sample splits should be archived at the storage facilities of the Geological Survey of Sweden where the ambient temperature does not exceed 30°C. This will be the topsoil reference sample collection for future use.
- ❑ *Randomisation of samples to reduce systematic errors*: Routine topsoil samples, field duplicate splits and corresponding routine sample splits, and URGE II standard sample splits are randomised and new numbers assigned. The randomisation procedure must be carried out very carefully and a record kept, because upon receiving the analytical results the samples will be re-assigned their field numbers. The laboratory must be informed not to randomise the samples.
- ❑ *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 issues about the analytical data should be included in the contract with the laboratory.
- ❑ *Quality control report*: A quality control report should be written to document the quality and integrity of the analytical data. This is important documentation, because in

- *Data processing and map plotting*: Data processing begins after the quality and integrity of analytical results is verified. 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 (parent material) map, geological map, lithogeochemical data (if available), soil map, 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 guideline value is contaminated. Sound evidence to support such a conclusion must be given.
- *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.

## ACKNOWLEDGEMENTS

We thank the EuroGeoSurveys Geochemistry Expert Group for entrusting us at the September 2014 Dublin annual meeting to write this manual for the URGE II project. We also acknowledge the assistance of the EuroGeoSurveys Brussels office staff, Isabel Pino de Juana (Scientific Officer), Céline Andrien (Office Manager) and Kim van Zanten (Administrative Officer) in making the necessary arrangements to obtain the ISBN number for this manual. We finally thank Francesca Siciliano (Communication Assistant) for the artistic design of the front and back covers of the manual.

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*Note: All web-links were checked on the 30th of May 2015.*

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## APPENDIX 1: Urban Topsoil Field Observations Sheet

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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): ..........................................................................................

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

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Sample number: ...........................................................

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

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

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

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

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

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

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

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

At the front 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 at the back 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 Topsoil Geochemical Mapping Manual (URGE II)

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

EuroGeoSurveys
European Geoscience for Society
The Geological Surveys of Europe

ISBN 978-90-822547-1-6