### Provided for non-commercial research and educational use. Not for reproduction, distribution or commercial use.

This article was originally published in Treatise on Geochemistry, Second Edition published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for noncommercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues who you know, and providing a copy to your institution's administrator.



All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

http://www.elsevier.com/locate/permissionusematerial

Demetriades, A., 2014. Basic considerations: *Sampling, the key for a successful applied geochemical survey for mineral exploration and environmental purposes*. Chapter 15.1 In: W. F. McDonough (volume Editor), Analytical geochemistry/Inorganic instrument analysis. In: H.D. Holland & K.K. Turekian (Executive Editors), Treatise on Geochemistry. Elsevier, Oxford, vol. 15, 1-31.

© 2014 Elsevier Ltd. All rights reserved.



# TREATISE ON GEOCHEMISTRY **SECOND EDITION**

# **VOLUME 15**

## ANALYTICAL GEOCHEMISTRY/ **INORGANIC INSTRUMENT ANALYSIS**



Volume Editor William F. McDonough H.D. Holland Executive Editors K.K. Turekian

## **15.1** Basic Considerations: Sampling, the Key for a Successful Applied Geochemical Survey for Mineral Exploration and Environmental Purposes

A Demetriades, Institute of Geology and Mineral Exploration, Athens, Hellas

© 2014 Elsevier Ltd. All rights reserved.

15.1.1	Introduction and Background Information	1
15.1.2	Design of a Geochemical Sampling Campaign	2
15.1.2.1	Desk Study	2
15.1.2.2	Orientation Survey	2
15.1.2.2.1	Orientation survey in mineral exploration	2
15.1.2.2.2	Orientation survey in a contaminated land investigation	3
15.1.2.3	Regional Geochemical Survey	4
15.1.2.4	Follow-up Geochemical Survey	5
15.1.2.5	Detailed Geochemical Survey	5
15.1.2.5.1	Detailed rock or soil geochemical survey	6
15.1.2.5.2	Detailed contaminated land investigation	6
15.1.3	Randomization of Samples	9
15.1.4	Quality Control – Duplicate Field Samples and Control Samples	9
15.1.5	Sampling	10
15.1.5.1	Stream Sediment Sampling	10
15.1.5.1.1	Wet sieving	12
15.1.5.1.2	Dry sieving	12
15.1.5.1.3	Without sieving	12
15.1.5.2	Overbank or Floodplain Sediment Sampling	12
15.1.5.3	Stream and Ground-Water Sampling	15
15.1.5.4	Rock Sampling	17
15.1.5.5	Soil Sampling	18
15.1.5.5.1	Soil sampling for mineral exploration	18
15.1.5.5.2	Soil sampling for environmental investigations	19
15.1.5.6	House-Dust Sampling	22
15.1.5.7	Attic-Dust Sampling	23
15.1.5.8	Road Dust Sampling	24
15.1.6	Sampling in the Laboratory	24
15.1.7	Conclusions	27
References		28

#### 15.1.1 Introduction and Background Information

Careful geochemical sampling is the key to any successful survey, carried out for either mineral exploration or environmental purposes (see Chapter 13.24). Geochemical sampling procedures are described in (1) many textbooks (e.g., Beus and Grigorian, 1977; Butt and Zeegers, 1992; Fletcher et al., 1986; Govett, 1983; Hale and Plant, 1994; Hawkes and Webb, 1962; Kauranne et al., 1992; Levinson, 1974, 1980; Rose et al., 1979; Siegel, 1974), (2) field manuals (e.g., EuroGeoSurveys Geochemistry Working Group, 2008; Johnson, 2005; Salminen et al., 1998), and (3) geochemical atlases (e.g., BGS, 1992, 2000; Bølviken et al., 1986; Fauth et al., 1985; Halamić and Miko, 2009; IGS, 1978; Kadūnas et al., 1999; Koljonen, 1992; Lahermo et al., 1990, 1996; Lis and Pasieczna, 1995; Lis et al., 1999; Locutura et al., 2012; Ottesen et al., 2000, 2010; Reimann et al., 1998, 2003; Salminen et al., 2004; Słowańska, 1997; Webb et al., 1978). Although the reported sampling procedures are aimed at mineral exploration, most of them can be used for environmental investigations as well. Sampling techniques applied in urban areas are described in atlases (De Vivo et al., 2003, 2005; Pasieczna, 2003; Šajn et al., 1998) and in Johnson et al. (2011). This chapter does not seek to replace the aforementioned detailed descriptions, but it will attempt to give a concise account of a practical approach to geochemical sampling of different media for mineral exploration and environmental purposes.

Every geochemical survey from the continental to the micrometer scale has eight independent, and yet interdependent, components:

- (1) planning,
- (2) sampling,
- (3) sample preparation,
- (4) laboratory analysis,
- (5) quality control,
- (6) data processing and map plotting,
- (7) interpretation, and
- (8) report writing.

Failure to perform correctly and efficiently any one of the aforementioned steps will have a detrimental effect on the

succeeding ones. Following the planning stage, the foremost parts are first sampling, and second sample preparation. Sampling is the most costly leg of the survey, and undoubtedly the most difficult to repeat, if it is not carried out properly. The next step that must be performed correctly is sample preparation. Any mistakes made during sampling and sample preparation are difficult to trace and correct afterwards. As sampling and sample preparation affect project success, both must be carried out by well-trained personnel, and supervised by an experienced applied field geochemist and chemist, respectively. Laboratory analysis of samples is another costly part of the geochemical survey, and a stage of considerable concern (see Chapters 15.5 and 15.6). If samples, however, have been collected and prepared properly, they can be reanalyzed until the results are of acceptable quality. Finally, data processing, map plotting, and interpretation, provided the previous stages of sampling, sample preparation, and analysis have given reliable results, are processes that can be repeated, depending on the skills of the applied geochemist. Consequently, an important basic consideration, for the successful execution of a geochemical survey, is the training of the applied geochemist. Apart from a good knowledge of geology and geochemical principles about the distribution of elements and geochemical survey methods, the applied geochemist should have a working knowledge of economic geology, mineral exploration methods, applied geophysics, mineralogy, hydrogeology, geomorphology, analytical methods, statistics, geostatistics, data processing by geographical information systems, and project management and good communication skills.

#### 15.1.2 Design of a Geochemical Sampling Campaign

The design of a geochemical sampling campaign depends largely on survey objectives, which range from the planetary to the laboratory micro- or even nano-scales. In order to be cost- and time-effective, a number of steps or phases have been established, that is, (1) desk study, (2) orientation survey, (3) regional survey, (4) follow-up survey, and (5) detailed survey. Each succeeding phase depends on the results of the previous ones. Failure to complete successfully one of the phases will affect the outcome of the succeeding steps, and essentially lead to the waste of financial and human resources.

#### 15.1.2.1 Desk Study

The purpose of the desk study is to collect and assess all available existing information and data, pertinent to the property under investigation, and to identify the potential for mineralization (if possible) or anthropogenic contamination (if any). In the past, apart from thorough literature search, aerial photographs were studied and a photo-geological interpretation made. Nowadays, with high-resolution Landsat imagery much more geological and land-use information can be obtained. Apart from the collection and evaluation of geological and environmentally sensitive data, there are many practical considerations involved in the field survey, such as accessibility of area, political situation, sanitary conditions, waterborne diseases, and suitable personnel (workers and field assistants), which should also be tackled. The collated data and information may enable, in the case of a contaminated land investigation, the development of a preliminary site conceptual model (Figure 1), which considers all potential contaminant sources, pathways, and receptors, and allows the identification of the existence of any pollutant linkage. This desk assessment of all available data and information should lead to the compilation of a concise draft report, which will be completed after the orientation survey and receipt of the initial analytical results.

For mineral exploration, it is not prudent to make any theoretical assumptions at this stage, apart from the potential for mineralization, based on available geological and geotectonic information. However, if applied geochemical data are available, then viable assumptions may be made.

#### 15.1.2.2 Orientation Survey

The orientation survey is a key component of phased exploration, since it determines the field, sample preparation, analytical, data processing, and interpretational procedures to be used in the detailed survey. An orientation survey should be carried out at each new area to be investigated, since its characteristic features may be somewhat different from other areas studied previously. In fact, each area is unique in terms of geology, geomorphology, and climate. Therefore, sound field information is required for each area to be investigated for planning the more costly follow-up or detailed phases. Since the purposes of the orientation survey for mineral exploration and contaminated land investigation differ, they are discussed under different headings. A more detailed description is given for contaminated land investigation, since orientation surveys for mineral exploration are covered adequately in exploration geochemistry textbooks (Hawkes and Webb, 1962; Levinson, 1974, 1980; Rose et al., 1979; Thomson, 1986; see also Chapter 13.24).

#### 15.1.2.2.1 Orientation survey in mineral exploration

In mineral exploration, two different orientation surveys should be carried out, both having the same objective to develop costeffective procedures to enhance the contrast of significant geochemical anomalies, and to subdue false patterns. The first concerns the regional or reconnaissance stream sediment survey and the second the detailed rock or soil geochemical survey. The former is comparatively easy, for in the prospective area the objective is to determine the sample density, grain-size fraction to be analyzed, and the optimum analytical method that gives the maximum geochemical contrast; for anomalous patterns to be considered significant they should be described by at least three samples. The latter, detailed survey is somewhat more complex for it involves many variables that should be determined in a potentially prospective area, that is,

- type of geochemical dispersion patterns (primary dispersion; secondary dispersion: clastic, hydromorphic, and biogenic);
- optimum sampling medium, rock or soil;
- optimum sampling interval to delineate potential mineralized structures; at least two orientation traverses should cross mineralization, and three to five samples collected over it; the traverses should cross all rock or soil types occurring in the area;



Figure 1 Site Conceptual Model of potential soil-contamination sources from airport activities, road traffic, military base, and agricultural activities: primary and secondary sources, transport mechanisms, exposure routes, and final receptors.

- soil horizon and depth from which soil samples shall be taken; soil samples should be collected from all distinct horizons; if the horizons are thick, samples should be taken every 20–25 cm (samples should never be taken from different horizons, because each horizon has its own peculiar physicochemical characteristics);
- grain-size fraction of soil to be analyzed;
- ore elements or suite of elements to be determined;
- optimum analytical method;
- effects of topography, hydrology, drainage, glacial history, climate, rainfall, etc., on secondary dispersion patterns;
- background variation in rock and soil, and establishment of local threshold values;
- data treatment methods; and
- presentation of results on maps, histograms, graphs, etc.

The above data and information will lead to the formulation of the standardized methodology to be used in the detailed survey. In order for the orientation survey to be effective, it should be carried out on that part of the prospective property that contains mineralization, and the geology is representative of the whole area.

### 15.1.2.2.2 Orientation survey in a contaminated land investigation

This is the second phase of a contaminated land investigation and the purposes are:

 to collect site-specific data and information about the characteristics of the potential soil polluting activities;

- to confirm the existence of soil contamination, by taking representative soil samples from pits and trenches from seemingly contaminated and uncontaminated parts of the property;
- to collect representative samples from the wastes produced, if any; at least three samples are required from each type of waste; and
- to refine the site conceptual model (Figure 1).

Ideally, all infrastructure on the property under investigation should have been removed, including asphalt and concrete roads, yards, etc., and the bare soil exposed over the whole property.

A significant point to remember is that soil is a very difficult medium to sample and analyze, because in most cases it is naturally heterogeneous, and the binding of contaminants to soil depends both on inherent soil properties, including soil type, redox condition, water saturation, etc., and on properties of contaminants (see Chapter 7.1). Local environmental influences affect, therefore, dispersion processes of contaminants. In addition to the more obvious effects due to climate and topography, the single most important factor is the parent material of soil within the investigated area.

In case airborne contamination is the dominant source, soil samples should not exceed a depth of 5 cm. Even this soil thickness may be too thick in some cases of predominantly airborne contamination, since it may be restricted to the very upper part in association with decayed organic matter. Hence, it is indeed very difficult to give guidelines about the depth interval of surface-soil samples. This is where the prudent investigator with a mineral exploration background carries out an orientation survey (Hawkes and Webb, 1962; Levinson, 1974, 1980; Rose et al., 1979), which will provide the characteristics of soil contamination in order to plan efficiently the detailed investigation, if this is considered necessary.

Samples should be collected from soil profiles down to a depth of 50 or 100 cm, or to the shallow water table, depending on soil properties and type of contamination. Soil samples should be taken from pits or trenches according to the following scheme: 0–5, 5–10, 10–15, 15–25, 25–50, 50–75, and 75–100 cm, provided the soil profile is uniform, something which is highly unlikely, unless the property is in the alluvial plain of a large river. Soil samples, as already stressed, must never be taken across soil horizons, since each horizon has its own peculiar physicochemical properties. Therefore, the above scheme may be varied across the property depending on soil profile characteristics at each location.

Pits and trenches are the best method to study in detail soil characteristics and potential contamination, since they are the only means to obtain a good three-dimensional picture of undisturbed soil. Drilling is not recommended at this stage, because it is costly, and does not give the three-dimensional information of pits and trenches.

'How does one proceed to take soil samples across the property, and how many should be collected?' These are two key questions, where no guidelines can, in fact, be given. One can attempt to model the situation by using 'hypergeometric probability' (Stanley, 2003). However, the question is: Can one model efficiently soil contamination, when all potential sources are not known? Therefore, the objective is to cover adequately the whole property, and the samples, or pits/trenches to be used afterwards in the detailed investigation, if the results justify this stage. This is a cost-effective method of planning by being able to use results (samples) or previous work (pits/trenches) in a subsequent stage of the investigation. The recommendation is to lay out a grid (see below), and to cover the whole property systematically by collecting soil samples from different grid nodes spaced widely apart, as far as this is possible, by taking into consideration, at this stage, the location of different potential soil-contaminating activities. During this orientation stage, the applied geochemist is acting like a detective, who is investigating the different sides of a case, with the objective of discovering the 'whereabouts' of contamination, and its three-dimensional characteristics.

If there are wastes on the property, they should also be sampled. At least three representative samples are to be taken from each waste type for its geochemical characterization.

#### 15.1.2.3 Regional Geochemical Survey

The aim of the regional reconnaissance geochemical survey is to evaluate the mineral potential of a large area of hundreds to thousands square kilometers by delineating anomalous geochemical patterns, and also to define the regional geochemical background values for each analyzed element (Figure 2). It is stressed that this phase is aimed at selecting potential prospective areas, and not to locate a specific deposit. The sampling medium that is commonly used is stream sediment, though rock surveys have been used as well, mostly in the Soviet Union and former Eastern Bloc countries. Regional stream sediment surveys are carried out at different sampling densities, depending on project objectives, as described in Section 15.1.5.1. As the results are going to be used for the potential resource evaluation of the area, collected samples should be analyzed for as many elements as possible. Currently, commercial laboratories offer packages of more than 45 elements. During the interpretation stage, at least three samples are required to



**Figure 2** Distribution of Pb in the <0.180-mm fraction of stream sediment, Eastern Macedonia, and Thrace, N.E. Hellas. Sampling density about 2 samples per km<sup>2</sup>. For follow-up stream sediment survey in the Virini-Pessani area see **Figure 3**, and for the detailed soil geochemical survey at Thermae see **Figure 4**.

define an anomalous pattern. Finally, geochemical anomalies should be grouped in a priority order to be investigated by the follow-up survey. Even single-element and single-sample anomalies should be listed, but a lower priority assigned.

Regional rock geochemical surveys outline prospective metallogenic provinces and favorable host rocks. Soviet geochemists developed methods of defining the properties of primary haloes by using zonal contrast coefficients (Beus and Grigorian, 1977; Govett and Nichol, 1979; Levinson, 1974, 1980). Using these techniques, it is possible to recognize primary haloes at great distances from mineralization, to interpret the depth of erosion level, and to make a prediction for concealed deposits. Since this is a highly specialized topic, Beus and Grigorian (1977) should be consulted.

#### 15.1.2.4 Follow-up Geochemical Survey

The aims of the follow-up geochemical survey are to define more precisely the potential mineralized area in order to carry out the more costly detailed survey. Planning of the follow-up survey is based on regional reconnaissance results, and highpriority areas are investigated first. The sampling media used are either stream sediment at a greater sample density, or residual soil at a wide sampling interval along wide-spaced traverses.

The follow-up stream sediment survey, carried out along an anomalous segment of a stream, aims to define a cutoff point close to the source of the anomaly. Thus, by defining cutoff points on neighboring streams, the potential mineralized area is delimited precisely (Figure 3).

#### 15.1.2.5 Detailed Geochemical Survey

Detailed rock or soil geochemical surveys for mineral exploration purposes are carried out over highly prospective areas, the limits of which have been defined by the follow-up survey, ranging from a few square kilometers to a few tens of square kilometers, with the objective of delineating as precisely as possible geochemical anomalies for evaluation by pitting, trenching, and drilling (see Chapter 13.24). However, detailed soil geochemical surveys for environmental contamination



Follow-up stream sediment survey

Figure 3 Follow-up stream sediment survey at a density of 17 samples per km<sup>2</sup>, Virini-Pessani, Thrace, N.E. Hellas. Lead distribution in the <0.180-mm grain-size fraction of stream sediment.

purposes are usually carried over very small areas of a few tens of square meters (factory and petrol station scale), with the aim to delineate precisely contaminated and uncontaminated parts of the property and to estimate the volume of contaminated soil.

The detailed geochemical survey is the most costly phase of a geochemical investigation, and it is imperative to be planned effectively. The following are the stages of an efficient design of a detailed geochemical survey for both mineral exploration, using rock or soil, and contaminated land investigation using soil:

- design of optimum sample layout for obtaining reliable information;
- randomization of samples to reduce systematic errors, and to distinguish between genuine and false geochemical patterns;
- sampling: field duplicates are taken to assess sample site representativeness and variability, and to estimate reliably measurement uncertainty;
- sampling: cross-contamination of soil samples in the field must be avoided, by using a good sampling procedure, and thorough cleaning of all equipment;
- sampling: each sample should be described and documented properly by completing the appropriate field observations sheet, and taking a general landscape and a site digital photograph;
- sampling: blank samples, such as a kaolin, bentonite, or pure quartz of known composition, should be used in a rock or soil geochemical survey (Schermann, 1990); this blank sample is packed in the field as the routine sample, and it should be taken through the whole process of sample preparation and analysis;
- sample preparation: insertion of control and blank samples to evaluate laboratory contamination; thorough cleaning of all apparatus and utensils at the end of preparation of each sample;
- analysis of samples in a certified laboratory: insertion of blank, replicate, and reference/standard samples in analytical batches:
  - blank samples assess laboratory contamination;
  - replicate samples estimate analytical precision, and
  - reference/standard samples determine analytical accuracy (see Chapter 15.3).

As the purposes of the detailed soil geochemical survey for mineral exploration and contaminated land investigation differ, they are discussed under different headings. Again, a more detailed description is given for the detailed contaminated land investigation, since the detailed soil geochemical survey for mineral exploration purposes is covered adequately in exploration geochemistry textbooks (Beus and Grigorian, 1977; Butt and Zeegers, 1992; Fletcher et al., 1986; Govett, 1983; Hawkes and Webb, 1962; Kauranne et al., 1992; Levinson, 1974, 1980; Rose et al., 1979; Thomson, 1986; see also **Chapter 13.24**).

#### 15.1.2.5.1 Detailed rock or soil geochemical survey

The objective of a detailed rock or residual soil geochemical survey is to locate precisely mineralized structures. For this purpose, a grid is laid over the prospective area, and systematic sampling of rock or residual soil is carried out. Grid dimensions depend on the estimated size of anomalous patterns and the orientation of the mineralized structures, defined by the follow-up survey or geological mapping. The requirement is at least three traverses to cross-cut the concealed mineralization, and its area extent delimited by the rock or soil geochemical anomaly (Figure 4).

#### 15.1.2.5.2 Detailed contaminated land investigation

The aims of the detailed site investigation on a contaminated property are:

- to define the level and extent of soil contamination over the whole property, to determine its spatial threedimensional characteristics, and also to delimit the uncontaminated parts,
- (ii) to assess the risks associated with identified hazards and receptors, and
- (iii) to evaluate the need for remediation in order to reduce or eliminate the risks of pollution to actual receptors according to the end land use.

The detailed phase is the most significant phase of a contaminated site investigation, because the polluted and unpolluted parts of a site must be delineated with a high degree of confidence, in both the horizontal and vertical sense, since recommendations will be made for remediation and the volume of contaminated material should be estimated precisely. The detailed site investigation, therefore, should be carried out in two stages:

- The first stage delineates the extent and level of surface-soil contamination down to a depth defined by the orientation survey by collecting soil samples in a systematic scheme. Site-specific guideline values of different determinands should be estimated depending on the end land use, and a human health-risk assessment should be carried out.
- The second stage involves the detailed investigation of sectors, where the site-specific guideline values are exceeded, by trenching and core drilling to a depth according to the nature of the soil and contaminating activity. Again, this stage will depend on results of the orientation survey.

The square sampling grid is considered the optimum for contaminated soil investigations and the design of block remediation, if the site is considered hazardous to human health.

Variations in the character of a geochemical response with changes in sampling point interval are shown in Figure 5. A critical examination of these distribution maps shows how under-sampling can lead to 'uncertainty' in interpreting a soil survey (Figure 5(b) and 5(c)).

Conversely, over-sampling is possible, but *is it worth the additional cost, or, rather, is the cost of an entire survey at that density warranted*? It is mentioned in some consultancy reports, which shall remain nameless, that one sample may represent up to 1 ha of land, provided that there are no marked changes in soil type (e.g., color, texture, stoniness, consistency, etc.). However, if a soil sample is taken down to a depth of 10 cm and is supposed to be representative of 1 ha, then this sample is equivalent to about 1300 tons of soil per 10-cm depth. The collected soil sample may be less than a millionth of this volume of material. Therefore, representativeness of the soil sample is something that should be considered very carefully when



Figure 4 Detailed soil geochemical survey, Thermae mineralized area, Thrace, Xanthi Prefecture, N.E. Hellas. Traverses at 80 m intervals, and sample sites at 20 m intervals.



**Figure 5** Sketch determinand distribution maps showing the mapping of a contaminated site with different square grid dimensions (numbers over the crosses represent Pb concentration values in mg kg<sup>-1</sup>). (a) The optimum grid for this case is  $25 \times 25$  m. (b) A grid of  $50 \times 50$  m gives a very generalised picture and misses an important 'hot spot.' (c) A grid of  $75 \times 75$  m finds no contamination, and the area is classed as uncontaminated.

investigating contaminated sites, because the natural soil heterogeneity has been influenced by unpredictable anthropogenic activities, thus making soil even more heterogeneous. Consequently, taking a representative soil sample in contaminated land investigations is indeed a difficult task.

Topsoil should 'never' be mixed with the underlying subsoil in one sample. If deeper sampling is required, then the different soil horizons must be kept separate from each other. As pointed out above, the field sampling survey is the most important part of a cost-effective and efficient soil survey, followed by the sample preparation. By and large, it is the most costly, and certainly the most difficult to repeat. Any deficiencies at the sampling stage will have fatal effects on the remainder of the contaminated land investigation. The same applies to sample preparation. Finally, although the analysis of soil samples is indeed costly, and another area of concern, the samples can be reanalyzed. However, a wrongly taken soil sample, and a wrongly prepared soil sample can never be corrected, except by repeating the field survey and bearing the cost. Therefore, it is important that the professional investigator pays attention not only to sampling, but he/she must ensure that samples are prepared correctly too.

The ideal soil geochemical survey for contaminated land investigations is based on a regular systematic sampling over the whole property (Figure 5(a)). The dimensions of the grid should be decided on the basis of the orientation survey results.

#### 15.1.2.5.2.1 Systematic versus random sampling

Systematic sampling refers to the collection of samples in a defined pattern, such as at intersection points on a square grid (Figure 5(a)). Because such a grid can be used to cover 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).

Random sampling refers to the independent collection of samples from random geographical locations. Such a collection of samples does not usually provide an even coverage of a specific area and it is, therefore, not suitable for areal studies. Random sampling is used in preference to systematic sampling, however, where the samples are to be used for the estimation of average values, or of degree of association of geochemical parameters (Open University, 1972).

#### 15.1.2.5.2.2 Square block sampling

A report published by the European Institute of the Joint Research Centre at ISPRA (Kuhnt and Muntau, 1994) recommends the use of a square grid (or square block) as the basic unit to characterize soil, since the geographical characteristics are averaged out for each grid square (or square block).

A variant of this sampling scheme is the philosophy of the IUGS and FOREGS grid-cell sampling scheme (Darnley et al., 1995; Salminen et al., 1998) (Figure 6(a)). The composite soil sample is made up from five subsamples taken randomly within the square block. In this case, each square block is subdivided into quadrants, and a subsample is collected randomly from each quadrant, and the fifth subsample is taken again randomly from the whole block. Thus, from one quadrant two subsamples of soil are collected (Figure 6(a)).

Another block-estimation scheme is to make a composite sample by collecting subsamples from the four grid nodes of each quadrant (Figure 6(b), red circles), and a fifth subsample taken from the center (magenta circle); in this case, a sort of 'moving' sampling scheme is developed, because subsamples are collected from the same grid nodes, shared by neighboring blocks (red circles). A variant of this sampling scheme is to make a composite soil sample from nine subsamples, that is, to take four additional subsamples from the semi-axial nodes of each quadrant (red, green, and magenta circles).

Block-estimation sampling schemes may seem ideal, but they are considered inappropriate in contaminated land investigations, since taking a composite soil sample to describe the geochemical characteristics of a large block of land, usually  $25 \times 25$  m or  $50 \times 50$  m, has a number of drawbacks, which are described in Section 15.1.2.5.2.3. Therefore, block soil sampling schemes are not recommended in contaminated land investigations.

#### 15.1.2.5.2.3 Composite versus spot sampling

A decision must be taken, whether to take composite or spot soil samples. This is, indeed, a dilemma, as already described above. A composite sample is assumed to be more representative of the site from which it is taken. Therefore, in this case, three to five points about the sampling site are randomly selected to collect subsamples to make the composite soil sample. Such a sampling scheme may be appropriate in natural conditions, but on land contaminated by human activities it is not considered suitable, because the distribution of contaminants is usually haphazard. Hence, one mixes subsamples of variable chemical composition, and contamination may either be enhanced or diluted, depending on the volume of contaminated and uncontaminated material collected. Consequently, one may either overestimate or underestimate contaminant concentrations. Therefore, to avoid such impasses, it is strongly recommended to take 'spot' soil samples, and to design the collection of a satisfactory number of duplicate 'spot' soil samples to estimate sampling variation, and relative expanded measurement uncertainty (Demetriades, 2011a; Ramsey, 1998;





Figure 6 Block soil sampling: (a) FOREGS grid-cell random sampling scheme (Salminen et al., 1998) and (b) quadrant grid-node sampling scheme.

see also **Chapter 15.2**). Spot soil sampling is considered more appropriate in the investigation of contaminated land, because the sample characterizes precisely the site from which it is taken, since there is no averaging involved, as with composite sampling.

#### 15.1.3 Randomization of Samples

Randomization of 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 (Fletcher, 1981; Fletcher et al., 1986; Plant, 1973; Reimann et al., 2008, 2009, 2011, 2012):

- contamination of uncontaminated soil/rock/sediment/ dust samples by contaminated samples during sieving;
- within-batch contamination of soil/rock/sediment samples from an external source during grinding and pulverization; and
- during the analysis of samples in the laboratory, changes in conditions may occur, for example 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 of distinguishing between false and genuine geochemical patterns.

Randomization of samples is the method devised by applied geochemists to remove any systematic relationship between order of analysis and geographical location (Darnley et al., 1995; Plant, 1973; Plant et al., 1975; Reimann et al., 2008, 2009, 2011, 2012; Thompson, 1983). By randomization of samples, any systematic between-batch variation in the analytical level is transformed to increased analytical variability. This converts data that would be reflected as areas of shifted geochemical background levels, and are artifacts of the lack of accuracy in the chemical analyses, into increased local noise. Care should, therefore, be taken to include a sufficient number of control reference samples, and to monitor their analysis, in order to detect between-batch variation (see Chapter 15.2). If such variations are identified, then the affected batches of samples should be submitted for reanalysis, and the new analytical results utilized, provided they are of acceptable quality.

During the planning of the field survey, the total number of samples is estimated. Then this number is randomized, and a list of random numbers is made. Number randomization can be performed by a digital computer software program, and an output produced. During the field survey, each sample is assigned in turn a random number from the list. Empty numbers should be left at random for the insertion of blank, standard, and replicate samples. In the laboratory, the samples are ordered in ascending numbers after sample preparation. At this stage, the blank, standard, and replicate samples of field duplicates are inserted.

Ideally all project samples should be analysed in a short time period. However, in a large project, involving thousands of samples, this may not be possible. Therefore, large batches of samples should be randomized. Such a large batch of samples could comprise 500–1000 samples (or more), depending on the project. When one batch of randomized samples is collected, it is placed in ascending order and sent to the laboratory for sample preparation and analysis. Again, empty numbers are left for the insertion of blank, standard, and replicate samples of field duplicates.

A third option is to collect the samples using a consecutive numbering system, and to assign random numbers in the laboratory together with the insertion of blank, standard, and replicate samples of field duplicates. This procedure, although practical, has a serious drawback as the samples are given new numbers, and there is the danger of making a mistake during their back-numbering to the original field-sample numbers. The number assigned in the field should remain through the whole process of sample preparation and analysis. Hence, the randomization of sample numbers should be done during the field sampling survey.

Batch collection and analysis of samples are recommended because of the advantage to monitor errors, and to correct data batchwise, and in this way to reduce the total spread of data errors to a minimum (Schermann, 1990). As already stressed, these batches of samples should be quite large, between 500 and 1000 samples.

Since many laboratories nowadays randomize samples prior to analysis, the applied geochemist should warn the laboratory to analyze the samples in the order they have been submitted.

#### 15.1.4 Quality Control – Duplicate Field Samples and Control Samples

Introduction of rigorous error-control procedures for regional geochemical programs from the 1960s onwards was one of the significant milestones in the progress of applied geochemistry (Bølviken and Sinding-Larsen, 1973; Brandvold and McLemore, 1998; Fletcher, 1981, 1986; Garrett, 1969, 1973, 1983; Garrett and Goss, 1978; Garrett et al., 1980; Howarth and Lowestein, 1971; Howarth and Thompson, 1976; Miesch, 1964, 1967, 1973, 1976; Plant and Slater, 1986; Plant et al., 1975; Reimann, 1989, 2005; Thompson and Howarth, 1976, 1978, 1980; Thompson and Maguire, 1993; see also Chapter 13.24). The procedures used are based on (1) the collection of field duplicate samples at every 10th or 20th sample site, depending on survey size, (2) the introduction of blank samples in the field, such as a kaolin, bentonite, or pure quartz of known composition (Schermann, 1990), (3) randomization of samples prior to submitting them for analysis (see Section 15.1.3), (4) the introduction of control reference samples (reference or project standards), unknown to, and unrecognizable by, the laboratory at a rate of 1 standard per 10-30 samples, depending on survey size and analytical batch, and (5) the insertion of analytical replicates of field duplicates at a rate of 1 in 10-20 samples (Fletcher, 1981; Garrett et al., 1980; Johnson, 2011; Plant, 1973; Plant et al., 1975; Reimann, 1989; Reimann and Wurzer, 1986; Reimann et al., 2008, 2009, 2011, 2012; Thompson and Howarth, 1978). In combination, these procedures allow the detection and evaluation of most quality problems that can occur during sample analysis, and which may seriously affect the success of all types of geochemical survey projects (see Chapter 15.2).

Duplicate field sampling is an inherent part of a field geochemical survey (regional, follow-up, and detailed), because the different types of variation of a determinand in the study area must be known, that is, the 'sampling and analytical noise' should be estimated. For this purpose, either a balanced or an unbalanced hierarchical sampling and analytical scheme (Figure 7) is followed for the estimation of geochemical sampling and analytical variance and relative expanded measurement uncertainty (Demetriades, 2011a; Demetriades and Karamanos, 2003; Garrett, 1969, 1973; Howarth and Thompson, 1976; Johnson, 2011; Miesch, 1964, 1967, 1973; Ramsey, 1997, 1998; Ramsey and Argyraki, 1997; Reimann et al., 2008, 2009, 2011, 2012; Thompson and Howarth, 1976).

The use of either a balanced or an unbalanced hierarchical sampling and analytical scheme depends largely on project size and budget available. The balanced design for a large project is more costly than the unbalanced scheme. The latter is preferred if classical analysis of variance is used. However, in small projects and, especially in contaminated land investigations, the balanced design is more appropriate, especially if robust analysis of variance is used (Lyn et al., 2007; Ramsey, 1998, 2009; Ramsey et al., 2002).

Robust analysis of variance is preferred as it is cost-effective and suitable for small areas, because of the small number of duplicate field samples required to be taken from a minimum of eight randomly selected sites (Lyn et al., 2007; Ramsey, 1998). Of course, the number of duplicate field sites depends on the total number of routine samples collected in the area under investigation. Normally, duplicate field samples are collected at every 10th, 20th, or 30th sampling site, depending on the total number of samples and project logistics. size to be placed on sample bags, sample number card of suitable size (normally  $5 \times 8$  cm), self-sealing bag for placing sample number card of solid samples, permanent ink marker (preferably black or blue), digital camera (>5 megapixels), extra memory cards and batteries for digital cameras, geographical positioning system (GPS), extra batteries for GPS, geological compass, scale ruler, binoculars, field observation sheets, mechanical pencil, permanent ink pen, rack sack for carrying samples, metal-free plastic crates or heavy-duty carton boxes for packing and transportation of samples, and rubbish bags.

At each sampling site, field observations should be recorded on simple field observation sheets, and at least two digital photographs taken (see EuroGeoSurveys Geochemistry Working Group, 2008; Salminen et al., 1998): the first showing the landscape about the sampling site, and the second characteristic features of the actual site (Photo 1). In order not to make any mistakes, the first photograph should be of the sample number, followed by the landscape and sample site photographs.

Apart from recording the GPS coordinates on the field observation sheet, before leaving the sampling site, the sample site should be transferred on the topographical map to ensure that the GPS coordinates are correct. Nowadays, with solidstate computers, it is possible to link a GPS to uploaded topographical maps and to locate in real time the precise position and sample site coordinates, or use Google Earth satellite imagery. In addition, digital cameras have a GPS, and the coordinates can be recorded on the photographs.

#### 15.1.5 Sampling

Representative sampling of different media will be described below. To begin with, the equipment to be used for sampling each medium is given, and then an outline of the sampling procedure. The following equipment is common to all sampling media: self-adhesive vinyl waterproof labels of suitable

#### 15.1.5.1 Stream Sediment Sampling

*Equipment*: Heavy-duty elbow-length rubber gloves; metal-free polyethylene funnel; metal-free plastic scoop; sieve set with two frames, preferably wooden or plastic, containing nylon 2.0-mm mesh and nylon 0.150-mm screens; metal-free gold pan or plastic bucket; kraft wet strength sample bag with wire closure; plastic bag for protection of kraft bag during transportation; metal-free plastic buckets or



Figure 7 (a) Unbalanced and (b) balanced ANOVA design for the estimation of random components of measurement uncertainty.

containers with lids; trenching tool – metal free, polyethylene or polypropylene; topographical maps, preferred scale 1:50000; chiselpoint geological hammer for semi-dry areas; and bristle brush (for cleaning equipment in dry-sediment sampling). Instead of kraft bags, trace-element-free Rilsan<sup>®</sup> bags may be used and plastic safety strips for their secure closing.

Active stream sediment is the sampling medium commonly used in regional and national geochemical reconnaissance surveys for the delineation of potentially mineralized areas, and also for defining geochemical baseline conditions. It can locate, however, anthropogenically contaminated areas as well. The technique involves sampling of fine- to medium-grained bed-load material (clayey–silty–sandy), which is transported by running stream or river water. This material represents the average geogenic composition of active erosion points at the time of sampling of the catchment basin upstream from the sampling site. Stream sediment is characterized by a variable mineralogical composition, grain size, and color. This



(c)

Photo 1 General and site view of soil sampling site, Mantoudhi, Euboea Island, Hellas.

variability is a function of geology, terrain, and climate of the upstream catchment basin.

Stream sediment samples are normally collected from minor tributaries (first- and second-order streams, according to the Strahler (1964) classification), which are subject to less complex dilution than the major, third-order, streams. However, fill-in sampling from third-order streams is carried out to cover segments between confluence points with second-order streams. Sample density varies according to survey objectives. For example, national stream sediment surveys vary from 1 to 2 samples per km<sup>2</sup> (BGS, 1992, 2000; Fauth et al., 1985; IGS, 1978; Smith et al., 1976; Webb et al., 1978), and continentalscale surveys may range from (a) 1 sample per 120 km<sup>2</sup> for the location of metallogenic provinces (Armour-Brown and Nichol, 1970; Garrett and Nichol, 1967) to (b) 1 sample per 500 km<sup>2</sup> (Ridgway et al., 1991), and (c) 1 sample per 4500 km<sup>2</sup> in the geochemical mapping of Europe (De Vos and Tarvainen, 2006; Salminen et al., 2005a).

The active stream sediment sample is collected from the lower-order stream at a suitable site above its confluence point with the higher-order stream; the lowermost sampling point should be selected sufficiently upstream of confluences with higher-order streams to avoid sampling sediment that may result from mixing of material from two adjacent streams during a flood event. Sampling sites should be located at least 100 m upstream from roads, railway lines, and settlements to avoid any potential contamination.

In rugged terrain, where collapsed bank material into the stream channel is probable, sediment from as near the center of the stream as possible is collected to avoid sampling bankslip material. However, in areas of low relief, where activestream sediment at the center of channels may be enriched in quartz, and depleted in clay should be avoided; in such cases, other fine-grained material, deposited along stream margins during flood events, is regarded as more suitable for sampling.

The stream sediment sample is normally a composite of 5–10 sampling points over a stretch of 50–100 m, depending on sampling density and stream geometry; in continental-scale mapping, however, the sampled stretch may vary from 250 to 500 m (Salminen et al., 2005b). Care should be taken for the composite stream sediment sample not to be made from material collected from streambeds of different nature.

In order to avoid any kind of metal contamination, no hand jewelry or dressings should be worn during sampling. If medical dressings are worn, heavy-duty rubber gloves are recommended to be worn at all times to avoid contamination of samples. Metal-free polyethylene or unpainted wooden spades/ scoops, metal-free nylon sieve meshes housed in an inert wooden or metal-free plastic frame, and metal-free funnels and sample collection containers are used. If it is not possible to use nonmetal equipment (e.g., spades and sieve frames), unpainted steel equipment should be used. Aluminum and brass equipment should be avoided. If contamination sources are observed in the vicinity of the stream, the sampling site should be moved.

There are three variants of composite stream sediment sampling, that is, (1) wet, (2) dry sieving in the field, and (3) collection of sample without sieving in the field. In the third case, a large volume of sample is collected to ensure that there is enough fine-grained material for analysis and storage.

#### 15.1.5.1.1 Wet sieving

For protection, rubber gloves are recommended to be worn throughout sampling. All stream sediment-sampling equipment (buckets, sieves, gold pans, funnels, gloves, and spades) are thoroughly washed with stream water before and after sampling. The gold pan or collection bucket is set up at a stable position on the stream bank (Photo 2). The sieve with the 0.150-mm aperture nylon cloth is placed in a stable position resting on the gold pan or bucket, and the sieve with the 2-mm aperture nylon cloth is set over it.

The amount of material to be wet sieved to obtain the required weight of <0.150 fractions for analysis and storage depends on the upstream geology and terrain. Fine- to medium-grained stream sediment is collected from different points, placed in buckets, thoroughly mixed with a plastic or wooden stirring rod, and carried to the sieving location, where they are left to stand, before draining off excess water. Stream sediment is subsequently loaded onto the top 2-mm sieve with a spade or plastic scoop. If more than one bucket of sediment is collected, equal amounts of sediment are loaded onto the top sieve from each bucket in turn.

The stream sediment material is rubbed through the top sieve wearing rubber gloves for protection. Large stones are removed by hand. Once the bottom sieve contains a reasonable quantity of <2-mm sediment, the top sieve is removed and the >2-mm material discarded. The <2-mm sediment in the bottom <0.150-mm sieve is washed and rubbed through the sieve with the aid of stream water and shaken down. In order to enhance the trace-element signature, a minimum amount of water is used to wash the sediment through the bottom sieve, all washing water is retained in a collection bucket, and fine-grained sediment allowed to settle. Once enough wet, finegrained sediment is collected, the lid is placed securely on the bucket. The sediment is then allowed to stand until all suspended material settles, and clear water sits on top of the sediment. Excess water is carefully decanted. The remaining sediment is thoroughly homogenized and mixed using the plastic stirring rod before being transferred into the kraft sample bags.

At the field base, kraft bags are air-dried for as long as possible. Samples are subsequently dried completely at <40 °C at the sample preparation laboratory. Freeze-drying is recommended as this helps to disaggregate the samples.

#### 15.1.5.1.2 Dry sieving

In Mediterranean and semiarid terrains, where there are long dry periods and streams are, therefore, seasonal, dry sieving is



A special case is sampling of small, first- and second-order seasonal streams in Mediterranean and semiarid terrains, which should be sampled with extreme care. Some of these seasonal streams have had no water flow for many years, and the streambed is covered with fallen bank material on which grass or other plants have grown. Since active-stream sediment must be sampled, the fallen bank material is removed by digging down to the old streambed, where the last activestream sediment was deposited. The pits at each subsite are dug near to the center of the channel.

All stream sediment-sampling equipment (buckets, sieves, gold pans, hammer, gloves, and spade) are thoroughly cleaned with a bristle brush in the field before and after sampling. At the field camp, all equipment is thoroughly washed with spring or tap water after sampling, and dried with clean, white cotton waste or cloth.

#### 15.1.5.1.3 Without sieving

Wet or dry sieving is normally a time-consuming and costly process. Therefore, a composite sample of the finest active stream sediment is collected from 5 to 10 points. The drawback of this technique is that a large volume of sample is taken to ensure that the required amount of <0.150-mm material for analysis and storage shall be obtained after sieving at the domestic lab. This is where the orientation survey becomes very important, since the approximate amount of sample material would have been already estimated.

#### 15.1.5.2 Overbank or Floodplain Sediment Sampling

*Equipment*: Kraft wet strength sample bag with wire closure; plastic bag for protection of kraft bag during transportation; metal-free plastic crates or heavy-duty carton boxes for packing and transportation of samples; disposable gloves (one per sample); unpainted spade;



**Photo 2** Wet sieving of a stream sediment sample, Euboia Island, Hellas.



Photo 3 Dry sieving of a stream sediment sample in Mediterranean and semiarid environments, Lavreotiki Peninsula, Hellas.

pickaxe; stainless-steel knife; metal-free plastic or stainless-steel scoop; chisel-point or rock pick geological hammer; wooden, folded 2-m long meter; permanent drawing ink marker (preferably black or blue); permanent ink pen; and topographical maps, preferred scale 1:50000. Instead of kraft bags, trace-element free Rilsan<sup>®</sup> bags may be used and plastic safety strips for their secure closing.

Overbank or floodplain sediments are deposited in layers during flood events in low-energy environments on the floodplain and levees (Alexander and Marriott, 1999; Ottesen et al., 1989, 2010); they should be devoid, therefore, completely of gravel, which indicates a high-energy environment. Since floods are recurring events in the geomorphological history of a drainage basin, a succession of almost horizontal layers is built up. Consequently, a vertical section through overbank sediment layers reflects the history of sedimentation (Photo 4). Due to channel shifting, apart from the fine-grained (silty-clay, clayey-silt) sediment layers, there may be in the section gravelly and sandy layers, representing the bottom channel load of high- to medium-energy environments, respectively.

During flood events, the heavy rainfall and resulting large quantity of water in the drainage basin increase the erosion capacity of a stream, thus activating many sediment sources. Consequently, a composite overbank sediment sample, comprising many layers, is representative of a large part or even the whole upstream drainage basin (Bølviken et al., 1996; Ottesen et al., 1989, 2010). In some cases, the sedimentation history may be complex due to erosion of former overbank sediment deposits, and their subsequent deposition further downstream. Therefore, younger overbank sediments, deposited downstream, may then be intermixed with material from older overbank sediment layers. This action does not reduce, however, the representativeness of overbank sediment, since the reworked sediment still represents material from the upstream drainage basin.



Photo 4 Overbank or floodplain sediment sections: (a) comparatively recent loose overbank sediment sequence, Euboea Island, Hellas; (b) old overbank sediment sequence with indurated sediments; note the channel shift from low-energy environment at the bottom with four fine-grained sediment layers, then a high-energy environment with variable-size bottom-load pebbles and sand (central part), and at the top again a low-energy environment with two recognizable fine-grained overbank or floodplain sediment layers, Lavreotiki peninsula, Hellas.

Surficial overbank sediments are normally affected by recent anthropogenic activities, and they may thus be contaminated (Figure 8). Deeper overbank layers, if deep enough, should normally be pristine and, therefore, depict the natural geochemical background variation of the upstream drainage basin (Bølviken et al., 1990, 1993, 1996; Demetriades et al., 1990, 1993, 1994; De Vos et al., 1996; Hindel et al., 1996; Ottesen et al., 2000).

Prior to sampling, the exposed overbank sediment sequence is first studied carefully in order to select a suitable section with many layers of fine-grained material (silty-clay or clayey-silt), with the objective of reaching pristine sediments. According to Ottesen et al. (2010), overbank sediment sample locations may be classified into three categories, depending on the river channel type:

- (i) In meandering or straight stream segments, the natural levee or slack water parts of the river floodplain may provide sampling sites for both recent and pristine or preindustrial overbank sediment samples.
- (ii) In braided rivers, the overbank sediment layer is generally thin and spreads out over large areas. The ages of braids vary across the channel. In such cases, a sufficient

knowledge of the sedimentation history is required to be able to distinguish between pristine and contaminated overbank sediments.

(iii) If river terraces occur, their relative stratigraphic ages have to be determined, in order to identify suitable sites for collecting older and younger overbank sediment samples.

Overbank sediment-sampling sites are selected at the lowermost points of floodplains of second-, third-, and fourthorder streams. Sites adjacent to roads or ditches (minimum distance 10 m) should be avoided. There are two variants of overbank sediment sampling, depending on project objectives, that is, (a) channel sampling of all layers resulting in a composite sample and (b) sampling of surface (top) and lowermost (bottom) layer. In both cases, a section is either cut in the exposed overbank sediment sequence or a deep enough pit is dug in the floodplain. Living surface vegetation and large roots are removed before taking the composite or top overbank sediment sample.

In systematic top and bottom overbank sediment sampling, 25-cm-thick sections are sampled from single layers only (Salminen et al., 1998, 2005b). If the layer is less than 25 cm,



**Figure 8** Distribution of Pb in the <0.180-mm reconnaissance stream sediment fraction, and in the <0.063-mm fraction of overbank sediment layers, Irene River, Thrace, N.E. Hellas. Note (a) the contamination train from the St. Philip mine and ore beneficiation plant, and (b) the two surface layers of overbank sediment that show contamination, and the lower layers tending toward background conditions.

then the actual thickness is recorded on the field observation sheet. Always, sample first the bottom overbank sediment, and then the top layer.

Sample weight depends on the grain size for analysis. If the natural <2-mm sediment fraction is to be analyzed, then a weight of 1 kg is sufficient; if, however, the natural 0.063-mm sediment fraction is to be analyzed, then a weight of at least 3 kg is required. For such decisions, however, the orientation survey will give the required answer for cost-efficient planning of systematic surveys.

#### 15.1.5.3 Stream and Ground-Water Sampling

Equipment: Hardened Nalgene™ trace-element-free bottles of different sizes; powder-free disposable vinyl gloves; disposable syringes; pyrogen-free disposable filters 0.45 µm; droplet bottles made of Teflon fluorinated ethylene propylene (FEP); pH-meter; electrical conductivity (EC)-meter; digital titrator with solution-delivery straws and appropriate titration cartridges, including 1.6 N and 0.16 N sulfuric acid or 1.6 N and 0.16 N H<sub>2</sub>SO<sub>4</sub> solutions; potassium dichromate solution for Hg preservation: 0.2 g of K2Cr2O7 (Pro analysis, PA, quality)/100 ml nitric acid HNO3 (Suprapure quality); buffer solutions for calibration of pH-meter; concentrated HNO3 65%, density 1.40 kg l<sup>-1</sup>; bromocresol green acid-base indicator solution (0.1 g of bromocresol green in 14.3 ml of 0.01 M NaOH+235.7 ml distilled and deionized water; distilled and deionized water and a washing bottle; volumetric flasks, capacity of 100 and 1000 ml; burette or equivalent equipment, 10 ml capacity; plastic 100-ml measuring cylinder (for alkalinity measurements); 250-ml plastic conical flask (for alkalinity measurements); two polyethylene (1 l) decanters for sample water to measure pH and EC; disposable Pasteur pipettes; cool boxes and their batteries, or a car refrigerator.

Stream and ground water are two sample types where their chemical composition varies with season. Hence, it is important to complete the sampling campaign in the shortest possible time in order to minimize, as much as possible, seasonal compositional variations. Overall, the temporal homogeneity of stream water is one of its outstanding features. Stream water coming from different sources with contrasting chemical and physical characteristics needs only a minor turbulence to mix thoroughly well. In the absence of turbulence, or where the stream is wide in proportion to its depth, lateral compositional variation of stream water may persist for considerable distances downstream (Rose et al., 1979). Such a lack of homogeneity occurs in broad, shallow channels of large rivers. The stream water sampling site should be selected, therefore, with great care.

Running stream water is always sampled, and never stagnant water from ponds, because its geochemistry is normally different from that of running water. Sampling of stream water during rainy periods and flood events should be avoided. If the stream water sample is collected at the same time as the stream sediment, it should be taken first for obvious reasons, that is, during stream sediment sampling, fine-grained material is agitated and transported in suspension. During sampling, disposable powder-free plastic gloves are worn all the time on both hands. Further, in order to avoid any kind of metal contamination, no hand jewelry is allowed, and smoking or having the vehicle running during water sampling is strictly prohibited.

Planning the next day's sampling campaign starts in the evening of the previous day by thoroughly rinsing two times all new sample bottles with deionized water. Ideally, new sample bottles should be used. In the case, however, of reused sample bottles, these must be thoroughly cleaned, that is, (1) each sample bottle is washed with a brush and phosphate-free detergent; (2) rinsed three times with cold tap water; (3) rinsed with 10% HCl acid, and (4) rinsed three times with deionized water. Disposable powder-free plastic gloves are worn during the cleaning of sample bottles.

Since water samples are going to be analyzed for different determinands, at each sampling site many bottles will be filled with filtered and unfiltered water. Hence, it is important to label them correctly with a permanent ink marker. At the sampling site, bottles for unfiltered water, decanters, syringes, and other equipment are rinsed twice with unfiltered stream water, and bottles holding filtered water are rinsed twice with filtered stream water.

During stream water sampling, stand facing upstream, and extra care should be made not to disturb bottom sediments. All samples of unfiltered water are collected first. Each bottle is uncapped, prior to sampling, then is completely submerged in the stream water, filled as full as possible, and capped tightly below water level (Photo 5). Extra care should be taken not to leave any air bubbles in bottles of unfiltered water samples that major ions are to be determined by ion chromatography.

For filtered water samples, the procedure is as follows: (1) a disposable syringe is rinsed with sample water by filling it up with unfiltered water and then pressing the plunger to eject the water (this process is repeated a second time); (2) the syringe is filled up again with water, and the 0.45-µm filter screwed onto the syringe; (3) the first 10-ml of filtered water is always discarded from each new filter, and (4) the bottle is filled up to its neck with filtered water, and closed tightly with the cap (Photo 6). It is noted that the filtered water sample should go straight into the bottle without contact with the sampler's hands. All samples are placed in the cooler box or car refrigerator, and kept refrigerated <4 °C until their analysis. At the field camp site, filtered water samples for trace-element analysis by ICP-MS and ICP-AES are acidified with ultrapure concentrated HNO3 acid (pH < 2); for example, for each 100 ml of filtered water 1 ml of concentrated nitric acid is added with a droplet bottle. Since the acid is extremely corrosive, powder-free vinyl gloves must be worn, and the brim of the Teflon FEP droplet bottle must not touch the water sample. The bottle is tightly closed and shaken thoroughly in order to mix well the acid with the water.

Water samples for the determination of Hg should be preserved by adding 2% ultrapure nitric acid. However, it is reported that a trace amount of gold chloride (AuCl<sub>3</sub>) added to the HNO<sub>3</sub> solution preserves all forms of mercury (USEPA, 2003). The gold acts as a strong oxidizing agent, converting or maintaining mercury as mercuric (Hg<sup>2+</sup>) ion, which remains in solution. An additional benefit of using AuCl<sub>3</sub> in 2% HNO<sub>3</sub> is the doubling of silver solubility, thus stabilizing Ag as well. It is recommended, therefore, to preserve water samples for Hg analysis by adding nitric acid with gold chloride to a final concentration of 2% HNO<sub>3</sub> and 1 mg kg<sup>-1</sup> AuCl<sub>3</sub>.

At the sampling site, pH, EC, and temperature are measured by appropriate instruments, and alkalinity is determined by titration. Total alkalinity is measured by titrating 100 ml of water with  $H_2SO_4$  to pH 4.5. Two methods may be used: (1) titration by a Hach<sup>®</sup> digital titrator and standard acid cartridges and (2) titration by an ordinary 10-ml burette. In both









(b)



(c)



**Photo 5** Sampling unfiltered water: (a) and (b) after rinsing the bottle and cap two times with stream water, (c) the bottle is submerged carefully in the stream, filled with water, and (d) it is capped tightly below water level. Care is taken not to leave any air bubbles in bottles of unfiltered-water samples.











Photo 6 Sampling filtered water: (a) and (b) rinsing the disposable syringe twice; (c) screwing a 0.45-µm filter onto the syringe; (d) discarding the first 10 ml of filtered water; (e) filling the bottle up to its neck with filtered water; and (f) tightly capping the bottle.

(Continued)



(e)



Photo 6 Cont'd

methods, bromocresol green is used as indicator, and normality of sulfuric acid is in both methods either 1.6 or 0.16 N. Total alkalinity is expressed as mg  $l^{-1}$  CaCO<sub>3</sub>. In some cases, sampled stream water is colored, because of high humus contents, and the titration endpoint is thus difficult to observe. In such cases, the pH-meter is used to determine the endpoint of titration at a pH of 4.5. A full description of the methods is given in the Geochemical Mapping Field Manual, used for the geochemical mapping of Europe (Salminen et al., 1998).

Apart from the duplicate field samples, blank water samples should be added in the field for checking cross-contamination of samples. Since contamination is most likely going to occur in filtered samples, the blank water samples are filtered. Blank water samples are made from distilled and deionized water, which is filtered in the same manner as the normal water sample, stored in a bottle of the same volume, and acidified with ultrapure concentrated HNO<sub>3</sub> acid (pH < 2).

Ground water samples are collected from natural springs, wells, and boreholes, using the same sampling techniques, and observing all precautions. In sampling wells and boreholes, care must be taken to flush pumps, pipes, casings, etc., prior to sampling.

Duplicate ground water samples are collected from the same drill-hole or well within 1 h from the first sample.

If water samples are going to be analyzed for organic contaminants, dark-brown bottles with double-secure caps should be used, since these will reduce photosensitive reactions to a considerable extent.

Finally, the applied geochemist before embarking in the sampling of stream and ground water is strongly recommended to discuss the analytical program with the laboratory



Photo 7 Area with outcropping limestone, suitable for rock sampling, Kefalonia Island, Hellas.

chemist, who may make additional recommendations on the preservation of samples.

#### 15.1.5.4 Rock Sampling

*Equipment*: Sledgehammer ( $\approx$ 5 kg), chisel-point geological hammer, chisel, heavy-duty plastic bags or cotton cloth bags, heavy-duty gloves, safety goggles, and topographical maps of suitable scale depending on survey objectives.

Sampling bedrock is probably the most difficult and timeconsuming field procedure, especially if planned to be carried out on a regular grid or regularly spaced traverses, since it is highly unlikely that an outcrop will be closed to each grid node. If suitable outcrops (Photo 7) are not within the range of sampling grid nodes, then pits may have to be dug down to bedrock. Therefore, during the planning stage of a rock geochemical survey, it is a good idea to know the availability of outcrops. This is where the information from the orientation survey becomes very important. Further, in mineral exploration programs, the prospective area will most likely be geologically mapped. Hence, the applied geochemist should ask the geologist to use the method of outcrop mapping, and to note also the granularity of rocks. By this method the distribution, size, and type of outcrops will be known, as well as any inherent heterogeneities and gross compositional variation. The applied geochemist will thus be able to plan cost-effectively the rock geochemical survey by deciding whether to use a regular grid or a random sampling design, based on the distribution of outcrops; if the outcrop distribution is poor a systematic residual soil geochemical survey may be opted for instead. In case, however, an orientation survey or geological mapping, is not carried out prior to the rock geochemical survey, then the applied geochemist should perform a preliminary survey for mapping the distribution of outcrops; time may be saved by consulting first aerial photographs and satellite images of the area. This information is vital for planning and cost estimation of the field sampling campaign, and also the viability and effectiveness of the rock geochemical survey.

The most common field method in rock geochemical surveys is the so-called rock chip sampling technique. In order for the rock chip sampling to be representative of each site, it is a good idea to decide beforehand on the optimum dimensions of the outcrop size to be sampled. This is where the

information from the orientation survey or geological mapping comes in handy. Once the dimensions of the outcrop have been decided, the most typical parts can then be selected for sampling. Breaking the outcrop with a sledgehammer at different places is the easiest way to reach fresh rock. A composite sample is then made by selecting rock chips from at least five to seven places on the outcrop surface. Each rock chip is examined and any weathered or oxidized surface material is removed with the chisel-point hammer. Here, the sledgehammer head may be used as an anvil on which the rock piece is placed for the removal of weathered parts. The size of rock chips vary from 4 to 8 cm. The field-sample weight depends on the analytical program and the amount to be retained in storage for future use. Normally, a weight of 500 g is sufficient from fine- to medium-grained rocks. If the rock is coarse grained and inhomogeneous, then, as a rule of thumb for the sample to be representative, the number of places from where the rock chips are collected, and the total weight, should be increased by at least a factor of 2. For the more statistically oriented, Govett (1983) gives an interesting statistical account about the grain size of rocks, and the volume of sample required to meet the condition of representativeness.

#### 15.1.5.5 Soil Sampling

*Equipment*: Handheld Dutch auger (provided the site conditions allow its use), pickaxe, shovel, chisel-point or rock pick geological hammer, metal-free plastic scoop, alternate color wooden or plastic folding meter (2 m).

Soil is the medium extensively used in applied geochemical programs for mineral exploration and environmental purposes. In mineral exploration, soil derived directly from the weathering of underlying rocks, known as residual soil, is used. For practical purposes, even soil that has been subject to minor creep is regarded as residual. Transported soil, of alluvial, glacial or aeolian origin, poses serious problems in interpretation, and will not be discussed here. Geochemical surveys in arctic, glaciated, and tropical-subtropical terrains are dealt with in specialized textbooks by Kauranne et al. (1992), McClenaghan et al. (2001), and Butt and Zeegers (1992), respectively.

For planning cost-effective soil investigations, the orientation survey is of paramount importance for determining the soil horizon to be sampled, selecting the optimum grain-size fraction for analysis and analytical method.

In all the different cases of soil sampling, the equipment is thoroughly cleaned after sampling in order to avoid any crosscontamination.

#### 15.1.5.5.1 Soil sampling for mineral exploration

Soil sampling may be used in the follow-up phase, but undoubtedly residual soil is the commonest medium in detailed geochemical surveys for the delineation of mineralized structures. For the planning of the detailed soil geochemical survey, as with any sampling program, attention must be paid to the results of the orientation survey, which determine the optimum soil horizon for sampling, the grain size for analysis, and the analytical method to be adopted for each specific geochemical exploration program.

In detailed soil geochemical exploration programs, a square or rectangular grid is laid over the property (Figure 4), and samples are collected at regular intervals (e.g., 20, 25, and 50 m) along the traverses. According to Hoffman (1986) line spacing and sampling interval are controlled by many factors, including:

- (i) anticipated size of mineral occurrence at the bedrockoverburden interface;
- (ii) local dispersion processes;
- (iii) geology;
- (iv) topography;
- (v) favorability of the prospective area;
- (vi) size of the area under investigation, and
- (vii) availability of funds for personnel and analysis.

Since exploration programs are cost- and time-sensitive, compromises are quite normal as, for example, sample density determined on scientific grounds must be reconciled with availability of funds, time, and personnel.

The sampling techniques that are normally used are either auguring or pitting. Pits are preferred, since they give a threedimensional view of the soil profile; also, collection of soil samples from single pits are recommended as the most costeffective technique. To begin with, it is important to ensure that the material to be sampled is residual, and then the pit is dug with the aid of pickaxe and shovel.

There are at least four main difficulties arising in soil surveys:

- (a) Changes in soil type within the area, since, apart from bedrock lithology, there are many factors controlling soil type. Even in sampling the same horizon from the same type of soil there may be differences, as for example the occurrence of Fe and Mn oxides that normally scavenge various elements. Hence, one must be careful to note changes between an Fe-leached and an Fe-enriched soil, because there will be differences in the variation of many elements, even though the bedrock lithology may still be the same.
- (b) Failure to sample consistently from a single soil horizon will most likely produce false geochemical anomalies. It is stressed that each soil horizon has its own peculiar physicochemical characteristics; hence, in systematic soil geochemical sampling the same horizon must be sampled. Sampling indiscriminately at a predetermined constant sampling depth must be avoided, since there is the danger of mixing soil horizons. Because of these problems, it is strongly recommended to sample the C-soil horizon, as this is easy to recognize, it is above bedrock, and in areas with a strong relief, soil creep is slight to none (Photo 8).
- (c) Failure to recognize the different types of layering in soil profiles, that is, distinction between residual soil, transported soil, or truncated soil. Hence, sampling C-soil horizon avoids such impasses.
- (d) Soil contamination and soil disturbance by anthropogenic activities may be difficult to observe when sampling in a remote area, as is the usual case in mineral exploration. Therefore, one must be on the lookout for any unusual signs and to make a note in order to verify any suspicions during the interpretation stage. For example, the ratio of element pairs, known to be associated in the parent bedrock and mineralization, may be used to check for any unnatural additions of any of the elements studied.

**15.1.5.5.2** Soil sampling for environmental investigations For environmental investigations, there are at least two different types of soil surveys:

(1) urban geochemical studies for the assessment of soil quality of different land-use types, that is, house gardens, allotments, road verges, open spaces, parks, sport fields, playgrounds, school yards, and especially nursery schools, or kindergartens, or







(a)



(b)





Photo 9 (a) Child playground, Athens, Hellas; (b) child day-care centre, Oslo, Norway; exposed parts of soil should be sampled to assess potential soil contamination; (c) house garden, Sutton Coldfield, United Kingdom – note roof flashing, that is, lead sheets on roofs to protect from water penetration are a potential source of urban soil contamination; (d) park, Athens, Hellas – sampling of exposed soil.

(Continued)



(d)

Photo 9 Cont'd



(a)



(b)

**Photo 10** (a) Massa brownfield site, Avenza-Carrara, Tuscany, Italy; chemical factory (1935–1984) producing different sulfur compounds (herbicides, pesticides, fertilizers, decoloring agents, etc.) from pyrite and arsenopyrite; (b) heavily contaminated soil with arsenic.

child-care centers, where child hand-to-mouth activity is quite common (Photo 9) and (2) contaminated land investigations at brownfield sites, which are sites with a former industrial or commercial use within the inner part of cities (Photo 10) and should be remediated before redevelopment.

#### 15.1.5.5.2.1 Urban soil sampling

There is no standard technique for collecting soil samples for urban geochemical studies. Johnson and Demetriades (2011) have reviewed urban soil sampling, carried out in different countries, and have noted that sampling depth varies considerably, from 0-2 cm to 0-25 cm. For example, (1) in Norwegian targeted investigations 'bare' surface soil from 0 to 2 cm was collected (Andersson et al., 2011; Jensen et al., 2011; Ottesen et al., 2011), while systematic urban geochemical surveys have used six different depths: (2) 0–5 cm (Demetriades, 2011b; Duriš, 2011; Šajn et al., 2011); (3) 0–10 cm (Gregorauskienė et al., 2011); (4) 0-15 cm (Abimbola and Olatunji, 2011; Albanese et al., 2011; Gosar et al., 2006; Li, 2011; Smith et al., 2011); (5) 0-20 cm (Batista et al., 2011; Birke et al., 2011a,b; Bityukova and Birke, 2011; Ďuriš, 2011; Locutura and Bel-lan, 2011; Pasieczna, 2003); (6) 5-20 cm (Flight and Scheib, 2011; Fordyce et al., 2005; Lax and Andersson, 2011), and (7) 0-25 cm (Tarvainen and Jarva, 2011). Each investigator hopefully decides on the sampling depth by assessing the results of an orientation survey.

Apart from the variable soil depth of urban geochemical surveys, there are differences in the sampling technique and design. Some prefer to make a composite sample from about five sites (Abimbola and Olatunji, 2011; Albanese et al., 2011; Batista et al., 2011; Birke et al., 2011a,b; Bityukova and Birke, 2011; Demetriades, 2011b; Ďuriš, 2011; Flight and Scheib, 2011; Fordyce et al., 2005; Gosar et al., 2006; 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 Aleksandra Gulan, 2011) and others single-site or spot samples (Andersson et al., 2011; Demetriades, 2011a; Jensen et al., 2011; Ottesen et al., 2011; Smith et al., 2011). Composite samples tend to average out the geochemical signal and may miss a highly anomalous point, because of dilution effects by the other subsamples with lower contaminant concentrations. The spot sample represents the geochemical composition of the individual site, and it is preferred. In both cases, the least disturbed area of open space is selected, and organic detritus removed before taking the sample.

The reason for the preference of spot to composite soil samples is the strong heterogeneous nature of urban soil, and especially in the inner older parts of cities. Archeological sites (Photo 11) or excavations for construction purposes (Photo 12) show this feature quite well.

The sampling design is either random or systematic using a grid. Whatever the sampling design, it is important to cover the urban area with a sufficient number of samples in order to define, with a high degree of confidence, background, and anomalous samples.

The recommendation is to use a systematic grid of either (1)  $500 \times 500$  m or (2)  $1000 \times 1000$  m dimensions, and to cover the whole urban area to be investigated. As the inner parts of cities are the most contaminated, a variable-size grid may be used, that is, a denser grid ( $500 \times 500$  m) for the inner city part, and a wider spaced grid ( $1000 \times 1000$  m) for the outer part. Suitable sampling sites are located as close to the grid node as possible, GPS coordinates recorded on the field observations sheet, and exact sample site marked on the cadastral map (1:5000). The regularity of the sampling grid in the urban environment depends largely on surface sealing, and thus availability of exposed soil.



**Photo 11** Archeological sites portray very well the heterogeneity of urban soil: (a) fourth century BC to third century AD bath complex and (b) shows close-up of a soil block left by the archeologists, Acropolis Museum, Athens, Hellas; (c) third to fourth century AD bath complex and (d) close-up of 'overburden' (soil and rubble) profile, Athens, Hellas.



Photo 12 Excavations show the strong heterogeneous nature of urban 'soil' - a mixture of soil and rubble: (a) Athens, Hellas and (b) Oslo, Norway.

The optimum sampling depth and dimension of spot to be sampled should be decided on the basis of orientation survey results. If this stage is missed, then the decision should be based on the fact that urban contamination is caused mainly by the settling of airborne dust. Hence, sample depth should never exceed 10 cm; sampling depths of either 0–2 or 0–5 cm are recommended. Samples should be taken from a square pit of  $25 \times 25$  cm or  $50 \times 50$  cm, depending on site conditions.

#### 15.1.5.5.2.2 Soil sampling for contaminated land investigations

Contaminated land investigations are difficult and costly, because of the haphazard distribution of contaminants, and lack of detailed information about the historical uses of a brown field site. The applied geochemist, during the desk study, should try to obtain as much information on the potential contaminants that could occur at the site from all previous activities. It is of paramount importance to carry out an orientation survey in order to decide on the sampling technique to be used, and the contaminants to be analyzed, during the systematic detailed phase of the investigation. A variety of methods are currently available for contaminated land investigations (BSI, 2005; Demetriades, 2011a; Demetriades and Karamanos, 2003; Ferguson and Kasamas, 1999; Ferguson et al., 1998; Taylor and Ramsey, 2006).

The detailed phase should be based on a systematic grid covering the whole property. Square grid dimensions may be  $10 \times 10$  m or even  $5 \times 5$  m, because it is important to cover the property sufficiently well in order not to miss any contaminated

parts (Figure 9), and also to delimit contaminated and uncontaminated parts of the property with a high degree of confidence so as to reduce remediation costs (Taylor and Ramsey, 2006).

Pitting is the preferred method of sampling, because it is the only technique that gives a three-dimensional view of the soil profile to be sampled (Photo 10(b)). The dimensions of the pit will be decided from the results of the orientation survey, and samples should never be taken from different soil horizons, because each horizon has its own peculiar physicochemical properties. Surface-soil samples are first collected down to the decided depth, and the soil surface is cleared from any organic material, before sampling. Following the interpretation of geochemical results of surface samples, sites for collecting soil samples from drill-holes down to the water table should be planned. The drilling results should define precisely depth of soil contamination in order to estimate the volume that requires removal and remediation.

#### 15.1.5.6 House-Dust Sampling

*Equipment*: High-volume cyclonic vacuum cleaner; Rilsan<sup>®</sup> bags and plastic safety strips for their secure closing.

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 (ATSDR, 1999; Lanphear et al., 1998, 2002; Laxen et al., 1987; Manton et al., 2000; Sterling et al., 1998; Succop et al., 1998; USEPA, 1986). It



**Figure 9** Map showing a sampling grid of  $5 \times 5$  m in order delineate effectively contaminated and uncontaminated parts of the property. The expected area with As contamination is shown in pink (see Photo 10). The map shows the As concentrations at each site and the probabilistic classification of contaminated land (Demetriades, 2011a).

has been shown that lead-contaminated house dust is the strongest predictor of blood-lead levels in children (Jacobs et al., 2002; Lanphear et al., 1998, 2002; Roberts and Dickey, 1995; Succop et al., 1998). 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 (1) to place in a given prenumbered bag all dust swept with a broom from the floor of the whole house for a period of 15-20 days, and (2) to use a new bag, if a commercial vacuum cleaner is available, for collecting the dust for again a period of 15-20 days (Photo 13), and at the end of the sampling period to place the vacuum-cleaner bag in a given prenumbered bag (Demetriades, 2011b). 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-standardized 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 recommends the use of high-volume cyclonic vacuum cleaners for collecting house dust (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 analyzed for Pb, pesticides, or other chemical compounds and elements, except asbestos fibers.

Houses to be sampled should be selected randomly. 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 specialized sampling design, it is recommended to use the expertise of a statistician. Finally, all house-dust samples should be collected within the same period of time.

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

#### 15.1.5.7 Attic-Dust Sampling

*Equipment*: High-volume cyclone vacuum, or paintbrush with a dustpan; Rilsan<sup>®</sup> bags and plastic safety strips for their secure closing.

In towns with traditional houses with tiled roofs and attics (Photo 14(a)), attic dust is a good sample medium to assess urban airborne contamination in the home environment (Gosar and Šajn, 2003; Gosar et al., 2006; Hensley et al., 2007; Šajn, 2003, 2005, 2006; USEPA, 2008). Šajn (2005) defines attic dust as the dust that accumulates on wooden carpentry of attics (Photo 14(b)), where the influence of inhabitants is minimized. 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 time 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 14(b)). 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 13 House-dust sampling: (a) House dust in vacuum-cleaner bag; (b) close-up of house dust showing its heterogeneous nature.





(b)

**Photo 14** Attic-dust sampling: (a) house with an attic; (b) attic dust.

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. As in all cases of geochemical sampling, the use of new sampling equipment for each sample is stressed. If the same equipment is going to be used, then it should be thoroughly cleaned between samples to avoid cross-contamination. It is strongly recommended to sample attic dust from houses of similar age, and all samples to be collected during the same time period.

#### 15.1.5.8 Road Dust Sampling

*Equipment*: Nylon brush and dustpan; vacuum cleaner; Rilsan<sup>®</sup> bags and plastic safety strips for their secure closing.

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

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 also during the same time period. Again all sampling equipment must be thoroughly cleaned after the collection of each sample to avoid cross-contamination.

#### 15.1.6 Sampling in the Laboratory

Sampling in the laboratory for chemical analysis of rock, soil, sediment, and dust samples, although it is an integral part of the analytical process and the responsibility of the chemist in charge, is of great concern to the applied field geochemist, because on the produced analytical results decisions will be taken, whether the investigated area has a potential for mineral exploration purposes, or if it is contaminated and hazardous to health to recommend remediation measures (see Chapter 15.6). The principles of representative sampling at the macroscale (continental, regional, and local) to micrometer scale are essentially the same. To appreciate the scale factor, geochemical patterns can be observed at all scales, as shown in the two examples of Figure 10; the distribution of Cu in the regional stream sediment on the island of St. Lucia (West Indies) is shown next to the Ni distribution in a mineral grain.

It is here assumed that the solid-field sample has been prepared in the laboratory and reduced to the required grain size for analysis (Fletcher, 1981, 1986; Hawkes and Webb, 1962; Levinson, 1974, 1980; Rose et al., 1979).

The first concern is how representative is the laboratory aliquot, the micro-sample, to the original bulk field sample. It is well known that there is an inherent natural heterogeneity of rock, soil, sediment, and dust within the sampling site itself. In the field, a bulk sample of 0.5–1.5 kg (or more) is taken and is considered to be representative of the sample site. However, because of the natural variation within the sample site itself, if a second sample is collected the analytical results will be slightly different. This within-sample site difference of the results between the first (routine sample) and the second (duplicate sample) must be quantified (see Section 15.1.4). Therefore, duplicate field samples are collected from an adequate number of randomly selected sites over the explored area in order to estimate the sample site variance ( $S_s^2$ ).

Let us now consider the laboratory analysis. Since it is impossible to analyze the whole bulk field sample, a very small aliquot is retrieved and analyzed, varying from 0.1 to 15 mg, depending on the analytical method used. To perform a meaningful chemical analysis, the chemical composition of this small aliquot must be representative of the larger bulk field sample with a certain degree of laboratory uncertainty. *How can this be achieved*?

As shown in the flowchart (Figure 11), following the fieldsample collection, the solid sample (rock, soil, sediment, and



**Photo 15** Road-dust 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 a 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.

dust) is prepared in the laboratory, homogenized, and split into subsamples by different methods: (1) coning and quartering by hand (for this laboratory personnel must be well trained), (2) riffle box splitting, and (3) spin riffling. Therefore, representative subsamples are made by any of these three methods. All these are well tested, and produce acceptable results, provided the staff is well trained.

Depending on the determinations to be performed, different subsample weights are prepared. In the example of Figure 11, subsamples of 50 and 100 g are prepared for laboratory use, and a subsample of 500-g weight is considered adequate for storage for reference and future use. The decision for the number of subsamples to be prepared for laboratory use depends on the analytical parameters to be determined and the amount of sample material required. Similarly, the amount of sample to be stored for reference purposes, and future use, depends again on project objectives, and also on the potential future use of archived samples. Here, it must be remembered that the cheaper investigation is the one that utilizes archived samples.

Since the first major concern is the representativeness of the aliquot analyzed with respect to the bulk field sample, let us see the logistics of the whole procedure. For argument sake, the laboratory receives a 50-g sample, and is going to use for analysis an aliquot of 0.5-g, which represents only 1% of the subsample weight. However, this is not the true picture, because the original field bulk sample is much larger. Again, to understand what has actually happened, let us say that the field bulk sample is 500 g, which means that the aliquot of 0.5 g used by the laboratory represents 0.1% of the total bulk weight of the sample. This very small sample of 0.5 g is supposed to represent the chemical composition of the original 500-g sample. It, of course, sounds absurd, and it becomes more illogical as the field bulk sample weight increases to 1.5 or 2 kg. The key is the aliquot retrieved from the laboratory subsample should be representative of the whole bulk field sample. One way to achieve this is to make a composite aliquot for analysis by collecting small portions from the whole laboratory sample. The procedure is as follows. At the weighing stage, the sample is poured onto a clean sheet of paper in the form of a cone (Figure 12). The cone is subsequently flattened to a thin circular slice with a spatula by rotating the spatula from the top of the cone and spreading the sample material until the required thickness is reached. The thin circular slice is then divided into small squares and the routine composite aliquot for analysis is made up by collecting randomly minute portions from different squares.

It is assumed that the laboratory sample is homogeneous. However, this should be tested. Hence, as with the field



**Figure 10** Geochemical patterns at all scales. On left, Cu in stream sediment, Island of St. Lucia, West Indies (Maassen and Bolivar, 1987, Photo I, p. 458); long axis is ~40 km. On left, micro-geochemical map of Ni distribution, by electron microprobe, in complex of platinum group mineral grain (Gunn et al., 1990, Photo 1, p. 38); long axis approximately 5  $\mu$ m (synthesis from Darnley et al., 1995, Photo 3-1, p. 7). Element concentrations increase from low (blue) to high (red) color, for example, Cu <34.50 mg kg<sup>-1</sup> (blue) to >124.50 mg kg<sup>-1</sup> (red).

sampling, a replicate aliquot is collected randomly from different squares in order to quantify the laboratory or analytical variance  $(S_a^2)$  (Figure 12(c)).

Hence, the total variance  $(T^2)$  is made up from the sampling  $(S_s^2)$  and analytical variance  $(S_a^2)$ , that is,  $T^2 = S_a^2 + S_s^2$ .

A balanced or an unbalanced hierarchical sampling and analytical scheme is followed (Figure 7), depending on project size and logistics. As has been already described in Section 15.1.4, if robust analysis of variance is applied (Lyn et al., 2007; Ramsey, 1998, 2009; Ramsey et al., 2002), then duplicate field samples from a minimum of eight random sites are required to estimate reliably the required parameters of sampling variance, analytical variance, and measurement uncertainty (Demetriades, 2011a; Lyn et al., 2007; Ramsey, 1998).

Apart from the sampling and analytical variance and measurement uncertainty, three other parameters should be determined, that is, detection limit, precision, and accuracy (Demetriades, 2011a; Fletcher, 1981, 1986; Johnson, 2011; Reimann et al., 2009, 2011, 2012). Regarding the 'lower limit of detection,' there are a number of definitions in the literature. In pure analytical chemistry, the 'detection limit' is the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated confidence limit, and the laboratory normally gives a value three times the standard deviation of this 'background count rate' of the method used. The laboratories have also other options, such as (1) to use six times the 'background count rate,' and this is called the 'limit of determination' and (2) to use an even more conservative value, the 'limit of quantification,' which is ten times the 'background count rate.' However, these are 'theoretical laboratory' detection limits, which are valid when analyzing a pure substance, and are of little interest when analyzing geological materials with a very complex matrix. In applied geochemical projects, the 'practical' detection limit (Reimann and Wurzer, 1986; Thompson and



Figure 11 Flowchart showing the different stages from field sampling to sample preparation and sample splitting.



Figure 12 Sampling scheme in the laboratory: (a) sample poured into a cone; (b) the cone is flattened with a wide spatula until a thin circular slice is formed; (c) the circular slice is divided into small squares and the routine aliquot for analysis is collected randomly from different squares. Similarly, the replicate aliquot is collected randomly.

Howarth, 1978) is in fact of relevance, and it is the value where the precision of replicate analyses of project samples gets better than +100% (Demetriades, 2011a; Fletcher, 1981, 1986; Reimann et al., 2009, 2011, 2012).

#### 15.1.7 Conclusions

Geochemical sampling methods for mineral exploration purposes have developed to a high standard over the past 60 years, and the present account has given a concise description of the methods used (see also Chapter 13.24). These methods can be applied from the large planetary to the submicron scale. An observation that has been made is that experienced exploration managers nowadays, in the attempt to reduce costs, tend to miss the orientation phase, which is the most important step in an applied geochemical exploration program. With the waning of mineral exploration, many postgraduate courses in exploration geochemistry have closed down or have modified their curriculum to accommodate environmental applications. This is a grave mistake that has been made by academics, because the best background for any applied geochemical survey, whether for mineral exploration or environmental purposes, is attained by the teaching of phased and systematic exploration methods used in mineral exploration. The applied geochemist with mineral exploration training is able to plan a more efficient cost-effective phased survey, than his/her counterpart with just environmental training.

One may ask, "What is happening at the present time with the market of multibillion euro/dollar contaminated land investigations?" The answer is that, at the present time, the majority of applied geochemical surveys are carried out mechanically by untrained personnel and with a little thought of suitability of the specialized techniques employed. Frequently, a stock 'recipe' is used – for example, soil samples are collected and analyzed for so many elements or compounds, and one looks only for the high numbers (Fletcher et al., 1986). No effort is made to increase significantly the effectiveness of the survey. Hence, time, effort, and money are lost for the production of questionable data.

To optimize an applied geochemical survey, a variety of techniques are available to the trained and experienced applied geochemist. The collective experience of over 60 years of applied geochemistry can be brought to bear on the problem at hand. This is something that is normally forgotten by people working in contaminated land investigations. In fact, many times they are trying to 'reinvent the wheel.' It is stressed that in the decision-making process it is necessary to be quite clear about what is wanted in an individual survey. The objectives must be, therefore, very clear.

There is a considerable difference between the investment made by a mineral exploration company in its attempt to find economic mineralization, and by the stakeholder of contaminated land. The former makes an investment in the 'hope' that there will be a return at some stage in the future, whereas the latter should understand that the investment made on a wellplanned systematic investigation will raise the value of his/her property directly after remediation. Therefore, the stakeholder has an almost immediate return on funds invested, and with a substantial profit.

In conclusion, the key to success of all types of applied geochemical surveys is good planning from the beginning to end. Apart from efficient planning, sampling and sample preparation are two significant parts of all phases of the applied geochemical survey, which must be executed with the utmost care; otherwise, the results will be of dubious quality.

#### **Acknowledgments**

I like to thank Professor William F. McDonough (Director of Graduate Studies, Department of Geology, University of Maryland, U.S.A.) for entrusting me to write this chapter, and to share my over 38 years of experience in sampling geological materials for geochemical exploration and environmental investigations, and for his constructive comments on the original manuscript.

#### References

- Abimbola AF and Olatunji AS (2011) Urban geochemical mapping in Nigeria with some examples from Southern Nigeria. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 32, pp. 571–580. Chichester: Wiley.
- Albanese S, Cicchella D, De Vivo B, et al. (2011) Advancements in urban geochemical mapping of the Naples metropolitan area: Colour composite maps and results from an urban brownfield site. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 24, pp. 410–422. Chichester: Wiley.
- Alexander J and Marriott SB (1999) Introduction. In: Marriott SB and Alexander J (eds.) *Floodplains: Interdisciplinary Approaches*, Special Publication No. 163, pp. 1–13. London: The Geological Society.
- Andersson M, Holt Y, and Eggen OA (2011) Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in urban surface soil in Norway. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 27, pp. 473–486. Chichester: Wiley.
- Armour-Brown A and Nichol I (1970) Regional geochemical reconnaissance and the location of metallogenic provinces. *Economic Geology* 65(3): 312–330.
- ASTM (2005) *Method D 5438–05: Practice for Collection of Floor Dust for Chemical Analysis*, p. 8. Philadelphia, PA: American Society of Testing and Materials.
- ATSDR (1999) Toxicological profile for lead. Agency for Toxic Substances and Disease Registry. Atlanta, G.A.: U.S. Department of Health and Human Services, Public Health Service. Available online at http://www.atsdr.cdc.gov/toxprofiles/tp13. pdf – Last accessed on 19 November 2012.
- Batista MJ, Fernandes J, Ramalho E, et al. (2011) Geochemical characterisation of soil and sediments of the city of Beira, Mozambique: A preliminary approach. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 31, pp. 546–569. Chichester: Wiley.
- Beus AA and Grigorian SV (1977) Geochemical Exploration Methods for Mineral Deposits, p. 287. Wilmette, IL: Applied Publishing Ltd.
- BGS (1992) Regional Geochemistry of the Lake District and Adjacent Areas, p. 98. Keyworth, Nottingham: British Geological Survey.
- BGS (2000) Regional Geochemistry of Wales and West-central England: Stream Sediment and Soil. Keyworth, Nottingham: British Geological Survey.
- Birke M, Rauch U, and Chmieleski J (2011) Environmental geochemical survey of the city of Stassfurt: An old mining and industrial urban area in Sachsen-Anhalt, Germany. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 18, pp. 269–306. Chichester: Wiley.
- Birke M, Rauch U, and Stummeyer J (2011) Urban geochemistry of Berlin, Germany. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) Mapping the Chemical Environment of Urban Areas, pp. 245–268. Chichester: Wiley.
- Bityukova L and Birke M (2011) Urban geochemistry of Tallinn (Estonia): Major and trace-elements distribution in topsoil. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 20, pp. 348–363. Chichester: Wiley.
- Bølviken B, Bergström A, Björklund A, et al. (1986) Geochemical Atlas of Northern Fennoscandia. NORDKALLOTT Project, Nordic Collaboration Supported by the Nordic Council of Ministers, 19 pp. + 155 maps.
- Bølviken B, Bogen B, Demetriades A, et al. (1993) *Final Report of the Working Group on Regional Geochemical Mapping 1986–93*. Geochemical Mapping of Western Europe Towards the Year 2000. Forum of European Geological Surveys (FOREGS). NGU Report 93.092, 18 pp., 6 appendices. Trondheim: Geological Survey of Norway.
- Bølviken B, Bogen J, Demetriades A, et al. (1996) Regional geochemical mapping of Western Europe towards the year 2000. *Journal of Geochemical Exploration* 56(2): 141–166.
- Bølviken B, Demetriades A, Hindel R, et al. (eds.) (1990) *Geochemical Mapping of Western Europe Towards the Year 2000*. Project Proposal. Western European Geological Surveys (WEGS). NGU Report 90.106, 12 pages and 9 appendices. Trondheim: Geological Survey of Norway.
- Bølviken B and Sinding-Larsen R (1973) Total error and other criteria in the interpretation of stream-sediment data. In: Jones MJ (ed.) *Geochemical Exploration* 1972, pp. 285–295. London: Institution Mining & Metallurgy.

- Brandvold LA and McLemore VT (1998) A study of the analytical variation of sampling and analysis of stream-sediments from areas contaminated by mining and milling. *Journal of Geochemical Exploration* 64: 185–196.
- BSI (2005) Investigation of Potentially Contaminated Sites Code of Practice, p. 83 British Standard Institute, BS 10175:2001.
- Butt CRM and Zeegers H (1992) Regolith exploration geochemistry in tropical and subtropical terrains. In: Govett GJS (ed.) *Handbook of Exploration Geochemistry*, vol. 4, p. 607. Amsterdam: Elsevier Scientific Publishing Co.
- Darnley AG, Björklund A, Bølviken B, et al. (1995) A global geochemical database for environmental and resource management. *Final Report of IGCP Project 259. Earth Sciences, 19,* 122 pp. Paris: UNESCO Publishing. Available online at http://www. globalgeochemicalbaselines.eu/files/Blue\_Book\_GGD\_IGCP259.pdf – Last accessed on 19 November 2012.
- De Vivo B, Cicchella D, Lima A, and Albanese S (2005) Geochemical Environmental Atlas of the Urban and Provincial Soils of Napoli, p. 313. Università degli Studi di Napoli 'Federico II', Napoli: Dipartimeto di Geofisica e Vulcanologia.
- De Vivo B, Lima A, Albanese S, and Cicchella D (2003) *Geochemical Environmental Atlas of Campania Region*, p. 214. Università degli Studi di Napoli 'Federico II', Napoli: Dipartimeto di Geofisica e Vulcanologia.
- De Vos W, Ebbing J, Hindel R, Schalich R, Swennen R, and Van Keer I (1996) Geochemical mapping based on overbank sediments in the heavily industrialised border area of Belgium, Germany and the Netherlands. *Journal of Geochemical Exploration* 56(2): 91–104.
- De Vos W and Tarvainen T (Chief Editors), Salminen R, Reeder S, De Vivo B, et al. (2006) Geochemical Atlas of Europe. Part 2 – Interpretation of Geochemical Maps, Additional Tables, Figures, Maps and Related Publications. 692 pp. Espoo, Finland: Geological Survey of Finland. Available online at http://weppi.gtk.fi/publ/ foregsatlas/ – Last accessed on 19 November 2012.
- Demetriades A (2011a) Understanding the quality of chemical data from the urban environment – Part 2: Measurement uncertainty in the decision-making process. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, pp. 77–98. Chichester: Wiley.
- Demetriades A (2011b) The Lavrion urban geochemistry study, Hellas. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 25, pp. 424–456. Chichester: Wiley.
- Demetriades A, Bølviken B, Bogen J, et al. (1994) The recording of environmental contamination by overbank sediment. In: Varnavas SP (ed.) Environmental Contamination, 6th International Conference, Delphi, Greece, pp. 340–342. Edinburgh: CEP Consultants Ltd.
- Demetriades A, Bølviken B, Hindel R, Ottesen RT, Salminen R, and Schermann O (1993) The geochemical implications of environmental pollution. 1st International Exhibition and Conference on Environmental Technology, *HELECO'93*, vol. 1, pp. 467–479. Athens: Technical Chamber of Greece.
- Demetriades A and Karamanos E (2003) Quality assurance and quality control (QA/QC) for in-situ geochemical methods, estimation of measurement uncertainty and construction of probability risk assessment maps. *Network Oriented Risk-assessment by In-situ Screening of Contaminated sites (NORISC)*, p. 20. European Commission co-financed Project, EVK4-CT-2000-00026. NORISC Consortium Report, Cologne.
- Demetriades A, Ottesen RT, Locutura J (ed.) (1990) Geochemical mapping of Western Europe towards the Year 2000. *Pilot Project Report*. Western European Geological Surveys. Open File Report 90.105, 9 pages and 10 appendices. Trondheim: Geological Survey of Norway.
- Duong TTT and Lee B-K (2011) Determining contamination level of heavy metals in road dust from busy traffic areas with different characteristics. *Journal of Environmental Management* 92(3): 554–562.
- Ďuriš M (2011) Geochemical and ecological survey of the Prague city area, Czech Republic. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 21, pp. 364–374. Chichester: Wiley.
- EuroGeoSurveys Geochemistry Working Group (2008) EuroGeoSurveys geochemical mapping of agricultural and grazing land soil of Europe (GEMAS) – Field manual. *Open File Report 2008.038*, 46 pp. Trondheim: Geological Survey of Norway. Available online at http://www.ngu.no/upload/Publikasjoner/Rapporter/2008/2008\_ 038.pdf – Last accessed on 19 November 2012.
- Farago ME, Kavanagh P, Blanks R, et al. (1998) Platinum concentrations in urban road dust and soil, and in blood and urine in the United Kingdom. *Analyst* 123: 451–454.
- Fauth H, Hindel R, Siewers U, and Zinner J (1985) *Geochemischer Atlas Bundesrepublik Deutschland*, p. 79. Hannover: Bundesanstalt für Geowissenschaften und Rohstoffe.
- Ferguson C, Darmendrail D, and Freier K, et al. (eds.) (1998) Risk Assessment for Contaminated Sites in Europe. Volume 1: Scientific Basis (CARACAS – Concerted Action on Risk Assessment for Contaminated Sites in the European Union), p. 165. Nottingham: LQM Press.

Ferguson C and Kasamas H (1999) Risk Assessment for Contaminated Sites in Europe. Volume 2: Policy Frameworks (CARACAS – Concerted Action on Risk Assessment for Contaminated Sites in the European Union), p. 223. Nottingham: LQM Press.

Fletcher WK (1981) Analytical methods in geochemical prospecting. In: Govett GJS (ed.) Handbook of Exploration Geochemistry, vol. 1, p. 255. Amsterdam: Elsevier.

Fletcher WK (1986) Analysis of soil samples. In: Fletcher WK, Hoffman SJ, Mehrtens MB, Sinclair AJ, and Thompson I (eds.) *Exploration Geochemistry: Design and Interpretation of Soil Surveys. Reviews in Economic Geology*, vol. 3, ch. 4, pp. 79–96. Texas: Society of Economic Geologists.

- Fletcher WK, Hoffman SJ, Mehrtens MB, Sinclair AJ, and Thompson I (1986) Exploration geochemistry: Design and interpretation of soil surveys. In: Robertson JM (ed.) *Reviews in Economic Geology*, vol. 3, p. 180. Chelsea, MI: Society of Economic Geologists.
- Flight DMA and Scheib A (2011) Soil geochemical baselines in UK urban centres: The G-BASE project. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 13, pp. 186–206. Chichester: Wiley.
- Fordyce FM, Brown SE, Ander EL, et al. (2005) GSUE: Urban geochemical mapping in Great Britain. *Geochemistry: Exploration, Environment, Analysis* 5: 325–336.
- Garrett RG (1969) The determination of sampling and analytical errors in exploration geochemistry. *Economic Geology* 64: 568–574.
- Garrett RG (1973) The determination of sampling and analytical errors in exploration geochemistry – A reply. *Economic Geology* 68: 282–283.

Garrett RG (1983) Sampling methodology. Howarth RJ (ed.) Statistics and Data Analysis in Geochemical Prospecting. In: Govett GJS (ed.) Handbook of Exploration Geochemistry, vol. 2, ch. 4, pp. 83–110. Amsterdam: Elsevier.

Garrett RG and Goss TI (1978) The statistical appraisal of survey effectiveness in regional geochemical surveys for Canada's uranium reconnaissance program. *Mathematical Geology* 12: 443–458.

- Garrett RG, Kane VG, and Zeigler RK (1980) The management and analysis of regional geochemical data. *Journal of Geochemical Exploration* 13: 115–152.
- Garrett RG and Nichol I (1967) Regional geochemical reconnaissance in eastern Sierra Leone. Transactions of the Institution of Mining and Metallurgy 76: B97–B112.

Gómeza B, Palacios MA, Gómeza M, et al. (2002) Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities. *The Science of the Total Environment* 299(1–3): 1–19.

- Gosar M and Šajn R (2003) Geochemical soil and attic dust survey in Idrija, Slovenia. Journal de Physique 107: 561–564.
- Gosar M, Šajn R, and Biester H (2006) Binding of mercury in soils and attic dust in the Idrija mercury mine area (Slovenia). *The Science of the Total Environment* 369: 150–162.

Govett GJS (1983) Rock geochemistry in mineral exploration. In: Govett GJS (ed.) Handbook of Exploration Geochemistry, vol. 3, p. 461. Amsterdam: Elsevier Scientific Publishing Co.

Govett GJS and Nichol I (1979) Lithogeochemistry in mineral exploration. In: Hood PJ (ed.) Geophysics and Geochemistry in the Search for Metallic Ores. Economic Geology Report 31, pp. 339–362. Geological Survey of Canada.

Gregorauskienė V, Taraškevičius R, Kadūnas V, Radzevičius A, and Zinkutė R (2011) Geochemical characteristics of Lithuanian urban areas. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 23, pp. 393–409. Chichester: Wiley.

Guney M, Onay TT, and Copty NK (2009) Impact of overland traffic on heavy metal levels in highway dust and soils of Istanbul, Turkey. *Environmental Monitoring and Assessment* 164(1–4): 101–110.

- Gunn AG, Styles MT, Stephenson D, Shaw MH and Rollin KE (1990) Platinum-group elements in ultramafic rocks of the Upper Deveron Valley, near Huntly, Aberdeenshire. *MRP Report 115*, 70 pp. Keyworth, Nottingham: British Geological Survey.
- Halamić J and Miko S (2009) *Geochemical Atlas of the Republic of Croatia*, p. 87. Zagreb: Croatian Geological Survey.

Hale M and Plant JA (eds.) (1994) Drainage Geochemistry. In Govett GJS (ed.) Handbook of Exploration Geochemistry, vol. 6, p. 766. Amsterdam: Elsevier.

- Hawkes HE and Webb JS (1962) *Geochemistry in Mineral Exploration*, p. 415. New York: Harper & Row.
- Hensley AR, Scott A, Rosenfeld PE, and Clark JJJ (2007) Attic dust and human blood samples collected near a former wood treatment facility. *Environmental Research* 105(2): 194–199.
- Hindel R, Schalich J, De Vos W, Ebbing J, Swennen R, and Van Keer I (1996) Vertical distribution of elements in overbank sediment profiles from Belgium, Germany and The Netherlands. *Journal of Geochemical Exploration* 56(2): 105–122.

Hoffman SJ (1986) Soil sampling. In: Fletcher WK, Hoffman SJ, Mehrtens MB, Sinclair AJ, and Thomson I (eds.) *Exploration Geochemistry: Design and*  Interpretation of Soil Surveys. Reviews in Economic Geology, vol. 3, pp. 39–77. University of Texas, El Paso, TX: Society of Economic Geologists.

- Howarth RJ and Lowestein PL (1971) Sampling variability of stream sediments in broad-scale regional geochemical reconnaissance. *Transactions of the Institution of Mining and Metallurgy* 80: B363–B372.
- Howarth RJ and Thompson M (1976) Duplicate analysis in geochemical practice, Part II. Analyst 101: 699–709.
- IGS (19<sup>7</sup>8) *Regional Geochemical Atlas: Shetland*. London: Institute of Geological Sciences. Jacobs DE, Clickner RP, Zhou JY, et al. (2002) The prevalence of lead-based paint
- hazards in U.S. housing. *Environmental Health Perspectives* 110: A599–A606. Jensen HKB, Eggen OA, Frøland SL, and Skårn JS (2011) Polycyclic aromatic hydrocarbons in urban surface-soil in Oslo, Bergen and Trondheim, Norway: PAH16 levels, compositions and ratios. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 26, pp. 457–472. Chichester: Wiley.
- Johnson CC (2005) 2005 G-Base field procedures manual. British Geological Survey, Internal Report IR/05/097, 130 pp. Available online at http://nora.nerc.ac.uk/5190/ 1/2005proceduresmanual.pdf – Last accessed on 19 November 2012.

Johnson CC (2011) Understanding the quality of chemical data from the urban environment – Part 1: Quality control procedures. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, pp. 61–76. Chichester: Wiley.

Johnson CC and Demetriades A (2011) Urban geochemical mapping: A review of case studies in this volume. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) Mapping the chemical environment of urban areas, pp. 7–27. Chichester: Wiley.

Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) (2011) *Mapping the Chemical Environment of Urban Areas*, p. 616. Chichester: Wiley.

Kadıoğlua YK, Üstündağ Z, Solak AO, and Gülseren Karabıyıkoğlu G (2010) Sources of environmental pollution in Ankara (Turkey): Geochemistry and traffic effects— PEDXRF applications. Spectroscopy Letters 43(3): 247–257.

Kadūnas V, Budavičius R, Gregorauskiene V, et al. (1999) Geochemical Atlas of Lithuania, p. 162. Vilnius: Geological Survey of Lithuania.

Kauranne LK, Salminen R, and Eriksson K (1992) Regolith exploration geochemistry in arctic and temperate terrains. In: Govett GJS (ed.) *Handbook of Exploration Geochemistry*, vol. 5, p. 443. Amsterdam: Elsevier.

Koljonen T (ed.) (1992) *The Geochemical Atlas of Finland, p. 218. Part 2: Till.* Espoo: Geological Survey of Finland.

Kuhnt G and Muntau H (eds.) (1994) EURO – Soils: Identification, Collection, Treatment, Characterisation, p. 154 Joint Research Centre, ISPRA: Environment Institute, European Commission Special Publication No. 1.94.60.

Lahermo P, Ilmasti M, Juntunen R, and Taka M (1990) The Geochemical Atlas of Finland, Part 1: The Hydrogeochemical Mapping of Finnish Groundwater, p. 66. Espoo: Geological Survey of Finland.

Lahermo P, Väänänen P, Tarvainen T, and Salminen R (1996) Geochemical Atlas of Finland. Part 3: Environmental Geochemistry – Stream Waters and Sediments, p. 149. Espoo: Geological Survey of Finland.

Lanphear BP, Hornung R, Ho M, Howard CR, Eberle S, and Knauf K (2002) Environmental lead exposure during early childhood. *Journal of Pediatrics* 140: 40–47.

Lanphear BP, Matte TD, Rogers J, et al. (1998) The contribution of lead-contaminated house dust and residential soil to children's blood lead levels. *Environmental Research* 79: 51–68.

Lax K and Andersson M (2011) Geochemical baseline levels and suggested local guideline values in urban areas in Sweden. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 14, pp. 207–222. Chichester: Wiley.

Laxen DP, Lidsay F, Raab GM, Hunter R, Fell GS, and Fulton M (1987) The variability of lead in dusts within the homes of young children. In: Thornton I and Culbard E (eds.) Lead in the Home Environment, pp. 127–139. Northwood: Science Reviews.

Levinson AA (1974) *Introduction to Exploration Geochemistry*, p. 614. Wilmette, IL: Applied Publishing.

Levinson AA (1980) Introduction to Exploration Geochemistry, 2nd edn., pp. 615–924, Wilmette, IL: Applied Publishing The 1980 Supplement.

Li X (2011) Geochemical mapping of trace metal pollutants in urban soils of Hong Kong. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) Mapping the Chemical Environment of Urban Areas, ch. 33, pp. 581–591. Chichester: Wiley.

- Lis J and Pasieczna A (1995) *Geochemical Atlas of Poland*, p. 36. Warsaw: Polish Geological Institute 7 tables, 76 maps.
- Lis J, Pasieczna A, Bojakowska I, et al. (1999) *Geochemical Atlas of Legnica-Głogów Copper District*. Warsaw: Polish Geological Institute, 31 pp. + 46 maps.
- Locutura J and Bel-lan A (2011) Systematic urban geochemistry of Madrid, Spain, based on soils and dust. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 19, pp. 307–347. Chichester: Wiley.

- Locutura J, Bel-lan A, García CA, Martínez S (2012). Atlas Geoquímico de España. 592 pp. (A3 size). Madrid: Instituto Geológico y Minero de España. Available on line at http://www.igme.es/INTERNET/actividadesIGME/lineas/CartoGeo/geoquimica/ geoquimicalng.htm#resu – Last accessed on 19 November 2012.
- Lyn JA, Ramsey MH, Coad DS, Damant AP, Wood R, and Boon KA (2007) The duplicate method of uncertainty estimation: Are eight targets enough? *Analyst* 132(11): 1147–1152.
- Maassen LW and Bolivar SL (1987) A geochemical survey of St. Lucia, West Indies. Journal of Geochemical Exploration 28(3): 451–466.
- Manton WI, Angle CR, Stanek KL, Reese YR, and Kuehnemann TJ (2000) Acquisition and retention of lead by young children. *Environmental Research* 82: 60–80.
- Mathur R, Balaram V, Satyanarayanan M, Sawant SS, and Ramesh SL (2010) Anthropogenic platinum, palladium and rhodium concentrations in road dusts from Hyderabad city, India. *Environmental Earth Sciences* 62(5): 1085–1098.
- McClenaghan MB, Bobrowsky PT, Hall. GEM, and Cook SJ (eds.) (2001) Drift Exploration in Glaciated Terrain, Special Publication 185, p. 350. London: The Geological Society.
- Miesch AT (1964) Effects of sampling and analytical error in geochemical prospecting. In: Parks GA (ed.) Computers in the Mineral Industry, Part 1. Stanford University Publications in Geological Sciences 9(1): 156–170.
- Miesch AT (1967) Theory of Error in Geochemical Data, p. 17. U.S. Geological Survey Professional Paper, 574-A.
- Miesch AT (1973) The determination of sampling and analytical errors in exploration geochemistry A reply. *Economic Geology* 68: 281–282.
- Miesch AT (1976) Geochemical Survey of Missouri: Methods of Sampling, Laboratory Analysis and Statistical Reduction of Data, p. 39. U.S. Geological Survey Professional Paper 954-A.
- Open University (1972) Geochemistry. In: *Second Level Course, S2-2, Units 1–3*. Bletchley, Bucks: The Open University Press.
- Ottesen RT, Alexander J, Langedal M, and Mikarlsen G (2011) Clean soil at child-care centres and public playgrounds – An important part of Norway's chemical policy. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 29, pp. 497–520. Chichester: Wiley.
- Ottesen RT, Bogen J, Bølviken B, and Volden T (1989) Overbank sediment: A representative sample medium for regional geochemical mapping. In: Jenness SE (ed.) Geochemical Exploration 1987. *Journal of Geochemical Exploration* 32(1–3): 257–277.
- Ottesen RT, Bogen J, Bølviken B, Volden T, and Haugland T (2000) Geochemical Atlas of Norway, Part 1: Chemical Composition of Overbank Sediments, p. 140 Trondheim: NGU.
- Ottesen RT, Bogen J, Finne TE, et al. (2010) Geochemical Atlas of Norway. Part 2: Geochemical Atlas of Spitsbergen – Chemical Composition of Overbank Sediments, p. 160. Trondheim: Geological Survey of Norway.
- Pasieczna A (2003) Atlas of Urban Soils Contamination in Poland. Warsaw: Polish Geological Institute, 83 pp. + 105 maps.
- Plant JA (1973) A random numbering system for geochemical samples. Transactions of the Institution of Mining and Metallurgy 82: B64–B65.
- Plant JA, Jeffery K, Gill E, and Fage C (1975) The systematic determination of accuracy and precision in geochemical exploration data. *Journal of Geochemical Exploration* 4: 467–486.
- Plant J and Slater D (1986) Regional geochemistry Potential developments. Transactions of the Institution of Mining and Metallurgy 95: B63–B70.
- Ramsey MH (1997) Measurement uncertainty arising from sampling. Implications for the objectives of geoanalysis. *Analyst* 122: 1255–1260.
- Ramsey MH (1998) Sampling as a source of measurement uncertainty: Techniques for quantification and comparison with analytical sources. *Journal Analytical Atomic Spectrometry* 13: 97–104. Article and software ROBCOOP4.EXE available online at http://pubs.rsc.org/en/Content/ArticleLanding/1998/JA/a706815h - Last accessed 19 November 2012.
- Ramsey MH (2009) Uncertainty in the assessment of hazard, exposure and risk. *Environmental Geochemistry and Health* 31(2): 205–217.
- Ramsey MH and Argyraki A (1997) Estimation of measurement uncertainty from field sampling: Implications for the classification of contaminated land. *The Science of* the Total Environment 198: 243–257.
- Ramsey MH, Taylor PD, and Jong-Chun L (2002) Optimized contaminated land investigation at minimum overall cost to achieve fitness-for-purpose. *Journal of Environmental Monitoring* 4: 809–814.
- Reimann C (1989) Reliability of geochemical analyses: Recent experiences. *Transactions of the Institution of Mining and Metallurgy* 98: B123–B130. Reimann C (2005) Sub-continental scale geochemical mapping: Sampling, quality
- control and data analysis issues. *Geochemistry, Exploration, Environment, Analysis* 5: 311–323.

- Reimann C, Äyräs M, Chekushin V, et al. (1998) Environmental Geochemical Atlas of the Central Barents Region, p. 745. Trondheim: Geological Survey of Norway.
- Reimann C, Demetriades A, Birke M, Eggen OA, Filzmoser P, Kriete C, and the 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<sup>®</sup>-extraction analysis and results of the GEMAS ring test for the standards Ap and Gr. Report No. 2012.051, 138 pp. Trondheim: Geological Survey of Norway. Available online at http://www.ngu.no/upload/Publikasjoner/Rapporter/ 2012/2012 051.0df – Last accessed on 19 November 2011.
- Reimann C, Demetriades A, Eggen OA, 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. Open File Report 2009.049, 92 pp. Trondheim: Geological Survey of Norway. Available online at http://www.ngu.no/upload/Publikasjoner/Rapporter/2009/ 2009\_049.pdf - Last accessed on 19 November 2012.
- Reimann C, Demetriades A, Eggen OA, Filzmoser P, and the EuroGeoSurveys Geochemistry Expert Group (2011) *The EuroGeoSurveys GEochemical Mapping of Agricultural and grazing land Soils project (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.* Open File Report 2011.043, 90 pp. Trondheim: Geological Survey of Norway. Available online at http://www. ngu.no/upload/Publikasjoner/Rapporter/2011/2011\_043.pdf – Last accessed on 19 November 2012.
- Reimann C, Filzmoser P, Garret RG, and Dutter R (2008) *Statistical Data Analysis Explained: Applied Environmental Statistics with R*, p. 343. Chichester: Wiley.
- Reimann C, Siewers U, Tarvainen T, et al. (2003) Agricultural Soils in Northern Europe: A Geochemical Atlas, p. 279. Stuttgart: E. Schweizerbart'sche Verlagsbuchhandlung.
- Reimann C and Wurzer F (1986) Monitoring accuracy and precision improvements by introducing robust and resistant statistics. *Mikrochimica Acta*, II 89(1–6): 31–42.
- Ridgway J, Appleton JD, and Greally KB (1991) Variations in regional geochemical patterns – Effects of site-selection and data-processing algorithms. *Transactions of the Institution of Mining and Metallurgy* 100: B122–B129.
- Roberts JW and Dickey P (1995) Exposure of children to pollutants in house dust and indoor air. *Reviews of Environmental Contamination and Toxicology* 143: 59–78.
- Robertson DJ and Taylor KG (2007) Temporal variability of metal contamination in urban road-deposited sediment in Manchester, UK: Implications for urban pollution monitoring. *Water, Air, and Soil Pollution* 186: 209–220.
- Rose AW, Hawkes HE, and Webb JS (1979) *Geochemistry in Mineral Exploration*, 2nd edn., p. 657. London: Academic Press.
- Šajn R (2003) Distribution of chemical elements in attic dust and soil as reflection of lithology and anthropogenic influence in Slovenia. In: Boutron C and Ferrari C (eds.) 12th International Conference on Heavy Metals in the Environment, 26–30 May, Grenoble, FranceJournal de Physique 107: 1173–1176.
- Šajn R (2005) Using attic dust and soil for the separation of anthropogenic and geogenic elemental distributions in an old metallurgic area (Celje, Slovenia). *Geochemistry: Exploration, Environment, Analysis* 5(1): 59–67.
- Šajn R (2006) Factor Analysis of Soil and Attic-dust to Separate Mining and Metallurgy Influence, Meza Valley, Slovenia. *Mathematical Geology* 38(6): 735–747.
- Šajn R, Bidovec M, Andjelov M, Pirc S, and Gosar M (1998) *Geochemical Atlas of Ljubljana and Environs*. Ljubljana: Inštitut za geologijo, geotehniko in geofiziko, 34 pp. + 37 maps.
- Šajn R, Gosar M, Bidovec M, Pirc S, and Alijagić J (2011) Geochemical mapping of Ljubljana urban and suburban area, Slovenia. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 22, pp. 375–392. Chichester: Wiley.
- Salminen R, Chekushin V, Tenhola M, et al. (2004) *Geochemical Atlas of the Eastern Barents Region*, p. 548. Amsterdam: Elsevier.
- Salminen R, Tarvainen T, Demetriades A, et al. (1998) FOREGS Geochemical Mapping Field Manual. Guide 47, 36 pp, 1 appendix. Espoo: Geological Survey of Finland. Available online at http://arkisto.gtk.fi/op/op47/op47.pdf – Last accessed on 19 November 2012.
- Salminen R. (Chief Editor), Batista MJ, Bidovec M, Demetriades A, et al. (2005) FOREGS Geochemical Atlas of Europe, Part 1: Background Information, Methodology and Maps. 526 pp. Espoo: Geological Survey of Finland. Available online at http://weppi. gtk.fi/publ/foregsatlas/ – Last accessed on 19 November 2012.
- Salminen R, Batista MJ, Demetriades A, Lis J, Tarvainen T (2005) Sampling. In: Salminen R. (Chief-Editor), Batista MJ, Bidovec M, Demetriades A (eds.) FOREGS Geochemical Atlas of Europe, Part 1: Background Information, Methodology and Maps, pp. 67–79. Espoo: Geological Survey of Finland. Available online at http://weppi.gtk.fi/publ/foregsatlas/- Last accessed on 19 November 2012.
- Schermann O (1990) Quality control. In: Bølviken B, Demetriades A, Hindel R, et al. (eds.) Geochemical Mapping of Western Europe towards the Year 2000. Project

Proposal. Open File Report 90–106, appendix 4, 6 pp. Trondheim: Geological Survey of Norway.

Siegel FR (1974) Applied Geochemistry, p. 353. New York: Wiley.

- Singh AK (2011) Elemental chemistry and geochemical partitioning of heavy metals in road dust from Dhanbad and Bokaro regions, India. *Environmental Earth Sciences* 62: 1447–1459.
- Słowańska B (ed.) (1997) Geology for environmental protection and planning in the Polish–Lithuanian cross-border area. Lithuanian Institute of Geology, p. 89. Warsaw: Polish Geological Institute, Geological Survey of Lithuania.
- Smith AY, Armour-Brown A, Olsen H, Lundberg B, and Niesen PL (1976) The role of geochemical prospecting in phased uranium exploration. A case history. In: IAEA (ed.) *Exploration for Uranium Deposits*, IAEA-SM-208/51, pp. 575–599. Vienna: International Atomic Energy Agency.
- Smith DB, Garrett RG, Closs LG, et al. (2011) Geochemical Mapping of the Denver, Colorado (USA) urban area: A Comparison of studies in 1972 and 2005.
  In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) Mapping the Chemical Environment of Urban Areas, ch. 30, pp. 521–546. Chichester: Wiley.
- Stanley CR (2003) Statistical evaluation of anomaly recognition performance. Geochemistry: Exploration, Environment, Analysis 3: 3–12.
- Sterling DA, Johnson DL, Murgueytio AM, and Evans G (1998) Source contribution of lead in house dust from a lead mining waste superfund site. *Journal of Exposure Analysis and Environmental Epidemiology* 8(3): 359–373.
- Strahler AN (1964) Quantitative geomorphology of drainage basins and channel networks. In: Chow VT (ed.) Handbook of Applied Hydrology: A Compendium of Water-Resources Technology, pp. 39–76. New York: McGraw-Hill Book Co, Section 4.
- Succop P, Bornschein R, Brown K, and Tseng C (1998) An empirical comparisons of lead exposure pathway models. *Environmental Health Perspectives* 106(S6): 1577–1583.
- Tarvainen T and Jarva J (2011) Using geochemical baselines in the assessment of soil contamination in Finland. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 15, pp. 222–231. Chichester: Wiley.
- Taylor PD and Ramsey MH (2006) Sampling strategies for contaminated brownfield sites. Soil Use and Management 21(Supplement s2): 440–449.
- Thompson M (1983) Control procedures in geochemical analysis. Howarth RJ (ed.) Statistics and Data Analysis in Geochemical Prospecting. In: Govett GJS (ed.) Handbook of Exploration Geochemistry, vol. 2, pp. 39–58. Amsterdam: Elsevier Scientific Publications.

- Thompson M and Howarth RJ (1976) Duplicate analysis in geochemical practice. Part 1. Theoretical approach and estimation of analytical reproducibility. *Analyst* 101: 690–698.
- Thompson M and Howarth RJ (1978) A new approach to the estimation of analytical precision. *Journal of Geochemical Exploration* 9: 23–30.
- Thompson M and Howarth RJ (1980) The frequency distribution of analytical error. *Analyst* 105: 1188–1195.
- Thompson M and Maguire M (1993) Estimating and using sampling precision in surveys of trace constituents of soils. *Analyst* 118: 1107–1110.
- Thomson I (1986) Getting it right. Fletcher WK, Hoffman SJ, Mehrtens MB, Sinclair AJ, and Thomson I (eds.) *Exploration Geochemistry: Design and Interpretation of Soil Surveys*. In: Robertson JM (ed.) *Reviews in Economic Geology*, vol. 3, pp. 1–18. Chelsea, MI: Society of Economic Geologists.
- USEPA (1986) Guidelines for carcinogen risk assessment guidelines. Risk Assessment Forum, 38 pp. Washington, DC: U.S. Environmental Protection Agency, EPA/630/ R-00/004/.
- USEPA (2003) Mercury Preservation Techniques, 2 pp. Las Vegas, NV: US Environmental Protection Agency. Available online at http://www.epa.gov/esd/ factsheets/mpt.pdf – Last accessed on 6th July 2011.
- USEPA (2008) Guidance for the Sampling and Analysis of Lead in Indoor Residential Dust for Use in the Integrated Exposure Uptake Biokinetic (IEUBK) Model, OSWER 9285.7-81, 23 pp. Las Vegas, N.V.: US Environmental Protection Agency. Available online at http://www.epa.gov/superfund/lead/products/dust\_sampling\_guidance\_ final.pdf – Last accessed 6 July 2011.
- Varrica D, Dongarrà G, Sabatino G, and Monna F (2004) Inorganic geochemistry of roadway dust from the metropolitan area of Palermo, Italy. *Environmental Geology* 44(2): 222–230.
- Vidojević D and Aleksandra Gulan A (2011) Soil Contamination in the urban area of Belgrade, Serbia. In: Johnson CC, Demetriades A, Locutura J, and Ottesen RT (eds.) *Mapping the Chemical Environment of Urban Areas*, ch. 28, pp. 487–496. Chichester: Wiley.
- Webb JS, Thornton Í, Thompson M, Howarth RJ, and Lowenstein PL (1978) The Wolfson Geochemical Atlas of England and Wales, p. 69. Imperial College of Science and Technology. Applied Geochemistry Research Group Oxford: Clarendon Press.
- Whiteley JD (2005) Seasonal variability of platinum, palladium and rhodium (PGE) levels in road dusts and roadside soils, Perth, Western Australia. *Water, Air, and Soil Pollution* 160(1–4): 77–93.