

Applied geochemistry—The how and why

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Abstract

The objectives of this chapter are to answer questions of how applied geochemical methods are planned and used for mineral exploration and environmental purposes by using material from actual examples. In the Supplementary material, most of the analytical results are provided for hands-on exercises for use by teachers and students alike. It starts by defining key geochemical terms, followed by the components of every applied geochemical survey that should be implemented for its successful completion. Emphasis is placed on the orientation survey, which is an important phase in any applied geochemical mapping study. It is followed by examples from reconnaissance stream sediment, follow-up and detailed geochemical surveys, contaminated land investigation, and ending with guidelines for the organization and execution of multi-purpose multinational continental-scale geochemical mapping. The question of how the quality of generated applied geochemical datasets is assured is answered, followed by data management, statistical, geostatistical, and compositional data analysis processing, 2D and 3D geochemical map plotting. Finally, useful guidelines for the organization and successful implementation of an applied geochemical mapping project at any scale and purpose are given.

Keywords

Compositional data analysis; Contaminated land investigation; Continental-scale geochemical mapping; Database management; Definitions of terms; Desk study; Detailed geochemical survey; Follow-up geochemical survey; Geostatistics; Map plotting; Orientation geochemical survey; Overbank sediment; Quality control; Randomization of samples; Reference materials; Rock; Sample preparation; Sample storage; Sampling; Soil; Statistical processing; Stream sediment

Key points

- Guidelines for the organization and successful implementation of an applied geochemical mapping project for mineral exploration and environmental purposes.
- Key geochemical terms defined.
- Emphasis is placed on the orientation geochemical survey with a case study example.
- Reconnaissance stream sediment geochemical survey.
- Follow-up stream sediment geochemical survey.
- Detailed soil geochemical survey.
- Contaminated land investigation.
- Multi-purpose continental-scale geochemical mapping.
- Instructions of how to assess the quality of generated applied geochemical datasets.
- Management of geochemical data.
- Geochemical results from actual geochemical surveys are provided in the Supplementary material for hands-on exercises.

Introduction

The format of this chapter will be questions and answers about 'Applied Geochemistry'. So, let us start with the first question:

How do we define 'Applied Geochemistry'? According to Kersten and Harmon (2021, p. 323) "Applied geochemistry is the area of the earth sciences that addresses the practical application of chemistry to any aspect of human endeavor. . . . Typical areas of application include the search for economic and energy resources, waste disposal, the effect of the environment on human health, and preservation of the environment". Of course, to reach such an all-embracing definition of applied geochemistry, it is important to recognize that there was considerable basic research from the 1920s onwards (Goldschmidt, 1923) for establishing the principles and methodologies that can then be applied to address the issues that are important to human endeavors. Some examples of basic research important to applied geochemists are: dispersion of elements in the surficial environment; water-rock interaction; chemical evolution in crystallizing magmas; element transport during soil formation; development of multi-element analytical methods, and many others, some of which will be described in this Chapter.

What does the word 'geochemistry' itself mean? It is a composite word made up from two Hellenic words 'geo' (γῆ—gēa) meaning 'earth' and 'chemistry' (χημεία—chimía) meaning, of course, 'chemistry'.

What is, therefore, 'geochemistry'? In simple terms, 'geochemistry' is the science that studies the chemistry of the Earth as a whole. Goldschmidt (1954, p. 1), the father of geochemistry, defined it as "the scientific discipline that studies the distribution and amounts of chemical elements in minerals, ores, rocks, soil, water, and the atmosphere, and is concerned with the study of the circulation of elements in nature, on the basis of the properties of their atoms and ions. The science is not strictly limited to the study of chemical elements as ultimate units in the classification of matter, but also covers the abundance and distribution of the various isotopes or atomic species, including the problems of nuclear frequency and stability in the universe".

We defined 'applied geochemistry' and 'geochemistry'. *Is this satisfactory?* Unfortunately, not, as scientists like to complicate matters instead of simplifying them. Geochemical techniques or methods developed specifically for the location and delineation of mineralization are classified under the terms 'exploration geochemistry' or 'geochemical prospecting' (Hawkes, 1957; Hawkes and Webb, 1962; Siegel, 1974; Rose et al., 1979; Levinson, 1974, 1980; Levinson et al., 1987). Geochemical techniques used for the delineation of anthropogenic contamination and its effects on the environment are referred to as 'environmental geochemistry' (Bowie and Thornton, 1985; Siegel, 2002). When such studies include environmental effects on human health, the term 'medical geochemistry' is often used (Dissanayake and Chandrajith, 1999; Censi et al., 2013). The branches continue with 'biogeochemistry', which deals with the effects of life processes on the distribution and fixation of chemical elements in the biosphere (Schlesinger and Bernhardt, 2014); 'organic geochemistry' is concerned with naturally occurring carbonaceous and biologically derived substances of geological interest (Kvenvolden, 2006); 'isotope' or 'nuclear geochemistry' studies radioactive and stable isotopes and their abundances (White, 2014).

Since there is apparently some confusion with the terminology about the scientific discipline that we are concerned with, the 'Association of Applied Geochemists' (formerly Association of Exploration Geochemists—<http://appliedgeochemists.org>) concluded that the scientific discipline is 'Applied Geochemistry', and the applied geochemical methods or techniques can be used in both the search for mineralization and for environmental purposes, tackling both contamination and health related issues (Demetriades, 2001). Therefore, the all-embracing science is 'Applied Geochemistry' as defined by Kersten and Harmon (2021), and all the supposed branches or disciplines are essentially applications (Thornton, 1983; Thornton and Howarth, 1986). Unfortunately, the Association of Applied Geochemists cannot control the international geoscientific community in establishing new branches of applied geochemistry. So, different geochemistry communities are continuously inventing new branches, with no link to the all-embracing discipline of 'Applied Geochemistry'. This drive, instead of advancing the discipline of applied geochemistry, causes serious gaps in basic principles and techniques that have been developed and tested from the 1950s in the use of applied geochemistry in integrated mineral exploration programs (Fersman, 1952; Hawkes, 1957; Ginzburg, 1960; Hawkes and Webb, 1962; Ward et al., 1963; Bradshaw et al., 1972; Siegel, 1974; Beus and Grigorian, 1977; Garrett and Nichol, 1967; Levinson, 1974,

1980; Rose et al., 1979; Thomson, 1976, 1986; Fletcher, 1981; Govett, 1983; Howarth, 1983; Levinson et al., 1987; Van Loon and Barefoot, 1989; Butt and Zeegers, 1992; Kauranne et al., 1992; Hale and Plant, 1994; Hale, 2000; Cohen and Howell, 2014). This lost link is observed in 'environmental geochemistry' and 'medical geochemistry', where their advocates are trying to reinvent the wheel, regrettably wasting time, effort, and money. Therefore, the aim of this chapter is to show that the well-tested methods of applied geochemistry can be used not only in mineral exploration but also for environmental and medical purposes, and what differs is the interpretation of the data according to the objectives of the geochemical survey.

Demetriades et al. (2014, p. 1) stated that "every geochemical survey from the continental to the micrometer scale has eight independent, and yet interdependent, components". However, as pointed out by Christopher C. Johnson (personal communication 2020) a ninth component should be added, which concerns the 'storage of samples', because the secure and well-organized storage of samples is very important for future investigations. Therefore, the nine components of every applied geochemical survey are:

- (1) Planning
- (2) Sampling
- (3) Sample preparation
- (4) Storage of samples
- (5) Laboratory analysis
- (6) Quality control
- (7) Data processing and map plotting
- (8) Interpretation, and
- (9) Report writing.

It is stressed that failure to perform correctly and efficiently any one of the aforementioned steps will have a detrimental effect on the succeeding ones.

How are key applied geochemical terms defined?

It is necessary to define a few key terms that will be used in this chapter, such as geochemical background (or background), threshold, geochemical anomaly (or anomaly), contrast, halo, pathfinder, primary and secondary geochemical dispersion, geochemical baseline (or baseline), and a few others.

In the applied geochemical methods used in mineral exploration, the normal spatial variation of element concentrations in barren (non-mineralized) earth materials are referred to as "normal background values", and any local abnormal deviation from the norm is defined as "anomalous" (Hawkes and Webb, 1962). These are simplistic definitions and more appropriate ones are given below, and pictorially presented in Figs. 1–3.

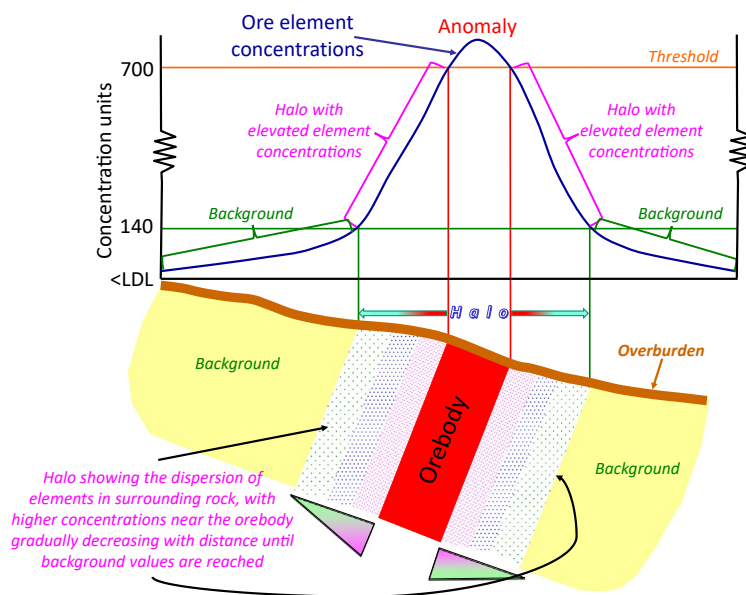


Fig. 1 Schematic representation of a cross-section across a vein deposit emplaced in a single type of host rock, e.g., a limestone, and covered by overburden (e.g., soil or till). The diagram shows the anomalous pattern over the orebody (>700 units), and the dispersion of elements in the surrounding host rock, the halo, which is indicated by elevated ore element concentrations gradually decreasing with distance from the orebody (700 to 140 units), until the unaffected rock is reached with background element concentrations (140 to <LDL units). Notation: LDL = lower detection limit of analytical method. Plotted with Microsoft® 365 PowerPoint.

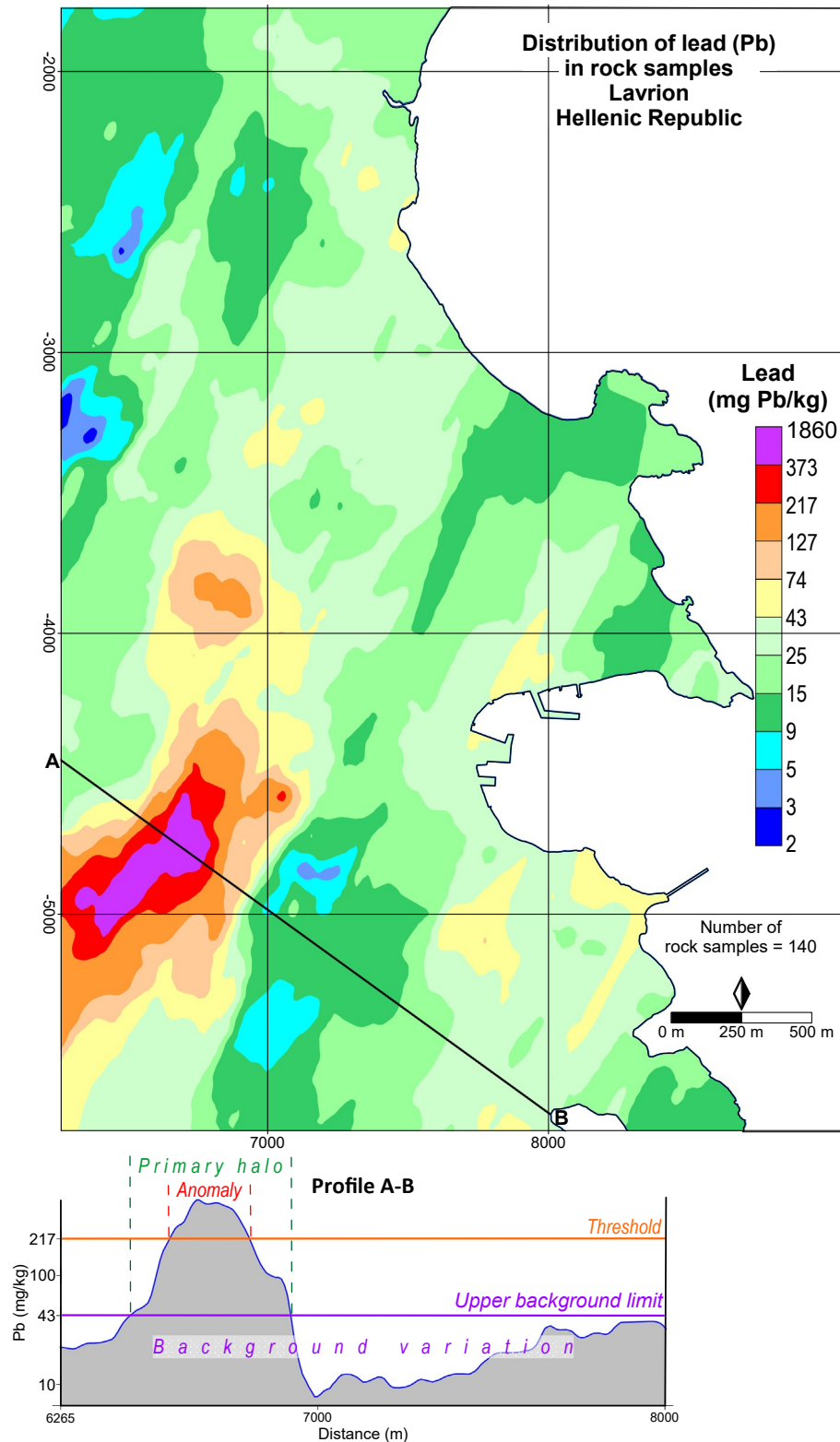


Fig. 2 Distribution of lead (Pb) in the <0.074 mm grain size of rock samples following a hot aqua regia extraction and determination by double-beam atomic absorption spectrometry (AAS) with a lower detection limit at 1 mg Pb/kg, Lavrion, Attiki Prefecture, Hellenic Republic (Demetriades, 2011a, Fig. 25.4, p. 435, modified). The color-surface geochemical map of Pb shows its primary dispersion in rocks. The profile displays the primary geochemical dispersion features caused by the polymetallic mineralization in the host rocks, namely anomalous concentrations of Pb (>217 mg/kg), the halo over and about the mineralization (>43 to 217 mg/kg), and the variable background concentrations (<43 mg/kg). The data were plotted with Golden Software's program Surfer™ v25.

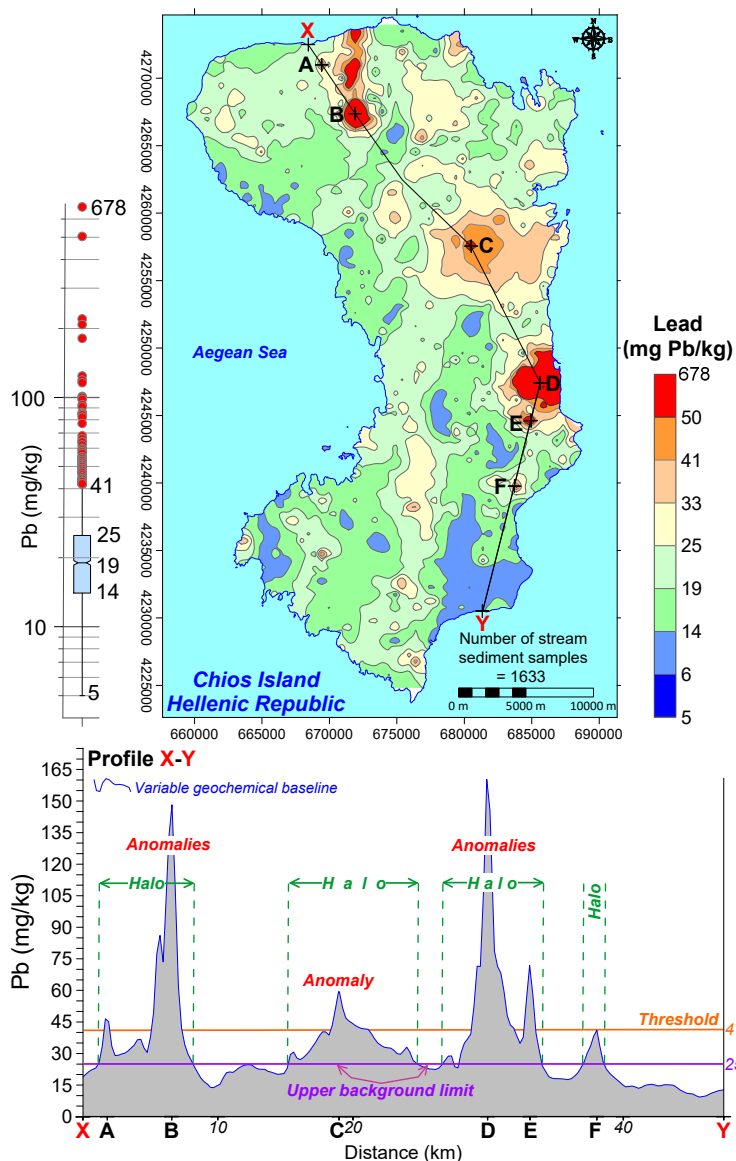


Fig. 3 Distribution of lead (Pb) in the <0.177 mm grain size of stream sediment following a hot aqua regia extraction and determination by double-beam atomic absorption spectrometry with a lower detection limit at 2 mg Pb/kg, Chios Island, Eastern Aegean Sea, Hellenic Republic (Kaminari and Labropoulos, 1989). The color-surface geochemical map of Pb shows the geochemical baseline of this area for the 1980s, the time of the sampling campaigns. The profile displays (i) the secondary geochemical dispersion features in stream sediment samples caused by the weathering and erosion of the polymetallic mineralization, namely anomalous concentrations of Pb (A, B, C, D, E), the haloes about the anomalies, and the background concentrations, and (ii) the variable geochemical baseline of Pb in stream sediment samples (blue color line). Anomaly F, although is below the threshold value, warrants further investigation. The notched-boxplot displays in the \log_{10} scale the statistical distribution of Pb concentrations. The upper background limit and threshold at 25 and 41 mg/kg Pb, respectively, were estimated by studying the spatial distribution, and the notched-boxplot. The map and notched-boxplot were plotted with Golden Software's program Surfer™ v25 and Grapher™ v21, respectively.

Geochemical background or *background*: The non-anomalous concentration range of an element or element combination in a particular sample type in a particular environment as measured on a particular grain size by a particular analytical technique. Background is a range, and not a single value.

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

Contrast: The ratio of the anomalous element concentration divided by the average geochemical background concentration.

Threshold: The limiting anomalous value of an element in a particular sample type in a particular environment as measured on a particular grain size by a particular analytical technique below which variations represent only normal background effects, and above which element concentrations are significant in terms of potential (i) mineralization, or (ii) environmental contamination.

Halo: A circular or crescentic spatial distribution pattern (in 2D plan view) with elevated element concentrations surrounding a mineral or ore deposit. Some halos are primary, formed either at the same time as the host rock or at the same time as associated mineral deposits, and some are secondary dispersion halos, either formed by surficial alteration of the associated mineral deposit or occur in the secondary environment such as soil, till, stream sediment, stream water, groundwater, or plants (Neuendorf and Mehl Jr, 2011, p. 291, slightly modified).

Pathfinder: In geochemical exploration, a relatively mobile element or gas that occurs in close association with an element or commodity being sought but can be more easily found because it forms a broader halo or can be detected more readily by analytical methods. A pathfinder serves to lead investigators to a deposit of a desired substance. Often called indicator element, but this latter term is restricted by some authors to elements that are important components of the ores being sought (Neuendorf and Mehl Jr, 2011, p. 475).

Primary geochemical dispersion or primary dispersion: The distribution of elements in rock that has arisen through ore-forming or rock-forming processes, regardless of whether the dispersion patterns are directly or indirectly associated with the ore-forming processes (Govett, 1983, p. 1).

Secondary geochemical dispersion or secondary dispersion: The distribution of elements in soil, sediments, and water caused by weathering, erosion or surface transportation by ice, frost, groundwater, animals, soil-forming processes, plant activity, and surface water (Hawkes, 1957, p. 225, slightly modified).

Geochemical baseline or baseline: The concentration at a specific point in time of a chemical parameter (element, species, or compound) in a sample of geological material, determined on a particular grain size by a particular analytical technique. It is a fluctuating surface (range of values) rather than a given value (Johnson and Demetriades, 2011a, Johnson and Demetriades, 2011b, p. 18, slightly modified).

Neoanomaly: This term was first used by Kovda (1974) to describe geochemical anomalies produced by human activities. It was subsequently introduced in the Western world by Davies (1980). It is a far better term than 'hotspot', which is used by other disciplines. See 'Hotspot'.

Hotspot: In contaminated land investigations, it is a spot with high hazardous element concentrations. Although this term is used extensively in applied geochemistry for environmental investigations, it should be avoided, because it is used by other scientific disciplines, especially in volcanology (Cloud Jr., 1974). See 'Neoanomaly'.

Routine sample: This is the sample collected according to the sampling plan of the applied geochemical survey.

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

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

Reference material: Reference materials are samples that have been collected, prepared, and analyzed according to documented procedures, and analyzed repeatedly, to give what become accepted 'true' values (Johnson, 2011; Lučivjanský and Mackových, 2022). Reference materials can be used to indicate the accuracy and precision of an analytical method and are particularly important for leveling results generated over a long period of time, often by different laboratories or analytical methods (Johnson et al., 2018; Johnson and Lister, 2022). There are two types of reference materials, primary and secondary, which are defined below.

Primary reference materials (PRMs): Primary reference materials are internationally certified standards with recognized and accepted elemental concentrations (Johnson, 2011; Lučivjanský and Mackových, 2022). The "true" element concentration values of PRMs are determined statistically on the basis of results from well-tested total analytical methods used by certified laboratories worldwide.

Secondary reference materials (SRMs): Secondary reference materials are generally in-house reference samples developed for internal use by projects and are kept 'blind' to the analyst (Johnson, 2011, p. 64; Lučivjanský and Mackových, 2022). They are cheaper than PRMs and are submitted at more frequent intervals in the analytical batch. They are for 'internal use' by the project and are referred to as 'external' reference materials because they are used by the applied geochemist to assess the quality of analytical results generated by the laboratory, and, most importantly, are kept 'blind' to the analyst. Laboratories usually have their own in-house secondary reference materials (Thompson et al., 2006; ISO, 2014; Gowing and de Hayr, 2020). The "accepted" element concentration values of SRMs are again statistically determined on the basis of results from the analytical methods used by the laboratories, which participate in the analysis of project samples.

In some of the above definitions the following qualification is made ". . . . in a sample of geological material, determined on a particular grain size by a particular analytical technique". The reason for this qualification is that if a different grain size of a particular sample type is analyzed by a different analytical technique the results will be different. Hence, the requirement when presenting geochemical results to state the sample type, the grain size used for analysis, and the analytical method.

How an applied geochemical survey is organized for mineral exploration purposes?

Mineral exploration for the location of economic mineralization typically follows a sequence of phases, or stages, and the applied geochemical survey is similarly designed. Fig. 4 shows the stages of a phased geochemical survey for mineral exploration.

It is important to recognize that each study area has its own characteristics with respect to geology, geomorphology, mineralization, and climate. Therefore, it is necessary to collect all available information, and after its evaluation to design the orientation survey for testing different sampling, sample preparation and analytical methods in order to decide on the optimum procedure to be followed in the succeeding geochemical survey phase or stage. Each phase is distinguished by the density of sampling and scale of maps used. Thus, the phases of applied geochemical surveys in mineral exploration are:

- *Desk study* involves the collection and evaluation of all available data and information, which are necessary for the cost-efficient planning of the phased geochemical survey.
- *1st Orientation survey* tests stream sediment sampling, sample preparation and analytical techniques for the successful execution of the reconnaissance and follow-up phases.

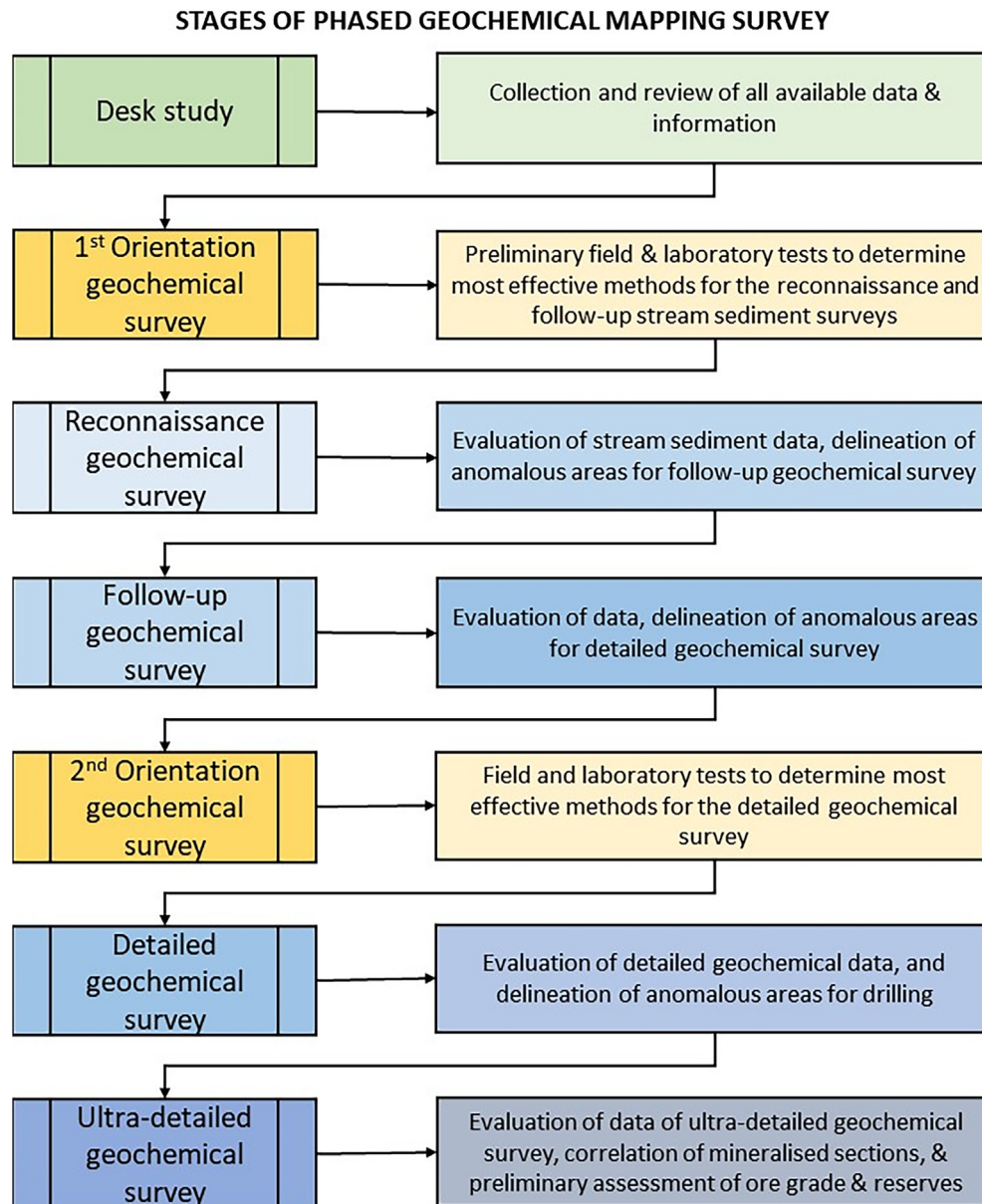


Fig. 4 Flow-chart showing the stages of phased geochemical survey in mineral exploration. From Demetriades A (2021) Geochemical mapping, in Alderton D and Elias SA (eds.), *Encyclopedia of Geology*, 2nd edn. vol. 6, pp. 267–280. Academic Press, doi: 10.1016/B978-0-08-102908-4.00059-X. Fig. 1, p. 268. Plotted with Microsoft® 365 PowerPoint.

- *Reconnaissance or regional phase* with an average density of 1 to 2 stream-sediment samples/km² and a map scale of $\geq 1:50,000$ to 1:100,000 is normally used. The aim of this phase is to evaluate the mineral potential of a region and to delineate potentially mineralized areas for conducting a follow-up geochemical survey. The reason that stream sediment is the usual sample medium in this phase is because it represents a composite product of weathering and erosion of the bedrock lithology of the source catchment basin above the sampling site and, thus, represents the geochemistry of a large area. So, it is a cost-effective method for the mineral exploration of a region.
- *Follow-up phase* with an average density from 10 to 20 stream sediment samples/km² and a map scale of around 1:25,000. The aim of this phase is to locate the anomalous areas with potential mineralization that warrant the execution of detailed geochemical surveys.
- *2nd Orientation survey* tests either soil or rock sampling, sample preparation and analytical techniques for the successful implementation of the detailed phase. The reason that the sample medium is changed from stream sediment to soil or rock is that the detailed phase is carried out along pegged traverses that crosscut the mineralized structures, which have been mapped by a geologist. Therefore, if there is a good development of soil over the prospective area, this sampling medium is used. If, however, soil is not well-developed in the study area, then rock is the preferable sampling medium. During the geological mapping of the prospective area, the geologist should be asked to map all the outcrops.
- *Detailed phase* with an average density that varies from 400 to 2500 soil (or rock) samples/km² and map scales of 1:5000 to 1:500. The objective of this phase is to precisely locate the mineralized structures to be evaluated by pitting, trenching and drilling, and
- *Ultra-detailed phase* where the drill-hole geochemical results are assessed, and a preliminary assessment of ore grade and reserves are made.

The 'ultra-detailed geochemical survey' is performed when the property under investigation reaches the core-drilling stage, and shall not be discussed in this account, except for showing a log of drillhole geochemistry.

According to Smith et al. (1976), two important concepts emerge from the stepwise development of a geochemical survey:

- Data arising from a survey at the reconnaissance level must be interpreted only at that level. Thus, data obtained from the sample density of the reconnaissance level must not be expected to locate economic mineral deposits, which is the function of data taken at the sample density of the detailed level, and
- As mineral exploration progresses from reconnaissance to follow-up and to detailed levels of sample density, survey costs per unit area increase proportionally.

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). The types of existing information may include previous investigation reports, topographical maps, remote sensing data, land ownership, access to the area, and any legal constraints. In the past, apart from the thorough literature search, aerial photographs were studied, and if a geological map was not available, a photo-geological interpretation was made. Nowadays, with high-resolution Landsat imagery, much more geological and land use information can be obtained, and a topographical map of quite good resolution can be constructed even from Google Earth Landsat imagery. Apart from the collection and evaluation of geological and mineralization (if any) 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, field assistants, drivers), which should also be tackled. The desk study assessment of all available data and information should lead to the compilation of a concise draft report, which will be completed after the evaluation of the orientation survey results.

Orientation survey

The orientation survey is a key component of phased applied geochemical exploration as its objective is to find a reliable and cost-effective methodology to clearly distinguish the anomalous element values related to mineralization from those of the background. An orientation survey should be carried out at each new area to be investigated, since each area has its own characteristic features with respect to lithology, mineralization type, geomorphology, and climate. Therefore, sound field information is required for each area to be investigated for planning the more costly subsequent phases. The principles of the orientation survey procedure are adequately covered in exploration geochemistry textbooks (Hawkes and Webb, 1962; Levinson, 1974, 1980; Rose et al., 1979), and here an outline will be given.

In mineral exploration, two different orientation surveys should be carried out, both having the same objective to develop reliable and cost-effective procedures to enhance the contrast of significant geochemical anomalies due to mineralization, and to subdue background and false patterns (Meyer et al., 1979). The first concerns the regional or reconnaissance stream sediment survey, and the second the detailed soil or rock geochemical survey (Fig. 4). The former is comparatively easy, for in the prospective area the objective is to determine:

- The sample density of the stream sediment survey, and
- The optimum grain-size of the stream sediment fraction to be analyzed and the most suitable analytical method that give the maximum geochemical contrast.

For anomalous patterns to be considered significant they should be described by at least three stream sediment samples. Of course, during the follow-up geochemical survey, even single stream sediment sample anomalies should be investigated but at a lower priority.

Case studies of stream sediment geochemical orientation surveys are provided by Plant (1971), Brundin and Nairis (1972), Ferguson and Price Jr. (1976), and Rose et al. (1982).

The second orientation survey to be carried out before the detailed soil or rock geochemical survey is somewhat more demanding. It involves many variables that should be determined in a potentially prospective area for the delineation of anomalous patterns for concealed or deep-seated mineralization, namely:

- Type of geochemical dispersion patterns (primary dispersion; secondary dispersion, i.e., clastic, hydromorphic, and biogenic).
- Optimum sampling medium, soil, or rock.
- Optimum sampling interval to delineate potential mineralized structures, which have already been geologically mapped; at least two orientation traverses should cross mineralization, and three to five samples to be collected over it; the traverses should cross all rock or soil types occurring in the area.
- Soil horizon and thickness from which soil samples shall be taken; soil samples should be collected from all distinct horizons; if soil horizons are thick, samples should be taken every 20 to 25 cm (samples should never include multiple 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 (different extraction methods are tested).
- Effects of topography, hydrology, drainage, glacial history, climate, rainfall, etc. on secondary dispersion patterns if soil is selected for the detailed geochemical survey.
- Background variation in soil and rock, and establishment of local threshold values.
- Data treatment methods, and
- Presentation of results on histograms, graphs, maps, etc.

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

Soil and rock geochemical orientation survey case studies for mineral exploration are described by Robertson and Gleeson (1981), Fletcher et al. (1986), Cook and Dunn (2006a, 2006b) and Benn et al. (2017).

How is an orientation survey conducted? A case study example

A good example of a geochemical orientation survey was performed on the 3Ts Gold (Au)-Silver (Ag) prospect area, which is in the Tommy-Adrian-Carter Lakes region of the Naglico Hills of central British Columbia in Canada (Fig. 5; Cook and Dunn, 2006a, 2006b; British Columbia, 2016). The property is situated about 125 km to the south-west of Vanderhoof, and 445 km NNW of Vancouver. Coordinates of the property center are: longitude 125.015355° West and latitude 53.024598° North.

It is a good case study and apart from the detailed reports all the analytical data are freely available. Below a brief description will be given, and additional information and data are provided in the Supplementary material in the online version at <https://doi.org/10.1016/B978-0-323-99762-1.00004-8>; it is denoted by consecutive numbers and with 'S' as prefix for each file, i.e., Microsoft PowerPoint®, Microsoft Excel® Table and Microsoft Word® Text files are referred to as PPT S1, Tables S1–S24, and Text S1 (includes Figs. S1–S11), respectively. It is noted that this notation refers to all the supplementary material provided in this account.

To begin with the objective must be defined. The objective of the soil geochemical orientation survey in the 3Ts Au—Ag prospect was to determine and recommend the most effective field and laboratory geochemical methods for property-scale evaluation of buried mineral targets in glacial drift-covered terrain by:

- (i) Comparing the results of commercially available analytical methods, and
- (ii) Identifying the most suitable soil horizon for field sampling.

What do we need to know about the area where an orientation geochemical survey is going to be carried out? As has already been discussed in the desk study, it is necessary to collect as much information as possible about the prospective area. For example, we need to know something about geology, mineralization, soil cover, and road access (refer to Supplementary material: PPT S1 and Text S1). A detailed description will be found in Cook and Dunn (2006a, 2006b), which should be consulted.

The soil geochemical orientation survey over the Tommy and Ted veins was required to answer the following questions:

- *What should be sampled and where should it be sampled?*
- *Which analytical methods reflect the presence of buried mineralization, and which do not?*
- *Which of the methods provide the greatest and optimal geochemical contrast for property-scale exploration?*
- *Which of the methods delineate the occurrence of epithermal Au mineralization?*

Answering the above questions should assist mineral exploration companies to conduct a highly effective geochemical exploration program in the British Columbia Interior Plateau for the delineation of blind or concealed targets of epithermal Au deposits. In fact,

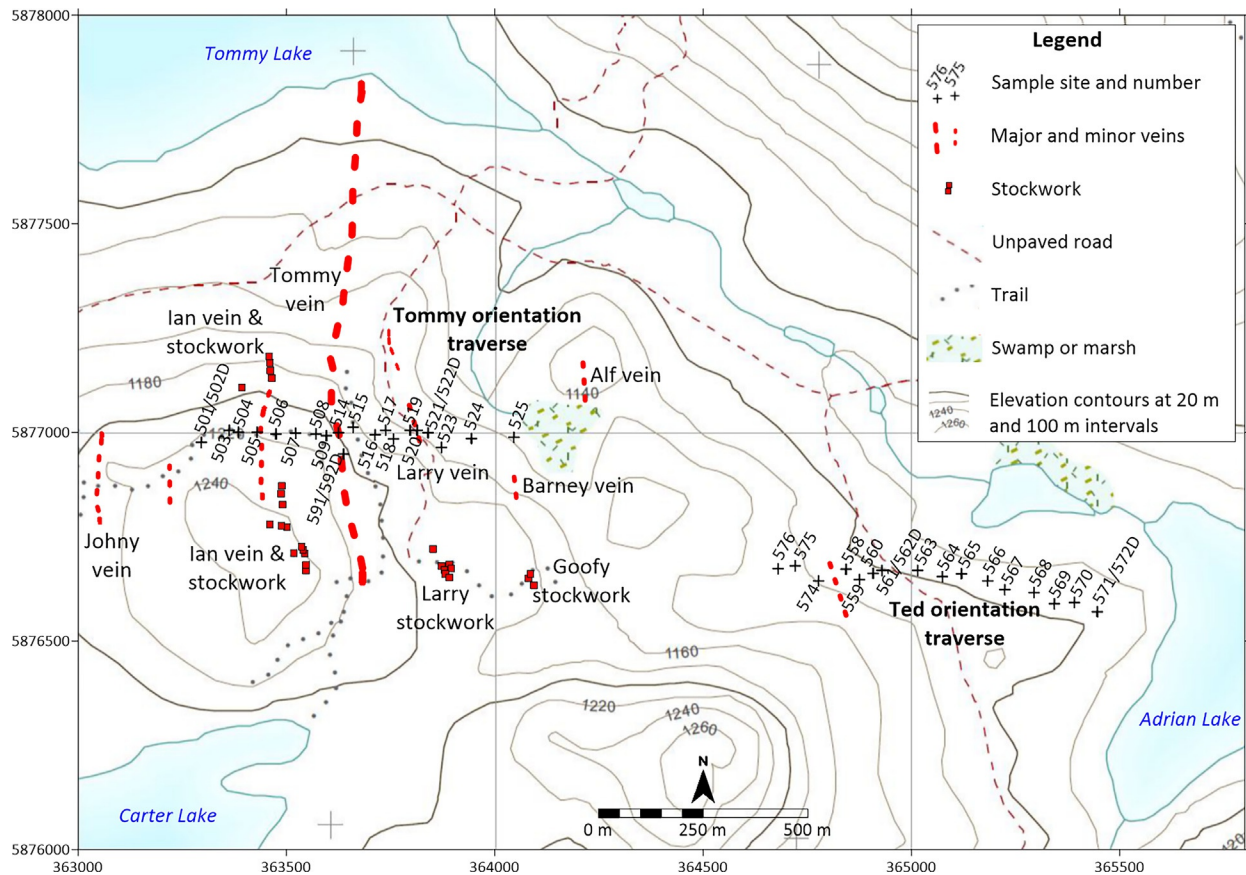


Fig. 5 Topographical map showing the routine and duplicated (D) sample sites of the Tommy and Ted soil orientation traverses, and the known mineralization, 3Ts prospect, British Columbia, Canada. Topographical map extracted from British Columbia (2016) *Map sheet 093F005* at a scale of 1:20,000. GeoBC of the Ministry of Forests, Lands, and Natural Resource Operation. Available at: <https://pub.data.gov.bc.ca/datasets/177864/pdf/093F/093F005.pdf>. 1:20,000 scale map sheet 093F005. The mineralization was digitized from Figs. 5 (p. 12) and 22 (p. 27) in Cook SJ and Dunn CE (2006b) *Final Report on Results of the Cordilleran Geochemistry Project: A Comparative Assessment of Soil Geochemical Methods for Detecting Buried Mineral Deposits - 3Ts Au-Ag Prospect, Central British Columbia*. Vancouver, BC: Geoscience BC, Open file Report 2007-7, 225 pp. Available at: <http://www.geosciencebc.com/reports/gbcr-2007-07/>; http://www.geosciencebc.com/i/project_data/GBC_Report2007-7/2007-7_Report.pdf; http://cmscontent.nrs.gov.bc.ca/geoscience/PublicationCatalogue/GeoscienceBC/GBCR2006-01-20_Cook.pdf. Plotted with Golden Software's Surfer™ v25.

project deliverables should end up with the provision of practical recommendations regarding the most appropriate field sampling, sample preparation and analytical techniques for the exploration of similar epithermal Au deposits in the British Columbia Interior Plateau, thereby increasing the likelihood of discovery.

After the evaluation of the results of previous geochemical surveys (refer to Cook and Dunn, 2006a, 2006b), two orientation geochemical traverses were planned over the Tommy and Ted veins (Fig. 5 and Fig. S3 in Text S1). The two orientation traverses were purposely chosen to crosscut the veins at rather arbitrary points to ensure that the sampling campaign was not biased towards those parts of the veins that were already known to be most prospective.

The Tommy and Ted orientation traverses comprised 20 and 16 sampling sites, respectively (Fig. 5). Sampling sites were spaced roughly at 50 m intervals, while nearer to the vein systems the spacing was close to 25 m. Distal sampling sites were at 75 to 100 m spacings. For quality control purposes, field duplicate soil samples were collected from five sampling sites, three on the Tommy and two on the Ted orientation traverses.

Three types of organic and mineral soil samples were collected at each sampling site (see Figs. S4–S9 in Text S1):

- LFH horizon humus (i.e., Litter, Fermentation, Humus horizon),
- B soil horizon, and
- C horizon till.

From each sampling site, a total of seven separate samples were collected for use by different analytical methods:

- A single LFH horizon humus sample (typically <5 cm thickness) comprising a mixture of partially decomposed twigs, needles, cones, moss, and other fine-grained organic debris above the underlying mineral soil; surface forest mosses over humus were removed prior to its collection.

- A total of five B horizon soil samples for aqua regia digestion (AR), enzyme leach (EL), soil gas hydrocarbons (SGH) and soil desorption pyrolysis (SDP) were collected; the fifth soil sample was taken from a constant depth of 10 to 25 cm at each sampling site according to the specifications of the laboratory that developed the Mobile Metal Ion (MMI[®]) analytical method. This constant depth range sampling procedure resulted in the collection of a mixed Bm and BC soil sample, i.e., Bm horizon and underlying transitional BC horizon; soil horizon nomenclature according to the Canadian soil system (Soil Classification Working Group, 1998). However, this constant depth range was not always observed. The Bm horizon is characterized by a relatively uniform brownening due to oxidation of iron (see Figs. S4–S9 in Text S1).
- A single C horizon till sample, obtained from a depth of approximately 45 to 60 cm on the Tommy traverse, and from about 40 to 60 cm on the Ted traverse.

Field duplicate samples ($N = 5$ pairs) were collected from all sample types.

A question arises about the constant depth sampling procedure:

- *Is collection of soil at constant depth a correct procedure (the case of samples for MMI[®])?*

The answer is '*definitely and emphatically not*' because each soil horizon has its own distinct physicochemical properties. Thus, the chemical composition of samples collected from mixed or different soil horizons are not comparable (Fig. 6a). Consequently, soil samples must always be collected from the same horizon in order to produce consistently comparable results between sites (Fig. 6b). Cook and Dunn (2006b), two experienced applied geochemists, collected horizon-based soil samples as can be observed in Table S1 with respect to the LFH and Bm horizons.

How were the samples collected? To answer this question, study the soil sample site numbers of the Tommy and Ted orientation traverses in Fig. 5, and then answer the following two questions:

- *What do you notice?*
- *Were the soil samples collected in a random order, or were they taken in a consecutive number sequence?*

It is obvious that the soil samples were taken in a consecutive number sequence, apart from the fill-in samples, i.e., 591/592D (Tommy traverse) and 574, 575, 576 (Ted traverse). The advice given for even such small geochemical mapping surveys is to take the samples in random order or, if they are not, to randomize them before their analysis (refer to Section "How is the quality of generated applied geochemical analytical datasets assured?").

How are the collected samples treated?

All samples following their collection were prepared in a suitably organized commercial laboratory, and subsequently analyzed. Firstly, they were dried in thermostatically controlled ovens at a temperature of 40 °C. Secondly, they were disaggregated with a porcelain mortar and pestle. Thirdly, all sample types were sieved through a stainless-steel sieve of different size, i.e., the LFH horizon humus samples through a 0.250-mm sieve, B horizon soil samples through a 0.180-mm sieve and C horizon till samples through a 0.063-mm sieve. These are standard sample preparation procedures of the Geological Survey of Canada and the British Columbian Geological Survey (Cook and Dunn, 2006a). If such standard procedures are not available, it will be necessary to determine the optimum grain size fraction for each of the sample types. The different laboratory methods used for the measurement of different determinands are concisely described below and tabulated in Table S2.

Is it appropriate to use a stainless-steel sieve? The chemical composition of stainless-steel, apart from Fe, includes mainly Cr, Ni, Mo, Mn, and minor amounts of Si, Cu, P, S, Ti, and C. Thus, the attrition of the stainless-steel sieve by the soil grains during sieving may contaminate to a variable extent the sieved sample by these elements (Thompson and Bankston, 1970). Hence, for major and multielement analyses certified trace element free nylon sieves are strongly recommended. However, in this case the use of a stainless-steel sieve does not affect the Au and Ag results, the two elements of interest.

During the orientation survey, different extraction methods are applied on different particle-sizes of soil to find the analytical method that gives the optimum contrast between anomalies and background for the elements of interest in the study area. The analytical methods used in mineral exploration are usually partial and not total extractions.

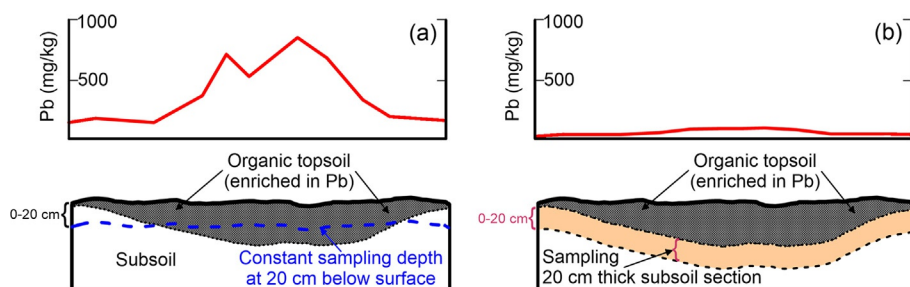


Fig. 6 Hypothetical examples of (a) non-significant geochemical anomaly due to collection of soil samples at a constant depth range that crosscuts different soil horizons (Open University, 1972, Unit 6 Applications of Geochemistry, Fig. 10, p. 14, modified) and (b) normal background values due to collection of soil samples from the same horizon and different depths according to its topographical morphology. Plotted with Golden Software's MapViewer[™] v8.

What is the difference between total and partial extractions? Total extraction methods determine the total element contents in a geochemical sample (e.g., rock, soil, sediment, plant), whereas partial or selective extraction or dissolution methods bring into solution the more readily available elements, depending on the type and degree of weathering, the expected chemical forms of the mineralization and of the pathfinding elements (Levinson, 1974, 1980; Rose et al., 1979; Fletcher, 1981; Chao, 1984; Hall, 1992; Cohen et al., 1998). The aim of the partial extraction methods is to enhance the contrast between anomalies and background of the pathfinder elements and to broaden their halo about the potential mineralized target.

All partial extraction methods must be carried out by experienced analysts because the analytical conditions in the laboratory must be exactly the same from day-to-day, and the analytical batches for a particular suite of samples monitored by the same reference samples to ensure that the analytical results are comparable.

In the orientation survey of the 3TS epithermal Au—Ag prospect area, the following partial extraction methods were used (Cook and Dunn, 2006a, 2006b): aqua regia (AR), enzyme leach (EL) and Mobile Metal Ion (MMI[®]). The latter two methods were developed by commercial companies, and the extractant solutions are proprietary. However, in general, the EL and MMI[®] digestions are designed only to extract those elements that are weakly adsorbed to grain surfaces or weakly bound to Fe—Mn oxides. As the results of soil gas hydrocarbons (SGH) and soil desorption pyrolysis (SDP) are not discussed here, their description can be found in Cook and Dunn (2006a).

Aqua regia method: Hot aqua regia digestion with inductively coupled plasma mass spectrometry (ICP-MS) finish was conducted on all prepared 3Ts Au—Ag property humus (LFH horizon), mineral soil (B horizon) and till (C horizon) samples. A 30-g aliquot of each sample was digested with 180 mL 2-2-2 HCl-HNO₃-H₂O at 95 °C for 1 h, diluted to 600 mL with deionized water, and then the supernatant solution analyzed for a 53-element suite by both ICP-MS and ICP-OES (inductively coupled plasma atomic emission spectroscopy) on Perkin-Elmer Elan 6000 and SpectroCirus instruments, respectively. This hot aqua regia digestion offers a partial recovery of numerous silicate-bound and refractory elements such as Ni, Ba and Cr. It provides, however, typically near-complete recovery for sulfide-associated elements such as Cu, Zn, Pb, Ag and Co.

Enzyme leach method: A 1-g subsample of <0.250 mm soil material was leached in a glucose oxidase solution containing a proprietary enzyme, which reacts with and dissolves any amorphous manganese oxides present (Clark, 1992, 1993; Bajc, 1998). Determined metals were reported to be complexed with gluconic acid, and the solutions were analyzed using a Perkin-Elmer Elan 6000 or 6100 ICP-MS unit.

Mobile Metal Ion method: This is a selective cold extraction method using 50 mL of a proprietary solution on a 50-g subsample, and an ICP-MS finish (Mann et al., 1998; Reimann et al., 2012a; Birke et al., 2014).

Fire assay method: The only total analytical method used was fire assay for the determination of Au. Fire assays were conducted on 30-g subsamples of <0.180 mm B horizon soil and <0.063 mm till, with an ICP-MS finish. The reason for the total decomposition of the samples was (i) to verify the presence of elevated Au concentrations in soil, and (ii) to ascertain what differences, if any, might exist between the partial (aqua regia digestion) and total Au determinations.

How is the quality of the analytical results assured?

As the orientation survey is a small project, *how is the quality of the analytical results assured?* It has already been mentioned that the samples must be randomized before they are sent to the laboratory, and field duplicate splits and standard samples inserted, and this procedure must remain blind to the analyst, namely:

- Duplicate-replicate pairs of samples (in this case, the five pairs of field duplicate samples, and two laboratory replicates), and
- Repeated analyses of control standards of known chemical composition.

Fig. 7a shows the scheme used by Cook and Dunn (2006b). Fig. 7b shows a random number sequence with the field duplicate-replicate pairs and standard, and when the 20-sample batch is placed in consecutive number order, they are randomly distributed in the batch (Fig. 7c).

Which is the first step upon receiving the analytical results from the laboratory? Before starting the processing of the soil orientation survey analytical data (or the results of any other geochemical mapping project) their quality must be assessed. As this is a small project, the assessment concerned the analytical results of:

- Duplicate-replicate pairs of samples, i.e., results of the five pairs of field duplicate samples (Table S3), and the two laboratory replicates (Table S4).
- Repeated analyses of control standards of known chemical composition (Table S5), and
- Laboratory replicate and standard replicate results (Table S6).

Cook and Dunn (2006b, pp. 39–99) studied in detail the quality assurance and quality control (QA/QC) results. Their procedure was limited, however, to a comparative assessment of analytical accuracy and precision for selected elements by aqua regia digestion relative to results achieved by other analytical methods. It is strongly recommended that these results should be studied. Here additional treatments are presented and discussed by using only the Ag and Au quality control results.

Tables S3 and S4 show the analytical results of Ag and Au on field duplicate, and laboratory replicate samples, respectively, and Table S5 the results of standard samples. The percentage relative standard deviation is given in all cases. The relative standard deviation (RSD or RSD%) is the absolute value of the coefficient of variation and is often expressed as a percentage [(Standard deviation × 100)/Mean]. It is a useful statistical parameter for comparing the uncertainty between different measurements of

(a)		(b)		(c)	
Sample	Analytical order	Sample	Analytical order	Sample	Analytical order
1	Field Duplicate 1	2	Field Duplicate 1	1	
2	Field Duplicate 2	14	Field Duplicate 2	2	Field Duplicate 1
3		7	Standard	3	
4		9	Field Duplicate 1	4	
5		20	Field Duplicate 2	5	
6		4		6	
7		19		7	Standard
8		17		8	
9		15		9	Field Duplicate 1
10	Standard	5		10	
11	Field Duplicate 1	1		11	
12	Field Duplicate 2	8		12	
13		6		13	
14		13		14	Field Duplicate 2
15		12		15	
16		10		16	
17		16		17	
18		11		18	
19		3		19	
20		18		20	Field Duplicate 2

Fig. 7 (a) Typical 20-sample batch of the quality assurance/quality control (QA/QC) scheme used for sampling and analysis of samples of Tommy and Ted traverses, 3Ts property, BC; (b) example of a random number list for sample number allocation; when the samples are sent to the laboratory are placed (c) in a consecutive number order (lower to higher). The brown and green color shades denote two different sample duplicates. Plotted with Microsoft 365 Excel® and PowerPoint®. (a) From Cook SJ and Dunn CE (2006b) *Final Report on Results of the Cordilleran Geochemistry Project: A Comparative Assessment of Soil Geochemical Methods for Detecting Buried Mineral Deposits - 3Ts Au-Ag Prospect, Central British Columbia*. Vancouver, BC: Geoscience BC, Open file Report 2007-7, 225 pp. Available at: <http://www.geosciencebc.com/reports/gbcr-2007-07/>; http://www.geosciencebc.com/i/project_data/GBC_Report2007-7/2007-7_Report.pdf; http://cmscontent.nrs.gov.bc.ca/geoscience/PublicationCatalogue/GeoscienceBC/GBCR2006-01-20_Cook.pdf, Fig. 21, p. 26.

varying absolute magnitude. The RSD% results of Ag and Au for field duplicate samples (Table S3), which combine field, sample preparation and analytical variation, are generally greater than the corresponding laboratory replicates (Table S4), and control standards (Table S5), which measure analytical variation only. The field duplicate results (Table S3) show that there is a large difference between the routine and duplicate samples, suggesting that the sampling variance is large. Cook and Dunn (2006b) concluded that the field duplicate Au results by aqua regia digestion and ICP-MS finish show poor reproducibility, despite elevated Au concentrations in humus directly over the Tommy vein mineralization.

Studying the results of the standard samples (Table S5) is realized that some of them are not suitable for the determination of Au by selective leach methods, e.g., standard LKSD-4, PEAT-1 and DS3 by Na-pyrophosphate extraction. By studying closely, the results of Table S5 you will find other inconsistencies.

Analytical precision can be calculated by different statistical methods as described by Fletcher (1981), Thompson (1983), Reimann et al. (2008), Johnson (2011), Demetriades (2011b) and Demetriades et al. (2022a).

Precision is a measurement of how closely the analytical results can be reproduced, and is independent of the true value (i.e., results can all show close agreement, but they may be a long way from the accepted value). A visual impression of precision can be given by simple X-Y graphs and Thompson-Howarth control charts (Thompson and Howarth, 1976, 1978; Thompson, 1983; Reimann et al., 2009, 2011, 2012a; Demetriades et al., 2022a). Further, overall precision at the 95% confidence level can be estimated quantitatively, based on the mean (\bar{x}) and standard deviation (SD) expressed as a percentage:

$$\text{Precision, } P(\%) = \frac{1.96 \times \text{SD}}{\bar{x}} \times 100 \quad (1)$$

$$\text{RSD or Coefficient of variation, CV}(\%) = \frac{\text{SD}}{\bar{x}} \times 100 \quad (2)$$

Substituting RSD or CV in Eq. (1):

$$P(\%) = 1.96 \times \text{CV} \quad (3)$$

Precision varies with concentration (Thompson and Howarth, 1976, 1978; Fletcher, 1981, 1986; Demetriades, 2011b). At low concentrations, near to the lower detection limit of the analytical method, precision is poor, and normally improves with increasing element concentration (see Fig. S10 in Text S1 and Table S6; refer to Demetriades et al., 2022a).

It is noted that the coverage factor at the 95% confidence level is 1.96 (the coverage factor, k , determines the confidence in the data values within a certain standard deviation value, e.g., for $k = 1$, there is a confidence that 68% of data points lie within one standard deviation, while $k = 1.96$ means that there is a confidence that 95% of the data values would lie within approximately two standard deviations). However, due to the uncertainty in the estimate of standard deviation of an analytical dataset of an element, the coverage factor of 2 is generally used, and this is at the 95.44% confidence level (JCGM 100, 2008; ISO/IEC, 2008, 2012; Ellison and Williams, 2012; Ramsey et al., 2019; Demetriades et al., 2022a).

Thompson and Howarth (1976, 1978) and Thompson (1983) describe a method of estimating analytical precision using duplicate-replicate sample pairs (Johnson, 2011, p. 70; Reimann et al., 2009, 2011, 2012a; Demetriades et al., 2022a). This is a graphical method, which can be used even for a single replicate pair that gives an immediate visual impression of the precision of the analytical method (Fig. 8). The mean of the replicate results is plotted against the absolute difference between the two replicate analyses. On the precision graph of $\pm 10\%$ and $\pm 20\%$ at the 95% confidence level, the fit-for-purpose criteria for the two precisions are defined by their corresponding 90th and 99th percentile lines (Fig. 8).

The replicated analytical results of the Tommy and Ted orientation traverses that can be plotted on the Thompson-Howarth control chart are the laboratory replicates, and the replicated determinations of standard samples (Table S7). The standard samples, as can be observed, have been analyzed from two to five times. In the case of repeated determinations (Table S5), the minimum and maximum values were considered in order to account for the largest variation.

The Ag Thompson-Howarth plot (Fig. 8a) shows that precision is generally good with only two pairs plotting above the 99th percentile at $\pm 20\%$ precision, and three pairs are above the 90th percentile at $\pm 10\%$ precision. Therefore, it can be concluded that the overall precision of Ag determinations for all analytical methods is better than $\pm 10\%$ at the 95% confidence level, because most values fall below the 99th percentile line.

The precision for Au is comparatively poor for all analytical methods (Fig. 8b), except the fire assay determinations on the standard samples, i.e., it is poorer than $\pm 20\%$ at the 95% confidence level. Of course, this is expected as fire assay is a much more vigorous digestion than the other methods used.

How are the orientation survey results treated after verifying their quality?

Upon verifying the quality of analytical results, the second step is to merge the analytical files with the sample site coordinates of the Tommy and Ted orientation traverses (Table S8); the field observations in Table S1 should be merged too.

Some basic statistical parameters of Ag and Au of the results of different analytical methods, used for the analysis of soil samples from the LFH organic humus horizon, B horizon soil and C horizon till, are given in Table S9, i.e., all data from the Tommy and Ted soil orientation traverses (Table S9a), and separately for the Tommy (Table S9b) and Ted (Table S9c) traverses. Multiple boxplots show the statistical distribution of Ag and Au in all soil samples collected from the Tommy and Ted orientation traverses (Fig. 9), and separately (Fig. 10).

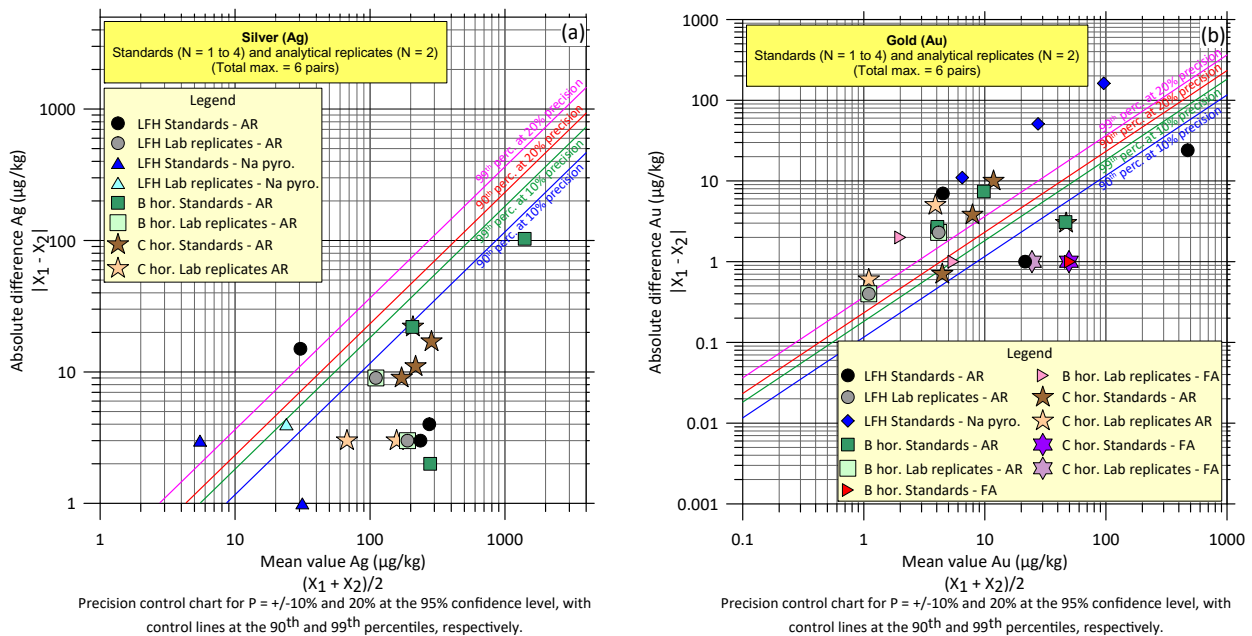


Fig. 8 Thompson and Howarth control charts of (a) Ag and (b) Au, using the results of laboratory replicates from the LFH horizon humus, B horizon soil and C horizon till of the Tommy and Ted traverses, 3Ts property, BC, and the results of standard replicates, and their determination by different analytical methods: AR = Aqua regia extraction; Na pyro. = Sodium pyrophosphate leach, and FA = Fire Assay. The control lines are for Precision (P) $\pm 10\%$ and $\pm 20\%$ at the 95% confidence level, with control lines at the 90th and 99th percentiles, respectively. In order to accommodate the results, the X- and Y-axes are logarithmic (base 10). Refer to Table S7 in the online version at <https://doi.org/10.1016/B978-0-323-99762-1.00004-8>. Plotted with Golden Software's Grapher™ v21.

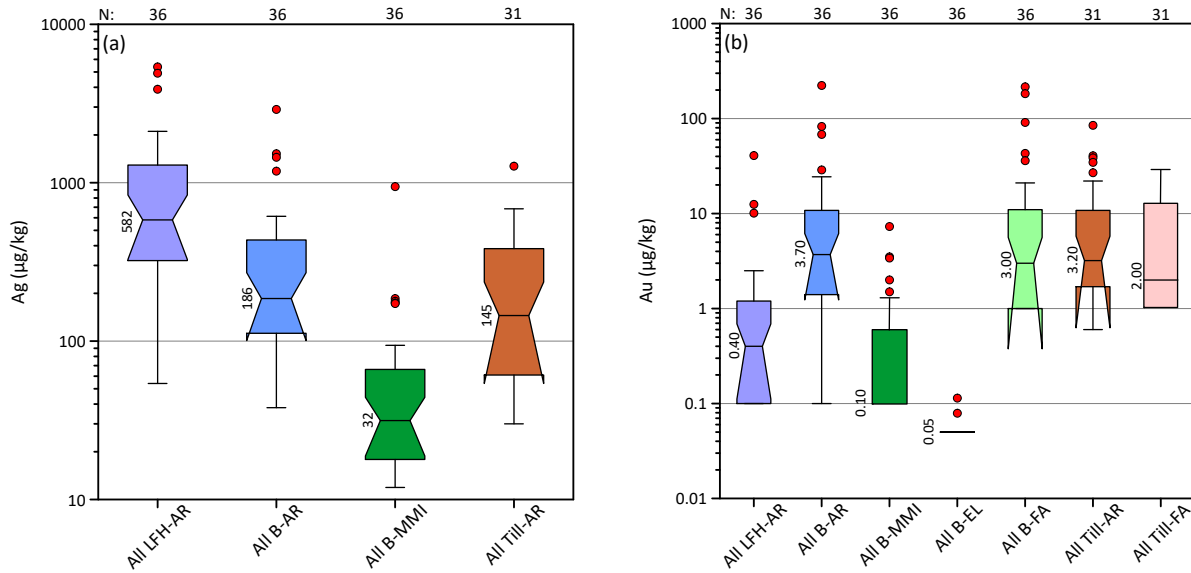


Fig. 9 Multiple notched-boxplot comparison of the statistical distribution of combined (a) Ag and (b) Au analytical results of different analytical methods in soil samples from the LFH horizon humus, B horizon soil and C horizon till of Tommy and Ted orientation traverses, 3Ts property, BC. Median Ag and Au concentrations are indicated by the horizontal line within the box and values displayed. The 95% confidence interval limits on the median are represented by the notch. Fifty per cent of the analytical results for each dataset lies within the box, i.e., between the 25th and 75th percentiles, the lower and upper limits of the box, respectively. Outliers beyond 1.5 times the interquartile range are indicated by red dots with a black rim. The Y-axis is logarithmic (base 10) in order to accommodate all results. Notation: AR = Aqua regia; MMI = Mobile Metal Ion; EL = Enzyme leach; FA = Fire assay. Plotted with Golden Software's Grapher™ v21.

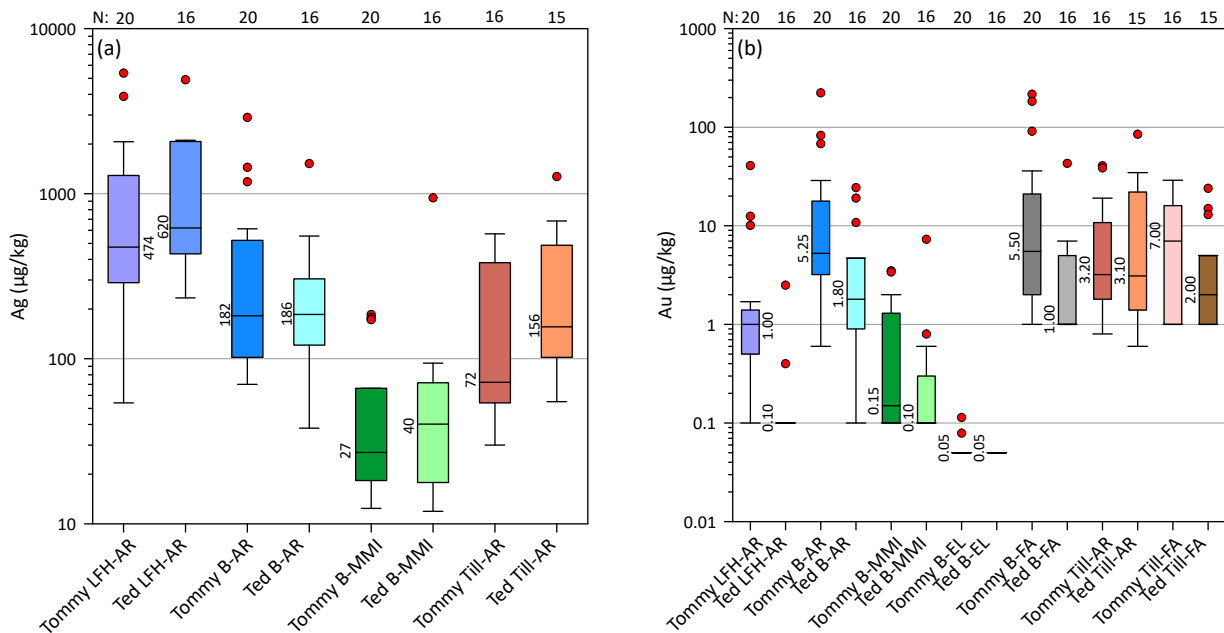


Fig. 10 Multiple boxplot comparison of the statistical distribution of individual (a) Ag and (b) Au analytical results of different analytical methods in soil samples from the LFH horizon humus, B horizon soil and C horizon till of Tommy and Ted orientation traverses, 3Ts property, BC. Median Ag and Au concentrations are indicated by the horizontal line within the box and values displayed. Fifty percent of the Ag and Au data for each dataset lies within the box. Outliers beyond 1.5 times the interquartile range are indicated by red dots with a black rim. The Y-axis is logarithmic (base 10) in order to accommodate all results. Notation: AR = Aqua regia; MMI = Mobile Metal Ion; EL = Enzyme leach; FA = Fire assay. Plotted with Golden Software's Grapher™ v21.

Boxplot comparison

The boxplot is a powerful pictorial tool of Exploratory Data Analysis (EDA), and is independent of statistical normal theory distributional assumptions (Tukey, 1977; Hoaglin et al., 1983). This graphical display was popularized for the statistical graphical presentation of geochemical results by Kürzl (1988). The boxplot summarizes five statistical parameters of geochemical datasets:

- (i) Location (minimum and maximum values, 25th, 50th (median) and 75th percentiles).
- (ii) Spread (scatter or variability or range).
- (iii) Skewness (depending on the position of the median within the box).
- (iv) Tail length (or whisker length) on either side of the box, which is conventionally extended to the most extreme data point up to a distance of $1.5 \times$ Interquartile range (IQR), defined by the difference between the values at the 75th and 25th percentiles, which are the upper and lower limits of the box, respectively, and
- (v) Outlying data points, which are beyond 1.5 times the interquartile range (Figs. 9 and 10).

It is noted that the visualization of the statistical distribution of geochemical data sets by boxplots is more powerful than histograms, because more information can be extracted from boxplots than histograms, and most importantly is much easier to compare different datasets. Further, histograms require a sample size of at least 30 to be useful, whereas boxplots need a sample size of only 5. The reason for this small number of samples, required by boxplots, is to estimate reliably the median.

Fig. 9 compares the combined Ag and Au analytical results of the Tommy and Ted soil orientation traverses using notched-boxplots. The notch shows the 95% confidence interval for the median (m), and its upper and lower limits are given by $m \pm 1.58 \times \text{IQR}/\sqrt{N}$ (where N is the number of samples in the dataset).

The first striking feature in Fig. 9a is that Ag concentrations are overall higher in the LFH horizon humus compared to the B horizon soil and C horizon till results. This can be explained by the fact that Ag is known to be absorbed by and form complexes with humic substances. The second distinct feature concerns the overall lower Ag concentrations extracted by the hot aqua regia digestion. Comparing the sample medians of Ag in Fig. 9a, and using the upper and lower notch limits, it is observed that there is a distinct difference at the 5% significance level between the median of LFH horizon humus aqua regia and B horizon soil MMI[®] results with those of the B horizon soil and C horizon till aqua regia data. The MMI[®] selective leach results have the lowest median, and the reason has been given already. The medians of B horizon soil and C horizon till Ag aqua regia results appear, however, to be comparable as the two notches overlap horizontally, suggesting that the medians of the two datasets are not significantly different at the 5% significance level.

Similarly, in Fig. 9b, the medians of Au in B horizon soil aqua regia and fire assay results appear to be comparable with those of C horizon till. The medians of LFH horizon humus aqua regia, B horizon soil MMI[®] and Enzyme leach Au results are lower and are not comparable.

An interesting feature is the folding-in or fold-back behavior of the 25th percentile for a few boxplots (e.g., All B-AR, All Till AR in Fig. 9a, and All B-AR, All B-FA and All Till-AR in Fig. 9b), which is caused by the lower limit of the 95% confidence interval on the median extending beyond the 25th percentile (or the 75th percentile, not in these cases). This feature suggests that additional data are required to define reliably Ag and Au low (background) concentrations, determined by aqua regia and fire assay. Most of the Enzyme leach Au analytical results on B horizon soil samples are below the method's lower detection limit, except two outliers (Table S8). Absence of lower whiskers in the boxplots of B horizon MMI[®] and C horizon till fire assay Au results, suggests that most of the Au data are near to the analytical method's lower detection limit (Fig. 9b; Table S8).

Outliers or anomalous Ag and Au concentrations are indicated in all soil horizon samples and by all analytical methods, except the Au fire assay C horizon till dataset (Fig. 9b). The organic-rich humus samples from the LFH horizon have the highest Ag concentrations, and mineral soil (B horizon and C horizon till) samples contain lower background Ag values (Fig. 9a). The highest anomalous Au contents occur in B horizon soil samples determined by aqua regia extraction and fire assay (Fig. 9b).

Multiple boxplots were plotted for the individual datasets of Tommy and Ted soil orientation traverses in order to study separately their statistical distribution (Fig. 10). Because of the small number of samples, it was not possible to plot notched-boxplots as the limits of the 95% confidence interval on the median extend beyond the 25th and 75th percentiles in most cases. By visual inspection, the aqua regia median values of Tommy and Ted traverses of (a) Ag (Fig. 10a), and (b) Au (Fig. 10b) results in B horizon soil and C horizon till samples, respectively, appear to be comparable. Outliers or anomalous Ag and Au samples occur in all soil horizons, and by all analytical methods, in both the Tommy and Ted traverses, except in the Tommy traverse C horizon till samples analyzed by aqua regia extraction and fire assay, and in the Ted traverse B horizon soil enzyme leach extraction.

In most sample types, the highest Ag and Au concentrations extracted by aqua regia are on the Tommy traverse (Fig. 10; Table S9b). Here, up to 5380 $\mu\text{g}/\text{kg}$ Ag and 40.8 $\mu\text{g}/\text{kg}$ Au are present in LFH horizon humus (median: 475 μg Ag/kg and 1 μg Au/kg), up to 2899 $\mu\text{g}/\text{kg}$ Ag, and 223 $\mu\text{g}/\text{kg}$ Au in B horizon soil samples (median: 182 μg Ag/kg and 5.25 μg Au/kg). Whereas, in C horizon till the Ag and Au aqua regia concentrations are lower compared to those of the Ted traverse (Tables S9a, b, and c), i.e., up to 1271 $\mu\text{g}/\text{kg}$ Ag and 84.9 $\mu\text{g}/\text{kg}$ Au, compared to 571 $\mu\text{g}/\text{kg}$ Ag and 40.6 $\mu\text{g}/\text{kg}$ Au in Tommy traverse C horizon till samples. Somewhat lower, but nevertheless elevated Au concentrations, are also present in Ted traverse sample media. These include up to 24.4 $\mu\text{g}/\text{kg}$ and 84.9 $\mu\text{g}/\text{kg}$ Au in B horizon soil (median: 1.80 $\mu\text{g}/\text{kg}$), and C horizon till samples (median: 3.10 $\mu\text{g}/\text{kg}$), respectively. In the case of C horizon till, samples from both the Tommy and Ted traverses report similar median values (3.20 and 3.10 $\mu\text{g}/\text{kg}$), respectively. Only LFH humus horizon samples on the Ted orientation traverse fail to report any elevated Au concentrations (maximum: 2.50 $\mu\text{g}/\text{kg}$; Fig. 10b; Table S9c).

Geochemical cross-sections

Cross-sections are used in the graphical portrayal of element concentrations at each sampling site along a pegged traverse. It is a powerful tool and can be plotted by hand. It can be used at any stage of a geochemical survey, and especially when the applied geochemist is in the field at remote locations without access to computers. Fig. 1 shows an annotated hypothetical representation of a geological-geochemical cross-section across a vein ore deposit emplaced in a single type of host rock, and the interpretation of the element concentrations.

Four different types of geochemical cross-sections of Ag and Au in soil samples from the Tommy and Ted orientation surveys were plotted for the study of the spatial distribution with reference to each sampling site:

- (i) Raw data of Ag and Au (Figs. 11 and 12).
- (ii) Response ratios of Ag and Au (Figs. 13 and 14).
- (iii) 3-term moving average (Figs. 15 and 16), and
- (iv) Comparisons of raw data, response ratios and residuals (Figs. 17 and 18).

All the raw Ag and Au analytical data performed on the Tommy and Ted soil orientation traverses were plotted in cross-sections, which show the position of mineralized veins and stockworks, and the samples near to mineralization (Figs. 11 and 12). The geochemical cross-sections are crowded, and this was done on purpose for the sake of reducing the number of diagrams. Ideally, each dataset should be plotted and studied separately, because of differences in the Ag and Au concentrations extracted by the different analytical methods. Further, for better interpretation, these geochemical cross-sections should be plotted over a geological and a topographical cross-section.

Always start by plotting the raw results, because it is important to understand first the spatial distribution of the actual element concentration patterns, before starting to process the results with other techniques.

To make easier the comparison of results of the different treatments, weak to strong anomalous samples in Figs. 11–18 have been assigned red color letters, and coinciding Ag and Au anomalies are given the same letter notation. Single element anomalies are denoted by N1, N2, N3, N4 and N5 in magenta color. When the same Ag or Au anomalous sample does not occur in either the Ag or Au cross-sections, or is subdued by the different data processing techniques, the letter notation is changed to blue color. As it is important to know exactly the sample sites, a blue color dot has been added on the connection line of the most prominent distribution.

There are no sample sites directly over the Ian vein, sample 505 is nearby (Fig. 11). While over the Tommy and Larry veins, there is one sample site directly above, i.e., samples 514 and 521, respectively, and two samples nearby, i.e., 591 and 520, respectively (Fig. 5).

The following notation is used in the underlying description (Figs. 11–18):

- Aqua regia = AR
- Fire assay = FA
- Enzyme leach = EL
- Mobile Metal Ion leach = MMI

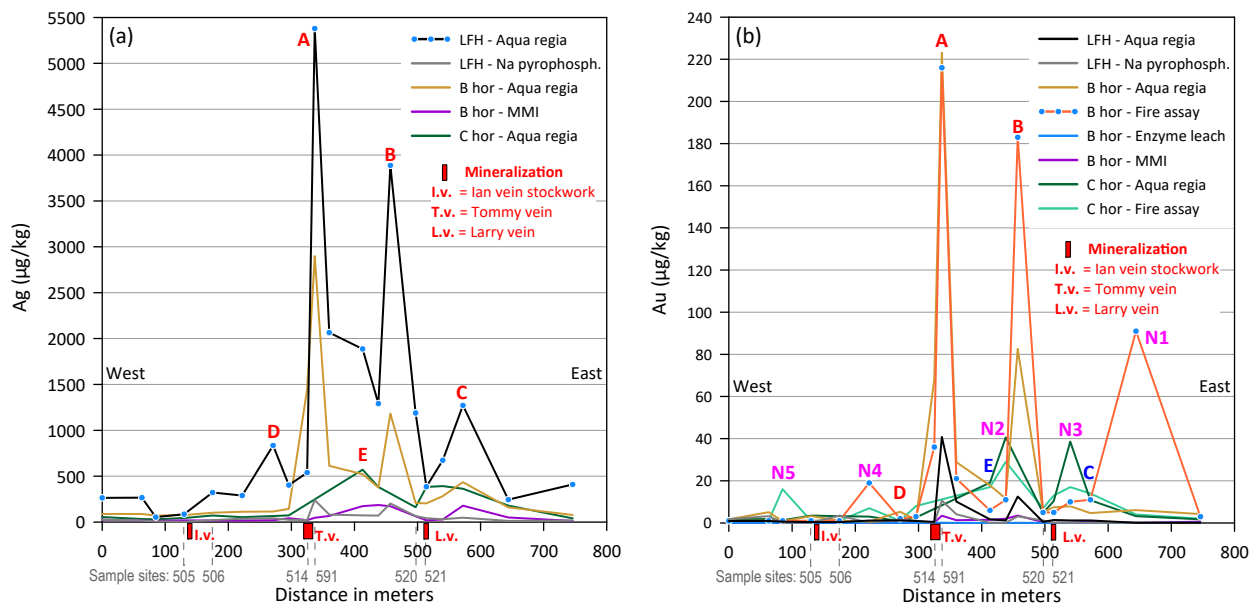


Fig. 11 Distribution of raw Ag and Au concentrations, analyzed by different methods, in samples of LFH humus, B horizon soil and C horizon till along the Tommy orientation traverse, 3Ts property, BC. The position of vein mineralization is shown. Letter notation: Red color letters denote weak to strong Ag and Au anomalous samples; blue color letters indicate subdued anomalous samples in the Au section (b); magenta color letters (N1 to N5) are new weak to strong Au anomalous samples (section b). Plotted with Golden Software's Grapher™ v21.

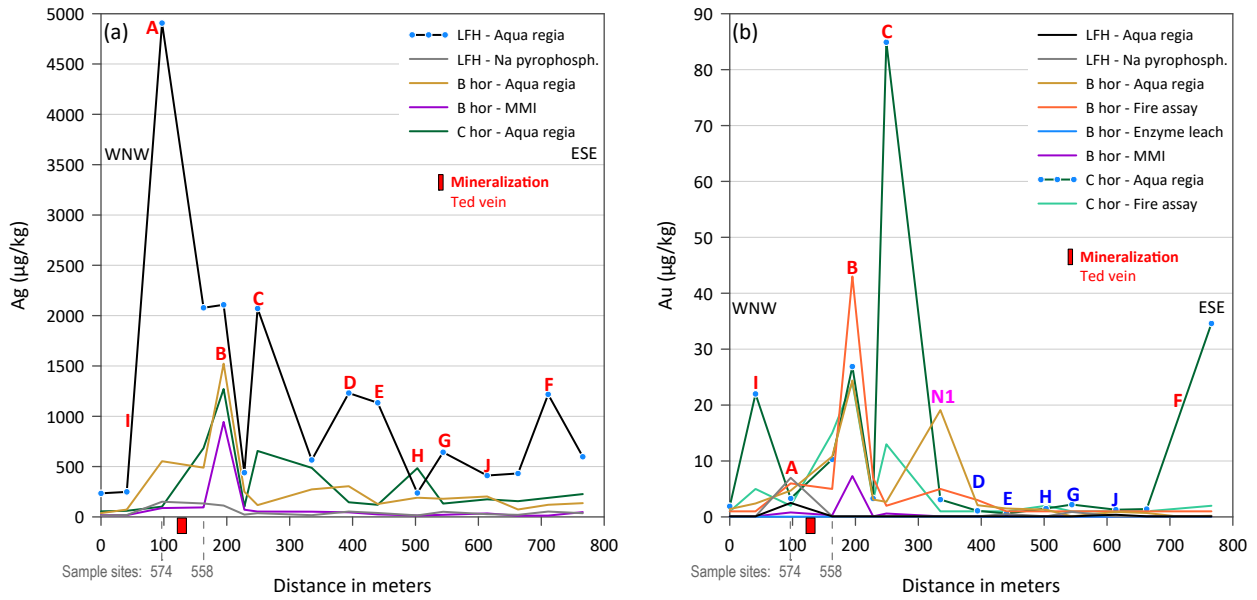


Fig. 12 Distribution of raw Ag and Au concentrations, analyzed by different methods, in samples of LFH humus, B horizon soil and C horizon till along the Ted orientation traverse, 3Ts property, BC. The position of vein mineralization is shown. Letter notation: Red color letters denote weak to strong Ag and Au anomalous samples; blue color letters indicate subdued anomalous samples in the Au section (b); magenta color letter (N1) is a new Au anomalous sample (section b). Plotted with Golden Software's Grapher™ v21.

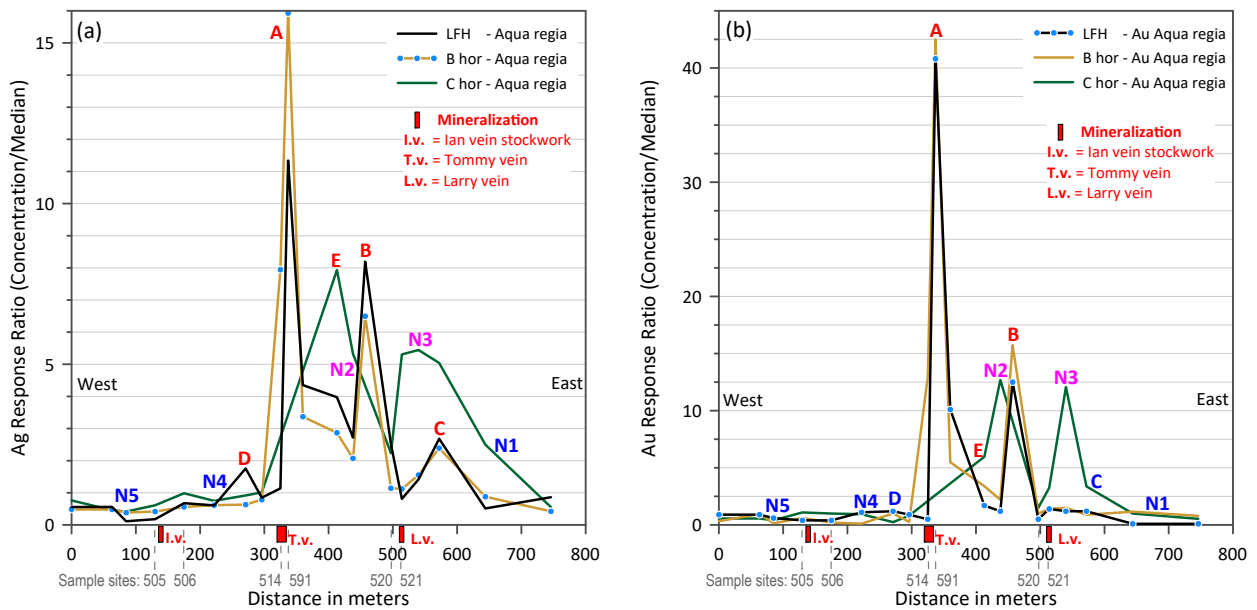


Fig. 13 Distribution of response ratios of Ag and Au hot aqua regia concentrations in samples of LFH humus, B horizon soil and C horizon till along the Tommy orientation traverse, 3Ts property, BC. The position of vein mineralization is shown. Letter notation is the same as in Fig. 11: Red color letters denote weak to strong Ag and Au anomalous samples; blue color letters indicate subdued anomalous samples in relation to the raw data sections; magenta color letter (N2, N3) are anomalies exhibited in Fig. 11b. Plotted with Golden Software's Grapher™ v21.

Fig. 11a and b show the raw Ag and Au distribution, respectively, along the Tommy soil orientation traverse. To begin with, there are no elevated Ag and Au concentrations directly over the Larry and Ian veins. As has already been mentioned, the orientation traverses over the Tommy and Ted veins were purposely chosen to crosscut them at rather arbitrary points to ensure that the sampling campaign was not biased towards those parts of the veins that were already known to be most prospective (Fig. 5). Further, the anomalous geochemical patterns may be slightly offset because of the topography and the overall west to east direction of the ice flow (Fig. S3 in Text S1).

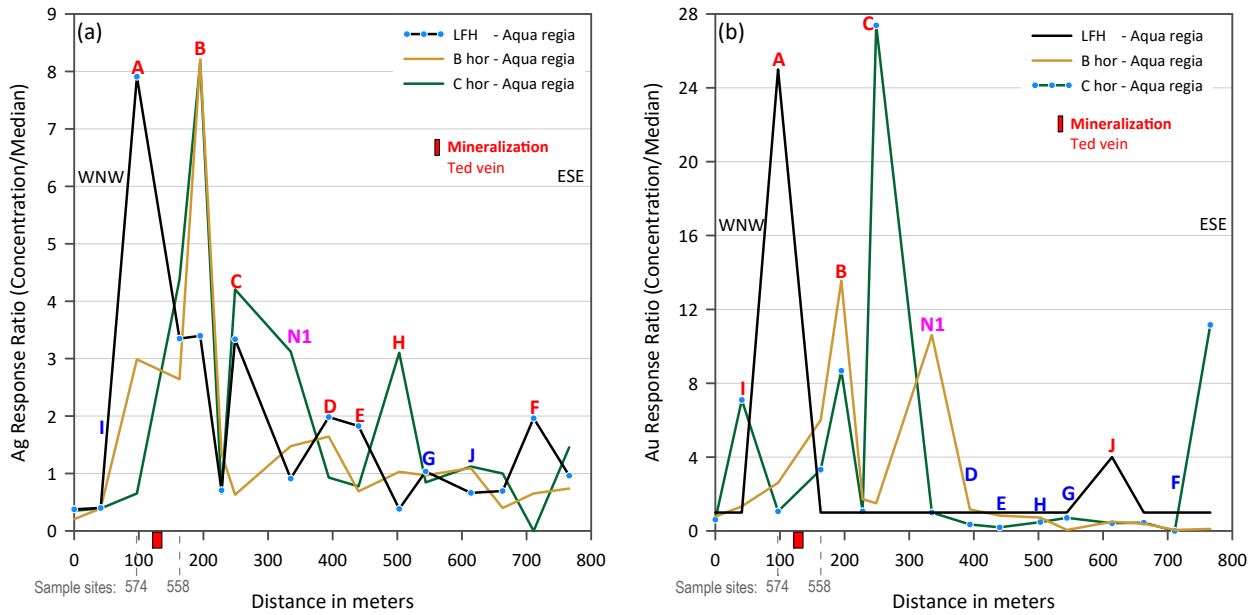


Fig. 14 Distribution of response ratios of Ag and Au hot aqua regia concentrations in samples of LFH humus, B horizon soil and C horizon till along the Ted orientation traverse, 3Ts property, BC. The position of vein mineralization is shown. Letter notation is the same as in Fig. 12: Red color letters denote weak to strong Ag and Au anomalous samples; blue color letters indicate subdued anomalous samples in relation to the raw data sections. The anomaly N1 (magenta color letter) displayed in (b) is the same anomaly exhibited in Fig. 12b. Plotted with Golden Software’s Grapher™ v21.

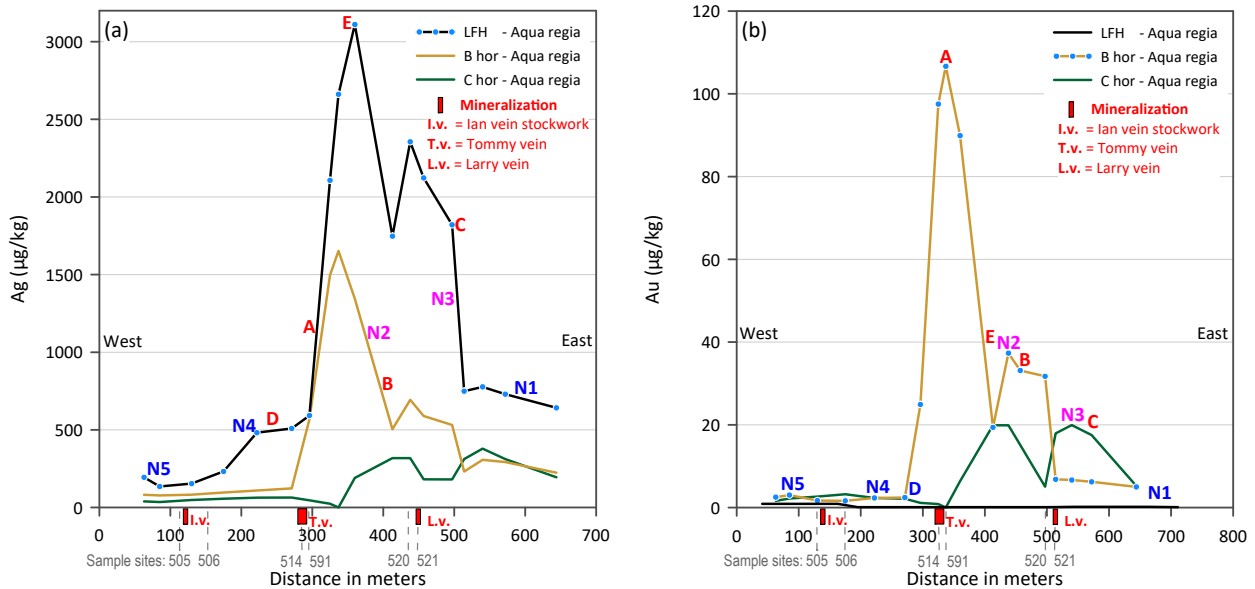


Fig. 15 3-term moving average of Ag and Au hot aqua regia concentrations in samples of LFH humus, B horizon soil and C horizon till along the Tommy orientation traverse, 3Ts property, BC. Letter notation is the same as in Fig. 11: Red color letters denote weak to strong Ag and Au anomalous samples; blue color letters indicate subdued anomalous samples in relation to the raw data sections; magenta color letter (N2, N3) are anomalies exhibited in Fig. 11b. Plotted with Golden Software’s Grapher™ v21.

The Tommy vein soil Ag and Au anomalous patterns coincide at the following sites:

- “A” anomaly is slightly to the east of the Tommy vein and is marked by (i) strong AR Ag in LFH humus and B horizon soil samples; (ii) weak Na-pyrophosphate Ag and Au in LFH humus samples; (iii) strong AR and FA Au, and very weak MMI Au in B horizon soil samples, and (iv) comparatively weak AR Au in LFH humus samples.

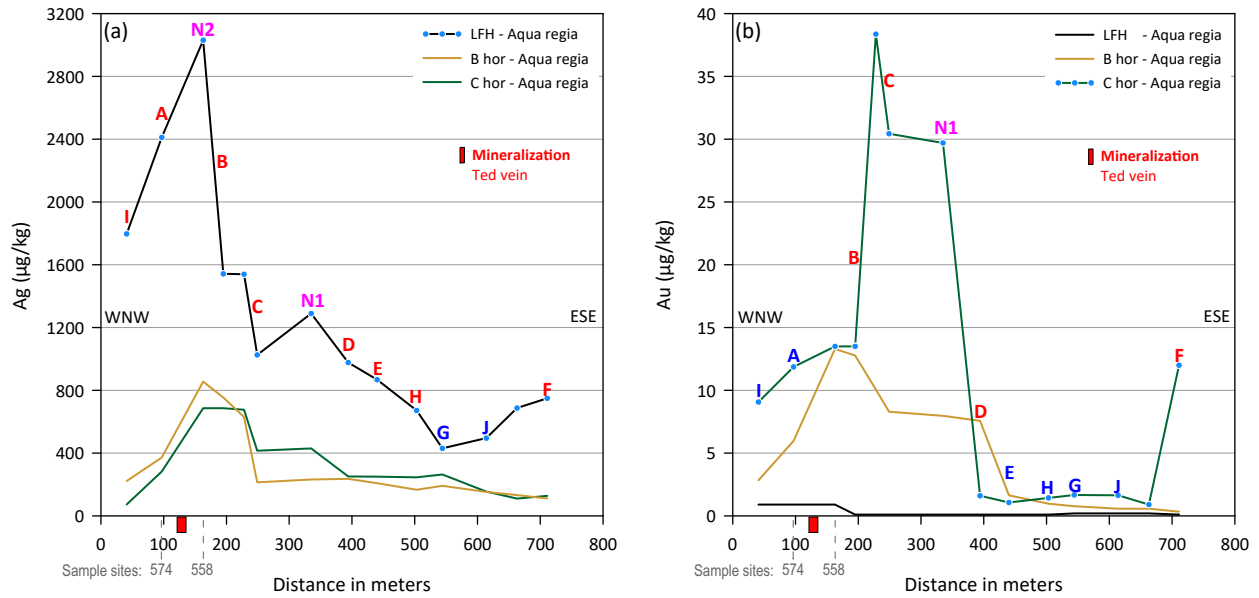


Fig. 16 3-term moving average of Au hot aqua regia concentrations in samples of LFH humus, B horizon soil and C horizon till along the Ted orientation traverse, 3Ts property, BC. Letter notation is the same as in Fig. 12: Red color letters denote weak to strong Ag and Au anomalous samples; blue color letters indicate subdued anomalous samples in relation to the raw data sections; magenta color letter (N1) is the anomaly exhibited in Fig. 12b. Plotted with Golden Software's Grapher™ v21.

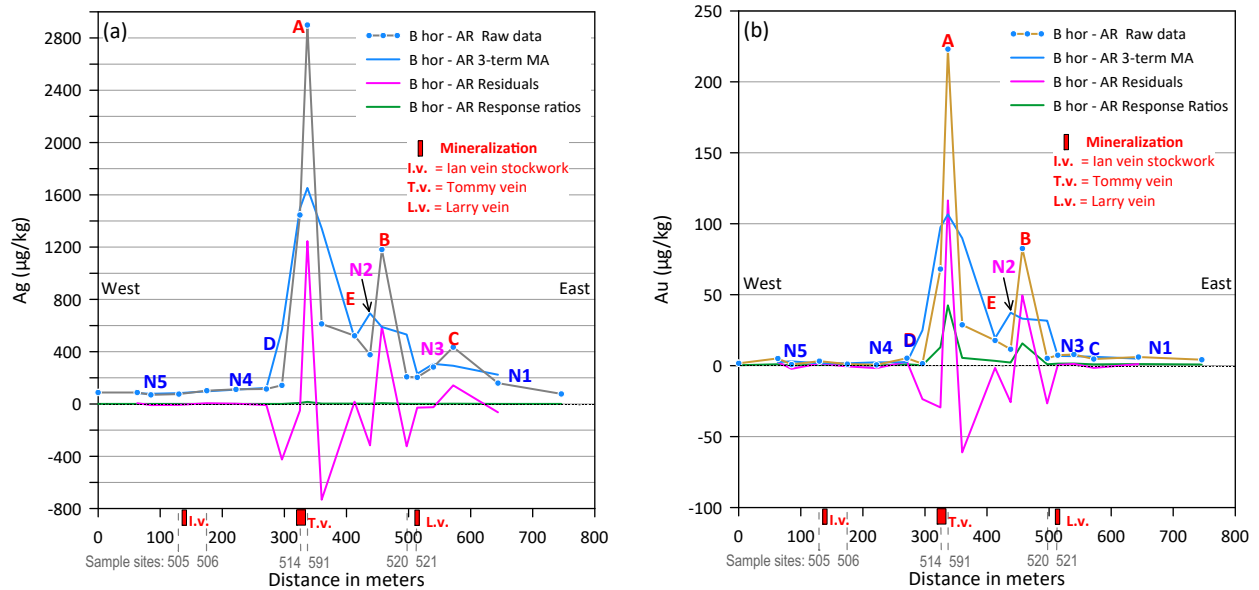


Fig. 17 Comparison of raw, 3-term moving average (MA) results, residuals, and response ratios of Ag and Au hot aqua regia (AR) concentrations in B horizon soil samples along the Tommy orientation traverse, 3Ts property, BC. It is noted that the response ratios line at this Y-scale is near to the zero line (see Fig. 13). Letter notation is the same as in Fig. 11: Red color letters denote weak to strong Ag and Au anomalous samples; blue color letters indicate subdued anomalous samples in relation to the raw data sections; magenta color letters (N2, N3) are anomalies exhibited in Fig. 11b. Plotted with Golden Software's Grapher™ v21.

- “B” anomaly to the west of the Larry vein is denoted by (i) strong AR Ag, weak AR Au, and weak Na pyrophosphate Ag in LFH humus samples; (ii) strong FA Au, moderate AR Ag and Au in B horizon soil samples. The MMI Ag results in B horizon soil samples show slightly elevated values between the Tommy and Larry veins, and MMI Au a very weak increase at site “B”.
- “C” anomaly to the east of the Larry vein is described only by AR Ag in LFH humus, AR and MMI Ag in B horizon soil samples.
- “D” anomaly to the west of the Tommy vein is marked only by a weak AR Ag in LFH humus, and very weak AR Au in B horizon soil samples.

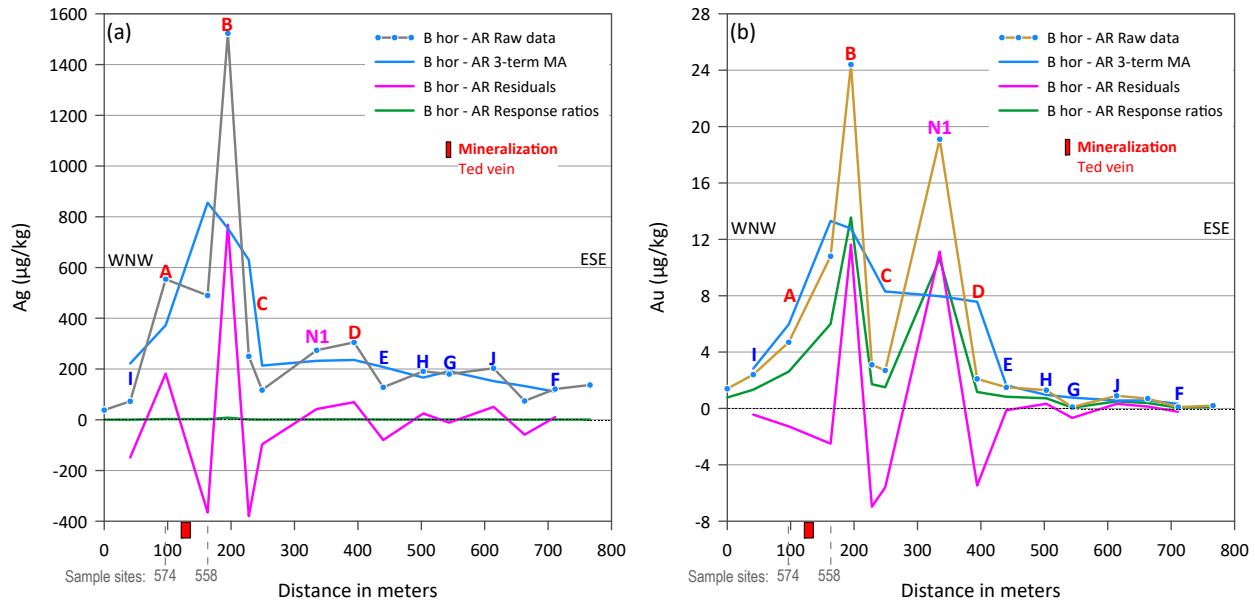


Fig. 18 Comparison of raw, 3-term moving average (MA) results, residuals, and response ratios of Ag and Au hot aqua regia (AR) concentrations in B horizon soil samples along the Ted orientation traverse, 3Ts property, BC. Letter notation is the same as in Fig. 12: Red color letters denote weak to strong Ag and Au anomalous samples; blue color letters indicate subdued anomalous samples in relation to the raw data sections; magenta color letter (N1) is the anomaly exhibited in Fig. 12b. Plotted with Golden Software's Grapher™ v21.

- “E” anomaly to the east of the Tommy vein is revealed only by AR Ag in C horizon till samples, while Au shows a rising trend with respect to AR and FA in C horizon till samples. The MMI Ag results in B horizon soil samples exhibit a weak increase from the Tommy vein, reaching a gentle peak at “E” and “B”, and then a decreasing trend towards the Larry vein.

The following weak anomalous patterns are displayed only by Au (Fig. 11b):

- “N1” anomaly to the east of the Larry vein is displayed only by FA Au in B horizon soil samples.
- “N2” and “N3” anomalies to the west and east of the Larry vein, respectively, are exhibited by AR and FA Au in C horizon till samples.
- “N4” anomaly to the west of the Tommy vein is marked by a weak FA Au in B horizon soil, and a very weak FA Au in C horizon till samples, and
- “N5” anomaly to the west of the Ian vein is denoted only by FA Au in C horizon till samples.

Fig. 12a and b show the raw Ag and Au distribution, respectively, along the Ted soil orientation traverse. The Ag and Au anomalous patterns coincide at the following sites:

- “A” anomaly displayed by AR Ag in LFH humus samples is over the Ted vein (sample sites 574 to 558), and extends to the ESE, encompassing the “B” anomaly. Gold shows a weak anomaly (site 574), which is described by Na pyrophosphate and AR in LFH humus samples, and an almost imperceptible rise in the MMI signal in B horizon soil samples.
- “B” anomaly to the ESE of the Ted vein is marked by AR Ag and Au in B horizon soil and C horizon till samples, MMI Ag and Au in B horizon soil samples, as well as by FA Au in B horizon soil and C horizon till samples.
- “C” anomaly further to the ESE of the Ted vein is displayed by AR Ag in LFH humus, AR (strong) and FA (weak) Au in C horizon till samples.
- “D”, “E” and “G” anomalous patterns still further ESE of the Ted vein are marked only by AR Ag in LFH humus samples.
- “F” anomaly is interesting as it is displayed by AR Ag in LFH humus samples, whereas with respect to Au the anomaly is exhibited by AR in C horizon till samples. The latter is described as an *open anomalous* Au pattern, meaning that it should be further investigated by extending the traverse to the ESE in order to locate the point at which the values fall to background.
- “H” anomaly is displayed only by AR Ag in C horizon till samples.
- “I” anomaly to the WNW of the Ted vein is marked by AR and FA Au in C horizon till samples, while Ag shows an elevated value in AR LFH humus samples.
- “N1” to the ESE of the Ted vein is a new anomaly displayed only by AR Au and FA in B horizon soil samples (Fig. 12b).

It is noted that the Enzyme leach method on B horizon soil samples did not show any anomalies.

Cook and Dunn (2006b), apart from plotting geochemical cross-sections, using the raw Ag and Au data, plotted geochemical cross-sections by using response ratios to enhance the anomalous patterns, and to subdue background variation. The Ag and Au response ratios are calculated by dividing the actual element concentration in each soil sample by the corresponding median of the combined results of Tommy and Ted orientation traverses (Figs. 13 and 14). They assumed that the median represents the geochemical background, which means that 50% of the sample values are considered as background.

So, *what does a response ratio mean?* A response ratio of 1 indicates a sample concentration at the median, or 50th percentile, of the different Ag and Au datasets; a response ratio of four implies a concentration of four times the median, regardless of the absolute magnitude of the concentration.

Is this an acceptable approach? During the processing of geochemical data, any logical approach is acceptable as long as it is explained, and its limitations are stated. This is, of course, a simplistic approach and a misconception, because the geochemical background is a range, and not a single value, in this case the median. Geochemical background is defined as “*the non-anomalous concentration range of an element or element combination in a particular sample type in a particular environment as measured on a particular grain size by a particular analytical technique*”.

As has already been pointed out, every rock type is characterized by different elements and, thus, has its own geochemical background variation and, of course, these characteristics are transferred to residual soil developed directly over bedrock (see Fig. 1). During the mineralization event, the neighboring rock types are affected to a variable degree, depending on their physicochemical characteristics and distance from the ore deposit. Consequently, the original background variation is modified by mineralization.

The main disadvantage of response ratios is that subtle geochemical anomalies, with values below the median of the studied element, will be undetected. Therefore, the response ratio technique should not be used at all, or if used it should be done with utmost care, and in combination with the results of other methods as described below.

In the case of the Tommy and Ted orientation traverses, plots of Ag and Au response ratios of aqua regia results appear to enhance the anomalies over the vein mineralization (Tommy and Ted veins). Anomalous patterns occur to the west of the Larry vein and to the east of the Ted vein. Although the response ratios have enhanced anomalies (Figs. 13 and 14), they have subdued some minor anomalies, which are displayed by the raw data (Figs. 11 and 12). Hence, the response ratios are after strong anomalies.

Are there any other plotting techniques that can be used in the processing of geochemical data along traverses? Of course, there are other plotting techniques that can be used for the processing of analytical results along pegged traverses in the attempt to enhance the anomalous pattern. One such technique is moving average (or rolling or running average), which smooths the ‘noise’ and emphasizes the trends. Depending on the number of sample sites along a traverse, a 3-term or a 5-term or a 7-term moving average (MA) can be used. The disadvantage of the moving average technique is that values at the beginning and end of the traverse are lost, i.e., the first and last value of the 3-term MA, the first and last two values of the 5-term MA, and the first and last three values of the 7-term MA. As is the usual case, the orientation traverses should extend well into background areas, so the loss of the first and last sample values does not cause any problems in the interpretation. Table S10 shows the calculation of the 3-term MA of Ag and Au aqua regia concentrations along the Teddy and Ted orientation traverses, and the estimation of residuals. Residuals are calculated by subtracting the result of the 3-term MA from the actual element concentration, and as expected in some cases there are negative values.

Plots of 3-term moving average for aqua regia extractable Ag and Au in samples of LFH humus, B horizon soil and C horizon till were plotted (Figs. 15 and 16). It is quite apparent from the 3-term moving average lines that the variable geochemical background of Ag and Au can be better defined. With respect to Ag, the LFH humus aqua regia results appear to have a better contrast than the B horizon soil and C horizon till samples for both the Tommy and Ted orientation traverses (Figs. 15 and 16). While for Au there are distinct differences, namely the Tommy traverse shows a better contrast for the aqua regia extractable B horizon soil samples, and the Ted traverse for the C horizon till samples. The aqua regia Au LFH humus 3-term moving average line is completely subdued in the Tommy and Ted traverses (Figs. 15b and 16b).

By studying the patterns of the 3-term moving average in Figs. 15 and 16, *can you see a feature that can be related to Fig. 1?* The Ted vein 3-term moving average lines show this feature better (Fig. 16). It appears that the secondary dispersion pattern of the aqua regia extractable Ag and Au concentrations along the Ted traverse start, in almost all sample media, at a distance of about 540 m and 400 m to the ESE of the Ted vein, respectively. The Ag and Au values increase gradually towards the Ted vein, and then drop at the end of the traverse. The Ag and Au anomalies at site “F” are open anomalies, suggesting the possibility of mineralization occurring to the ESE that should be investigated by extending the profile and, of course, collecting and analyzing new samples. The 3-term moving average lines of Ag and Au along the Tommy traverse (Fig. 15) display patterns over the Tommy and Larry veins, and the anomaly between the two veins.

If you now compare the Ag and Au patterns resulting from the response ratio (Figs. 13 and 14), and the 3-term moving average (Figs. 15 and 16) techniques, you will most likely prefer the latter.

Comparison cross-sections of the B horizon aqua regia Ag and Au results in samples of the Tommy and Ted orientation traverses were plotted showing the raw results, 3-term moving average, residuals, and response ratios (Figs. 17 and 18). The response ratios because of the linear Y-scale are not registering any visible patterns. This comparison shows that the 3-term moving average smooths out the “noise” and effectively defines the variable background. Fig. 17a and b display Ag and Au anomalies, respectively, over the Tommy vein, and to the west of the Larry vein. Fig. 18a and b show Ag and Au anomalies along the Ted traverse to the east of the Ted vein. In all cases, the residuals exhibit very well the anomalous patterns, especially the Ag and Au anomaly to the west of the Larry vein (Fig. 17), and to the ESE of the Ted vein (Fig. 18).

Geochemical maps

Geochemical maps show the spatial distribution of chemical elements and other physicochemical properties of natural sample media, such as rock, stream sediment, soil, floodplain or overbank sediment, vegetation, and even human tissues. Geochemical maps are in fact the end product of the systematic collection and processing of geochemical mapping surveys. Cook and Dunn (2006b) for the 3Ts property soil orientation survey plotted simple symbol type maps by using the combined Tommy and Ted traverse data to calculate six percentile ranges, i.e., minimum value to 25th, 25th to 50th, 50th to 75th, 75th to 90th, 90th to 95th, and 95th to maximum value. Here only the aqua regia extractable Ag and Au maps for the B horizon soil samples are shown (Figs. 19 and 20).

How are analytical data organized for plotting geochemical maps? The use of percentile range classes for plotting geochemical maps is quite common nowadays, because they are parameters of exploratory data analysis (Reimann et al., 2008). The advantage of percentiles is that the spatial distribution of determinands can be compared by using the same percentile levels. Percentiles for a given dataset can easily be calculated with Microsoft Excel[®]. However, for a thorough study of the spatial distribution, especially for mineral exploration purposes, the estimation of class ranges by using probability graphs is recommended (Cassie, 1954; Tennant and White, 1959; Williams, 1967; Lepeltier, 1969; Sinclair, 1974, 1976, 1983, 1986; Reimann et al., 2008). Although the recent trend is to use compositional data analysis in the statistical treatment of geochemical datasets (e.g., Aitchison, 1982, 1986, 1997, 2008; Egozcue et al., 2003; Aitchison and Egozcue, 2005; Buccianti et al., 2006; Reimann et al., 2012b; Filzmoser et al., 2014; Pawlowsky-Glahn and Buccianti, 2011; Pawlowsky-Glahn et al., 2015; Grunsky et al., 2018; Greenacre, 2018, 2021; Greenacre et al., 2021), well-established techniques should not be forgotten.

The probability or cumulative frequency plot is a powerful tool for the statistical treatment of the analytical results of continuous variables (or determinands or measurands), and their splitting into statistical populations. For example, the aqua regia concentrations of Ag and Au in B horizon soil samples of the combined Tommy and Ted orientation traverses vary from 38 to 2899 µg/kg Ag, and 0.10 to 223 µg/kg Au, respectively (Table S9). Hence, it is theoretically assumed that any intermediate value between these limits may occur in a soil sample. In contrast to continuous variables, there are those referred to as discrete, which are individually

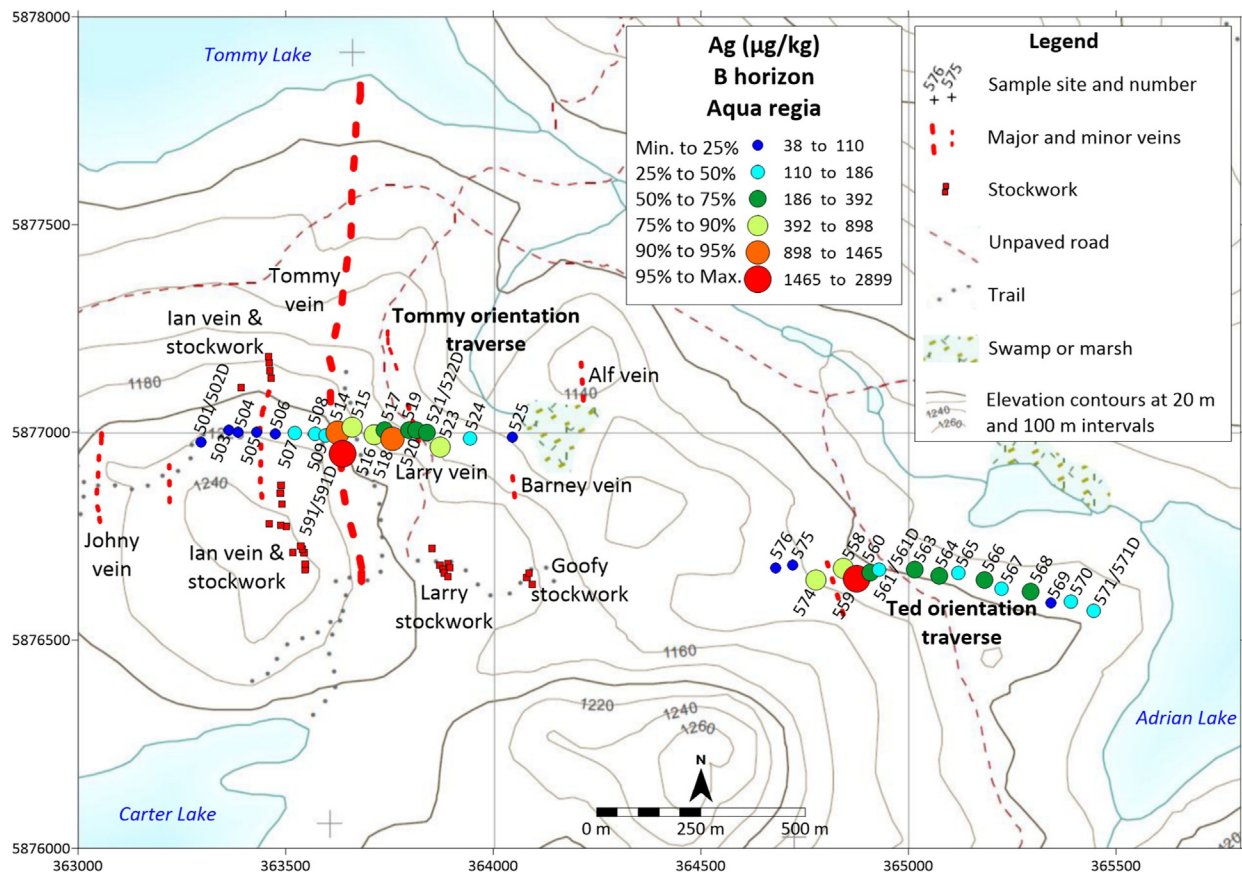


Fig. 19 Distribution of hot aqua regia extractable Ag in B horizon soil samples by using the combined data of the Tommy and Ted orientation traverses to estimate the percentile class ranges, 3Ts property, BC. Plotted with Golden Software's Surfer[™] v25. Data from Cook SJ and Dunn CE (2006b) *Final Report on Results of the Cordilleran Geochemistry Project: A Comparative Assessment of Soil Geochemical Methods for Detecting Buried Mineral Deposits - 3Ts Au-Ag Prospect, Central British Columbia*. Vancouver, BC: Geoscience BC, Open file Report 2007-7, 225 pp. Available at: <http://www.geosciencebc.com/reports/gbcr-2007-07/>; http://www.geosciencebc.com/i/project_data/GBC_Report2007-7/2007-7_Report.pdf; http://cmscontent.nrs.gov.bc.ca/geoscience/PublicationCatalogue/GeoscienceBC/GBCR2006-01-20_Cook.pdf.

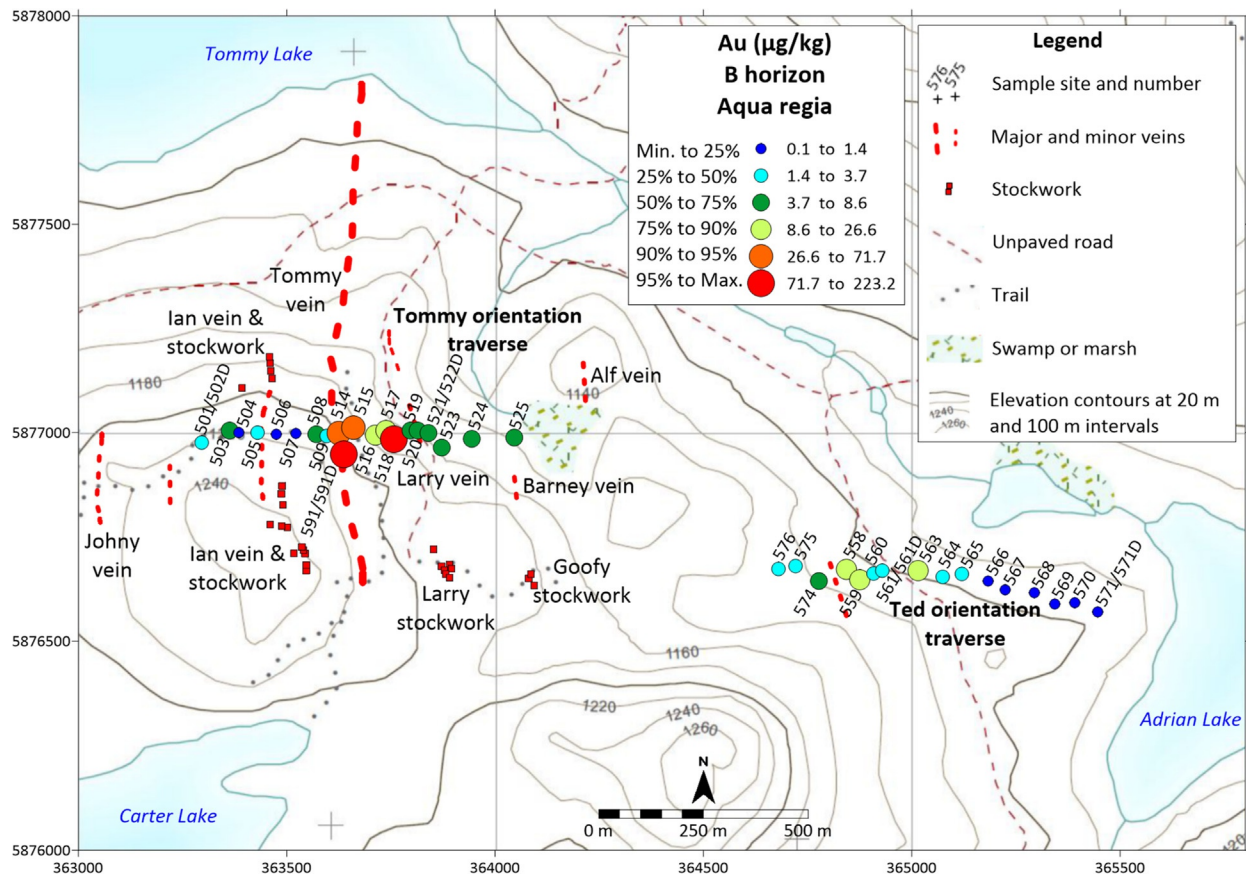


Fig. 20 Distribution of hot aqua regia extractable Au in B horizon soil samples by using the combined data of the Tommy and Ted orientation traverses to estimate the percentile class ranges, 3Ts property, BC. Plotted with Golden Software's Surfer™ v25. Data from Cook SJ and Dunn CE (2006b) *Final Report on Results of the Cordilleran Geochemistry Project: A Comparative Assessment of Soil Geochemical Methods for Detecting Buried Mineral Deposits - 3Ts Au-Ag Prospect, Central British Columbia*. Vancouver, BC: Geoscience BC, Open file Report 2007-7, 225 pp. Available at: <http://www.geosciencebc.com/reports/gbcr-2007-07/>; http://www.geosciencebc.com/i/project_data/GBC_Report2007-7/2007-7_Report.pdf; http://cmscontent.nrs.gov.bc.ca/geoscience/PublicationCatalogue/GeoscienceBC/GBCR2006-01-20_Cook.pdf.

distinct or are discontinuous. For example, the number of minerals in a polished section of an ore is a discrete variable, because the number of minerals in a given polished section may be 1, 2, 3, etc. minerals, but not 1.372 mineral types (Sinclair, 1976).

Fig. 21 displays the cumulative frequency or probability plots of aqua regia extractable concentrations of Ag and Au in B horizon soil samples of combined Tommy and Ted orientation traverses, which have been plotted on a \log_{10} -probability template. The distribution maps, using the class intervals, determined by the cumulative frequency plots, are shown in Figs. 22 and 23. If the Ag and Au percentile maps (Figs. 19 and 20) are compared with the cumulative frequency class intervals maps (Figs. 22 and 23), it will be observed that the anomalous patterns are better defined by the latter. Therefore, the proficient applied geochemist should use all the available tools for the statistical processing of geochemical data, and the subsequent plotting of the spatial distribution on maps.

What is the reason for using a \log_{10} -probability template in population splitting? The reason for using a \log_{10} -probability template is because geochemical data usually approach a log-normal distribution (e.g., Ahrens, 1954a, 1954b; Tennant and White, 1959; Lepeltier, 1969; Sinclair, 1974, 1976, 1983, 1986). As can be observed, the cumulative frequency % curve of Ag and Au is made up of straight-line sections and breaks or inflection points between the straight-line parts. Each straight-line section is assumed to define a distinct \log_{10} -normal population. The break between two adjacent straight-line sections, indicates the end of one population and the beginning of the next. The cumulative frequency plots of Ag and Au suggest the probable existence of 7 and 9 distinct populations, respectively. Of course, each population should be verified, using a rather tedious stepwise procedure. For this purpose, a simple worked example is given in Table S11, and the results plotted in Fig. 24. The interpretation of the three populations has already been presented in the geochemical section of Fig. 1.

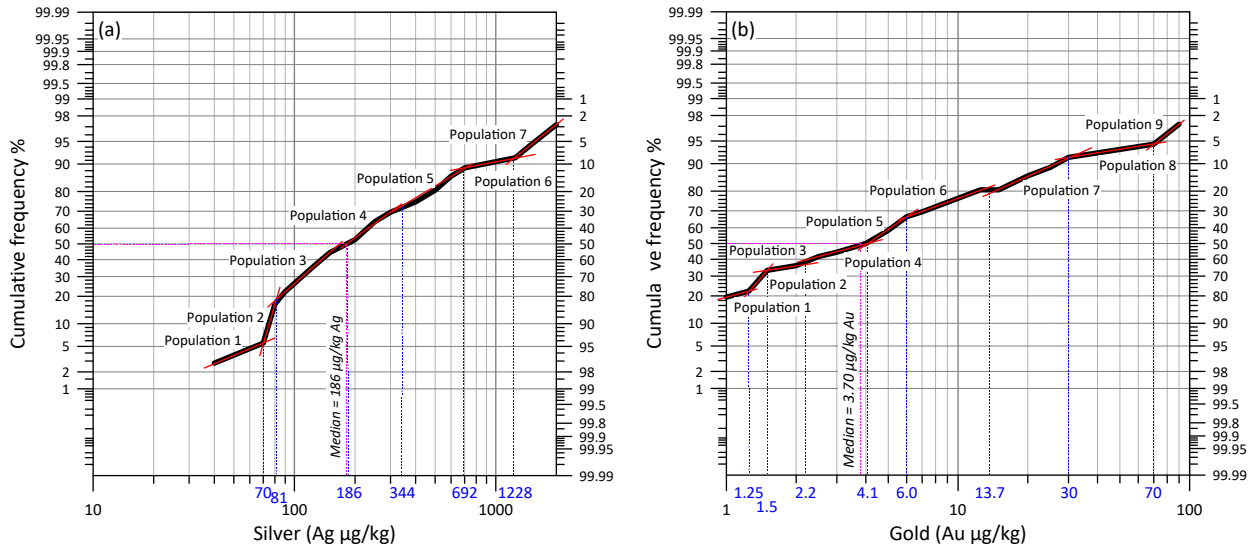


Fig. 21 Cumulative frequency (probability) plots of hot aqua regia extractable concentrations of (a) Ag and (b) Au in B horizon soil samples of combined Tommy and Ted orientation traverses, 3Ts property, BC. X-axis scale is in log (base 10), and Y-axis is in Probability %. The % cumulative frequency line is in black color, and the different straight-line segments, denoting possible populations, are marked by red lines. The breaks between each population are marked by blue dotted lines down to the X-axis, and the limits are given in blue color numbers. Plotted with Golden Software’s Grapher™ v21.

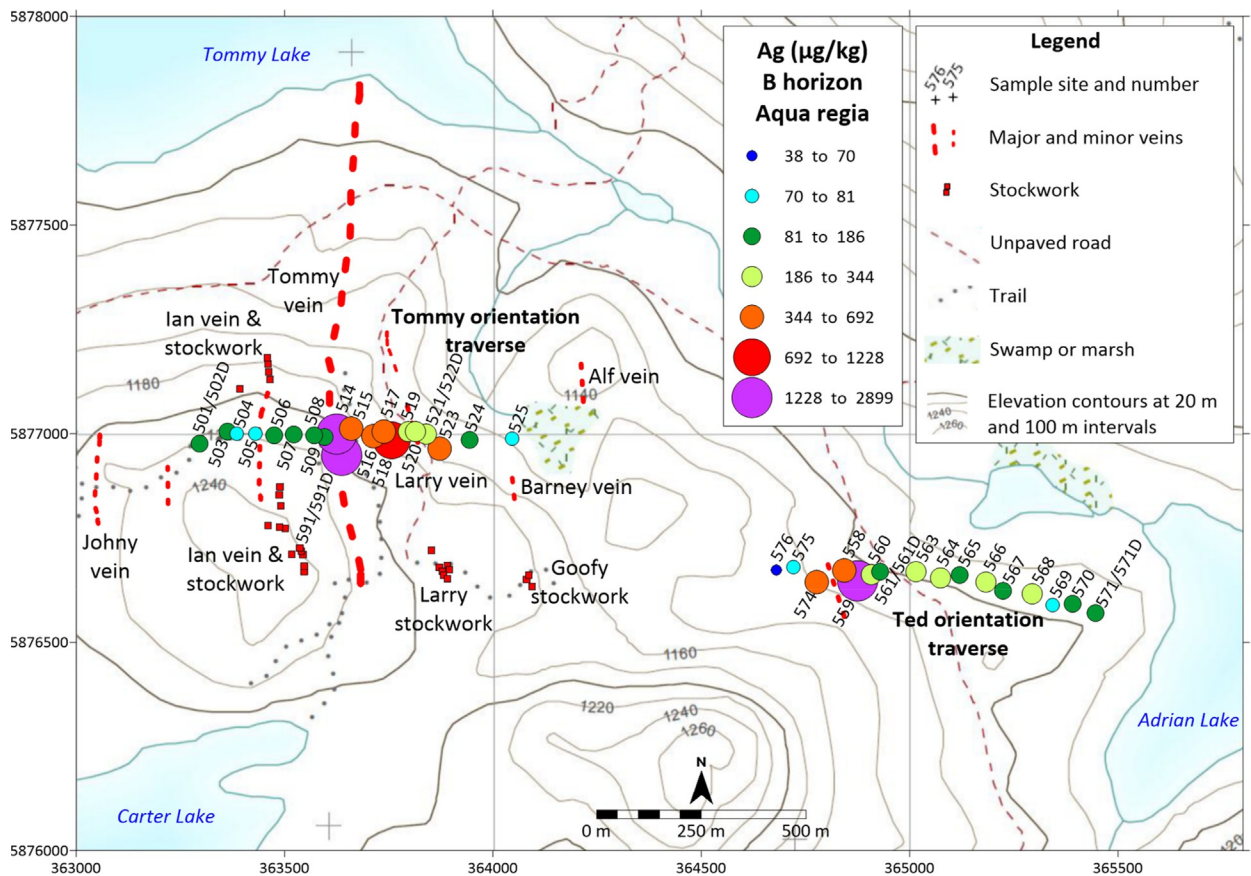


Fig. 22 Distribution of hot aqua regia extractable Ag in B horizon soil samples by using the combined data of the Tommy and Ted orientation traverses to estimate the class ranges by log₁₀-probability graphs, 3Ts property, BC. Refer to Table S9 in the online version at <https://doi.org/10.1016/B978-0-323-99762-1.00004-8> for basic statistics, and Fig. 21a for the log₁₀-probability distribution. Plotted with Golden Software’s Surfer™ v21. Data from Cook SJ and Dunn CE (2006b) Final Report on Results of the Cordilleran Geochemistry Project: A Comparative Assessment of Soil Geochemical Methods for Detecting Buried Mineral Deposits - 3Ts Au-Ag Prospect, Central British Columbia. Vancouver, BC: Geoscience BC, Open file Report 2007-7, 225 pp. Available at: <http://www.geosciencebc.com/reports/gbcr-2007-07/>; http://www.geosciencebc.com/i/project_data/GBC_Report2007-7/2007-7_Report.pdf; http://cmscontent.nrs.gov.bc.ca/geoscience/PublicationCatalogue/GeoscienceBC/GBCR2006-01-20_Cook.pdf.

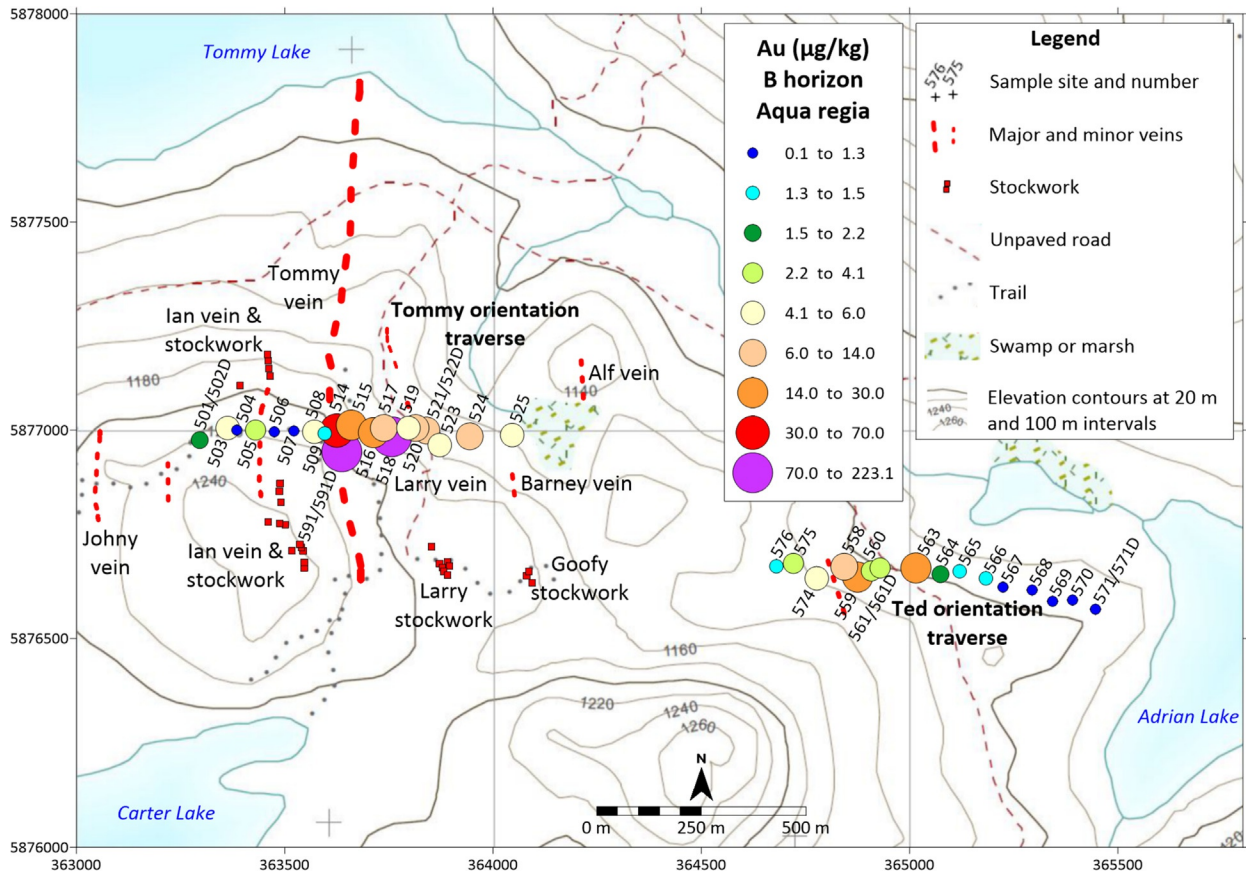


Fig. 23 Distribution of hot aqua regia extractable Au in B horizon soil samples by using the combined data of the Tommy and Ted orientation traverses to estimate the class ranges by \log_{10} -probability graphs, 3Ts property, BC. Refer to Table S9 in the online version at <https://doi.org/10.1016/B978-0-323-99762-1.00004-8> for basic statistics, and Fig. 21b for the \log_{10} -probability distribution. Plotted with Golden Software's Surfer™ v21. Data from Cook SJ and Dunn CE (2006b) Final Report on Results of the Cordilleran Geochemistry Project: A Comparative Assessment of Soil Geochemical Methods for Detecting Buried Mineral Deposits - 3Ts Au-Ag Prospect, Central British Columbia. Vancouver, BC: Geoscience BC, Open file Report 2007-7, 225 pp. Available at: <http://www.geosciencebc.com/reports/gbcr-2007-07/>; http://www.geosciencebc.com/i/project_data/GBC_Report2007-7/2007-7_Report.pdf; http://cmscontent.nrs.gov.bc.ca/geoscience/PublicationCatalogue/GeoscienceBC/GBCR2006-01-20_Cook.pdf.

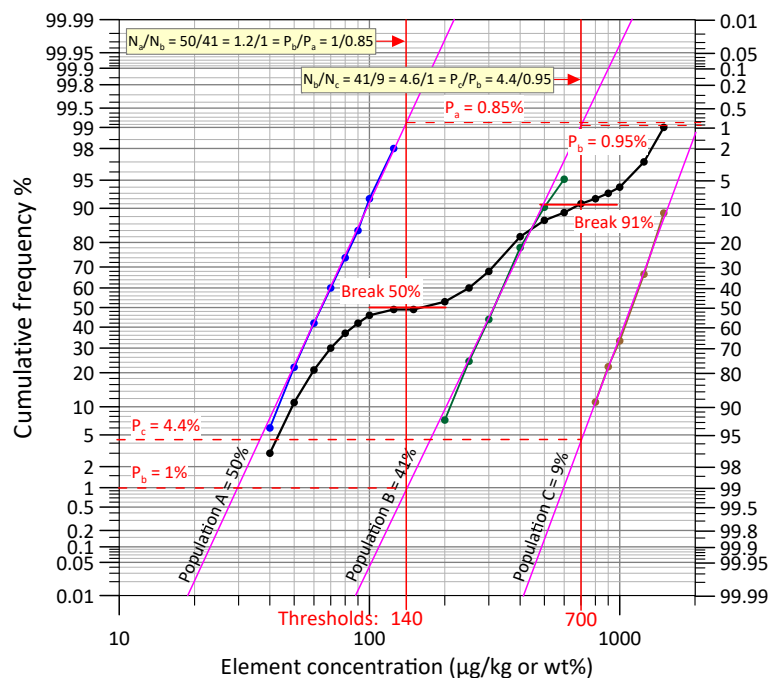


Fig. 24 An example of a partitioned \log_{10} -probability graph showing the % cumulative frequency curve (black color), the two breaks or inflection points, and the verification of the 3 populations by recalculation and plotting of the results which are aligned in a straight line, thus proving that the 3 populations are log-normal. Refer to Table S11 in the online version at <https://doi.org/10.1016/B978-0-323-99762-1.00004-8> showing the calculations, and to Fig. 1 for the interpretation. Plotted with Golden Software's Grapher™ v21.

Have the results of the soil orientation survey answered the questions posed?

Now let us see if the results of the soil orientation survey have answered the questions that have been posed, namely:

- (i) *Where and what should be sampled?*
- (ii) *Which analytical methods reflect the presence of buried mineralization, and which do not?*
- (iii) *Which of the methods provide the greatest and optimal geochemical contrast for property-scale exploration?*
- (iv) *Which of the methods delineate the occurrence of epithermal Au mineralization?*

The answers to the above questions, according to Cook and Dunn (2006b), are:

- (i) The orientation survey results suggest that B horizon mineral soil and LFH horizon organic-rich humus provide similar levels of geochemical contrast for hot aqua regia digestible Ag and Au, with the former sample medium giving a slightly better overall contrast. Hence, the recommendation is the collection of B horizon mineral soil samples, provided the samplers can distinguish the soil horizons. They recommend, however, that for regional reconnaissance sampling of till is the best choice, because of producing more comparable results, which are largely unaffected by soil forming processes. Note that in this case till is the C horizon.
- (ii) The Mobile Metal Ion and Enzyme leach methods, and particularly the base metals (Zn, Cu, Pb, Cd) provide a better geochemical contrast over known Au—Ag mineralization, because their contrast levels are superior to those of hot aqua regia digestion. Hence, these two methods may be suitable substitutes for aqua regia digestion and ICP-MS and ICP-OES finish.
- (iii) For the near-surface Au—Ag epithermal mineralization targeted in this study, the hot aqua regia digestion combined with ICP-MS multi-element analytical suite provides a more effective combination of (a) suitable geochemical contrast over the Tommy and Ted vein mineralization, and (b) a wide range of reported elements critical to epithermal Au—Ag deposits, including Au and Ag, precious metal pathfinders as, for example, As and Sb, and relevant base metals such as Zn, Cu, Pb and Cd.
- (iv) In general, the partial extraction analytical suites tested in this project provide most, but not all, of the key elements needed for the detection of epithermal Au—Ag deposits beneath soil and till cover. Some elements are lacking in the selective extraction suites, or if present are at concentrations below stated analytical detection limits; examples include As—Sb (MMI[®]-suite) and Ag—Au (EL suite). Positive aqua regia results are, however, strongly influenced by the relict lithological signature, in thin soil, of near-surface outcropping and subcropping of resistant quartz veins. The MMI[®], EL, SGH and SDP analytical methods might prove more useful than AR for detecting more deeply-buried deposits, where such inherited lithological signatures are not present in surface soil.

Reconnaissance geochemical survey

Which are the aims of a regional reconnaissance geochemical survey? The aims are:

- (i) To evaluate the mineral potential of an area hundreds to thousands of km² in size by delineating anomalous geochemical patterns, and
- (ii) To define the regional geochemical background values for each analyzed element (Fig. 25).

It is stressed that this phase is for selecting potential prospective areas, and not to locate a specific mineral deposit.

Which is the most common sampling medium used in reconnaissance geochemical surveys? The sampling medium that is commonly used is active stream sediment, though rock has been used as well, mostly in the former Soviet Union and Eastern Bloc countries (e.g., Beus, 1976; Beus and Grigorian, 1977; Földvári-Vogl, 1978; Koval, 1984; Chuman et al., 2013).

Regional stream sediment surveys are carried out at different sampling densities, depending on project objectives. As the results are going to be used for the potential resource evaluation of a region, and the establishment of national geochemical baseline element concentrations, collected samples should be analyzed for as many elements as possible. Currently, commercial laboratories offer packages of more than 50 elements. During the interpretation stage, at least three samples are required to define an anomalous pattern. Geochemical anomalies should be grouped in a priority order to be investigated by a follow-up stream sediment survey. Even single element and single sample anomalies should be listed but assigned a lower priority.

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 (Levinson, 1974, 1980; Beus and Grigorian, 1977; Govett and Nichol, 1979). 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.

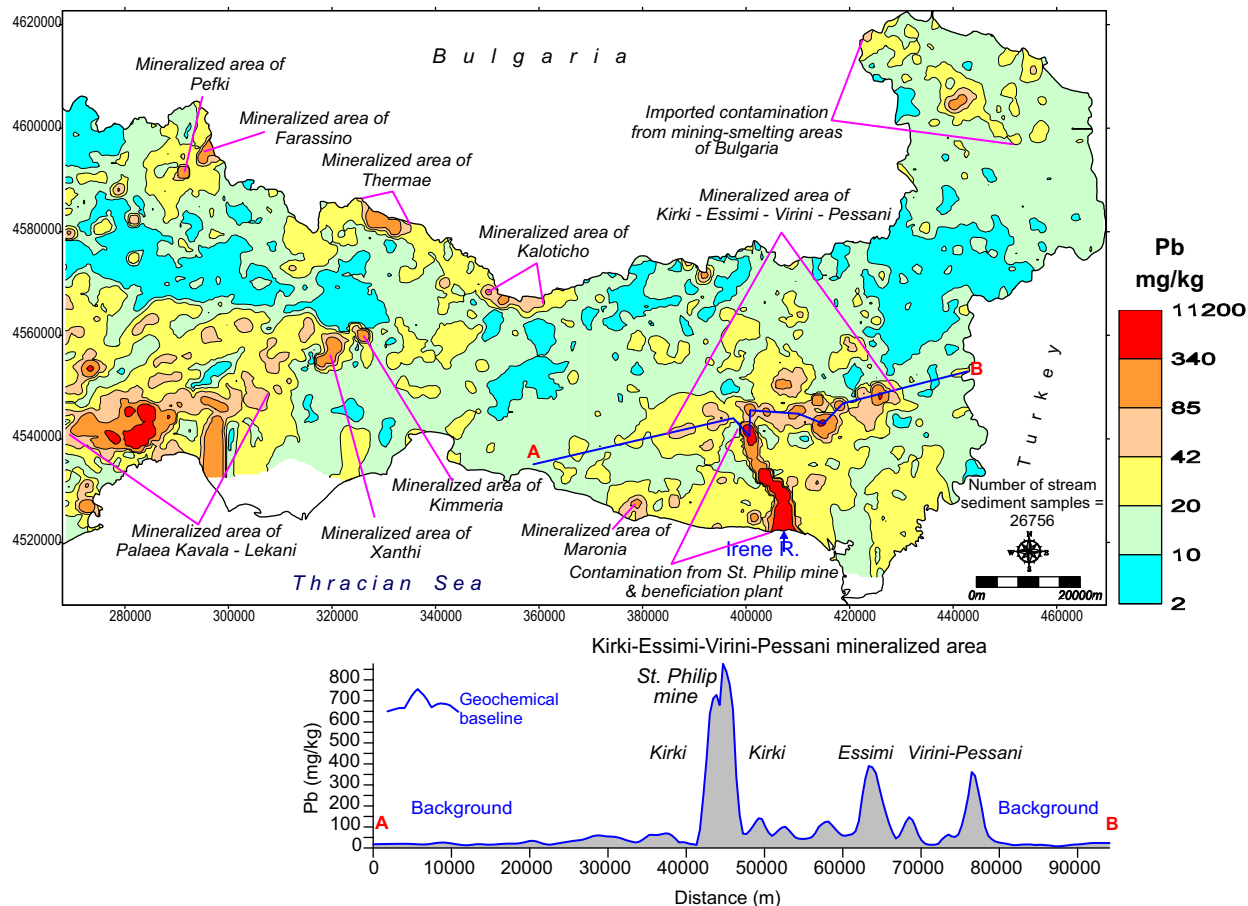


Fig. 25 Distribution of hot aqua regia extractable Pb in the <0.177 mm grain size fraction of active stream sediment, reconnaissance stream sediment survey of Eastern Macedonia and Thrace, Hellenic Republic, at an average density of 2 to 3 samples/ km^2 . The major polymetallic mineralized areas are indicated. The A-B geochemical section shows the background variation and anomalous patterns of Pb in mineralized areas. The Irene River anomalous train is caused by the St. Philip polymetallic sulfide mine and the ore beneficiation plant (see Fig. 26). Plotted with Golden Software's Surfer™ v25.

Fig. 25 shows the distribution of hot aqua regia extractable Pb in the <0.177 -mm grain size fraction of active stream sediment in Eastern Macedonia and Thrace (Hellenic Republic) at an average density of 2–3 samples/ km^2 (Table S12). The major Pb anomalous patterns related to polymetallic mineralized areas are indicated on the map. The A-B geochemical cross-section begins from background areas in the south-west and crosses the mineralized area of Kirki-Essimi-Virini-Pessani, with the pronounced anomaly over the St. Philip mine area, and the background areas to the north-east. Imported contamination from Bulgarian mining and smelting areas is indicated in the north-east part of the map.

The anomalous train along the Irene River, shown in Fig. 25, is caused by the activities at the St. Philip polymetallic sulfide mine and the ore-beneficiation plant (Fig. 26; Table S13). In order to better define the natural anomalous patterns of Pb, 30 contaminated stream sediment samples were removed from the database of the Irene River catchment basin. Apart from the Pb anomaly near the St. Philip mine, there are other anomalies to its south, and north-west of Essimi village. When plotting regional reconnaissance stream sediment maps, as shown in Fig. 25, it is strongly recommended to study the geochemical distribution of analyzed chemical elements within each catchment basin (Demetriades, 2008), because the anomalous patterns are better defined (Fig. 26).

The inset in Fig. 26 shows the distribution of Pb concentrations in different overbank sediment layers, which were sampled from a vertical section at the lowermost site of the Irene River outlet to the North Aegean Sea.

What does the geochemistry of individual overbank sediment layers show? Individual overbank sediment layers, deposited during different flood events, show that the top two layers have been affected by the mining and ore-beneficiation activities at the St. Philip mine, while the Pb concentrations in the lower three layers tend towards natural background (Fig. 26 inset). Hence, overbank

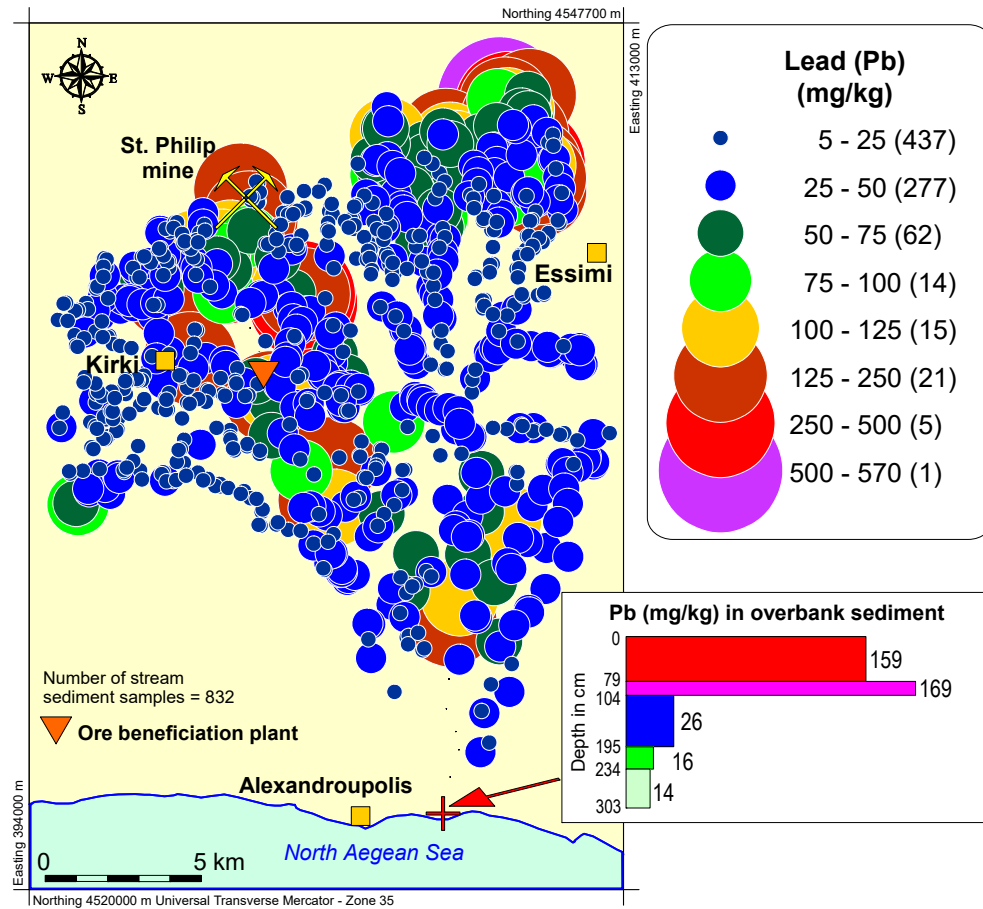


Fig. 26 Distribution of hot aqua regia extractable Pb in the <0.177 mm grain size fraction of active stream sediment, Irene River catchment basin, Thrace, Hellenic Republic (for its location see Fig. 25). The stream sediment samples contaminated by the St. Philip mine and ore beneficiation plant activities were removed in order to show the natural anomalies. The inset shows the distribution of Pb in the <0.063 mm grain size fraction of five overbank sediment layers. Plotted with Golden Software's MapViewer™ v8.

sediment can document the geochemical history of a drainage basin, provided that individual overbank sediment layers are sampled (Ottesen et al., 1989; Bølviken et al., 1996; Hindel et al., 1996; Swennen et al., 1998; Macklin et al., 2006; Demetriades, 2008; Adáñez-Sanjuán et al., 2021).

Follow-up geochemical survey

Which is the aim of a follow-up geochemical survey? The aim of a follow-up geochemical mapping survey is to define more precisely the potential mineralized area in order to carry out the costlier detailed survey. In fact, the follow-up active stream sediment survey, carried out along an anomalous segment of a stream, aims to define a cut-off point close to the source of the anomaly (Open University, 1972, Figs. 11–13, pp. 14–15; Rose et al., 1979, Fig. 14.22, p. 379; Levinson, 1974, Figs. 1–5, p. 20). Thus, by defining cut-off points on neighboring streams, the potential mineralized area is delimited precisely.

How and where is the follow-up geochemical survey planned and executed? Planning of the follow-up survey is based on regional reconnaissance results, and high priority areas are investigated first. The sampling media used are either active stream sediment at a higher sampling density, or residual soil or till at a wide sampling interval along wide-spaced traverses.

Fig. 27 (Table S14) displays the aqua regia extractable Pb in the <0.177 grain-size fraction of active stream sediment in the area of Virini-Pessani, which has been delineated by the reconnaissance stream sediment survey (Fig. 25). The variable-size dots show the Pb concentrations at each stream sediment sampling site. The color-surface defines the limits of the Pb anomalous areas. In this follow-up stream sediment survey, the average density was 17 samples/km².

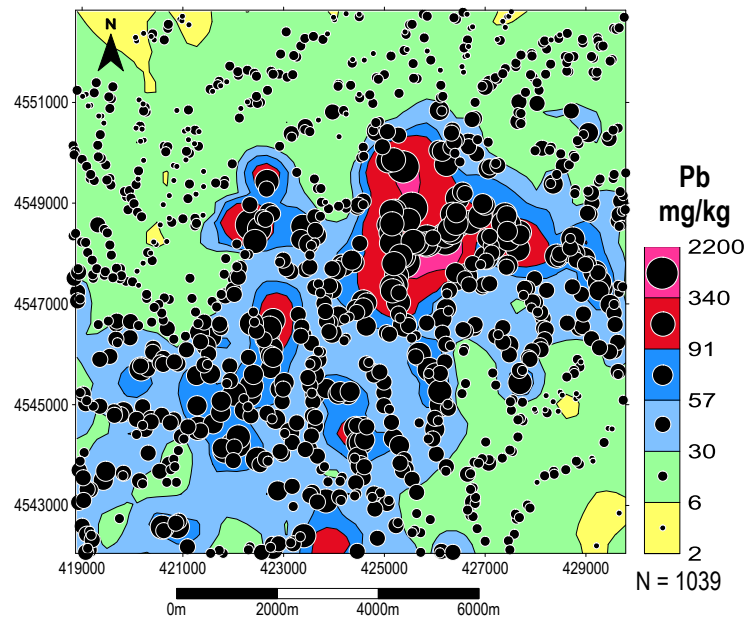


Fig. 27 Distribution of hot aqua regia extractable Pb in the <0.177 mm grain-size fraction of active stream sediment, follow-up stream sediment survey, Virini-Pessani area, Thrace, Hellenic Republic (for its location see Fig. 25). Plotted with Golden Software's Surfer™ v25.

Detailed geochemical survey

Where is the detailed geochemical survey carried out? 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 and geological (lithological and structural) mapping, ranging from a few km² to a few tens of km², with the objective of delineating, as precisely as possible, geochemical anomalies for evaluation by pitting, trenching, and drilling.

The detailed geochemical survey is the costliest phase of a geochemical investigation, and it is imperative to be planned effectively by designing the optimum sample layout to obtain reliable information. The purposes of the detailed rock and soil geochemical surveys for mineral exploration are concisely discussed below, and more extensively in exploration geochemistry textbooks (Hawkes and Webb, 1962; Levinson, 1974, 1980; Beus and Grigorian, 1977; Rose et al., 1979; Govett, 1983; Fletcher et al., 1986; Butt and Zeegers, 1992; Kauranne et al., 1992).

Detailed soil geochemical surveys are also carried out for environmental contamination purposes (i) in urban areas (refer to Johnson, 2011 and case studies therein), and (ii) over very small areas of a few tens of m² (factory and petrol station scale), with the aims of precisely delineating the contaminated and uncontaminated parts of the property or properties, and of estimating the volume of contaminated soil (Demetriades, 2014). An example of a detailed contaminated land investigation is discussed in Section "How is an applied geochemical survey organized for the assessment of contaminated land?" of this Chapter.

Detailed rock or soil geochemical survey

What is the objective of a detailed geochemical survey for mineral exploration purposes? The objective of a detailed geochemical survey using rock or residual soil or 'till' in glacial terrains is to locate precisely mineralized structures.

How is a detailed geochemical survey for mineral exploration purposes planned and executed? In most cases, a grid is laid over the prospective area, and systematic sampling of rock or soil or till is carried out along pegged traverses. Grid dimensions and orientation of the traverses depend on the estimated size of anomalous patterns, and the orientation of the mineralized structures, defined by the follow-up survey, geophysical data, or geological mapping. The requirement is at least three traverses to crosscut the concealed mineralization, and its area extent delimited by the rock or soil or till geochemical anomaly (Fig. 28). However, as pointed out above, even single element and single sample anomalies should be listed for further study but assigned a lower priority.

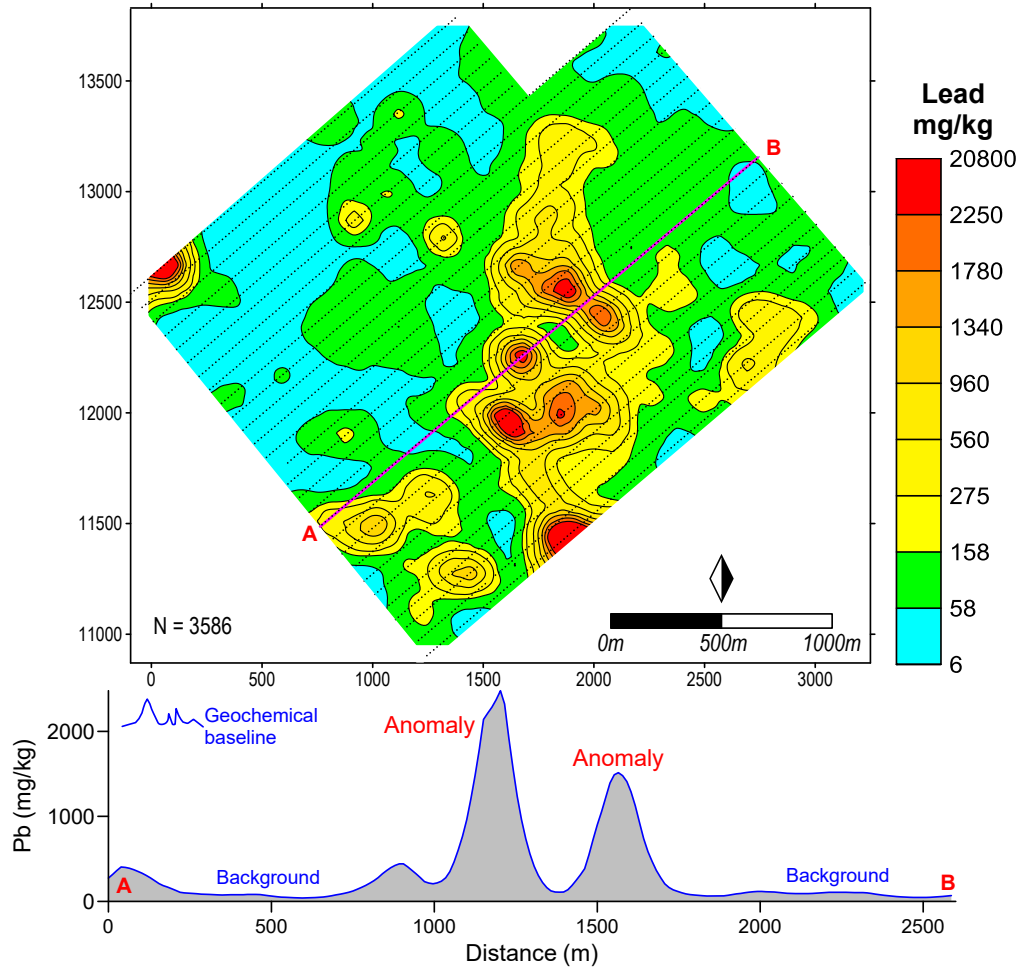


Fig. 28 Distribution of hot aqua regia extractable Pb in the <0.177 mm grain-size fraction of C-horizon soil, detailed soil geochemical survey, Thermae, Xanthi Prefecture, Thrace, Hellenic Republic (for its location see Fig. 25). The A-B geochemical cross-section shows the anomalous patterns, the variable background and geochemical baseline. Plotted with Golden Software's Surfer™ v25.

As has already been pointed out, survey costs are increased considerably from the regional reconnaissance to the follow-up and detailed geochemical stages. Compare the average sampling densities of the discussed geochemical surveys:

- (i) Regional reconnaissance stream geochemical survey at an average density of 2 to 3 samples/km² (Fig. 25).
- (ii) Follow-up stream sediment geochemical survey at an average density of 17 samples/km² (Fig. 27), and
- (iii) Detailed soil geochemical survey at an average density of 679 samples/km² (Fig. 28).

Fig. 28 shows the distribution of hot aqua regia extractable Pb in the <0.177 mm grain-size fraction of C horizon soil. The Pb anomalous patterns have been mapped in detail. Below the map, the A-B geochemical cross-section shows the background and anomalous patterns of Pb along one of the pegged traverses, as well as the geochemical baseline variation. Following the delineation of the anomalous patterns in the Thermae area, the next stage involved digging trenches down to a depth of approximately 2 m in order to examine the mineralization. Subsequently, few anomalies were investigated by diamond core drilling. Due to lack of funding, the mineral exploration effort in this area was terminated.

How is an applied geochemical survey organized for the assessment of contaminated land?

In the investigation of contaminated land, a stepwise approach is commonly followed, because it is the most cost-effective and efficient way to assess contamination. Fig. 29 is a flow chart representing a typical approach to a site or property investigation (BSI, 2005). The phased approach typically comprises:

1. *Preliminary investigation (desk study and walkover survey)*: The objective of the desk study and walkover survey is to determine if the property under investigation is posing an unacceptable risk to people or the environment, and to formulate a preliminary Site

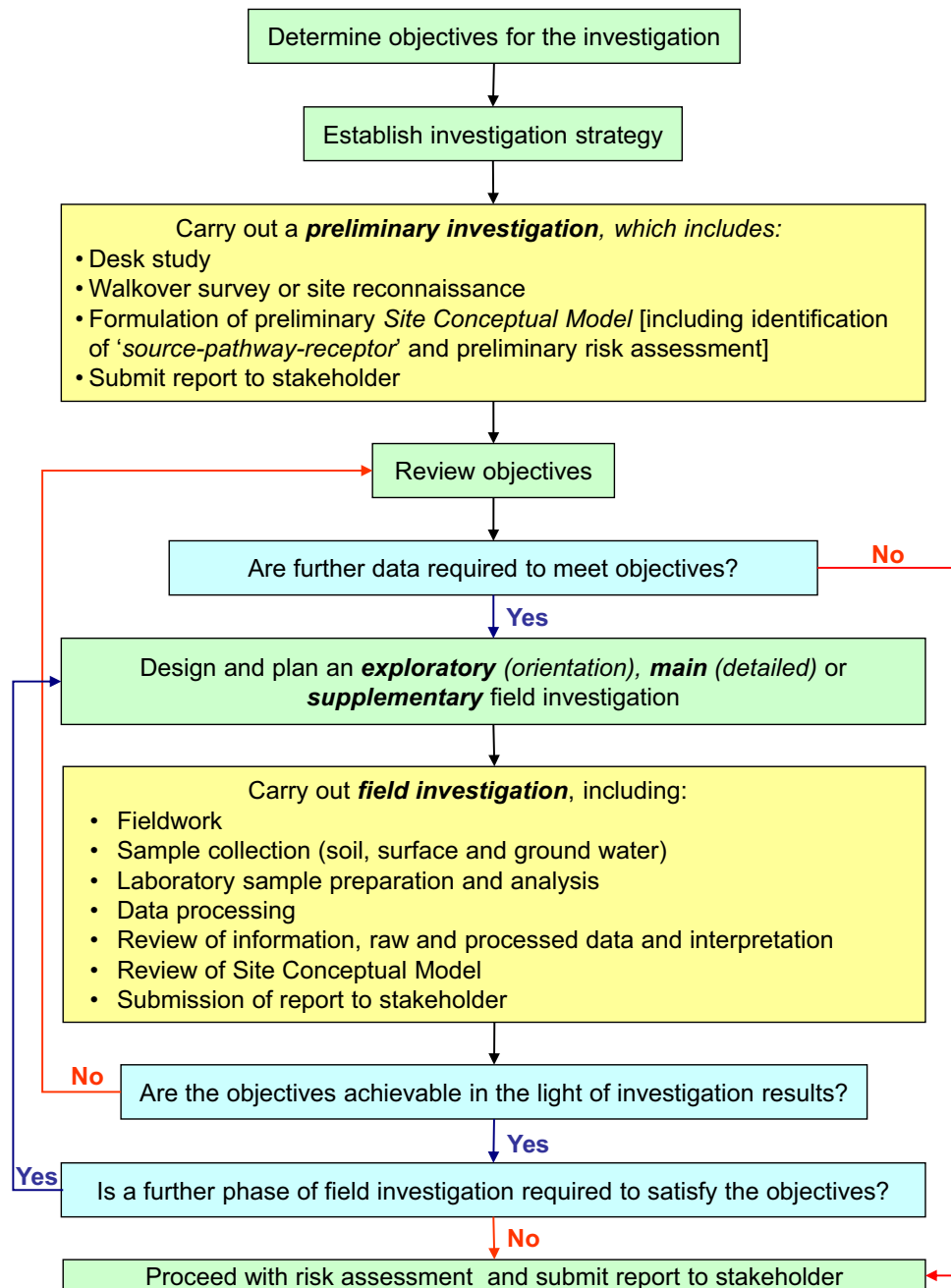


Fig. 29 Flow-chart showing a typical approach of contaminated land or property investigation, including the various stages of a stepwise phased investigation. It illustrates how data and information obtained at each stage is reviewed to determine if the investigation strategy requires modification, or the objectives have been met. The review process also enables the revision of the Site Conceptual Model (see Fig. S11 in Text S1 in the online version at <https://doi.org/10.1016/B978-0-323-99762-1.00004-8>), the requirements of risk assessment and the objectives of site or property investigation. Plotted with Microsoft 365 PowerPoint®. Modified from BSI (2005) *Investigation of Potentially Contaminated Sites – Code of Practice*. British Standard Institute, BS 10175:2001, 76 pp, Fig. 1, p. 7).

Conceptual Model, using the 'source-pathway-receptor' scenario (see Fig. S11 in Text S1; Demetriades, 2014). Essentially, a desk study involves a review of all available site-specific and historical information. Whereas a walkover survey is concerned with an inspection of the property and its vicinity for the collection of information about other potential contaminating activities, which may have a contribution in the contamination.

2. *Exploratory or orientation site investigation*: The aim is to collect site-specific data and information about the characteristics of the potential soil contaminating activities, to confirm the existence of soil contamination by collecting and analyzing soil samples from pits and trenches dug-up at different locations in the property under investigation, and to refine the Site Conceptual Model.

3. *Detailed or main site investigation:* The aims of the detailed site investigation are: (i) to define the level and extent of soil contamination over the whole property, and to examine if the contamination has affected groundwater; (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 contamination to actual receptors according to the end land use.

It is noted that implementation of remediation measures is outside the scope of this article.

Example of a contaminated land investigation

How is a contaminated land investigation tackled by a geochemical mapping survey? The answer lies in the objective of the property owner, and the specifications of the national environmental legislation. In this case study example, the property is a dry-cell battery factory that produced mercury-zinc batteries. Mercury batteries use either pure mercuric oxide or a mixture of mercuric oxide with manganese dioxide as the cathode, and the anode is made of zinc. The factory owner’s plan was to remediate the property and sell it to a contractor for building a housing estate. So, the objectives were to define (i) the three-dimensional extent of contamination, and to estimate the volume of contaminated soil that needed remediation, and (ii) if the groundwater was contaminated and to what extent. In this case study example, only the surface soil results will be presented and discussed.

The information provided by the property owner was that the factory operated for about 20 years, before it was closed down and turned into a temporary storage depot. The whole property was situated on the alluvial plain of the local river, and had a shallow water well.

Since the industrial site was going to be remediated and used for housing, an orientation soil survey was carried out first by testing different square block dimensions to arrive at the optimum block size of 25 × 25 m for covering the property, and each block given a random sample number (Fig. 30). Further, the thickness of the surficial alluvial soil horizon was also examined by digging pits at a number of sites. This was an essential test to ensure that the surface horizon was sampled at all sampling sites.

What is the reason for using a block for sampling? The decision for selecting a block for the geochemical mapping of this property was that the owner intended to remediate the contaminated soil before selling it, according to the national legislation in force. Hence, defining the blocks that were contaminated was considered to be the optimum cost-effective procedure.

How was the soil sampling carried out? A composite surface sample (0–20 cm) was collected with an auger of 1.5 in. diameter (3.81 cm) from five locations, i.e., the four corners of each square block, and the fifth location was randomly selected within each block of 25 × 25 m. The soil sample from the corners of each square block was split into four equal portions, and placed in the

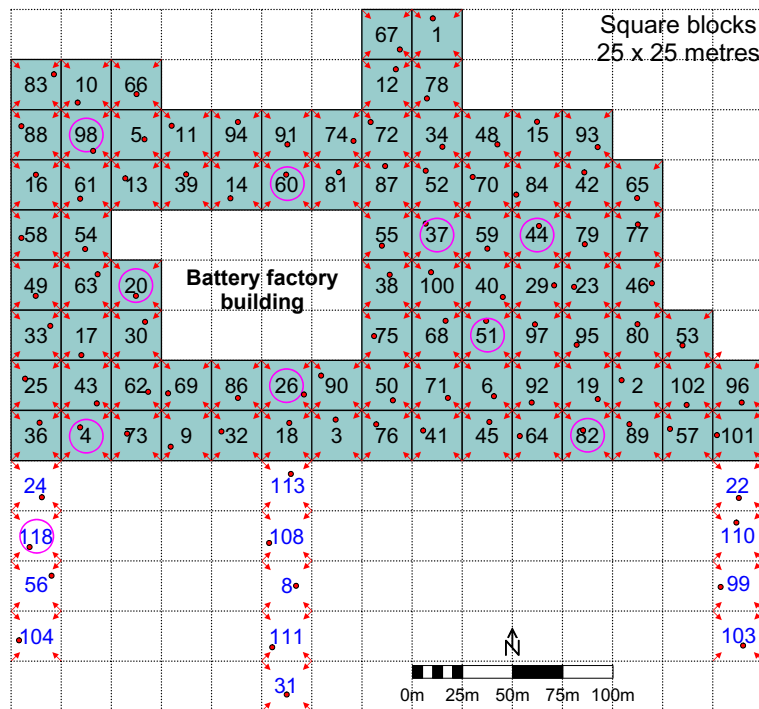


Fig. 30 Map showing the square block sampling scheme over the battery factory property. Each square block has been given a random number for the sampling, and the 10 duplicate field samples were again randomly selected and are indicated by magenta color circles. The composite soil samples were collected from the four corners of each block, and the fifth sampling site (red dot with black rim) was randomly selected within each square. The red arrows at the corner of each square block show how each corner soil sample was split into equal portions and placed in the sampling bag of the neighboring square block. The blue color sample numbers show the soil samples collected outside the factory property. Plotted with Golden Software’s MapViewer™ v8.

sampling bag of the neighboring square block, and the fifth sampling site was randomly selected within each block. By using this rolling sampling scheme, there was a relationship among adjacent square blocks, and the difference was made by the random sample collected within each square block.

In total, 102 routine composite surface soil samples were taken, and 10 field duplicate soil samples, which were collected from a single spot within each square block. The auger was very thoroughly cleaned before taking the next soil sample. The average weight of each sample was 1.5 kg. As shown in Fig. 30, the soil samples were collected in a random order and analyzed in a consecutive number sequence.

How was the quality of the analytical results achieved? As this is a small geochemical survey, the quality of analytical results relied on (i) the duplicate-replicate analyses of field quality control samples using a balanced ANOVA design (Fig. 31), (ii) the commercial laboratory's reference samples, (iii) method blank samples, and (iv) the repeated analysis of the 10th sample in each analytical batch.

How were the samples prepared and analyzed? In the commercial laboratory, the samples were dried at a temperature of $<35^{\circ}\text{C}$ in thermostatically controlled ovens. The reason for drying the samples at this temperature is that Hg can be lost at higher temperatures. After drying, the soil samples were disaggregated with a porcelain mortar and pestle and sieved through a 0.177 mm nylon screen. An aliquot of 4 g weight of the <0.177 mm grain size of each sample was digested by aqua regia, and Ca, Cd, Co, Cu, Fe, Hg, Mg, Mn Ni, Pb, Sb, Zn were determined by double-beam atomic absorption spectrophotometry (AAS). While As and Sb were determined via hydride generation, and Hg by flameless AAS.

What should be the first step upon receiving the analytical results from the laboratory? Upon receipt of the analytical results, one must resist the temptation to start the computer processing of quality control data, or even the sample results. The first step is to visually study the quality control data, including replicate analyses, method blanks and certified reference sample results. It is important to know your data, and to understand the variation, if it exists. This is an incredibly significant key step that is normally overlooked. In this case study example, during the visual quality control check of the analytical data, it was found that the laboratory analyzed Hg with reagents contaminated by mercury, i.e., the reagent blanks had values in the order of $50\ \mu\text{g}/\text{kg}$ Hg (see Table S16). Hence, all the Hg analyses were not acceptable.

How should the professional applied geochemist react in this situation? As the laboratory results are unacceptable the laboratory was asked to reanalyze all the samples and to bear the cost.

How was the reanalysis of the samples achieved? Prior to sending the samples for analysis to a commercial or an institutional laboratory, a contract must be signed with the condition that if the analytical results do not meet the required quality, the laboratory will be obliged to reanalyze batches or the whole sample suite, and to bear the cost of reanalysis. This is an important safety precaution, otherwise the applied geochemist will be exposed to severe criticisms for not anticipating such problems. In this case study example, however, there was in the contract the condition that if the analytical results were not of acceptable quality, the commercial laboratory was obliged to reanalyze them and bear the cost. Hence, the laboratory has undertaken to reanalyze all samples a second time with improved lower detection limits, i.e., for Hg at $10\ \mu\text{g}/\text{kg}$, and most importantly with reagents that were certified as Hg free.

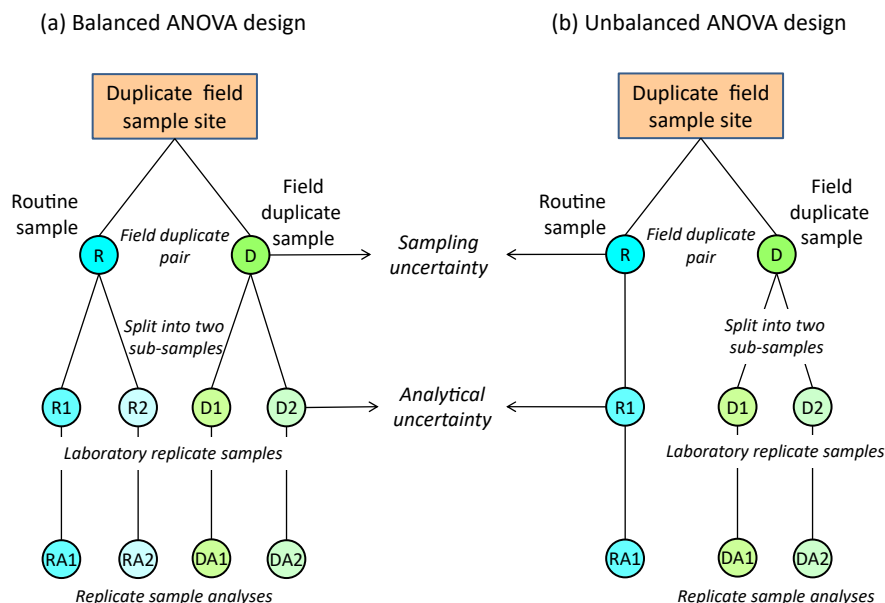
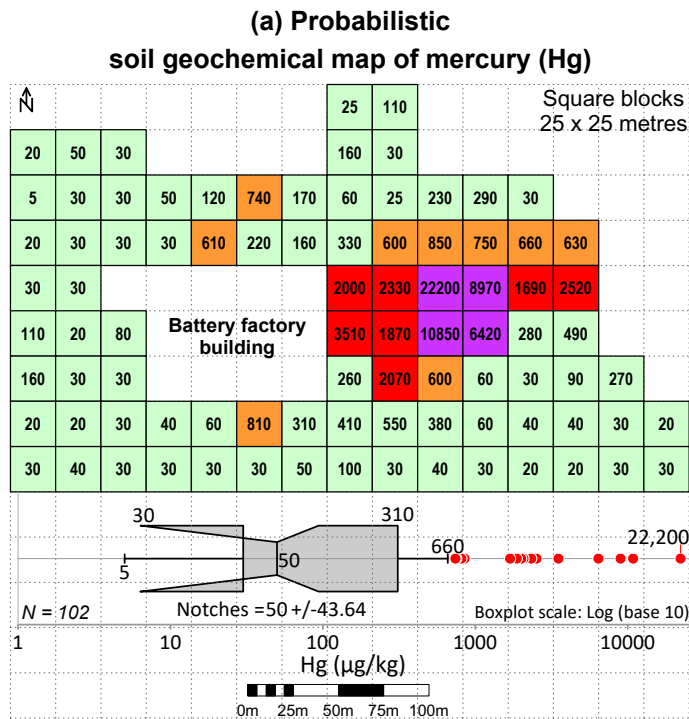


Fig. 31 (a) Balanced and (b) unbalanced ANOVA sampling and analytical designs for the estimation of sampling, analytical and geochemical variance, and measurement uncertainty. Plotted with Microsoft® 365 PowerPoint.



Using the "short-cut" method the uncertainty is expressed on the threshold value of 1000 µg/kg Hg, i.e.,

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

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

Mercury (µg Hg/kg soil)
Contaminated:
4263 to 22,200

Expanded uncertainty at the 95% confidence level is
 $U\% = 76.54\%$
 $U = 76.54/100 = 0.7654$

Probably contaminated:
1000 to 4263

Probabilistic classification is calculated by:

Possibly contaminated:
566 to 1000

Contaminated:
 $C = T + U$ or $C - U = T$
 $C - 0.7654 \cdot C = 1000$
 $0.2346 \cdot C = 1000$
 $C = 4263 \mu\text{g/kg Hg}$

Uncontaminated:
5 to 566

Uncontaminated:
 $C = T - U$ or $C + U = T$
 $C + 0.7654 \cdot C = 1000$
 $1.7654 \cdot C = 1000$
 $C = 566 \mu\text{g/kg Hg}$

Fig. 33 (a) Probabilistic risk assessment geochemical map showing how the results of the balanced quality control design of duplicate field sampling were used to estimate measurement uncertainty, and to classify the blocks into (i) uncontaminated, (ii) possibly contaminated, (iii) probably contaminated, and (iv) contaminated using the guideline value of 1000 µg/kg Hg as threshold. Map and notched-boxplot plotted with Golden Software's MapViewer™ v8 and Grapher™ v21, respectively. Modified from Demetriades A (2011b) 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, Ottesen RT (eds.), *Mapping the Chemical Environment of Urban Areas*, pp. 77–98. Chichester, UK: John Wiley & Sons Ltd. doi: 10.1002/9780470670071.ch6, Fig. 6.5, p. 91.

The second and third types are probabilistic maps (Figs. 33 and 34), which use the estimated relative expanded measurement uncertainty and expanded uncertainty factor at the 95% confidence level, respectively, to define four class intervals: uncontaminated, possibly contaminated, probably contaminated, and contaminated.

- (ii) Possibly contaminated
- (iii) Probably contaminated, and
- (iv) Contaminated.

How are the class intervals of Hg concentrations estimated? The programs ROBCOOP4 (Ramsey, 1998), RANOVA (Rostron and Ramsey, 2012), ROBCOOP4A (Vassiliades, 2022) and any other robust ANOVA program can process the quality control data, and provide the required class intervals of Hg concentrations in soil. In this case study, the ROBCOOP4A program was used. The output of the ROBCOOP4A program is tabulated in Table S17 together with equations for understanding the computations leading to the classification of soil into:

- (i) Uncontaminated
- (ii) Possibly contaminated
- (iii) Probably contaminated, and
- (iv) Contaminated.

In order to understand the contribution from sampling and chemical analysis to the total measurement uncertainty the following calculations can be made:

- Proportion of robust expanded relative measurement uncertainty, u , caused by sampling = $(s_{\text{samp}}^2/s_{\text{meas}}^2) \times 100 = (107.9/108.2) \times 100 = 99.72\%$, and
- Proportion of robust expanded relative measurement uncertainty, u , caused by analysis = $(s_{\text{anal}}^2/s_{\text{meas}}^2) \times 100 = (8.91/108.2) \times 100 = 8.23\%$.

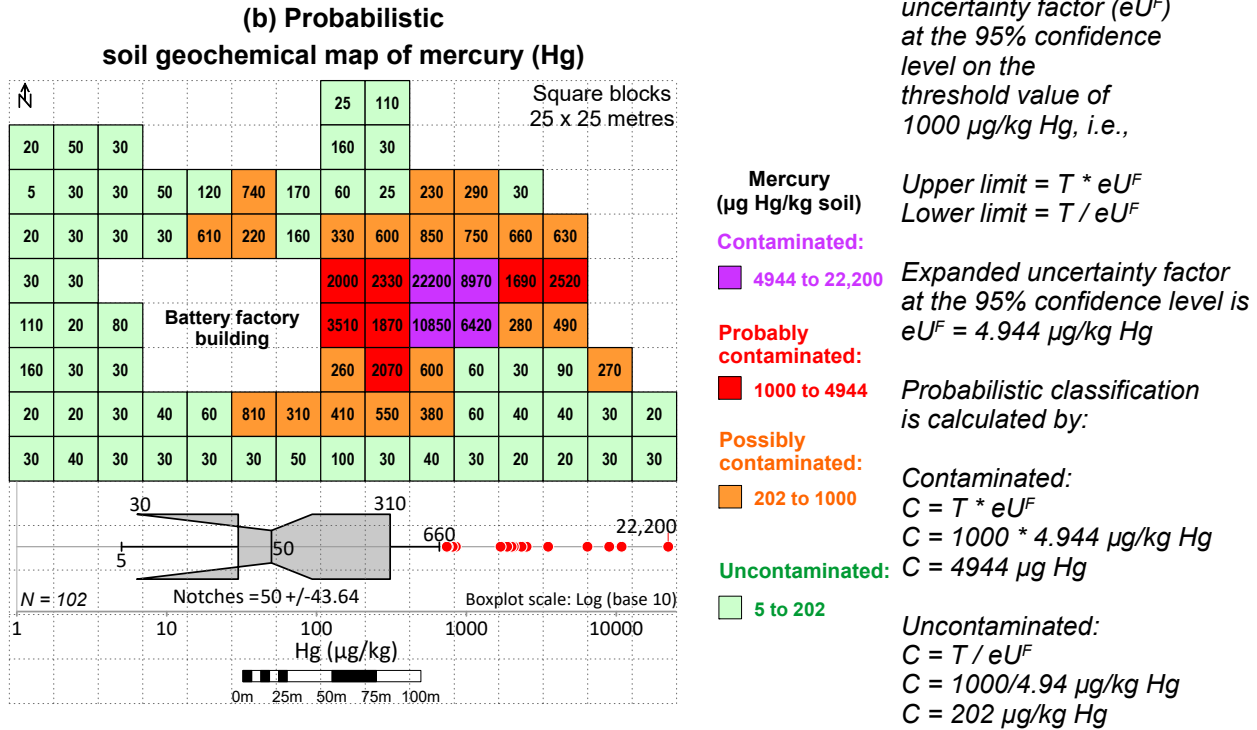


Fig. 34 (b) Probabilistic risk assessment geochemical map showing how the results of the balanced quality control design of duplicate field sampling were used to estimate the expanded uncertainty factor (eU^F), and to classify the blocks into (i) uncontaminated, (ii) possibly contaminated, (iii) probably contaminated, and (iv) contaminated using the guideline value of 1000 µg/kg Hg as threshold. Map and notched-boxplot plotted with Golden Software’s MapViewer™ v8 and Grapher™ v21, respectively. Modified from Demetriades A (2011b) 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, Ottesen RT (eds.), *Mapping the Chemical Environment of Urban Areas*, pp. 77–98. Chichester, UK: John Wiley & Sons Ltd. doi: 10.1002/9780470670071.ch6, Fig. 6.5, p. 91.

Where:

s_{samp}^2 = sampling variance
 s_{anal}^2 = analytical variance
 s_{meas}^2 = sampling variance (s_{samp}^2) + analytical variance (s_{anal}^2).

It is, therefore, quite evident from the above calculations that sampling is the greater contributor to total measurement uncertainty (Table S18).

Most environmental contamination investigators plot a simple deterministic Hg distribution map by using the recommended statutory guideline value for residential or industrial land use. In this case study example, the residential guideline value of 1000 mg/kg Hg was used to classify surface soil into uncontaminated and contaminated blocks (Fig. 32). The deterministic map shows that 11 blocks are contaminated, and the Hg neanomaly has a west-east trend, which has been caused by stack emissions, since the dominant wind direction in this area is westerly.

The first probabilistic Hg distribution map was plotted using the relative measurement uncertainty of 76.54% at the 95% confidence level on the threshold value of 1000 µg/kg Hg (Fig. 33). The calculations for the classification of soil into (a) uncontaminated (69 blocks), (b) possibly contaminated (9 blocks), (c) probably contaminated (7 blocks), and (d) contaminated (4 blocks) are displayed in Fig. 33 and Table S18.

The second probabilistic Hg distribution map (Fig. 34) was plotted using the expanded uncertainty factor of 4.94 at the 95% confidence level (Ramsey et al., 2019; Demetriades et al., 2022a). In this case, the uncontaminated blocks are reduced from 69 to 57, and the possibly contaminated blocks are increased from 9 to 21, while the number of probably contaminated and contaminated blocks remains the same at 7 and 4 blocks, respectively. The contaminated land investigator will have to decide how to handle the possibly contaminated blocks depicted by the second probabilistic Hg distribution map.

It is concluded that the two probabilistic Hg distribution maps (Figs. 33 and 34) define the contaminated blocks more reliably than the deterministic approach (Fig. 32).

Upon completion of the first phase, the depth of contamination was investigated, and whether the contaminants reached the groundwater table. The second phase results are not presented here. However, it can be stated that the intense surface contamination

(0–20 cm) was progressively reduced towards 100 cm depth, with three 25 × 25 m blocks showing contamination below this depth. The collected groundwater samples did not show any contamination. Finally, the volume of contaminated soil was estimated, and recommendations for its remediation were submitted to the property owner.

How and why are multinational continental-scale applied geochemical surveys carried out?

Let us first start with what the aim is of multinational continental-scale geochemical mapping surveys (the Why). The aim is to study the concentration and spatial distribution of chemical elements at the terrestrial surface of the Earth in order to:

- Understand the processes controlling their spatial distribution.
- Define the variable geochemical background across political boundaries.
- Define the variable geochemical baseline across political boundaries.
- Delineate anomalous geochemical patterns hundreds to thousands of km² in size representing metallogenetic provinces.
- Delineate areas with element deficiency and toxicity, and
- Establish a harmonized global geochemical reference network for leveling data of regional geochemical surveys (Darnley et al., 1995; Demetriades et al., 2022b).

The sampling media used in multinational continental-scale geochemical mapping surveys are:

- Till, stream sediment, stream organic matter, stream moss, and heavy mineral fraction for the Nordkalott region geochemical atlas (Bølviken et al., 1986).
- Soil, humus, and terrestrial moss for the Geochemical Atlas of the Central Barents region, also known as the Kola Ecogeochemistry project (Reimann et al., 1998; Reimann, 2022).
- Agricultural soil for the Geochemical Atlas of Baltic countries (Reimann et al., 2003; Reimann, 2022).
- Soil, terrestrial moss, and stream water at all sampling sites, and at selected sites stream sediment, vegetation, O-horizon, and complete soil profile for the Geochemical Atlas of Eastern Barents Region (Salminen et al., 2004).
- Active stream sediment, stream water, floodplain sediment and residual soil (or till in glaciated parts) for the Geochemical Atlas of Europe, which is known as the FOREGS Geochemical Atlas of Europe or just the FOREGS Atlas (FORum of European Geological Surveys) (Salminen et al., 1998; Salminen et al., 2005; De Vos et al., 2006).
- Mineral bottled water used as a proxy for the European Groundwater Geochemistry (EGG) atlas (Reimann and Birke, 2010), and
- Agricultural and grazing land soil in Europe, which is known as the GEMAS Atlas (GEOchemical Mapping of Agricultural Soil) (EuroGeoSurveys Geochemistry Working Group, 2008; Reimann et al., 2014a, 2014b).

Apart from the above multinational continental-scale geochemical surveys, there are, to my knowledge, three completed national continental-scale surveys, which used:

- Floodplain sediment in China (Xie et al., 2012).
- Catchment outlet sediment, which is similar to floodplain sediment, for the geochemical atlas of Australia (Caritat and Cooper, 2011; Caritat, 2022), and
- Soil for the geochemical atlas of the conterminous United States of America (Smith et al., 2019; Smith, 2022).

What are the most important components for the successful implementation of multi-national continental-scale geochemical surveys? For their smooth and effective execution, teamwork is the most important with the following components: transparent cooperation, communication, assertiveness, dedication, mutual trust and respect and, last but not least, coordination, prudent and ethical leadership. As Norsen et al. (1995) have stated “Without trust and respect cooperation cannot exist, assertiveness becomes threatening, responsibility is avoided, communication is hampered, autonomy is suppressed, and cooperation is haphazard.”

Examples from three European geochemical atlases are presented herein, because of their multinational nature (the How). All three were completed successfully because of the excellent conditions, which had the aforementioned teamwork components.

Sampling manuals, sample preparation and storage

Before starting a multinational continental-scale geochemical mapping survey it is important to agree on the sampling, sample preparation, quality control and analytical protocols. It is, therefore, strongly recommended to consult the published sampling manuals (Salminen et al., 1998; EuroGeoSurveys Geochemistry Working Group, 2008; Demetriades et al., 2020), which were compiled by applied geochemistry experts, and tested during dedicated field workshops with participants from almost all participating countries. Using this experience, the “International Union of Geological Sciences Manual of Standard Methods for Establishing the Global Geochemical Reference Network” (Demetriades et al., 2022b) was compiled as an authoritative work, which includes separate chapters providing extensive information on sampling protocols for rock, residual soil, humus, stream water, stream sediment, and overbank and floodplain sediments. There are also chapters discussing sample site selection; sample preparation; quality control procedures, including development of project reference materials; data management; map preparation; project

management; and information on how to level existing geochemical datasets. Any applied geochemist considering carrying out a geochemical mapping project at a global scale, or any other scale, should find a wealth of useful information within these pages.

Safe and well-organized long-term storage of samples in a secure and clean storeroom is important and an absolute must (Mackovych et al., 2022; BGS, 2023). Ideally, the archive samples should be stored in silica glass vials. However, as these are prone to break, certified trace-element free polyethylene vials should be used. To begin with, the samples should be divided after homogenization to the number of sub-samples required for laboratory analysis, and a number of larger sub-samples for permanent storage. All samples should be labeled with their alpha-numeric number, as well as a specialized bar or quick response (QR) code tracking system to allow their speedy location and retrieval when needed. Of course, the samples of all geochemical surveys must be stored safely, and to be readily available for future studies. Among explorationists the following opinion exists: “the cheapest geochemical survey is the one that uses archive samples”.

Quality assurance/quality control procedure

For analytical quality control in continental-scale multi-national geochemical mapping projects in Europe, established procedures are based on:

- Collection of a field duplicate sample at every 30th sample site (FOREGS Atlas) and at every 20th sample site (GEMAS Atlas).
- Randomization of all samples prior to submitting them for analysis.
- Introduction of control reference samples (project standards or Secondary Reference Materials, SRMs), unknown to, and unrecognizable by, the laboratory at a rate of one standard per 10 to 30 samples, and
- Insertion of analytical replicates or project duplicate splits at a rate of one in 10 to 20 samples.

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 multi-national continental-scale geochemical mapping projects. The quality control procedures and results are described and discussed in articles and reports, which should be consulted (Sandström et al., 2005; Reimann et al., 2009, 2011, 2012a; Reimann and Birke, 2010; Demetriades et al., 2014, 2022a; Johnson and Lister, 2022).

The FOREGS Atlas used a balanced ANOVA design (Fig. 31a), and the GEMAS Atlas project an unbalanced ANOVA design (Fig. 31b), although the original intention was to use the former scheme (EuroGeoSurveys Geochemistry Working Group, 2008), but due to cost this was not possible. Similar quality control procedures should be installed for all applied geochemical mapping projects at any mapping scale (Johnson, 2011; Johnson et al., 2018; Demetriades et al., 2022a; Johnson and Lister, 2022).

Database management and map production

The database management and map production procedures used for the FOREGS, EGG and GEMAS atlases are described by Tarvainen et al. (2005), Reimann and Birke (2010), Filzmoser et al. (2014) and Filzmoser and Reimann (2014), and by Tarvainen et al. (2022) for the establishment of the Global Geochemical Reference Network (Demetriades et al., 2022a).

Examples of continental-scale geochemical maps

Nickel is selected as an example because, apart, of its interpretation in the published European Geochemical Atlases (De Vos et al., 2006; Reimann and Birke, 2010; Reimann et al., 2014a), there are two published papers by Albanese et al. (2015) and Jordan et al. (2018), which should be consulted. Further, it is an element of interest not only for mineral exploration and geology, but also for the environmental and medical sciences (Macomber and Hausinger, 2011; Sreekanth et al., 2013; Genchi et al., 2020; Begum et al., 2022). The Ni analytical data sets of the European Geochemical Atlases are provided in Table S19.

What are the anthropogenic sources of Ni? The anthropogenic sources of Ni include fertilizers, smelters, steel works, metal plating and coinage, fuel combustion and detergents (e.g., Cempel and Nikel, 2006; Begum et al., 2022). In the presence of some organic complexing agents, Ni can form neutral or negatively charged complexes, making the metal highly mobile in relation to other trace elements. Consequently, Ni concentrations may be high in stream water contaminated by sewage and leachate from waste tips.

What is the role of Ni in biota, and its effects with respect to toxicity and deficiency? Nickel has been shown to be essential for microorganisms and has been implicated as having an essential role in human metabolism. Most Ni²⁺ compounds are relatively non-toxic, but some compounds are highly toxic, and extreme excesses of Ni are both toxic, causing dermatitis and gastric irritation, and carcinogenic (Ware, 1988; ATSDR, 2005). The World Health Organization recommends a prophylactic guideline value of 80 µg Ni/L for a body weight (bw) of 60 kg (13 µg/kg bw/day x 60 kg bw, with water consumption of 2 L/day), which is protective of chronic systemic Ni toxicity (WHO, 2021, p. 23). Nickel deficiency retards growth and impairs iron uptake, and low Ni blood levels are found in people with cirrhosis of the liver and chronic kidney failure. High Ni blood levels occur in people that have suffered a heart attack or a stroke, those with serious burns and lung cancer, in women with toxemia of pregnancy, and cancer of the uterus. Deficiency of Ni in animals impairs Fe absorption leading to low iron levels in tissues and organs, and to iron-deficiency anemia.

Table 1 gives the basic statistical parameters of Ni in samples of (i) topsoil, subsoil, stream sediment, floodplain sediment and stream water from the FOREGS Geochemical Atlas of Europe (Salminen et al., 2005), (ii) groundwater from the EGG Atlas (Reimann and Birke, 2010), and (iii) agricultural and grazing land soil from the GEMAS Atlas (Reimann et al., 2014a). In addition, Fig. 35 displays a notched-boxplot statistical comparison of all datasets, and Figs. 36–38 show the corresponding

Table 1 Basic descriptive statistical parameters of hot aqua regia extractable Ni in samples of (a) topsoil, subsoil, stream sediment, and floodplain sediment from the FOREGS Geochemical Atlas of Europe (Salminen et al., 2005), and (b) agricultural and grazing land soil from the GEMAS Atlas (Reimann et al., 2014a); also (c) stream water from the FOREGS Geochemical Atlas of Europe, and (d) groundwater from the EGG Atlas (Reimann and Birke, 2010).

Statistical parameters	Ni (mg/kg)						Ni (µg/L)	
	Topsoil	Subsoil	Stream sediment	Floodplain sediment	Agricultural soil	Grazing land soil	Stream water	Ground water
N	837	784	845	747	2108	2023	808	884
Grain size (mm)	<2 → <0.063	<2 → <0.063	<0.150	<2 → <0.063	<2	<2	—	—
Detection limit	2 ^a	2 ^a	2 ^a	2 ^a	0.10 ^b	0.10 ^b	0.005 ^a	0.02
Minimum	<2.00	<2.00	2.00	2.00	<0.1	0.276	0.030	<0.02
5th percentile	3.00	4.00	4.20	4.00	1.85	1.84	0.250	0.022
10th percentile	4.00	5.00	6.00	6.00	3.06	2.79	0.390	0.029
25th percentile	7.00	9.00	10	10	6.81	6.35	0.948	0.063
Median	14.0	18.0	16.0	18.0	14.7	14.4	1.91	0.178
75th percentile	26.0	30.3	29.0	28.0	27.3	27.5	3.00	0.642
90th percentile	40.4	47.0	46.0	43.0	42.7	43.1	4.72	2.01
95th percentile	63.2	72.8	69.0	78.4	65.9	65.7	6.33	4.34
97.5th percentile	121	128	111	131	120	102	8.54	7.37
Maximum	2565	2586	1201	942	2475	2466	24.6	94.6
MAD ^c	9.00	10.0	8.00	8.00	9.26	9.59	1.00	0.143
Order of magnitude ^d	3.11	3.11	2.78	2.67	4.39	3.95	2.91	3.67

The original and analytical grain-size fractions in millimeters (mm) are indicated.

^aLimit of quantification (LoQ).

^bPractical detection limit (PDL).

^cMAD = Median absolute deviation.

^dThe Order of Magnitude is estimated by converting to logarithms (base 10) the minimum and maximum values, and subtracting the log of the minimum value from the log of the maximum value, e.g., the minimum and maximum values of Ni in Topsoil samples are used as example: $\log_{10} 2565 - \log_{10} 2 = 3.409 - 0.301 = 3.108$ (3.11 to two decimal places).

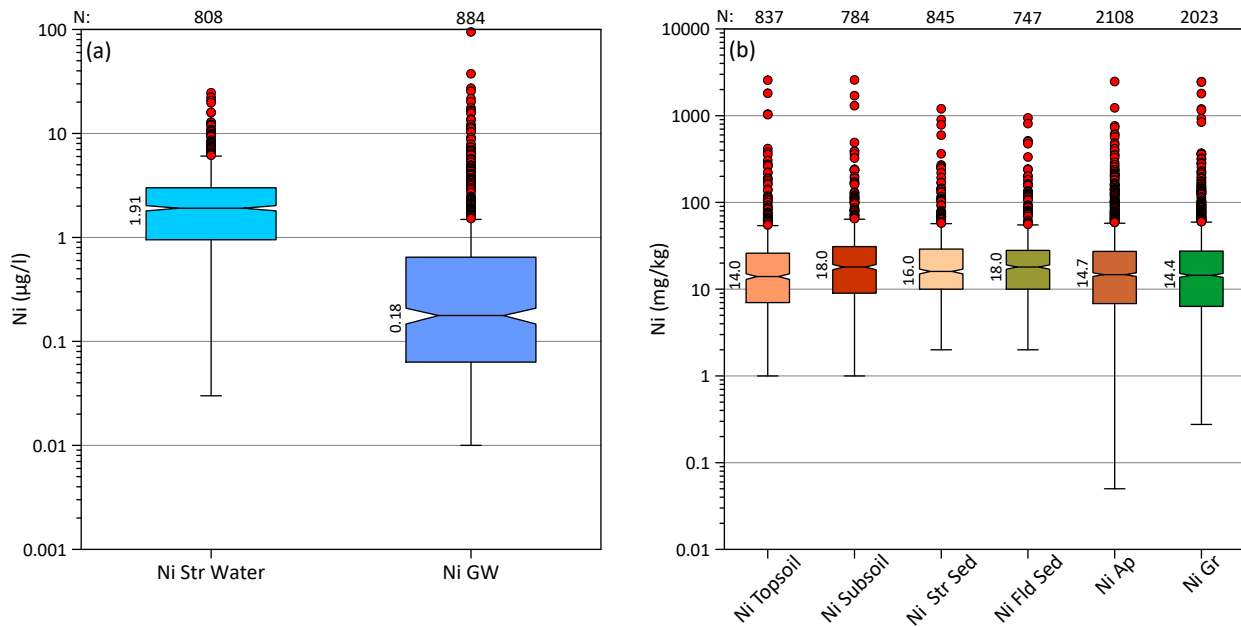


Fig. 35 Multiple boxplots comparing the statistical distribution of Ni in (a) Stream water (Str Water) and groundwater (GW) samples, and (b) hot aqua regia results in samples of Topsoil, Subsoil, Stream sediment (Str Sed), Floodplain sediment (Fld Sed), Agricultural soil (Ap), and Grazing land soil (Gr). Data from the FOREGS, EGG and GEMAS atlases. Median Ni concentrations are indicated by the horizontal line within the box and values displayed. Fifty percent of the Ni data for each data set lies within the box. Outliers beyond 1.5 times the interquartile range are indicated by red dots with black rim. The y-axis is logarithmic (base 10) in order to accommodate all results. Plotted with Golden Software's Grapher™ v21.

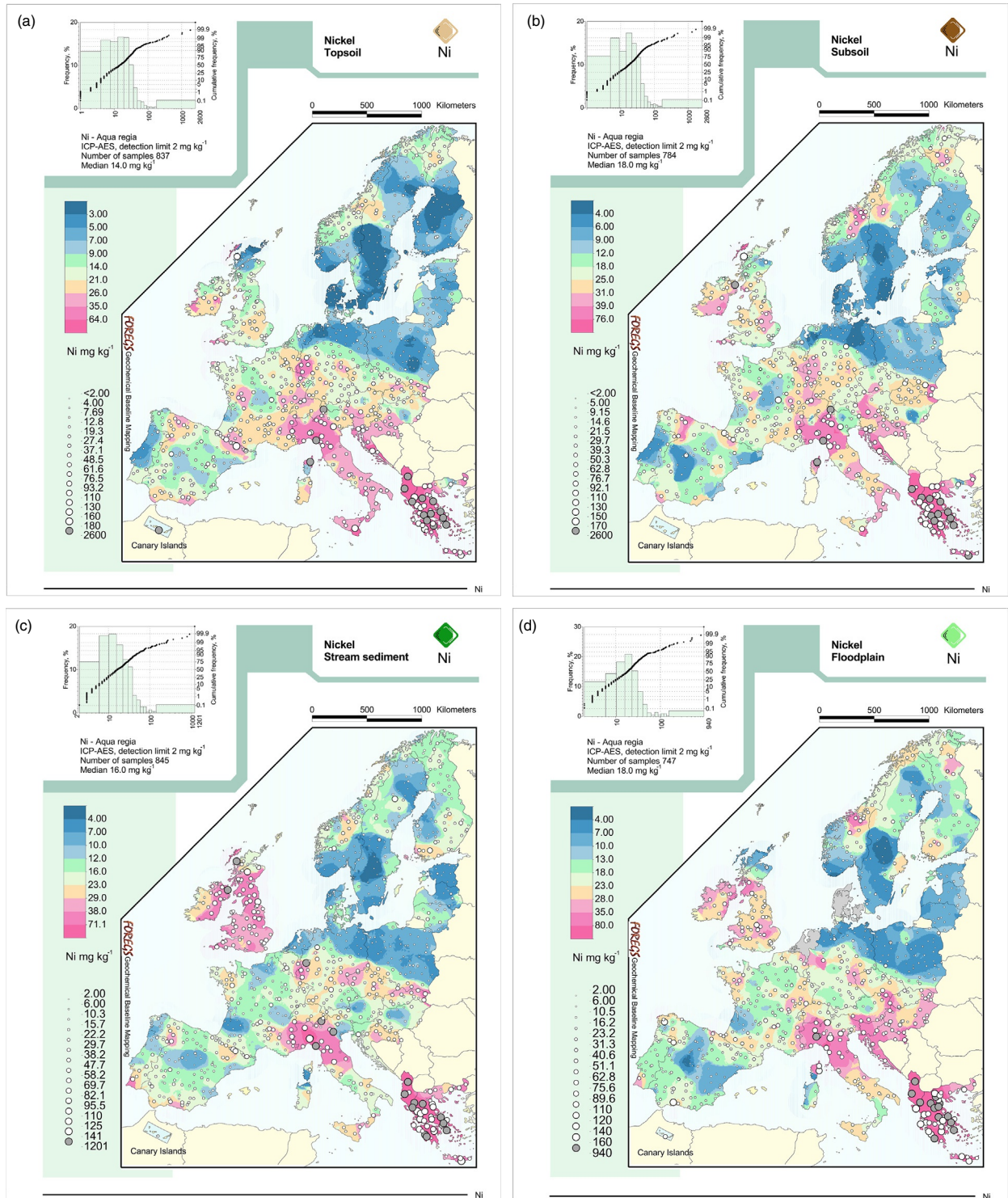


Fig. 36 Maps from the FOREGS Geochemical Atlas of Europe showing the distribution of hot aqua regia extractable Ni in samples of (a) <2 mm Topsoil, (b) <2 mm Subsoil, (c) <0.150 mm Stream sediment, and (d) <2 mm Floodplain sediment (Salminen et al., 2005; De Vos et al., 2006). Refer to Table 1 for basic descriptive statistics. Plotted with Alkemia (Gustavsson et al., 1997) and ESRI's ArcView (Tarvainen et al., 2005).

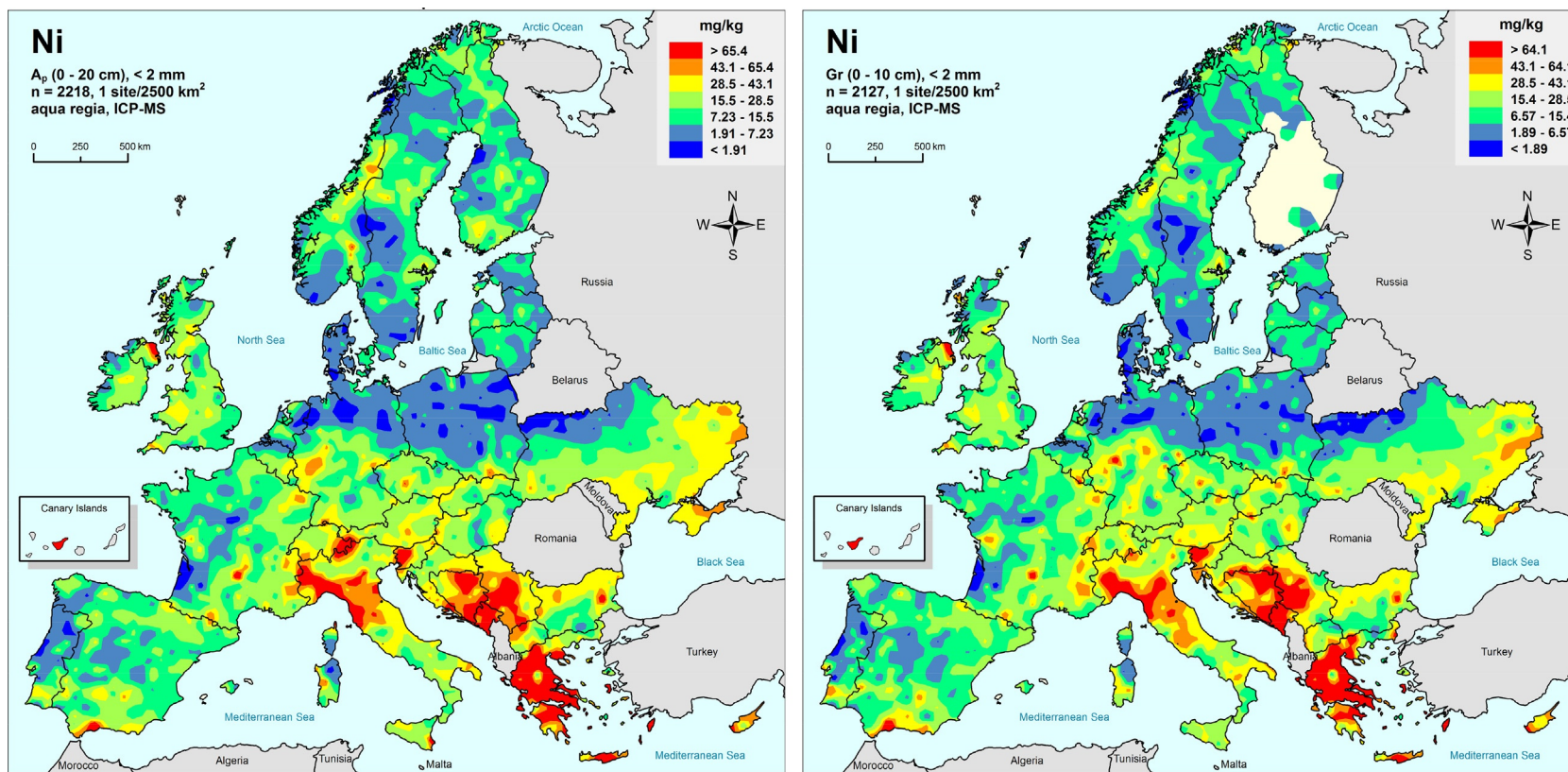


Fig. 37 Maps from the GEMAS Atlas of Europe showing the distribution of hot aqua regia extractable Ni in the <2 mm grain-size fraction of (a) Agricultural soil, and (b) Grazing land soil samples (Reimann et al., 2014a, Figs. 11.39.5, p. 329). Refer to Table 1 for basic descriptive statistics. Plotted with ESRI's ArcGIS.

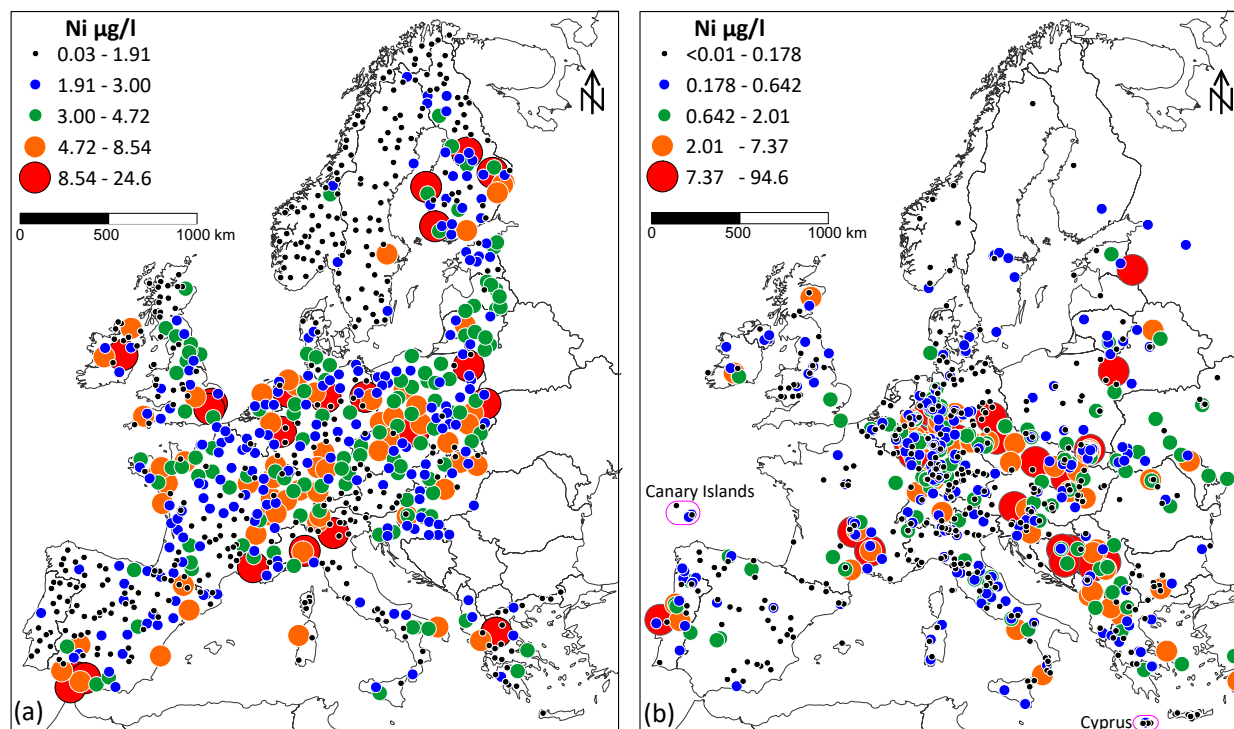


Fig. 38 Growing dot or variable-size dot maps from the FOREGS and EGG Atlases showing the distribution of Ni in samples of (a) stream water and (b) groundwater using bottled mineral water as proxy. Refer to Table 1 for basic descriptive statistics. Plotted with Golden Software's MapViewer™ v8. (a) Data from Salminen R, Batista MJ, Bidovec M, Demetriades A, De Vivo B, De Vos W, Gilucis A, Gregorauskiene V, Halamic J, Heitzmann P, Lima A, Jordan G, Klaver G, Klein P, Lis J, Locutura J, Marsina K, Mazreku A, Mrnkova J, O'Connor PJ, Olsson SA, Ottesen RT, Petersell V, Plant JA, Reeder S, Salpeteur I, Sandström H, Siewers U, Steenfelt A and Tarvainen T (2005) *FOREGS Geochemical Atlas of Europe, Part 1 – Background Information, Methodology, and Maps*. Espoo: Geological Survey of Finland, 525 pp. Available at: <http://weppi.gtk.fi/publ/foregsatlas/>; (b) Data from Reimann C and Birke M (eds.) (2010) *Geochemistry of European Bottled Water*. Stuttgart: Borntraeger Science Publishers, 268 pp. Available at: <http://www.schweizerbart.de/publications/detail/artno/001201002>.

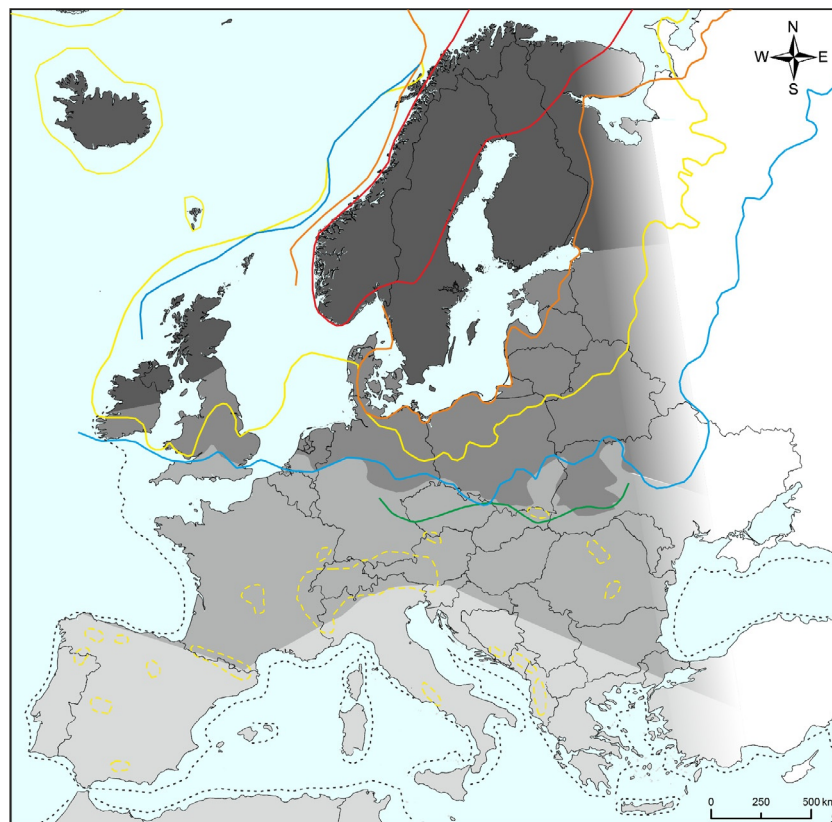
geochemical maps. Further, for the interpretation of the Ni geochemical maps, three additional maps are included, namely, Quaternary ice sheets (Fig. 39; Jähne, 2014), distribution of major intermediate, mafic, and ultramafic rocks (Fig. 40), and Ni mineralization and deposits (Fig. 41).

The analytical results demonstrate that natural Ni concentrations at the European scale vary from 2.67 to 4.39 orders of magnitude for the solid sample media (topsoil, subsoil, stream sediment, floodplain sediment, agricultural and grazing land soil), and from 2.91 to 3.67 orders of magnitude in stream and groundwater, respectively (Table 1). The tabulated results imply that there are outliers or anomalous samples in all datasets, which can be observed in the notched-boxplots (Fig. 35), and the anomalous patterns on the geochemical maps (Figs. 36–38). An interesting observation in the boxplot comparison is that the Ni medians of topsoil of the FOREGS Atlas, and the agricultural and grazing land soil of the GEMAS Atlas appear to be comparable, as the three notches overlap horizontally, suggesting that the medians of the three datasets are not significantly different at the 5% significance level (Fig. 35b). Similarly, the Ni medians of subsoil and floodplain sediment samples are comparable. The Ni median of stream sediment samples appears to be the odd one out. The Ni medians of stream and groundwater samples are not comparable (Fig. 35a).

A remarkable feature shown by Ni in all solid sample media geochemical maps is the southern border of the last ice age, running through The Netherlands, Germany, Poland, and northern Ukraine, marked by exceptionally low Ni-values to its north, and much higher values to its south (Figs. 36 and 37). This feature is verified by the map of Quaternary ice sheets (Fig. 39).

Low Ni values in all solid sample media occur in most of Fennoscandia, Estonia, Latvia, and Lithuania, and over the glacial drift area in Poland, northern Germany, and Denmark. Low Ni concentrations also occur in Portugal and central Spain, and small areas in central Hungary, and central and southern France. The relatively low Ni values in Finland are indeed interesting, given the presence of greenstone belts (Fig. 40) and Ni-deposits (Fig. 41). This feature is explained by the extensive glacial till cover.

High Ni values occur over most of Hellas and Albania (Figs. 36–38), caused by mineralized ophiolitic rocks (Figs. 40 and 41), and sedimentary rocks derived from them. An example is the Vourinos Ni—Cr deposit in northern Hellas. There are also high values of Ni over ophiolites in Liguria (Italy) and Corsica, over Slovenia and Croatia (including terra rossa soil over carbonate rocks), the Rheno-Hercynian, the Carpathians, Northern Ireland (Antrim basalt), central Norway and a large area with greenstone belts in northern Scandinavia. In Hellas, the high Ni values, apart from their relationship with ophiolites, are associated with bauxite, Fe—Ni and polymetallic sulfide mineralization. In southern Europe, some high Ni values are explained by coprecipitation with



Edited by Jähne (2012), based on Plant et al. (2003, 2005), Anderson and Borns (1997), Spielhagen et al. (2004), Svendsen et al. (2004)

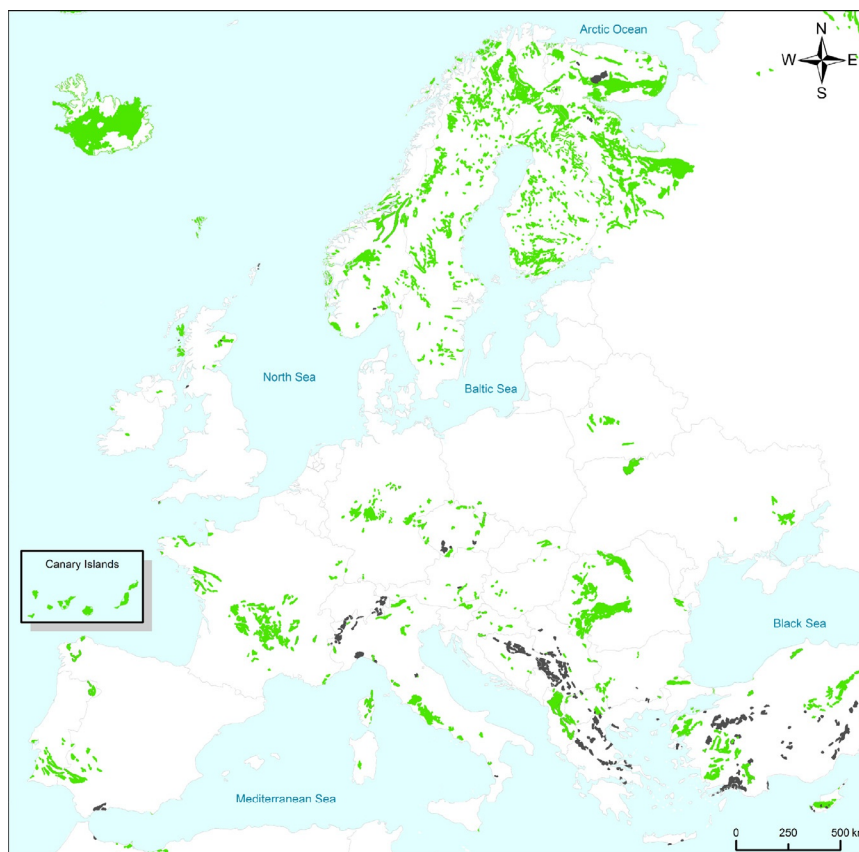
Maximum extent of the European ice sheets during different glacial periods:

Fig. 39 Map showing the maximum extent of the Quaternary ice sheets. From Jähne F (2014) *Geology of Europe*. In: Reimann C, Birke M, Demetriades A, Filzmoser P and O'Connor P (eds.), *Chemistry of Europe's Agricultural Soils—Part B: General Background Information and Further Analysis of the GEMAS Data Set*. Hannover: Geologisches Jahrbuch (Reihe B103), Schweizerbart, ch. 2, pp. 47–70. Available at: https://www.schweizerbart.de/publications/detail/isbn/9783510968473/Geologisches_Jahrbuch_Reihe_B_Heft_B103_Chemistry, Fig. 2.11, p. 69. Plotted with ESRI's ArcGIS.

Fe—Mn oxides of supergene origin, for example, in north-west Spain. Gran Canaria shows a local high Ni value due to basaltic volcanic rocks. The high Ni values in the central Pyrenees are associated with black shale of Ordovician, Silurian, and Carboniferous age.

The high Ni values in western Finland are related to (Litorina) clay soil, whereas the ones in eastern Finland are ascribed to black schist and sulfide deposits (Fig. 41). The high Ni value in north-western Sardinia is associated with polymetallic sulfide deposits. The single high Ni anomaly in northern Hellas is most likely due to the ophiolitic lithology. Anomalous Ni values in eastern Poland are related to peat lands.

Generally, the lowest Ni values in stream and groundwater are found in central and western Iberian Peninsula, and in southern France and Corsica on Variscan terrane; in Scotland and Norway on Caledonides, and in Sweden on Precambrian terrane (Fig. 38). For a terrane map refer to Fig. 1 in Plant et al. (2005, p. 25). Elevated Ni concentrations in stream water ($>4.72 \mu\text{g/L}$) occur in southern Spain on Alpine Orogen (Baetics) terrane; in France (Brittany) on Variscan terrane; in central and eastern Ireland, south-eastern England and northern Germany on Caledonides; in southern Germany on Variscan terrane; in southern Finland,



Edited by Jähne F., based on Asch K. (2003). IGME 5000: International Geological Map of Europe and Adjacent Areas

Rock units at the surface (e.g., ophiolite complex) with intermediate to ultramafic igneous rocks and their metamorphic equivalents

	Intermediate - mafic
	ultramafic

Fig. 40 Generalized map of intermediate, mafic, and ultramafic igneous rocks in Europe. From Jähne F (2014) Geology of Europe. In: Reimann C, Birke M, Demetriades A, Filzmoser P and O'Connor P (eds.), *Chemistry of Europe's Agricultural Soils—Part B: General Background Information and Further Analysis of the GEMAS Data Set*. Hannover: Geologisches Jahrbuch (Reihe B103), Schweizerbart, ch. 2, pp. 47–70. Available at: https://www.schweizerbart.de/publications/detail/isbn/9783510968473/Geologisches_Jahrbuch_Reihe_B_Heft_B103_Chemistry, Fig. 2.6c, p. 59. Plotted with ESRI's ArcGIS.

northern Germany, central and eastern Poland on Precambrian terrane, and in north-western (Liguria), north-eastern (isolated high value), and southern (Apulia and Sardinia island) Italy on Alpine Orogen (Fig. 38a). Anomalous Ni concentrations in stream water in southern Spain are related to ultramafic rocks of the Ronda, Ojén and Carratraca massifs and to Fe—Cu and Ni—Cr mineralization in these massifs (Figs. 40 and 41).

The interpretation of Ni distribution in groundwater requires good knowledge of aquifer lithology, which was not available at the time of publication of the EGG Atlas (Fig. 38b). Therefore, only assumptions can be made from the generalized geological and mineralization maps (Figs. 40 and 41). High Ni concentrations in groundwater occurring in central Portugal, Massif Central in France, the extensive belt from northern Hellas through Albania, Serbia, Bosnia and Herzegovina, Croatia, Slovenia to southern Austria may be associated with the occurrence of mafic-ultramafic rocks. The highest value of 94.6 µg/L was reported from a well in Bosnia and Herzegovina. In Germany, several of the groundwater samples, with enhanced Ni-concentrations, are reported from wells that draw water from important tectonic faults.

The geochemical maps of Ni in stream and groundwater show that there is no correlation in the patterns, except of a single anomalous sample in north-east Poland near to the border with Belarus (Fig. 38). Further, the maps show that Ni concentrations in samples of solid sample media and in stream and groundwater do not necessarily correlate (Figs. 36–38).

All geochemical maps do not provide evidence for widespread anthropogenic Ni contamination at the European scale. Almost all variations visible on the continental-scale geochemical maps find their explanations in natural factors. However, on the local scale human influences may occur as, for example, the point Ni geochemical anomaly in eastern Spain on the Mediterranean coast at Cap de la Nau, which has been caused by industrial activities. Also, the high Ni concentrations in stream water in the Czech Republic are most likely caused by atmospheric deposits of fly ash from coal burning power plants.

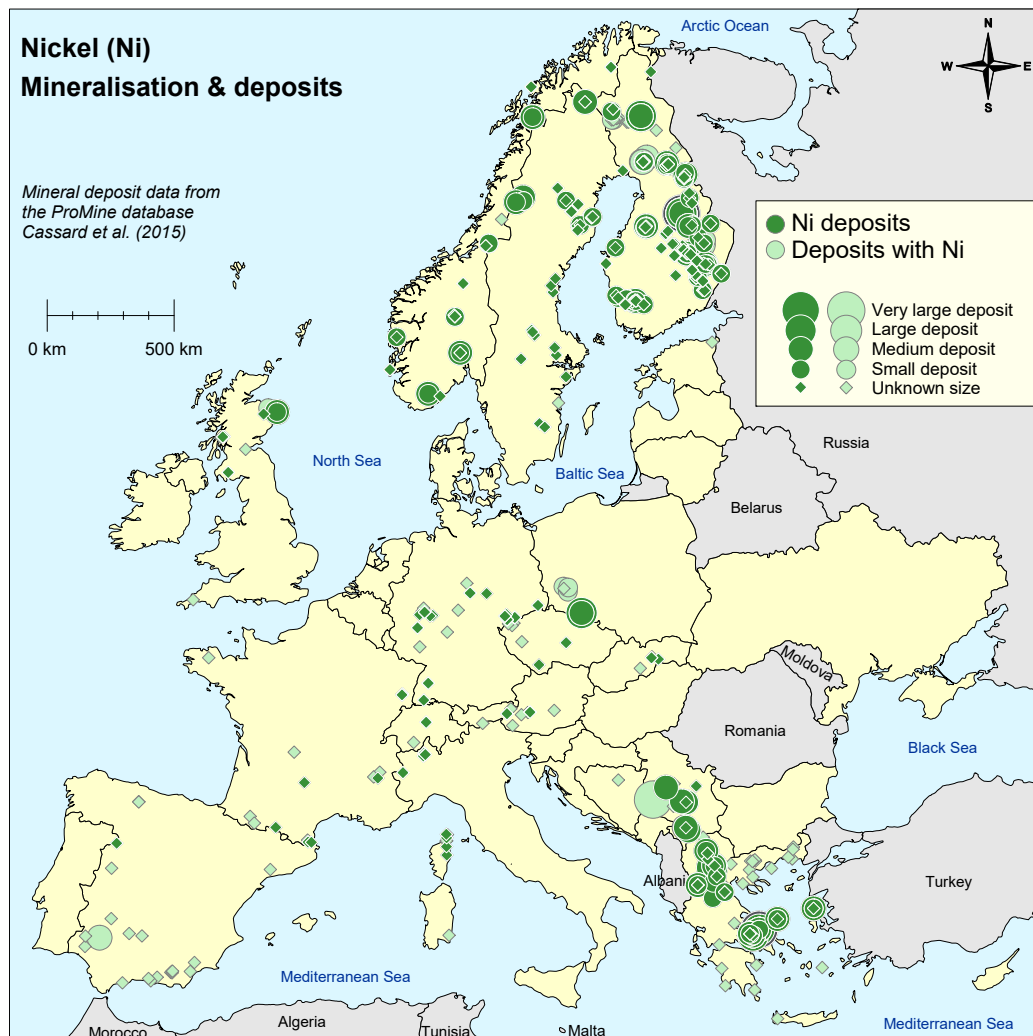


Fig. 41 Distribution of Ni mineral deposits and mineralization in Europe (Demetriades and Reimann, 2014, Fig. 3.7, p. 77 – slightly modified). Source ProMine mineral deposit database (Cassard et al., 2015). Plotted with Golden Software's MapViewer™ v8.

In conclusion, the European Geochemical Atlases provide to the scientific community, and decision-makers databases of high quality and integrity about the geochemistry of soil, stream and floodplain sediment, stream water and groundwater for multi-purpose use. Most importantly, they have shown distinct geographical differences in the levels of potentially harmful elements from natural geogenic sources, including lithology and mineralization. Finally, geochemical maps could be used to identify potential geohazard and geohealth risks for more detailed investigations.

After studying the soil, sediment, and water Ni distribution maps of Europe, do you think that it is possible to establish a single guideline value for the whole of Europe? The answer is, of course, 'definitely not', because the geochemical variation illustrates the difficulty in defining a single guideline value for 'water', 'soil' and 'sediment' to be applied all over Europe. However, this was the intention of some bureaucrats within the European Commission in Brussels. Fortunately, the FOREGS Geochemical Atlas of Europe was published at the right time and put a stop to this plan.

How is the quality of generated applied geochemical analytical datasets assured?

Quality control procedures have already been mentioned in different sections of this account, and here additional details are given because of their importance in the generation of analytical results of good quality for specific and multi-purpose use.

What does actually define 'quality', when carrying out an applied geochemical survey at any mapping scale? Is it enough that samples are taken and prepared according to harmonized protocols, and then analyzed for an agreed number of parameters in accredited laboratories?

The problem with the attribute of ‘quality’ is that it is somewhat subjective and may thus be understood differently by different people (Demetriades et al., 2014). In modern times, it is most often defined as ‘fitness-for-purpose’. The question is *how can one measure and document this ‘fitness-for-purpose’?*

Procedures to guarantee the quality of sampling and sample preparation are relatively straightforward and easy to implement, if these are carried out by well-trained personnel, and supervised by experienced laboratory analysts and field applied geochemists. It is at the analytical stage, where most quality problems for geochemical mapping projects arise.

For an effective analytical quality assurance/quality control (QA/QC), established procedures are based on:

- Collection of a field duplicate sample at a rate depending on the total number of samples collected in a geochemical mapping survey, and the rate varies from every 5th, 10th, 20th or 30th sample site, i.e., 20%, 10%, 5% or $\approx 3\%$ duplication, respectively.
- Following sample preparation, two different designs can be used for splitting the field duplicate samples: (a) balanced ANOVA, and (b) unbalanced ANOVA (Fig. 31). Although the unbalanced ANOVA design is more economical, because only the field duplicate sample is split into two replicate samples, the balanced ANOVA design is recommended as it is more efficient for the estimation of quality control parameters (Ramsey, 1998; Sandström et al., 2005; Demetriades, 2011b; Ramsey et al., 2019; Demetriades et al., 2014, 2022a; Johnson et al., 2018; Johnson and Lister, 2022).
- Introduction of project control reference or standard samples (Secondary Reference Materials, SRMs), unknown to, and unrecognizable by, the laboratory at a rate of one project standard per 10 to 30 samples. It is strongly recommended to insert randomly at least two to three SRMs (Johnson et al., 2018; Johnson and Lister, 2022) with different element concentrations.
- Insertion of analytical replicates or duplicated splits of project samples (Fig. 7b and c) at a rate of one in 10 to 20 samples.
- Randomization of all samples prior to submitting them for analysis (Fig. 7c), and
- Arrangement with the analytical laboratory to include in the analytical batches, apart from method blanks, its internal reference materials, PRMs and the reanalysis of project samples at an agreed rate, i.e., usually every 10th or 20th sample.

In combination, the above procedures allow the detection and evaluation of most quality problems that can occur during sample analysis, and which may seriously affect the success of geochemical mapping projects. It is strongly recommended to consult the following publicly available reports by Reimann et al. (2009, 2011, 2012a).

Although analytical quality has increased tremendously over the last 20 to 30 years, and at present many commercial laboratories are ‘accredited’ for the analyses they carry out, there is still a need for independent and project related quality control, the so called ‘external’ quality control. In a way, the spatial determinand distribution, as displayed on the geochemical maps, is the ‘final’ stage of the applied QA/QC procedure in a geochemical mapping project. ‘Noisy’ geochemical maps are caused either by a too low sampling density or, more often, by poor quality data, i.e., insufficient quality control at all stages of the geochemical mapping project.

It is particularly important to understand that an ‘accredited’ laboratory does not mean that the analytical results it produces are of high quality. Accreditation forces the laboratory to follow a documented and traceable procedure, and nothing more. Therefore, it is the job of the applied geochemist to verify the quality of the geochemical project’s analytical results. It is important to understand that you should not rely only on the quality control results of the laboratory. Never accept analytical results on face value without first carrying out a thorough check of your own ‘external’ quality control results and, of course, thoroughly check those generated by the laboratory. When the applied geochemist is satisfied that the analytical results are of acceptable quality (fitness-for-purpose), then and only then should data processing begin.

Randomization of samples

Of course, you may ask: *What are the reasons for randomizing the samples prior to their analysis by the laboratory?* Systematic errors may occur in the laboratory during sample preparation and analysis (Plant, 1973; Plant et al., 1975; Fletcher, 1981, 1986). Some of these systematic errors are:

- Contamination of uncontaminated project samples by contaminated samples during sieving.
- Within-batch contamination of project samples from an external source during grinding and pulverization, and
- During analysis of project samples in the laboratory, changes in the conditions may occur, namely weighing balance drifting, analytical instrumental drift, interferences, etc., such changes are monitored by the analysis of reference or standard samples introduced in every analytical batch.

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

Randomization of geochemical mapping project samples is the method devised by applied geochemists to remove any systematic relationship between order of analysis and geographical location (Plant, 1973; Plant et al., 1975; Fletcher, 1981, 1986; Thompson, 1983; Reimann et al., 2009, 2011, 2012a; Johnson, 2011; Demetriades et al., 2014, 2020, 2022a; Demetriades and Birke, 2015a, 2015b; Johnson et al., 2018). By randomization of project samples, any systematic between-batch variation is increased in the analytical data, meaning that any systematic errors are spread randomly over all samples. This converts data, which 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 be taken, therefore, to include enough control samples, and to monitor their

analyses, in order to detect between-batch variation. If such variations are identified, then the affected batch or batches of soil samples (or other sample types) should be submitted to the laboratory for re-analysis, and the new analytical results utilized, provided they are satisfactory according to fitness-for-purpose. Furthermore, randomization of samples has another advantage, which is project and international reference samples, and project replicate samples can be hidden in the batches and, thus, not recognized by the laboratory.

In order to understand what can go wrong in a project when the applied geochemist does not install an effective QA/QC procedure, study Fig. 42. You will see that the cobalt (Co) distribution map in stream and lake sediment samples of Alaska, displays, according to Smith et al. (2013, p. 171): “Large blocks of data, readily identifiable by their straight edge boundaries, show the effects of uncorrected bias in the analytical results. For example, the Co map shows a rectangular block (four 1° by 3° quadrangles) in the center of the state where the results are elevated with respect to the surrounding areas despite the fact that the surrounding quadrangles were analyzed by the same laboratory and method. This problem is even more pronounced in areas where different laboratories and methods were employed”. It was very unfortunate because the Geochemical Atlas of Alaska was published by Weaver et al. (1983) and distributed to many institutions all over the world, without the authors realizing the grave mistake that they have made. When this was reported, the atlas was withdrawn, but the damage done could not be repaired. It is surprising that recently a second version of the Geochemical Atlas of Alaska has been published (Lee et al., 2016), and the problem is still visible if you compare the new and old Co distribution maps (Fig. 42). It is quite apparent that the authors did not have the necessary reference materials to level the different batches of analytical data as has been done in the United Kingdom stream sediment regional geochemical survey (Lister and Johnson, 2005; Johnson and Lister, 2022). Fig. 43a shows the La stream sediment geochemical map, which was plotted with the combined datasets from La determined by Direct Current Optical Emission Spectrometer (DC-OES) in the northern part of Scotland, and by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in the southern part of Scotland and northern England. In this case, because of the lack of control samples, a different leveling methodology was applied by using cumulative percentiles (Everett et al., 2019; Johnson and Lister, 2022), and the resulting seamless La geochemical map is shown in Fig. 43b.

Other leveling procedures are described by Darnley et al. (1995, Section 8.4, p. 75–78), Daneshfar and Cameron (1998), Amor et al. (2019), and Main and Champion (2022).

Randomization of samples can be done in two different ways:

- (i) During the planning of the field geochemical mapping survey the total number of routine and duplicate field samples, and their replicated splits, is estimated, as well as the number of project reference samples (SRMs) and blanks that will be inserted for analysis. Then this number is randomized, and a list made of the random numbers generated. A computer software program can perform randomization of sample numbers, and an output produced. During the field survey, each sample is assigned in turn a random number from the list. In the preparation laboratory, the samples are ordered in ascending numbers, and the project reference and blank samples, and routine and field duplicate-replicate sample splits, are inserted at the appropriate reserved places using the same coding, and a record kept.
- (ii) If the samples are not collected in a random sequence, then the randomization of routine project samples, and external control samples is done before submission to the laboratory. Project samples are assigned new numbers, taking into account the number of places to insert project control samples (reference and blank samples and project replicate splits). This procedure has a major disadvantage, because the samples lose their identity, as completely new numbers are assigned. Hence, the procedure must be done very carefully, and a good record kept of the project sample numbers, and their corresponding new random numbers, because upon receiving the analytical results the original sample numbers must be reassigned.

How are applied geochemical datasets processed?

Following the verification of the quality of the analytical results, their computer processing starts by first compiling the database file by merging the analytical results with the sample site coordinates and field observations. As stressed by Tarvainen et al. (2022) the merged data file should be checked and validated, especially with respect to the sample site coordinates (Demetriades et al., 2022b).

How data below the detection limit are handled?

Before answering this question, it is pointed out that arrangements should be made with the laboratory to provide uncensored (recorded) values for the estimation of the practical detection limit for each determinand. Detailed instructions for the estimation of the practical detection limit of each element from uncensored values are given by Demetriades (2011b) and Demetriades et al. (2022a), using a modified version of the method proposed by Howarth and Thompson (1976) and Thompson and Howarth (1976, 1978). If this is impossible for any reason, the laboratory will apply a fixed lower detection limit (LDL) for each element (censored or truncated or reported value). In such a case, the laboratory should provide information of how the lower detection limit was determined, i.e., (i) the instrumental detection limit (IDL), which refers to the analyte concentration that is required to produce a signal greater than 3 times the standard deviation of the noise level, and (ii) the limit of quantification (LoQ) defined as 10 times the standard deviation of the method blank value.

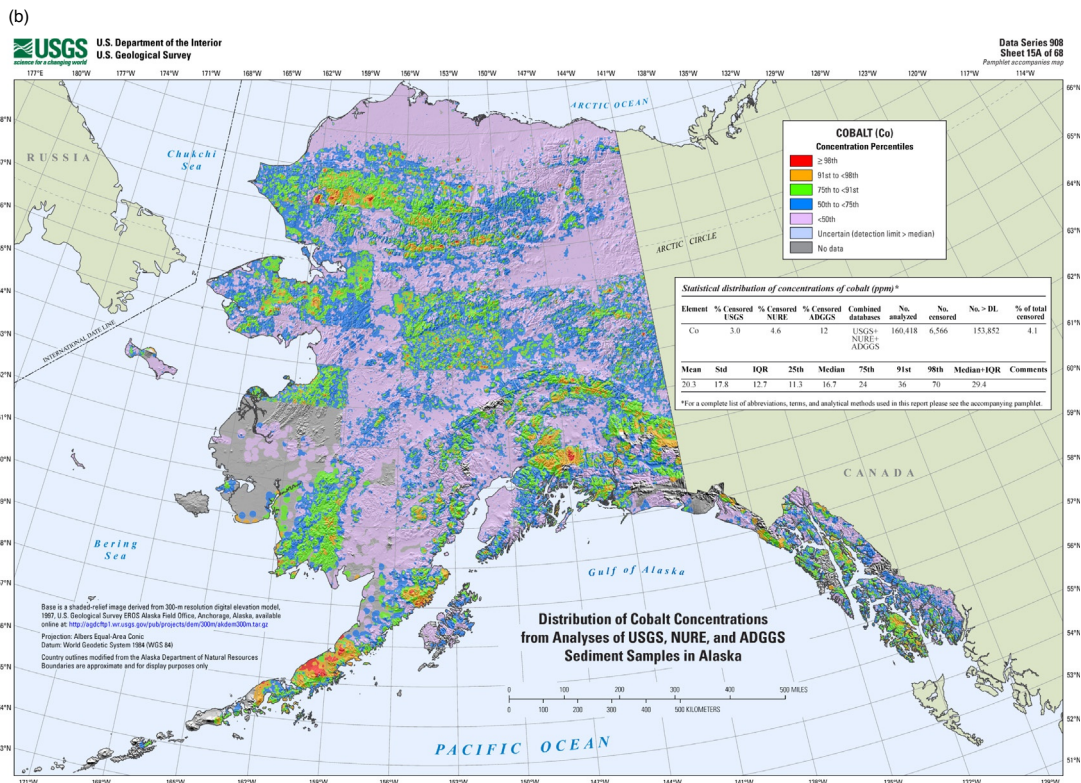
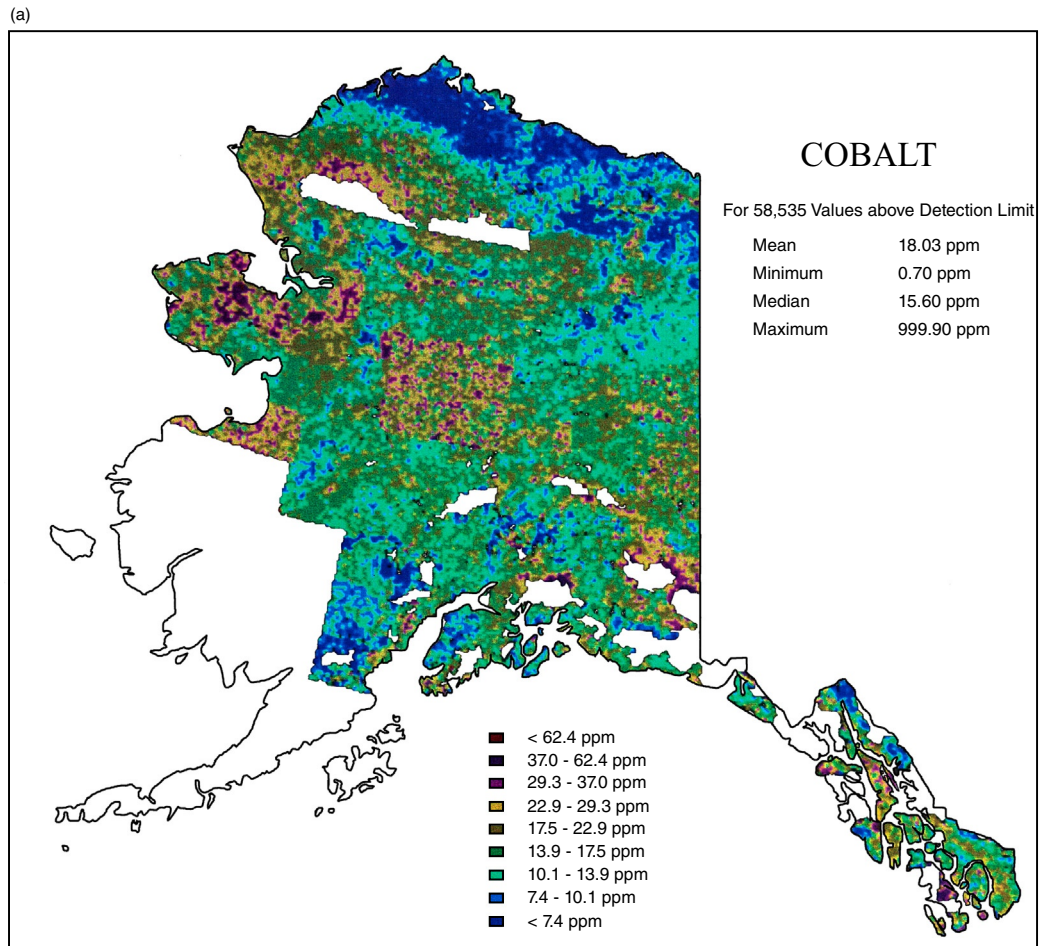


Fig. 42 (a) Cobalt distribution map from the original Geochemical Atlas of Alaska (Weaver et al., 1983) and (b) new map plotted by Lee et al. (2016). Large blocks of unleveled data, identifiable by their straight-edge boundaries (map sheet boundaries), show the effects of uncorrected bias in the analytical results. Modified by Smith DB, Smith SM and Horton JD (2013) History and evaluation of national-scale geochemical data sets for the United States. *Geoscience Frontiers* 4(2): pp. 167–183. doi: 10.1016/j.gsf.2012.07.002, Fig. 4, p. 172.

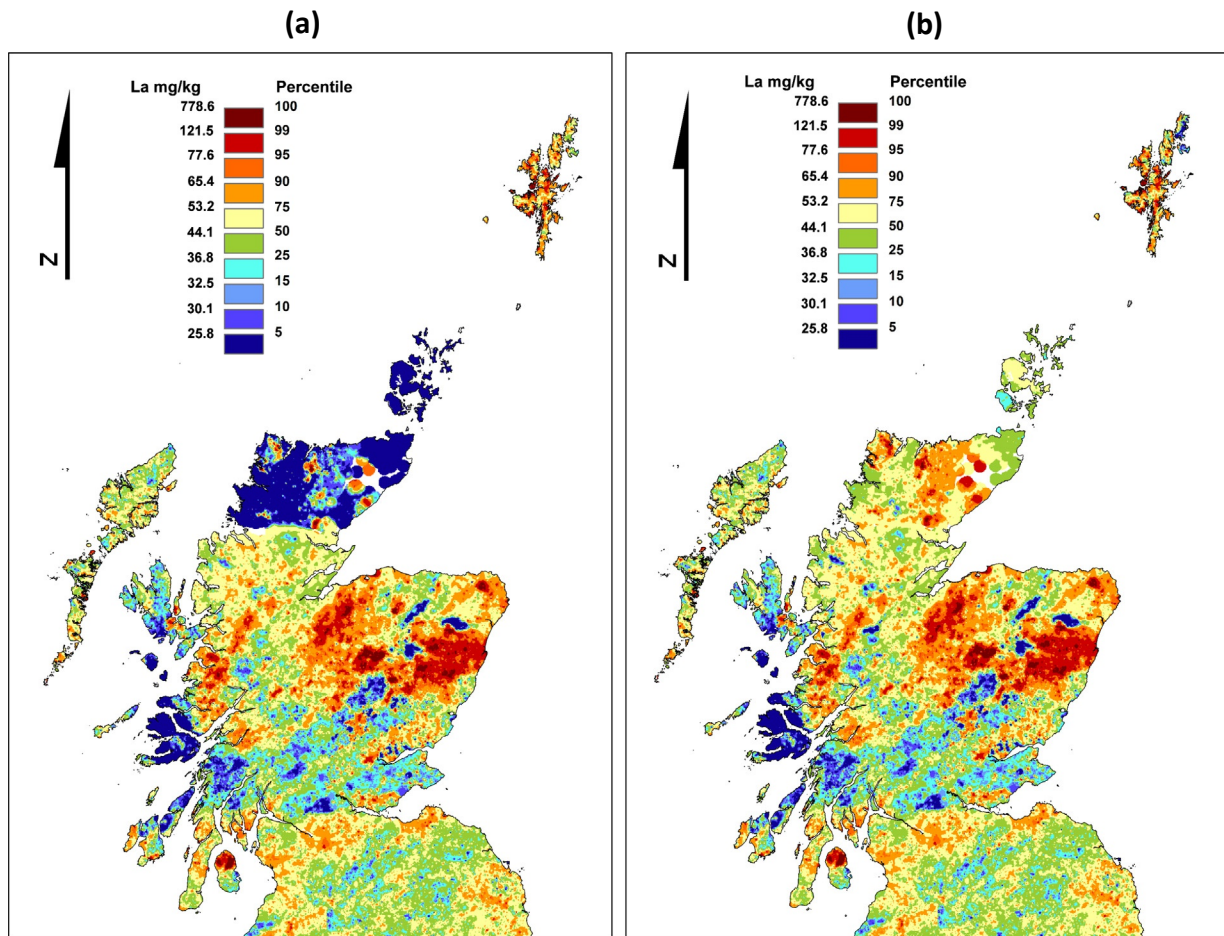


Fig. 43 Lanthanum in stream sediment samples from northern Britain based on combined datasets from La determined by DC-OES and ICP-MS. Maps with (a) Unleveled ICP-MS La results, and (b) Leveled ICP-MS La results. From Johnson CC and Lister TR (2022) Data Conditioning Methods: Generating Time Independent Geochemical Data. In: Demetriades A, Johnson CC, Smith DB, Ladenberger A, Adanez Sanjuan P, Argyraki A, Stouraiti C., de Caritat P, Knights KV, Prieto Rincon G and Simubali GN (eds.) *International Union of Geological Sciences Manual of Standard Methods for Establishing the Global Geochemical Reference Network*. Athens, Hellas: IUGS Commission on Global Geochemical Baselines, Special Publication, 2, pp. 429–456. ch. 8, doi: 10.5281/zenodo.7307696, Fig. 8.13, p. 448.

In Table 1 the hot aqua regia extractable Ni concentrations of the FOREGS atlas top- and sub-soil samples, which have been determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), have a reported lower detection limit of 2 mg Ni/kg; in this case, it is the LoQ (Sandström et al., 2005). Thus, all Ni values reported <2 mg/kg were converted to half the value of the detection limit, i.e., 1 mg/kg Ni. However, if the analytical results are plotted on a cumulative probability plot as shown in Fig. 44, the real lower detection limit of this method appears to be lower as indicated by the flattening of the curve below the reported detection limit. This example, and others that can be found in Demetriades et al. (2022a) and Johnson and Lister (2022), emphasize the importance of using the recorded (uncensored) rather than the reported (censored or truncated) analytical results.

What tables and diagrams should be compiled and plotted during the processing of geochemical datasets?

Table 1 shows the basic descriptive information and statistical parameters that should be given or estimated for each element, i.e., number of samples, grain size (sieved fraction and analytical), detection limit, minimum and maximum values, the 5th, 10th, 25th, Median (50th), 75th, 90th, 95th, 97.5th, median absolute deviation (MAD) and order of magnitude. Of course, other percentiles could be used, e.g., 2nd, 5th, 10th, 25th, 50th, 75th, 90th, 95th, 98th.

The histogram is the most widely used diagram for displaying the statistical distribution of geochemical results (Till, 1974; Koch Jr. and Link, 1970; Sinclair, 1983; Reimann et al., 2008). The concentration of the studied element is plotted on the X-axis (abscissa), and the frequency of occurrence (or the % frequency) on the Y-axis (ordinate). The selection of class intervals is an important issue because this will show the statistical distribution of the studied determinand, and the key is the bin width and number of bins. Hence, some experimentation is required for finding the optimum histogram structure for the dataset of each element. The histogram is also used by some researchers for the visual estimation of populations and the threshold between background and anomalous values. Fig. 45 shows a histogram and the difficulty of estimating populations. Hence, if the histogram is going to be

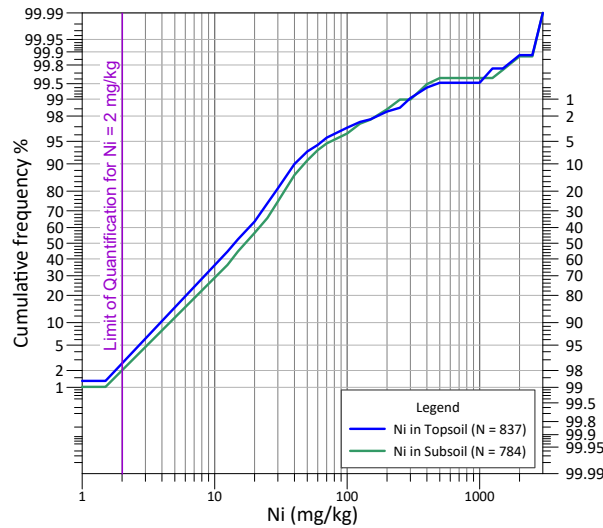


Fig. 44 Cumulative probability plot indicating the true detection limit for the FOREGS atlas Topsoil and Subsoil samples determined by hot aqua regia (Sandström et al., 2005). The plot demonstrates that the real detection limit (i.e., the point at the lower end of the cumulative distribution curve where the curve becomes horizontal) is lower than that cited by the analyst, which is indicated by a vertical magenta color line on the plot. Plotted with Golden Software's Grapher™ v21.

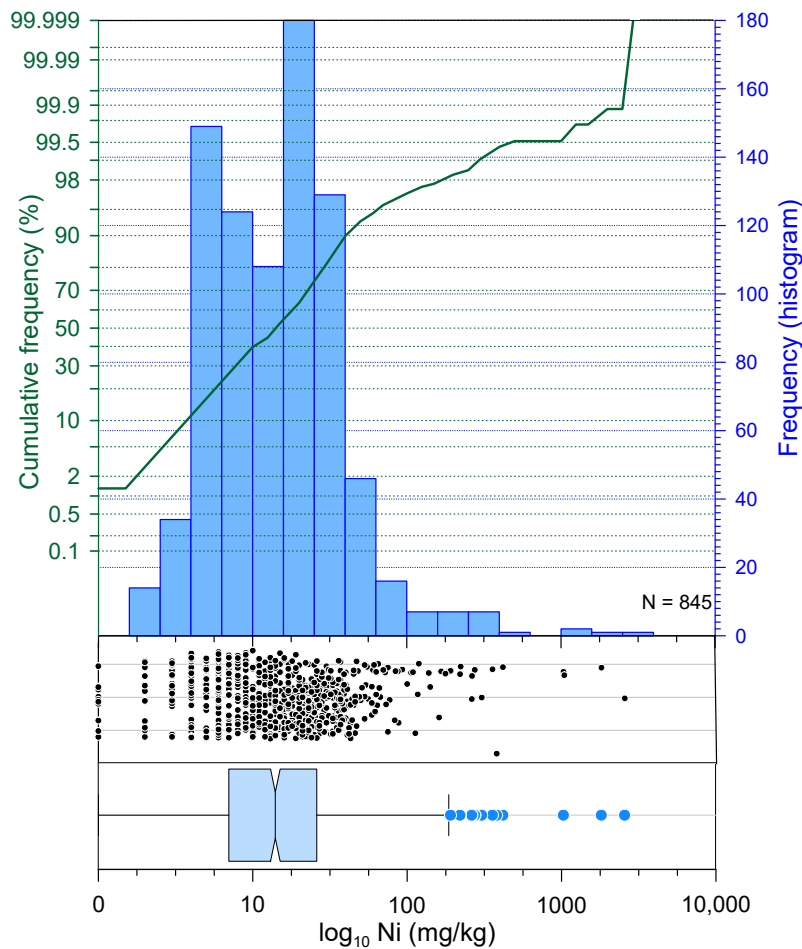


Fig. 45 Histogram, cumulative frequency % curve (green line), one-dimensional scattergram and notched box-and-whisker plot of \log_{10} -transformed aqua regia Ni concentrations in topsoil, determined by ICP-AES, FOREGS Geochemical Atlas of Europe (Salminen et al., 2005). The left Y-axis shows the cumulative frequency % (probability scale), the right Y-axis the histogram frequency, and the X-axis the class interval bins. The advantage of using \log_{10} -transformed data is that the statistical distribution is more symmetric and lower and upper outliers of the notched-box-and-whisker plot are displayed if, of course, they exist. Plotted with Golden Software's Grapher™ v21.

used for population splitting, it is better to be combined with the cumulative frequency curve, the one-dimensional scattergram and the boxplot as displayed in Fig. 45. This combination provides a powerful insight of the statistical distribution of element concentrations (Reimann et al., 2003, 2008; Reimann and Birke, 2010; Filzmoser et al., 2014; Tarvainen et al., 2022). Of course, the cumulative frequency plot (Figs. 21 and 24) could be used for a more detailed study of the statistical distribution of an element (Cassie, 1954; Tennant and White, 1959; Williams, 1967; Lepeltier, 1969; Sinclair, 1974, 1976, 1983, 1986).

It is stressed that the arithmetic mean, and standard deviation no longer have a place in geochemistry, as it is well-known that geochemical data do not follow the normal Gaussian distribution (Ahrens, 1954a, 1954b; Reimann and Filzmoser, 2000; Reimann et al., 2008). Hence, for the central value and standard deviation, statistical estimators based on ranks should be used, such as the median and median absolute deviation (MAD), respectively (Table 1).

How are geochemical data presented on maps?

The most common types of geochemical maps are:

- (i) Point-symbol maps showing determinand values at the sample locations (Figs. 19, 20, 22, 23, 26, 38).
- (ii) Color-surface contour maps based on interpolated and smoothed data (Figs. 2, 3, 25, 28, 37, 43).
- (iii) Color-surface contour maps with superimposed variable-size dots at the sample locations (Figs. 27 and 36),
- (iv) Color-surface contour ratio maps with superimposed variable-size dots at the sample locations (Fig. 46) and
- (v) Multi-component maps display the simultaneous variation of a few elements of interest, and these include factor analysis scores maps (Fig. 47; Batista et al., 2006).

Color-surface geochemical maps

Color-surface geochemical maps are produced by interpolation of point element concentrations into unsampled space. The methods used for interpolation of sample element concentrations or measurements into unsampled space for the generation of a grid of estimated measurements assume that there is an autocorrelation between or among them. Interpolation of point geochemical results into unsampled space must be carried out with the utmost care. Nowadays software packages offer numerous spatial interpolation methods, and you must be aware that many factors affect the predictive performance of each method. Therefore, it is strongly recommended to study the advantages and disadvantages of each interpolation method. The commonest interpolation method used in geochemical map production is inverse distance weighting (Davis, 1973, 1986; Howarth, 1983; Reimann et al., 2008). The best interpolation method, which is no longer available, was the Alkemia Smooth interpolation procedure developed by Gustavsson et al. (1994, 1997). This method applied a moving weighted median, instead of the commonly used weighted mean. The Alkemia Smooth interpolation method was used for plotting the color-surface maps of the FOREGS Geochemical Atlas of Europe (see Fig. 36; Salminen et al., 2005; Tarvainen et al., 2005, 2022). An important addition on the color-surface geochemical maps is the superimposed proportional or variable-size dots at the sampling points. The dots are centered at the sampling points and their size varies continuously with the concentration of the presented element. As pointed out by Gustavsson et al. (1997) the continuous dot size function avoids the problem of subjectively classifying observations into discrete classes and generating artificial levels. The dots are always surrounded by a thin white girdle, which keeps them visible even when clustered on the map (Figs. 36, 46, 47). An important piece of advice is to order the element concentrations from higher to lower and to plot them in a descending size order, thus avoiding the small dots of being covered by the larger ones.

Since the 1980s, geostatistics began to be used in the processing of geochemical data, and plotting of maps with kriging algorithms (e.g., Clark, 1979; Royle, 1992; Reis et al., 2003; Reimann et al., 2008; Paz-Ferreiro et al., 2010). Kriging is the general name of geostatistical interpolation methods. Kriging is the recommended interpolation method, because the predicted values in unsampled space are estimated from the values of nearby samples using sophisticated weighted average techniques, which minimize estimation errors. Even if you use kriging to plot color-surface geochemical maps, again it is strongly recommended to superimpose on the color-surface map a proportional or variable-size dot map (see examples in Figs. 27 and 36). The reason is to show the actual concentrations at each sample site, verifying indirectly the validity of the interpolation method used.

Geostatistical data processing

Geostatistical methods are based on statistical models, which assume spatial autocorrelation between the variables, and in the case of geochemical mapping the variables are:

- (i) The concentration of an element or value of any determinand (or measurand) in spatial samples, and
- (ii) The distance between the samples (geographical location of the sample).

What is the meaning of the above two variables? It is assumed that when the samples are near to each other the (auto)correlation between or among them is high. In contrast, as the distance between or among samples increases (auto)correlation is reduced.

Why should geostatistics be used for plotting color-surface geochemical maps? Kriging is considered to be an optimal spatial interpolator or predictor of regionalized variables, provided the data meet certain criteria (Clark, 1979; Royle, 1979, 1992; Hengl, 2007).

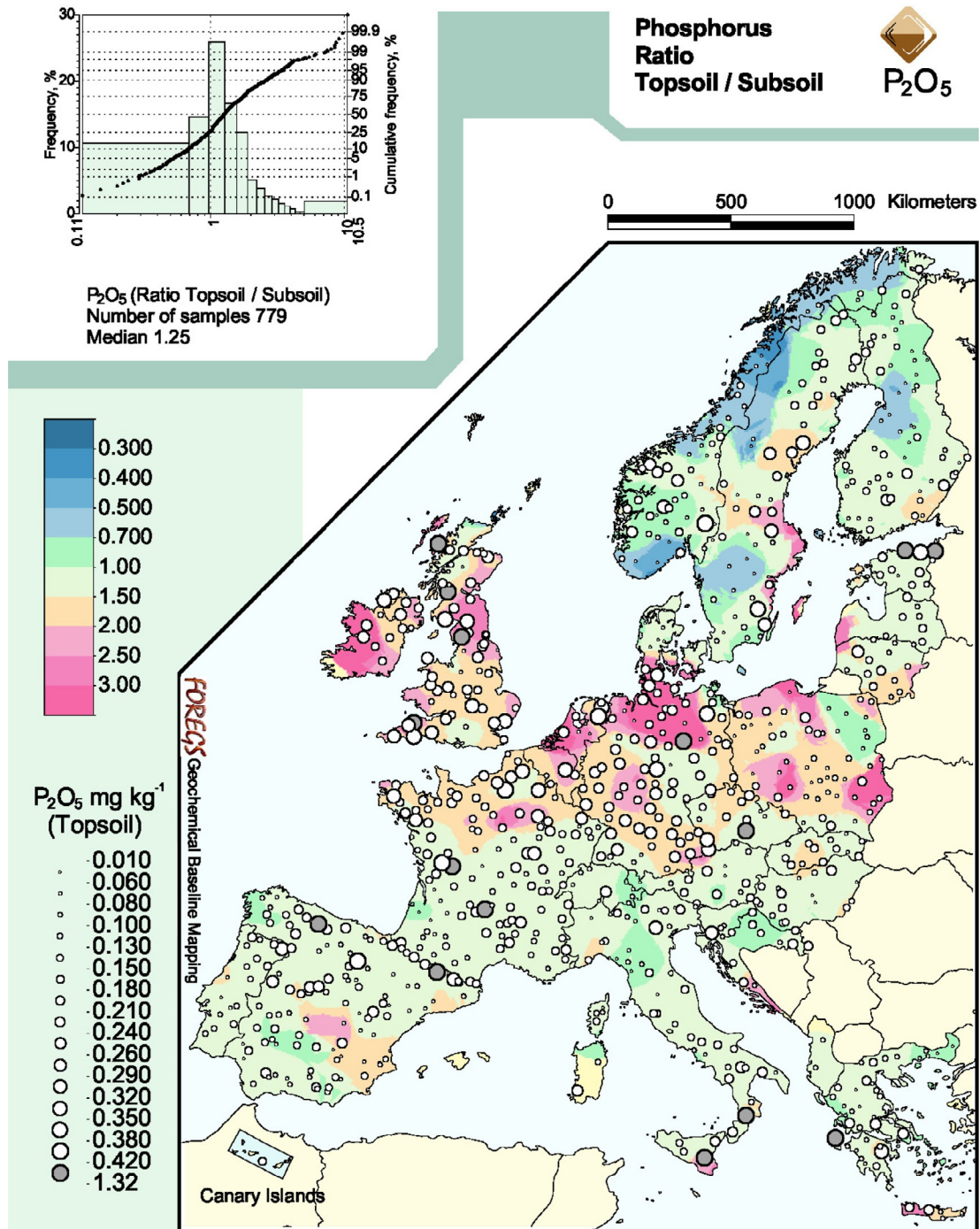


Fig. 46 Color-surface ratio map of P_2O_5 concentrations in topsoil/subsoil with superimposed variable-size or proportional dots, FOREGS Geochemical Atlas of Europe. The contrast between subsoil and topsoil points to different mineral phases carrying the phosphate (notably a weaker association with phyllosilicate minerals in topsoil) and could generally be related to fertilizer use (anthropogenic contamination in topsoil). From De Vos W, Tarvainen T, Salminen R, Reeder S, De Vivo B, Demetriades A, Pirc S, Batista MJ, Marsina K, Ottesen RT, O'Connor PJ, Bidovec M, Lima A, Siewers U, Smith B, Taylor H, Shaw R, Salpeteur I, Gregorauskiene V, Halamic J, Slaninka I, Lax K, Gravesen P, Birke M, Breward N, Ander EL, Jordan G, Duris M, Klein P, Locutura J, Bel-Lan A, Pasieczna A, Lis J, Mazreku A, Gilucis A, Heitzmann P, Klaver G and Petersell V (2006) *Geochemical Atlas of Europe. Part 2 – Interpretation of Geochemical Maps, Additional Tables, Figures, Maps and Related Publications*. Espoo: Geological Survey of Finland, 692 pp. Available at: <http://weppi.gtk.fi/publ/foregsatlas/>, Map 10, p. 279.

What is meant by regionalized variable and optimal spatial interpolator? A regionalized variable is a random variable that takes different values according to its spatial position (sample site) within a specific geographical region. Geochemical data are a good example of regionalized variables. The kriging algorithm, which is based on the parameters extracted from the variogram (Fig. 48), can predict unbiased values in unsampled space with the minimum errors of estimation. Incidentally, the variogram is the graphical representation of the spatial continuity of a geochemical dataset. The unbiased nature of geostatistical interpolation methods is especially important in the data processing of geochemical data. Further, geostatistics can help optimize sampling density.

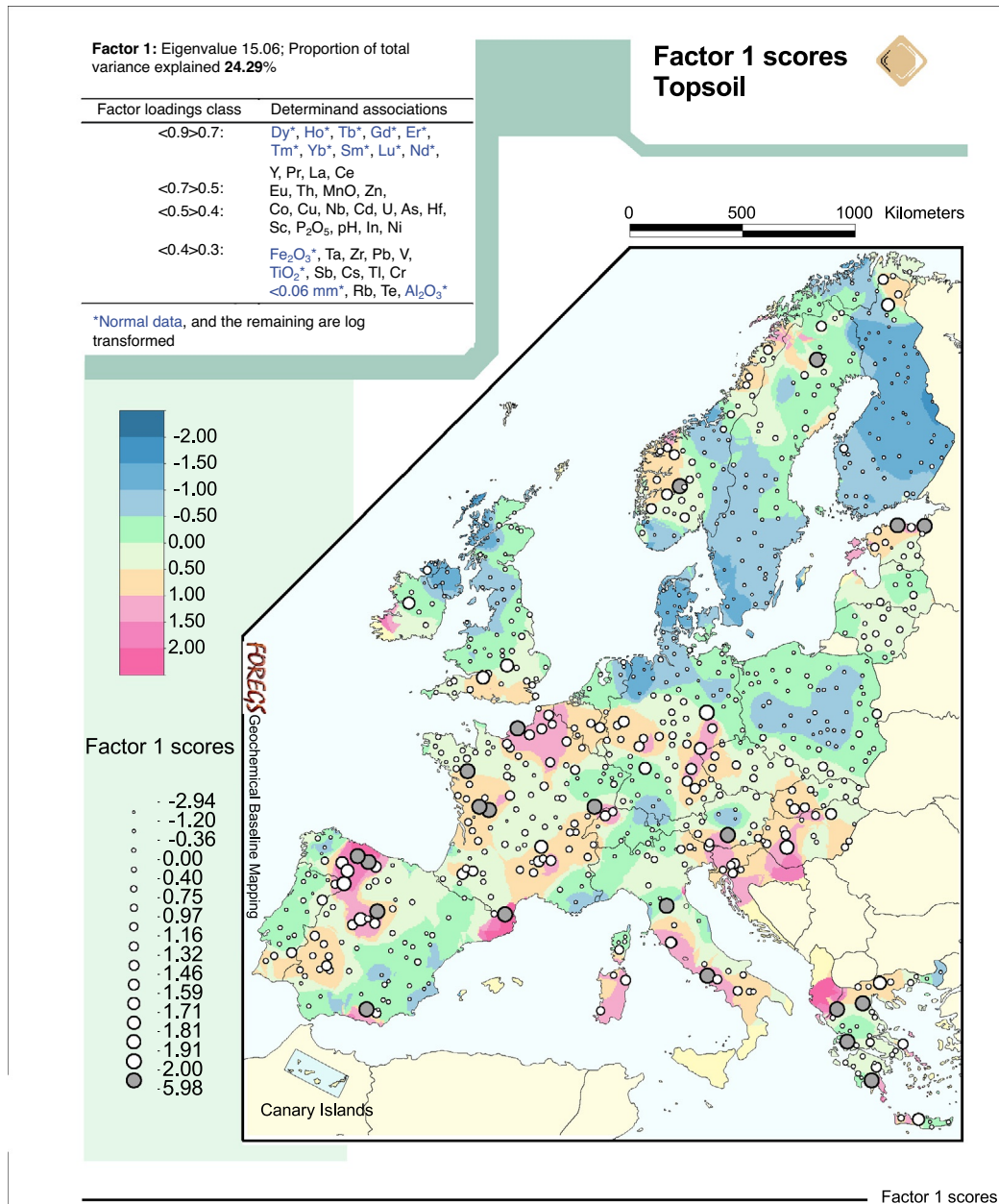


Fig. 47 Color-surface multicomponent map with superimposed variable-size or proportional dots of Factor 1 Varimax rotated scores in topsoil, FOREGS Geochemical Atlas of Europe. See text for an explanation of map construction. From Batista MJ, Demetriades A, Pirc S, De Vos W, Bidovec M and Martins L (2006) Factor analysis interpretation of european soil, stream and floodplain sediment data. Annex 5. In: De Vos W, Tarvainen T, Salminen R, Reeder S, De Vivo B, Demetriades A, Pirc S, Batista MJ, Marsina K, Ottesen RT, O'Connor PJ, Bidovec M, Lima A, Siewers U, Smith B, Taylor H, Shaw R, Salpateur I, Gregorauskiene V, Halamic J, Slaninka I, Lax K, Gravesen P, Birke M, Breward N, Ander EL, Jordan G, Duris M, Klein P, Locutura J, Bel-lan A, Pasieczna A, Lis J, Mazreku A, Gilucis A, Heitzmann P, Klaver G and Petersel V (eds.) *Geochemical Atlas of Europe. Part 2 - Interpretation of Geochemical Maps, Additional Tables, Figures, Maps, and Related Publications*. Espoo: Geological Survey of Finland, pp. 567–617. Available at: <http://weppi.gtk.fi/publ/foregsatlas/articles/Annex5.pdf>, Fig. 6, p. 582).

How many samples are needed for the geostatistical processing of geochemical data? The answer of my tutor in geostatistics, A.G. Royle, is “When geostatistics appears not to work, the reason is usually precisely that the data were insufficient in the first place” (Royle, 1979, p. 101). Therefore, he recommends starting by plotting a variogram of sample values. If the results do not produce an interpretable variogram, it can be concluded that the sampling interval is too large, or there is something else wrong with another characteristic of the dataset, such as small number of samples, as already pointed out. Even an apparently meaningful variogram should be examined very carefully.

Fig. 48 shows an example of a variogram with all features labeled, i.e., the magenta line is the experimental variogram with the pair of values at each lag distance; the blue curve is the fitted spherical model. It appears to be a perfect fit. However, if the variogram

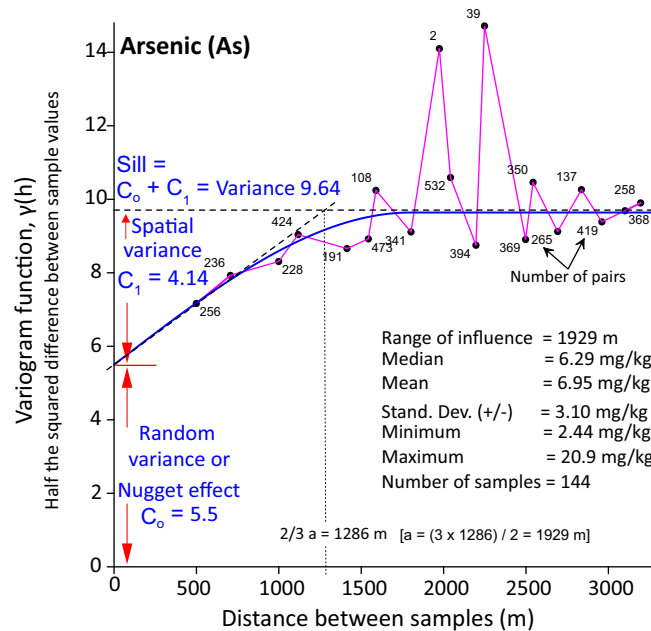


Fig. 48 Experimental (magenta line) and spherical model (blue line) variogram of As showing different features. The spherical model appears to fit perfectly well the experimental variogram. However, a careful study reveals that the random variance (or nugget effect) is larger than the spatial variance. This means that this particular As dataset, has a large sampling and analytical variance (random variance), suggesting that the data cannot be interpolated into unsampled space. From Demetriades A (2021) Geochemical mapping. In: Alderton D and Elias SA (eds.), *Encyclopedia of Geology*, 2nd edn. vol. 6, pp. 267–280. Academic Press, doi: 10.1016/B978-0-08-102908-4.00059-X., Fig. 2, p. 271. Plotted with Golden Software's Surfer™ v25.

is studied carefully, the experienced researcher will see that the random variance (or nugget effect) is larger than the spatial variance. This means that this particular As dataset has a large sampling and analytical variance (random variance), which implies that the data cannot be interpolated into unsampled space. In fact, the careful applied geochemist should have never reached this stage of data processing, because the quality control data would have shown that the sampling and analytical variances are extremely high, and the dataset is unsuitable for interpolation. Hence, with such data it is pointless to use geostatistics or any other interpolation method to predict values in unsampled space. However, there is a solution for such datasets, and this is the plotting of a point symbol map, using either exploratory data analysis (EDA) symbols (Tukey, 1977; Reimann et al., 2008; Tarvainen et al., 2022) or variable-size dots.

Guidelines for geostatistical data processing

The applied geochemist that would like to use geostatistics should follow first a course in geostatistics, because it is important to know the theory and procedures used in geostatistical data processing. Here only concise guidelines will be given, and a detailed account of geostatistical processing of geochemical data is outside the scope of this article. So, it is assumed that you have followed a course in geostatistics, and you would like to be given some tips of how to proceed in the geostatistical processing of geochemical data.

How does one carry out a geostatistical structural analysis on a geochemical dataset? To begin with, study the statistical distribution of the dataset. If the data are log-normal, then use logarithms (base-10 or base-e). Then many variograms should be plotted in different directions and, of course, studied very carefully to extract the necessary parameters for use in the kriging algorithm. The objective of this exercise is to discover if there is an interpretable geostatistical structure and if there are directional anisotropies in the dataset. This used to be a tedious and time-consuming process, especially if the variograms were plotted in the field camp with just a simple programmable hand-held calculator. Nowadays, different software packages provide a useful procedure for plotting a variogram surface (Fig. 49) with even a laptop computer (the analytical data are in Table S20). Variograms can be plotted either automatically or using a dedicated computer routine. In both cases, variograms at 1-min intervals can be plotted. In total, 179 variograms are plotted for the first two quadrants, and as the variograms in the other two quadrants are a mirror image, they can be easily transposed, and the final result is a very detailed geostatistical structural analysis of the studied dataset. The variogram surface reveals the existence of any directional spatial anisotropies of the dataset.

The first step with most software packages is the plotting of an experimental omnidirectional variogram, and directly afterwards the variogram surface. The omnidirectional variogram with a directional tolerance of 90 degrees takes into consideration all sample points and is able to detect the existence of spatial continuity in a sample dataset (Barnes, 2023).

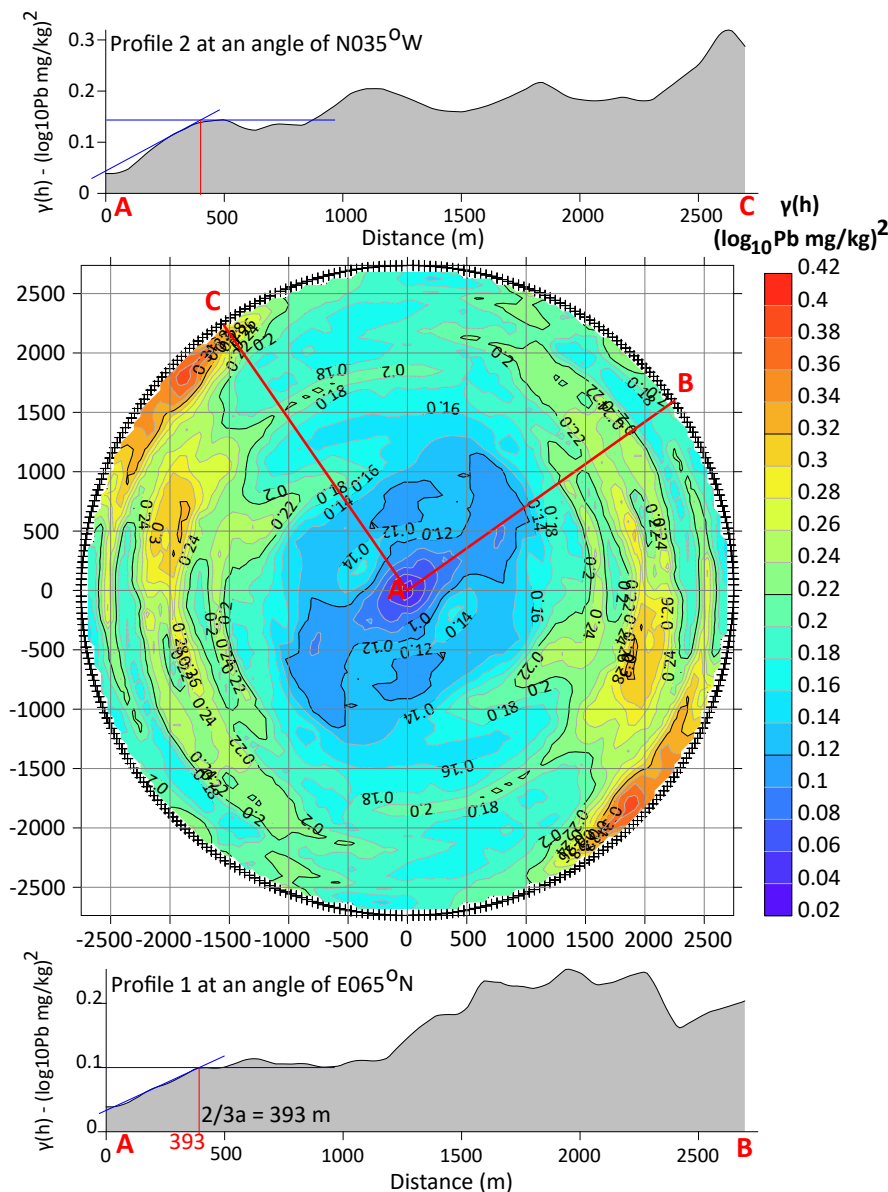


Fig. 49 Experimental variogram surface of total Pb (log base 10) in surface soil, Lavrion urban area, Hellenic Republic. Profiles 1 (A-B) and 2 (A-C) show the features of the major and minor axes, respectively, and the initial estimates of the range of influence in both directions, using a spherical model. Plotted with Golden Software's Surfer™ v25. See soil geochemical map of Pb in Fig. 50.

Fig. 49 shows the geostatistical structure of Pb concentrations in surface soil (overburden) of the Lavrion urban area (Fig. 50), a town situated to the southwest of Athens, the capital of the Hellenic Republic (Latitude 37.710635°; Longitude 24.052526°). The variogram surface, as observed in Fig. 49, helps in the identification of any anisotropy in the studied dataset, and the determination of the direction of anisotropic axes. In this case, it shows an elliptical shape at the center, with the major axis at E035°N, and the minor axis at N035°W, with the final range of influence at 684 and 573 m, respectively (Fig. 51). This means that the spatial dependence (autocorrelation) changes with respect to both distance and direction between two sample points. This feature is called anisotropy, as opposed to isotropy, which implies that the spatial variability does not vary along different directions, and the shape of the spatial variance is near circular.

The second step is to draw profiles along the major and minor axis of the ellipsoid. In Fig. 49, the variogram structure of the major and minor axes of the ellipsoid are shown (Profiles 1 and 2), together with the first rough estimation of the range of influence by fitting a spherical model.

The third step is to draw variograms along these two directions to study in detail the spatial geostatistical structure of the dataset, and to extract the necessary parameters to perform anisotropic kriging. It may be necessary to remove trends by applying either a linear or a quadratic filter. In this case, no filters were applied. The variogram surface and the two profiles 1 and 2 show that there are

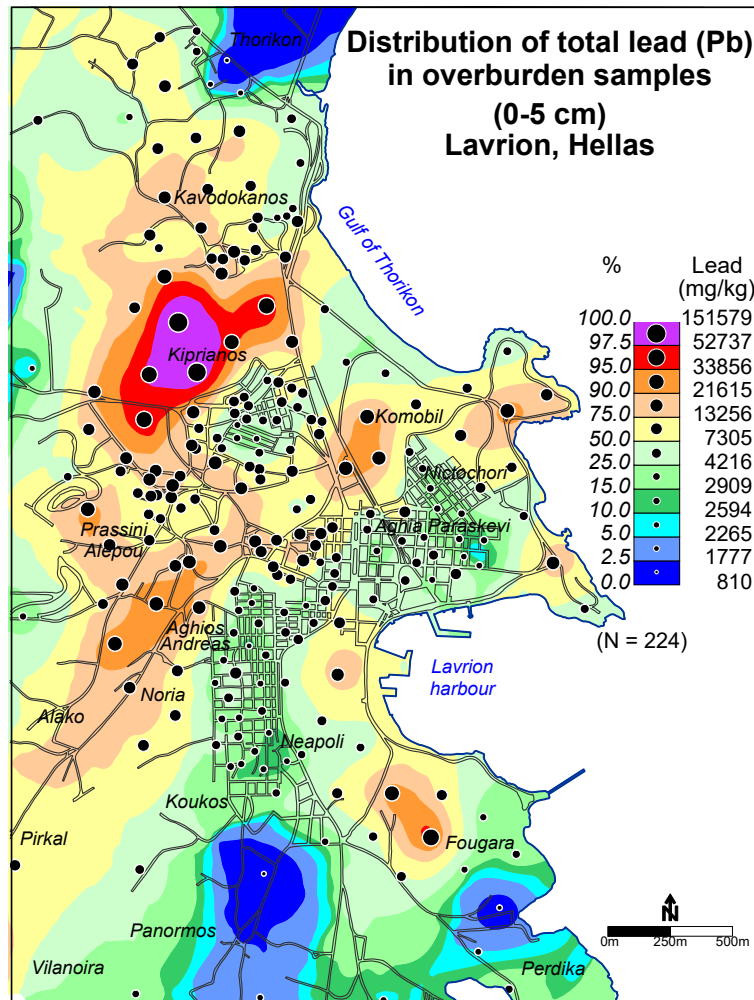


Fig. 50 Distribution maps of Pb in samples of overburden (0–5 cm), Lavrion urban area, Hellenic Republic. From Demetriades A (2011a) The Lavrion urban geochemistry study, Hellas. In: Johnson CC, Demetriades A, Locutura J and Ottesen RT (eds.), *Mapping the Chemical Environment of Urban Areas*. Chichester: Wiley-Blackwell, John Wiley & Sons Ltd., ch. 25, pp. 424–456. doi:10.1002/9780470670071.ch25, Fig. 25.8, p. 444. Plotted with Golden Software’s Surfer™ v25.

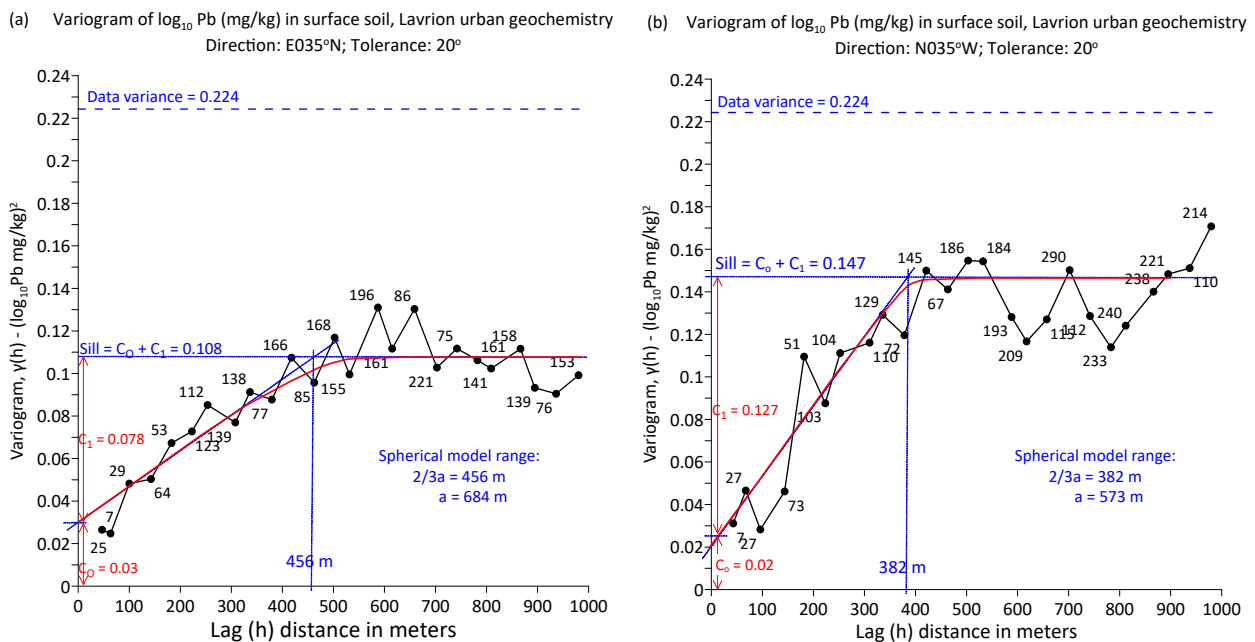


Fig. 51 Variograms of \log_{10} Pb (mg/kg) along the two directions indicated by the variogram surface (a) major axis at $E035^{\circ}N$, and (b) minor axis at $N035^{\circ}W$, Lavrion urban geochemistry (Demetriades, 2011a). Plotted with Golden Software’s Surfer™ v25. See soil geochemical map of Pb in Fig. 50.

structures beyond 1000 m (Fig. 49). So, experimental variograms were plotted up to 1000 m (Fig. 51), because it is considered unlikely, in such a contaminated environment, the range of influence to extend beyond this limit.

The variograms, indicated by the variogram surface in the two directions, (Fig. 49) were plotted, i.e., along the major axis at E035°N (Fig. 51a), and along the minor axis at N035°W (Fig. 51b). A spherical model was fitted, and the range of influence in both directions estimated. It can be observed that there are changes in the range influence, which was initially roughly estimated from the profiles drawn from the variogram surface (Fig. 49) with respect to the ones estimated from the directional variograms (Fig. 51), i.e., (i) first rough estimation 428 m and 320 m in comparison to (ii) 684 m and 573 m, respectively. This is, of course, expected during the modeling stage. It is also expected that these estimations will most likely change during the kriging interpolation, because they are validated by a cross-validation procedure.

What does cross-validation mean? Cross-validation uses the experimental variogram parameters to estimate the actual sample values. It removes each sample value one at a time and tries to predict its actual value by using nearby sample values, and the estimated experimental variogram parameters. This procedure is carried out for all actual sample values. The objective is to predict the actual sample value with the minimum error, or kriging variance. If the error between the actual sample value and the predicted is large, it means that the variogram parameters used are not correct, and they are changed until the best fit is achieved. The results of the cross-validation procedure can be examined either in a table or on an X-Y plot of original versus estimated values. The experimental variograms (Fig. 51) show that the random variance (C_0), which includes the sampling and analytical errors, varies from 0.02 to 0.03 ($\log_{10}\text{Pb mg/kg}$)². Hence, the aim is to achieve an error kriging variance in this order of magnitude. For plotting the color-surface map of Fig. 50 the final parameters (a) major axis at E032°N and a range of influence at 630 m, and (b) minor axis at N032°W, and a range of influence at 435 m, were used. These parameters are slightly different from the ones that have been estimated by the variogram modeling (Fig. 51), because several tests were made until the optimum geostatistical model was reached.

It is finally stressed that cross-validation is an important validation procedure, which was first introduced in the geostatistical processing of data. Nowadays, it has been built in almost all interpolation methods, and should always be used for the verification of interpolated values into unsampled space.

Compositional data analysis

Geochemical data are usually reported as concentrations in units of $\mu\text{g/kg}$, mg/kg or weight percent (wt%) and are, thus, a classic example of compositional (closed) data (Aitchison, 1982, 1986, 1997, 2008; Aitchison and Egozcue, 2005; Buccianti et al., 2006; Egozcue and Pawlowsky-Glahn, 2011; Pawlowsky-Glahn and Buccianti, 2011; Pawlowsky-Glahn et al., 2015; Grunsky et al., 2018; Greenacre, 2018, 2021; Greenacre et al., 2021).

What are compositional data? Compositional data are non-negative data carrying relative, rather than absolute, information—these are often data with a constant-sum constraint on the sample values (Greenacre, 2021).

What is meant by closed data? If all chemical elements in a sample of rock, soil, sediment, or water are analyzed, the analytical results sum up to a constant, i.e., 1,000,000 mg/kg or 100 wt%. Hence, no single chemical element is free to vary separately from the rest of the total chemical composition. Even if not all chemical elements in the periodic table are analyzed, the total element concentrations still depend on each other. Such data are called “compositional” or “closed” data (CoDA)—and they do not belong to the classical Euclidean space. Here we have a little problem, because almost all classical statistical methods are built around Euclidean distances for unconstrained data. Compositional or constrained data have their own geometry on the Aitchison simplex (Aitchison, 1986). Therefore, geochemical data must be transformed before statistics, based on Euclidean distances, are used. However, the skeptical applied geochemist may wonder:

- We have been using classical statistics for data processing of geochemical data, and the derived results were interpretable.
- We know that geochemical data do not follow a Gaussian distribution, and that if we want to use conventional classical statistics the data must be logarithmically transformed to approach lognormality, and the derived results were again interpretable.
- We have been told that few extreme measurements, which deviate from the main body of a geochemical dataset, can influence significantly classical statistical parameters, such as the mean and standard deviation, and it is better to use non-parametric statistical techniques, such as Exploratory Data Analysis (EDA), for the statistical processing of geochemical data. The reason is that EDA has no conditions about the statistical distribution of data, and that the median and median absolute deviation are not affected significantly by extreme values, and again the derived results were interpretable.
- For the past few years, we have seen many papers that use compositional data analysis for the treatment of geochemical data. So, “*What goes wrong when we apply multivariate statistical methodology designed for unconstrained data to our constrained data and how can the unconstrained methodology be adjusted to give meaningful inferences?*”, a question asked by John Aitchison himself during his lectures.

So, let us now examine the advantage of using compositional data analysis with two examples from the European atlas of Agricultural and Grazing land soil, the GEMAS Atlas project (Reimann et al., 2014a, 2014b; Table S21).

To process statistically the constrained or closed geochemical data, they need to be ‘opened’. Presently, there are three ‘opening’ transformations, all based on log-ratios:

- *Additive log-ratio (alr) transformation* (Aitchison, 1986): the alr transformation sacrifices one element (e.g., Ti), and the analytical results of each sample are divided by the analytical result of the sacrificed variable (e.g., Ti), and the quotient is then log transformed; it is noted that if any other variable from the dataset is sacrificed, then different results are expected.

- *Centered log-ratio (clr) transformation* (Aitchison, 1986): the log-ratios of the results of each element in a sample are estimated by dividing the individual values of each element by the geometric mean of all the determined elements for that sample, and the quotient is then log transformed, and
- *Isometric log-ratio (ilr) transformation* (Egozcue et al., 2003): the expressions for the calculation of ilr are more complex and there are different rules on how to generate them; the ilr transformation preserves all geometric properties for multivariate data analysis but the direct relation to the elements is lost, although it is possible to back-transform the data to the original data space for interpretation; the results, however, are not always easy to interpret geologically.

Fig. 52 shows four variable-size dot maps displaying the distribution of total K and P in agricultural soil determined by X-ray fluorescence (XRF). It was expected that the distribution patterns of total K and P will be disturbed by input from nitrogen-phosphorus-potassium (NPK) fertilizers, especially in the north-central European plain, extending from Ukraine through Poland and northern Germany to The Netherlands and Belgium (Fig. 52a and c).

There are many areas with high total K concentrations in agricultural soil, such as (i) areas underlain by granitic rocks (e.g., northern Spain/Portugal, Massif Central in France, Bohemian-Moravian Massif in Czechia); (ii) the alkaline volcanic rocks in southern-central Italy, and (iii) felsic metamorphic rocks in Sweden, southern Norway, and Finland (Fig. 52a). In southern Sweden

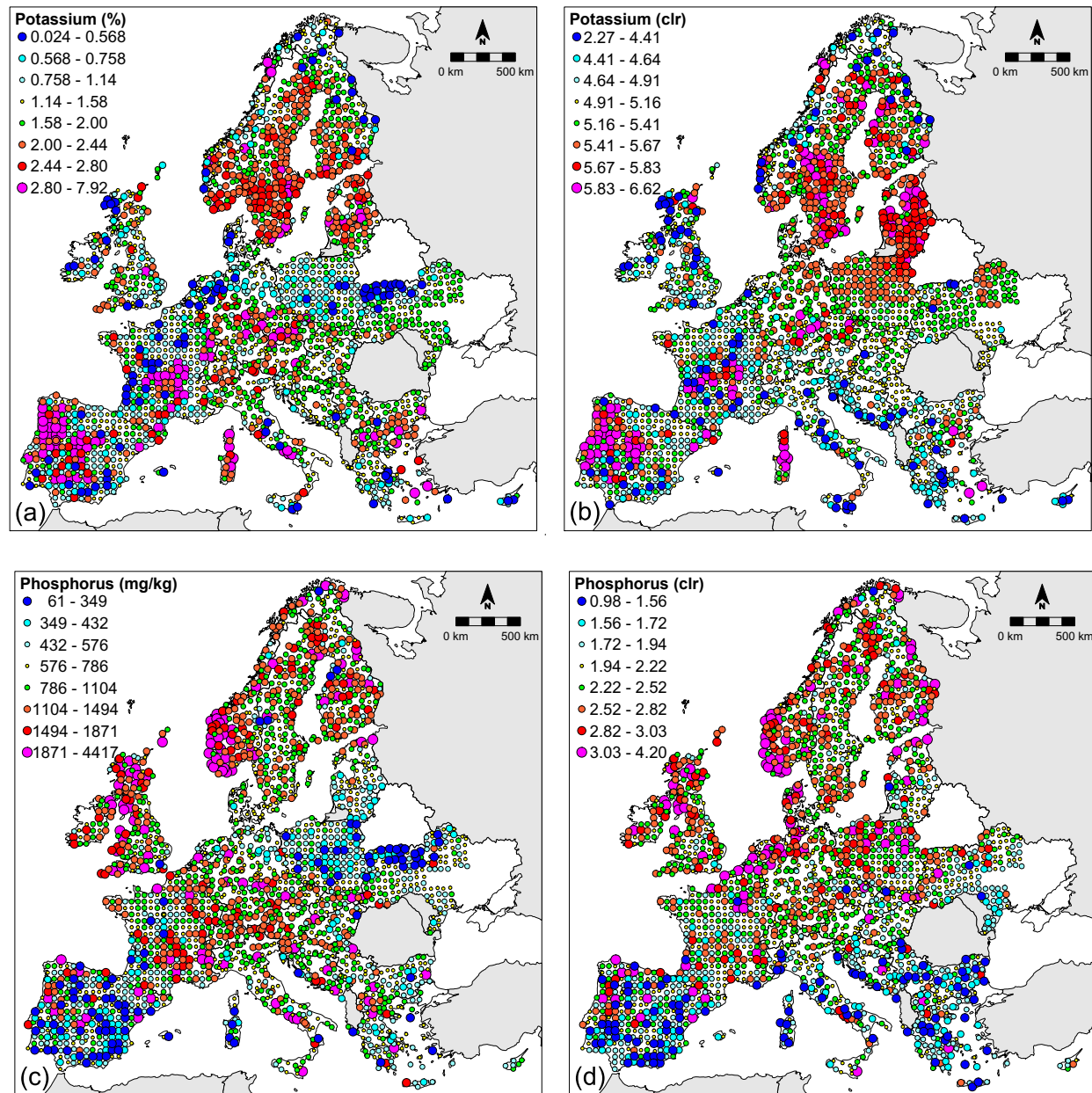


Fig. 52 Geochemical maps comparing the distribution of total K and P determined by XRF in European agricultural soil in two different treatments: (a) K raw data, (b) log-ratio transformed clr K, (c) P raw data, and (d) log-ratio transformed clr P. Data from Reimann C, Birke M, Demetriades A, Filzmoser P and O'Connor P (eds.) (2014a) *Chemistry of Europe's Agricultural Soils—Part A: Methodology and Interpretation of the GEMAS Data Set*. Hannover: Geologisches Jahrbuch (Reihe B 102), Schweizerbart, 528 pp. + DVD. Available at: <https://www.schweizerbart.de/publications/detail/isbn/9783510968466>. Plotted with Golden Software's MapViewer™ v8.

and Finland, high K concentrations are often due to the occurrence of clay-rich soil. It is concluded that the total K patterns, as determined by XRF, are clearly driven by geology (Reimann et al., 2014a).

High total P values in agricultural soil occur in parts of Fennoscandia and the United Kingdom (Fig. 52c). This spatial distribution is probably related to climatic conditions (a wet and cold climate favors the build-up of organic material rich in P). The Alpine Region (especially the western part) is marked by somewhat enhanced P concentrations. This is most likely related to the Crystalline Massifs and to the big tectonic lines with associated magmatic rocks (Rhône-Simplon-Insubria-Periadriatic Line). It appears somewhat surprising that geology and climatic factors so completely dominate the geochemical map of P, where it was expected that its distribution will be influenced by anthropogenic activities (Reimann et al., 2014a).

Agricultural soil, occurring on top of glacial sediments in the northern European plain (but note the difference in Baltic States), gives uniformly low total K and P concentrations (Fig. 52a and c). The effects of agricultural practice on these agricultural soil samples are, thus, not immediately deducible from the total K and P maps. However, the patterns change significantly on the maps showing the distribution of centered log-ratio K and P (Fig. 52b and d). It suddenly becomes visible that, relative to the geometric mean of these two major elements, they are highly abundant in the glacial sediments of north-central Europe.

What is the reason for the visible effect of the NPK fertilizers in the soil of the north-central European plain? The reason for the low total K and P values displayed in the raw data concentration maps is that the collected soil samples occur over the glacial sediments, which contain more than 75% SiO₂ (also known and discussed in the geosciences as “the quartz dilution effect” see, for example, Bern (2009)). Hence, there is not much room for all other elements to vary. The relatively high clr(K) and clr(P) may be an indication of high input of fertilizers on this rather poor agricultural soil (Reimann et al., 2012b; Filzmoser et al., 2014). It is worth comparing the clr(P) map (Fig. 52b) with topsoil/subsoil P₂O₅ ratio map (Fig. 46), which shows similar features. The reason that they are similar is because the P₂O₅ concentrations in topsoil are compared with the subsoil samples.

The disadvantage of log-ratio data transformation is that the concentration units are lost. However, log-ratio (clr) maps show the relative abundance of an element with respect to the geometric mean of all elements measured on each sample. Experience shows that sometimes clr(Element) maps look similar to the usual element concentration maps, while in other cases very different patterns can become visible, as has already been shown by the two examples (Filzmoser et al., 2014). Geochemists believed for many years that there would be a strong effect only for the major elements, like Si and possibly Al. However, whether there is an effect is not only dependent on the absolute concentration of the elements, but also from the geometric mean of all variables determined on each sample.

Therefore, it is worth plotting the usual element concentration and the log-ratio maps. For best results, the clr-transformation should be performed where more than 97% of all analytical results are above the lower detection limit (Reimann et al., 2012b; Filzmoser et al., 2014).

3D geochemical mapping

Computer technology and software have advanced considerably during the last decade, and it is now possible to process geochemical data quite easily from drill-hole cores from mineral exploration and environmental contamination projects. Further, to model in 3D surface geochemical data.

Fig. 53 is a 3D surface geochemical distribution map of hot aqua regia extractable Pb concentrations in the <0.177 mm grain-size fraction of C-horizon soil, which can be compared with the 2D color-surface map of Fig. 28.

Figs. 54–56 show the results of the ultra-detailed phase where drill-hole geochemical results are used in the preliminary assessment of ore grade and the estimation of reserves.

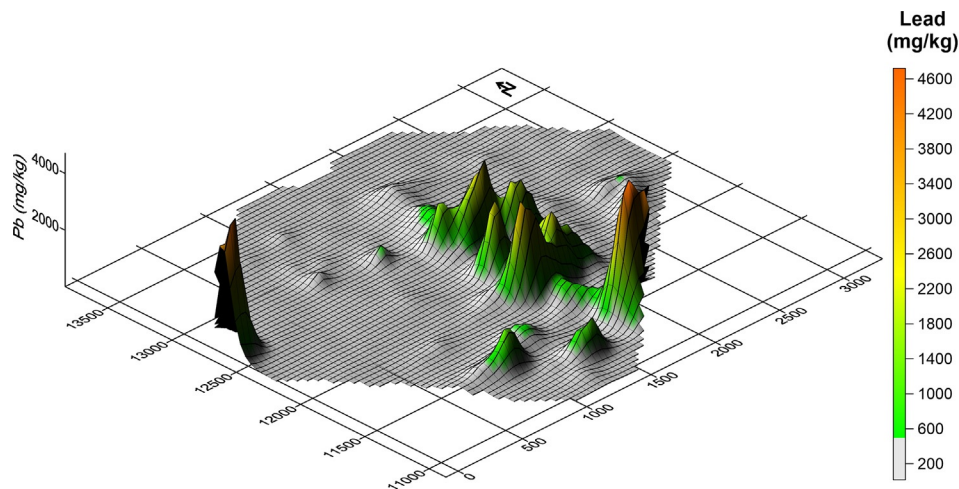


Fig. 53 Three-dimensional (3D) surface geochemical map of hot aqua regia extractable Pb concentrations in the <0.177 mm grain-size fraction of C-horizon soil, detailed soil geochemical survey, Thermae, Xanthi Prefecture, Thrace, Hellenic Republic (compare with Fig. 28; for its location see Fig. 25).

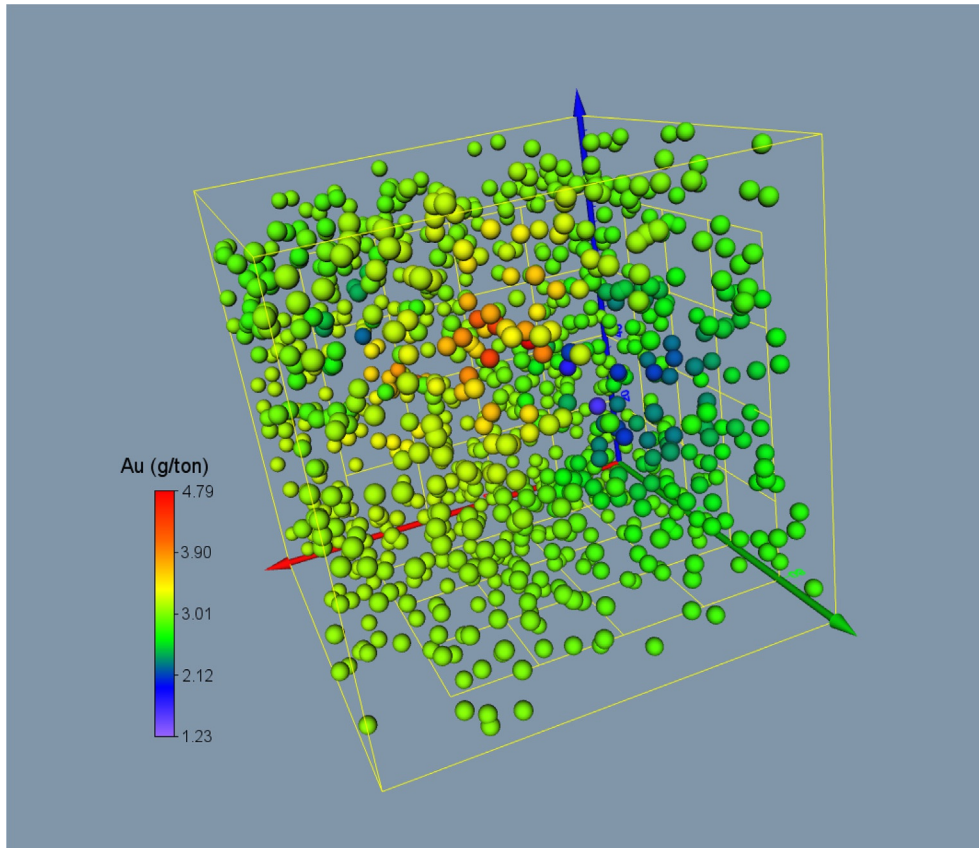


Fig. 54 Three-dimensional (3D) geochemical distribution map of Au. The data are provided as an example dataset by Golden Software (<https://www.goldensoftware.com/>). Plotted with Golden Software's Voxler™ v4.

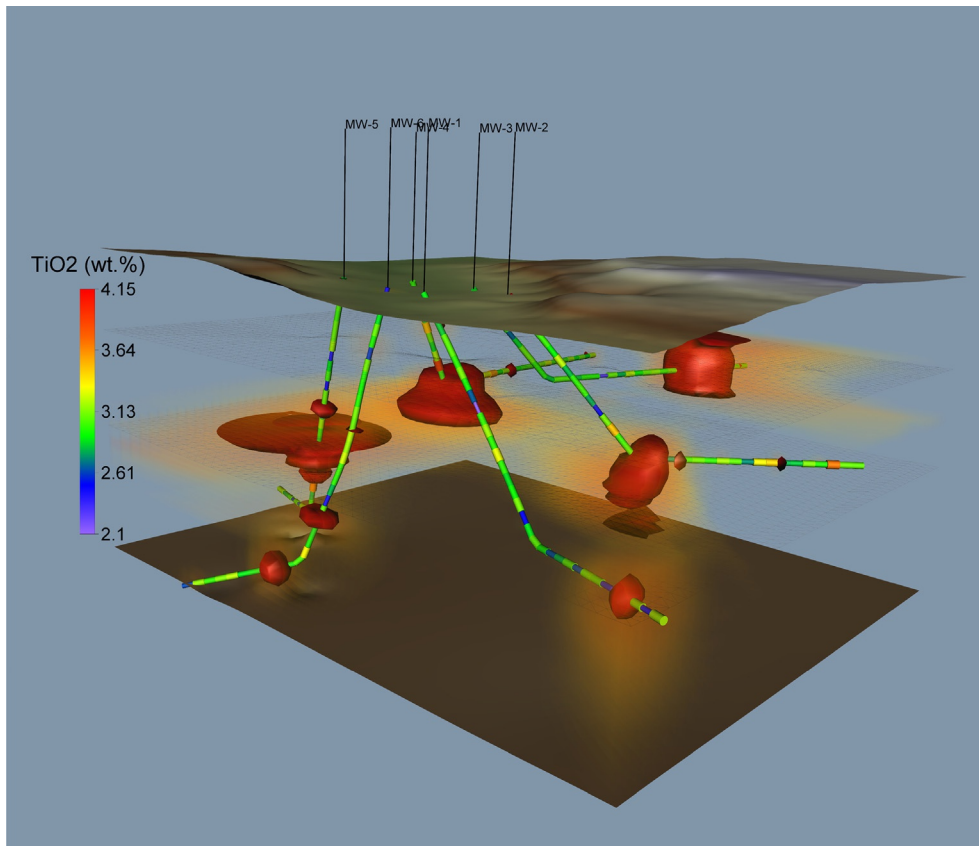


Fig. 55 Three-dimensional (3D) geochemical distribution map of TiO₂ distribution. The data are provided as an example dataset by Golden Software (<https://www.goldensoftware.com/>). Plotted with Golden Software's Voxler™ v4.

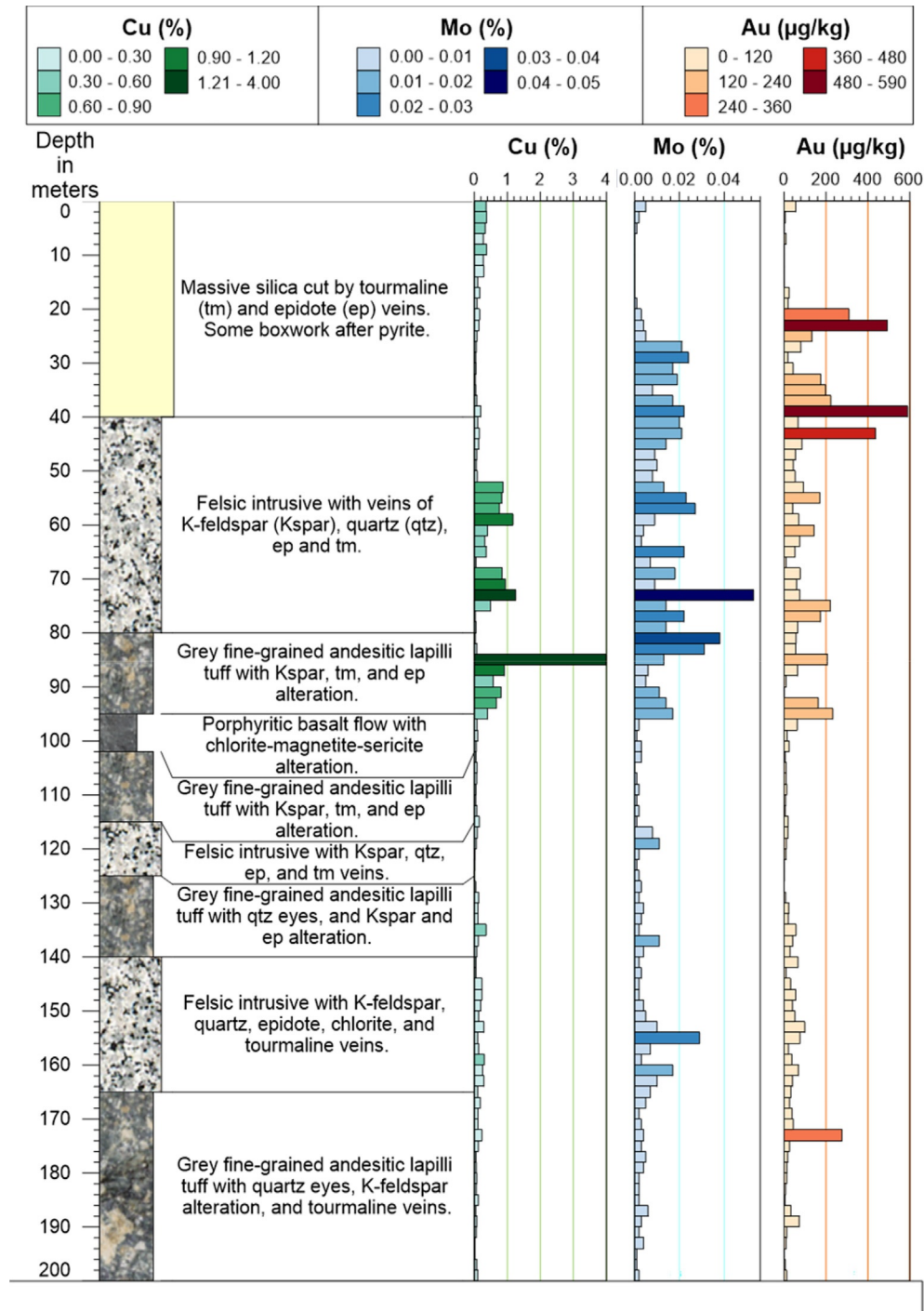


Fig. 56 Drillhole sample geochemistry. The drillhole log shows the lithology, and the assay results of Cu, Mo and Au of core samples collected every 2-cm down to a depth of 200 m without considering in a few cases that the sample is from two different rock units. *Is this a correct sampling procedure to mix two different rock types?* The results are provided as an example dataset by Golden Software (<https://www.goldensoftware.com/>). Plotted with Golden Software's Strater™ v5.

Fig. 54 is a 3D geochemical distribution map of Au concentrations in samples collected from different depths of a mineralized body (refer to Table S22). The richest parts of the ore body are displayed by the green, yellow, orange, and red shades.

Fig. 55 is a 3D geochemical distribution map of TiO₂ concentrations of contiguous core samples collected along the whole length of six drill-holes (refer to Table S23). The richest sections >3.64% TiO₂ are indicated with red color and their possible extensions by orange shades.

Fig. 56, although not strictly a 3D geochemical map, shows the Cu, Mo and Au concentrations of contiguous core samples and the lithology of a porphyry Cu—Mo—Au deposit (e.g., Berger et al., 2008). You will observe that core samples are collected every

2-cm down to a depth of 200 m, i.e., a total of 100 samples, which is an ultra-detailed sampling procedure (refer to Table S24). Another observation is that samples are collected in a few cases from two different rock types.

Is this an acceptable sampling procedure according to the instructions given earlier? The sampling instructions given for rock geochemical surveys are that a rock sample always consists of chips of the same rock type.

What is the reason for not observing this rule in this case? The reason is that the rock types hosting the mineralization will be mined in large sections (benches) from an open-pit mine. So, the average ore grade of each section will be estimated independent of the host rock.

You will observe that this is a comparatively rich porphyry Cu—Mo—Au deposit and shows a zonation, with a rich Cu zone at depth, followed above it by a Mo rich zone, and nearer to the surface there is a Au rich zone.

Concluding remarks

The attempt made in this article was to answer many questions, which are usually asked by university students, early career and even professional applied geochemists, and to give useful guidelines for the organization and successful implementation of an applied geochemical mapping project at any scale and purpose. An outline of the most important guidelines is given below:

- **Orientation survey:** In the systematic development of phased geochemical mapping, the orientation survey is important, because it provides the necessary information to successfully plan the succeeding follow-up stream sediment stage. A second orientation survey is usually required for the successful planning and execution of the detailed geochemical survey.
- **Sampling and sample preparation:** These are the most important parts of any geochemical mapping project, and they must be carried out by well-trained personnel with extremely strict supervision by an experienced field applied geochemist (Fig. 57). It is again stressed that any mistakes during these two stages cannot be corrected afterwards, and the consequence will be the failure of the whole geochemical mapping survey (Demetriades, 2014, 2021). Mistakes during the laboratory analysis of samples can be corrected by their reanalysis, provided there is enough archive sample material available. Hence, it is significant to store safely a large sample split or splits in a well-organized storage facility.
- **Rock sampling:** Always collect fresh and unweathered samples of the same rock type (Batista et al., 2022a). Never mix different rock types in a sample because their geochemistry is different. Never mix fresh and unweathered rock samples with weathered and oxidized rock samples, because their geochemistry is again different.
- **Soil sampling:** Always collect samples from the same soil horizon (Batista et al., 2022b). Never collect samples that include material from different soil horizons, because each horizon has different physico-chemical properties. The same applies to overbank and floodplain sediment layers.
- **Stream sediment sampling:** Always collect active stream sediment from the center of perennial, intermittent and ephemeral streams to avoid nearby falling bank material (Fordyce et al., 2022). The sample site should be selected either well above the confluence with another stream or well below it to avoid mixing of sediments from either source. Always collect stream sediment samples at least 25 m above obvious human made contamination.
- **Quality assurance/Quality control procedure:** This is another important procedure that must be set up from the beginning of the geochemical mapping project (Johnson, 2011; Demetriades, 2011b; Johnson et al., 2018; Demetriades et al., 2022a; Johnson and Lister, 2022). You are advised to study the quality control reports of the GEMAS Atlas project (Reimann et al., 2009, 2011, 2012a). Here the decision that you will have to make is whether to follow a balanced or unbalanced ANOVA design (Fig. 31). The recommendation is to use the former. Apart from the collection of field duplicate samples, another important aspect is the insertion of either Certified Reference Materials (CRMs) or project standards (Secondary reference materials, SRMs). For small geochemical mapping projects, it is too costly to make SRMs, but for big and long duration projects it is advisable to make at least five large SRMs with different chemical composition (Johnson and Lister, 2022; Lučivjanský and Mackových, 2022).

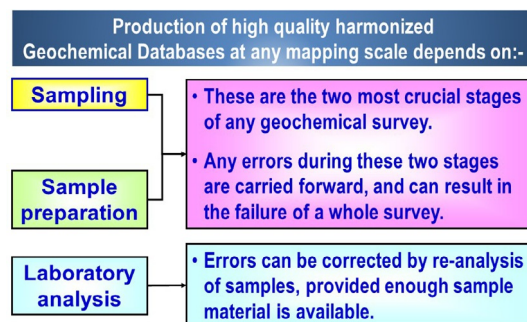


Fig. 57 Stages of a geochemical mapping survey, stressing the importance of carrying out efficiently the sampling and sample preparation procedures. Plotted with Microsoft® 365 PowerPoint.

- *Field blank water samples*: Field blank water samples from laboratory grade deionized water are usually made for stream and groundwater geochemical mapping projects, and their purpose is to detect and identify any potential contamination of water samples from the sampling to the analytical stages. Before using the laboratory grade deionized water, it is advisable to make a few analyses to ensure that it is contaminant free. Instead of using laboratory grade deionized water, it has been found that “Water for Injection” is certified trace element free, and it can be purchased from pharmacists, and is a good alternative.
- *Solid blank samples*: Solid blank samples can be made either from pure silica sand or fine-grained kaolin tailings for monitoring contamination of solid field samples during the sampling and sample preparation stages (Schermann, 1990; Lučivjanský and Mackových, 2022). The problem here is that you will have to carry in the jeep a sack full of these solid blank samples, and pack aliquots in the field in the same bagging material as the routine field samples. Subsequently, these solid blank samples will go through the sample preparation and analytical stages as the other geochemical mapping project samples.
- *Bagging materials*: It is important to ensure that the bags for solid samples, and the bottles for water samples are certified trace-element free.
- *Randomization of project samples*: Randomization of project samples, including field duplicate-replicate splits, aliquots of SRMs or CRMs, and aliquots of blanks, is a procedure that must be followed in all geochemical mapping projects.
- *Sampling density*: It depends on project objectives, mapping scale, and dimensions of the target size.
- *Laboratory analysis*: This is another significant part of the geochemical mapping project. As most of you will be using commercial laboratories, it is necessary to sign a contract or an agreement of the analytical method or methods that will be used for the analysis of your project samples. You should select an analytical method capable of analyzing a large sample weight, i.e., between 15 and 50 g, as the aim is for the analytical aliquot to be more representative of the sample. In the contract, the following clauses should be included: (i) reanalysis of 10% or 15% of the samples; (ii) inclusion of at least three CRMs or laboratory standards per 100 samples (the first and last sample in each batch, and the third in between); (iii) inclusion of at least three method reagent blanks (i.e., acid mixture plus deionized water) per 100 samples, and (iv) reporting of uncensored values (see below). The results of all these laboratory control samples to be reported together with the results of project samples in the order analyzed, and date of analysis per batch. An important clause is that if mistakes are found during the checking of the quality of analytical results, the laboratory will be obliged to reanalyze the samples of specific batches, and in case all the results are of unacceptable quality to reanalyze all project samples. Final payment will be made subject to the verification of the quality of analytical results.
- *Reporting of analytical results*: The analytical laboratory must not censor values at its internal lower detection limit for each element. The uncensored values of each element (even negative values) must be submitted in order to estimate its practical detection limit (Thompson and Howarth, 1976, 1978; Demetriades, 2011b; Demetriades et al., 2022a).
- *Quality control check of laboratory results*: Upon receipt of the analytical results, their quality must be checked first. Never start the statistical processing of analytical results, and map plotting before checking first their quality (Johnson, 2011; Demetriades et al., 2022a). When you are absolutely certain that the quality of the results is fit-for-purpose, then and only then should you start data processing.
- *Data processing*: First the sample site coordinates are merged with the analytical results, and field observations. It is recommended that you start plotting boxplots (Figs. 9, 10, 35) and cumulative probability plots (Figs. 21, 24, 44) in order to study the statistical distribution of each determinand, and then to plot Exploratory Data Analysis symbol maps or growing (proportional) dot or variable-size dot maps (Figs. 19, 20, 22, 23, 26, 38 and 52). These maps portray the actual geochemical variation within the study area. It is recommended to plot the symbol maps over a lithological base map or a topographical map.
- *Color-surface maps*: This map type is more pleasing to the eye than point symbol black and white maps. They are needed for decision and policy makers. It can be said that the color-surface maps are essential for marketing purposes of your work. There are many interpolation techniques, and their advantages and disadvantages are discussed by Reimann et al. (2008). It is recommended to use geostatistics for the interpolation of values into unsampled space, and for this you must have a good working knowledge of geostatistical procedures. If you cannot avoid the plotting of color-surface maps, it is strongly recommended that you superimpose on the color-surface variable-size dots, which display the actual geochemical variation at each sampling site (Figs. 27, 36, 46, 47 and 50).
- *Report writing*: The Association of Applied Geochemists has published a particularly good instruction booklet for writing professional geochemical reports (Bloom and Lavin, 2022), which should be consulted.

If you follow the instructions in this article, you should be able to plan an efficient and quality controlled geochemical mapping project, either for mineral exploration or environmental purposes, and to process, present, and interpret the data, and to write a good professional report.

Finally, *why is applied geochemistry important to our quality of life?* Apart from using the applied geochemical methods for mineral and environmental purposes, applied geochemistry provides us with sound evidence of our close relationship with the materials of our home planet Earth (Fig. 58). It is, therefore, appropriate to end this chapter with the following timeless statements from Darnley et al. (1995, p.x): “Everything in and on the earth—mineral, animal, and vegetable—is made from one, or generally, some combination of, the naturally occurring chemical elements. Everything that is grown, or made, depends upon the availability of the appropriate elements. The existence, quality and survival of life depends upon the availability of elements in the correct proportions and combinations. Because natural processes and human activities are continuously modifying the chemical composition of our environment, it is important to determine the present abundance and spatial distribution of the elements across the Earth’s surface in a much more systematic manner than has been attempted hitherto”.

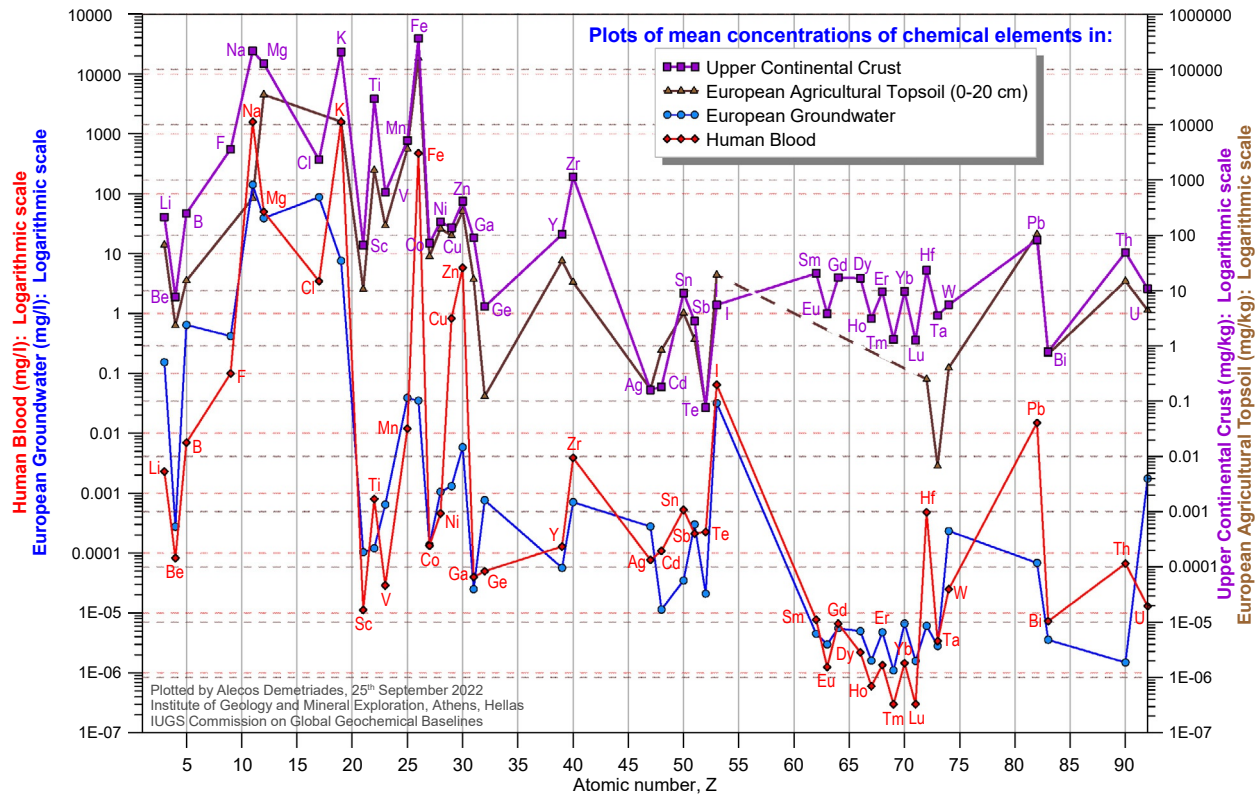


Fig. 58 Graph showing the relationship between selected major and trace element mean concentrations in the upper continental crust, European agricultural topsoil and groundwater, and human blood. Their similar trend indicates that there is a close relationship between the chemical composition of human blood and the materials of the upper continental crust, topsoil and groundwater, although there is a significant difference in magnitude. Data sources: Upper Continental Crust (Reimann et al., 2014a, Table 11.1, p. 105); European Agricultural Topsoil (Reimann et al., 2014b); European Groundwater (Reimann and Birke, 2010); Human blood (ALS Global, 2021). Drawn with Golden Software's Grapher™ v21.

Supplementary material

Supplementary material associated with this article can be found in the online version at <https://doi.org/10.1016/B978-0-323-99762-1.00004-8>, and includes:

Text S1: Information about the 3Ts Gold-Silver prospect area and additional figures (Figs. S1 to S11).

PPT S1: It contains all figures of main text and supplementary material.

Table S1: Field observations, 3Ts Gold-Silver prospect.

Table S2: Laboratory methods, 3Ts Gold-Silver prospect.

Table S3: Analytical results of duplicate-replicate pairs, 3Ts Gold-Silver prospect.

Table S4: Analytical results of laboratory replicates, 3Ts Gold-Silver prospect.

Table S5: Repeated analyses of control standards, 3Ts Gold-Silver prospect.

Table S6: Duplicate-replicate results for exercise.

Table S7: Replicated determinations of standard samples, 3Ts Gold-Silver prospect.

Table S8: Analytical results, 3Ts Gold-Silver prospect.

Table S9: Statistical parameters of Ag and Au, 3Ts Gold-Silver prospect.

Table S10: 3-term moving average, 3Ts Gold-Silver prospect.

Table S11: Cumulative frequency example.

Table S12: Pb data, Eastern Macedonia & Thrace Reconnaissance stream sediment.

Table S13: Pb data, Irene River catchment basin, Thrace, Hellenic Republic.

Table S14: Pb data, Virini-Pessani follow-up stream sediment, Thrace.

Table S15: Pb data, Thermae detailed geochemical survey, Thrace.

Table S16: Hg data, Battery factory.

Table S17: Battery factory QC duplicate-replicate Hg analyses.

Table S18: Battery factory ROBCOOP4A Hg output.

Table S19: Ni data from European Geochemical Atlases.

Table S20: Pb data, Lavrion urban geochemical study.

Table S21: GEMAS Ap soil XRF raw and clr-transformed data.

Table S22: Au analytical results.

Table S23: Drillhole TiO₂ and MnO data.

Table S24: Porphyry Cu drillhole data.

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