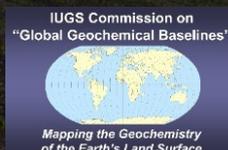


International Union of Geological Sciences Manual of Standard Geochemical Methods for the Global Black Soil Project

edited by Alecos Demetriades, Dai Huimin, Liu Kai, Igor Savin,
Manfred Birke, Christopher C. Johnson and Ariadne Argyraki

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Front cover photograph: Black soil landscape, Hailun county, Suihua city, Heilongjiang Province, P.R. China. Taken by Liu Kai, Shenyang Centre of China Geological Survey, Shenyang, Liaoning Province, P.R. China.

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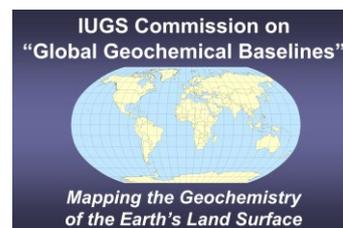
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**INTERNATIONAL UNION OF GEOLOGICAL SCIENCES
MANUAL OF STANDARD GEOCHEMICAL METHODS
FOR THE
GLOBAL BLACK SOIL PROJECT**

Edited by

Alecos Demetriades^{1,2}, Dai Huimin³, Liu Kai³, Igor Savin⁴, Manfred Birke^{1,5},

Christopher C. Johnson^{1,6} and Ariadne Argyraki^{1,7}

¹ IUGS Commission on Global Geochemical Baselines

² Institute of Geology and Mineral Exploration, Athens, Hellas (retired)

³ Shenyang Centre of China Geological Survey, Shenyang, Liaoning Province, P.R. China

⁴ V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation

⁵ Federal Institute for Geosciences and Natural Resources, Hannover, Germany

⁶ GeoElementary, Derby, United Kingdom

⁷ Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Hellas

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The aims of the International Union of Geological Sciences Commission on Global Geochemical Baselines are:

- To provide high quality geochemical baseline data for the terrestrial part of our home planet Earth;
- To establish a Geochemical Reference Network for levelling data sets of existing regional geochemical projects, and
- To provide reference samples and sites for future monitoring of the chemical state of the World's terrestrial surface.

Hence, the generated geochemical data must be of high quality, integrity and consistency.

Sampling of Black Soil (chernozems), *sensu stricto*, is not included in the programme of the International Union of Geological Sciences (IUGS) Commission on Global Geochemical Baselines, because it is an agricultural soil impacted by human activities. However, it is an important agricultural soil, and as is considered to be among some of the most productive soil types in the World, it should quite rightly be studied separately from other agricultural soil types.

The aim of the Global Black Soil Critical Zone Geo-ecological Survey (BASGES) is to study, in a holistic approach, the serious degradation problems that Black Soil types are facing all over the world because of several decades of intensive cultivation. Their present chemical state shall be studied by following the principles of the IUGS Commission on Global Geochemical Baselines for producing an internally consistent high quality geochemical database. The requirements are to use standardised sampling and sample preparation methods, and all samples must be analysed in the same laboratory for the same suite of determinands/parameters, following a strict quality control protocol.

The present manual contains comprehensive instructions for sample site selection, sample collection and preparation, recommendations for preparation of project reference samples, laboratory analysis, quality control procedures that should be implemented, checking the quality of analytical data, required supporting information for interpretation of geochemical data, and need for the establishment of site-specific guideline values for Black Soil in the different regions of its occurrence.

Keywords: black soil, chernozems, mollisols, geochemical survey, baseline study, quality control, BASGES, manual

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Reijo Salminen (Geological Survey of Finland, retired), Project manager of the ‘*Geochemical Atlas of Europe*’ (<http://weppi.gtk.fi/publ/foregsatlas/>);

David Smith (United States Geological Survey, retired), Project manager of the ‘*Geochemical and Mineralogical Survey of Soils in the Conterminous United States of America, North American Soil Geochemical Landscapes Project*’ (<https://pubs.usgs.gov/sir/2017/5118/index.html>), and

Patrice de Caritat (Geoscience Australia), Project manager of the ‘*National Geochemical Survey of Australia*’ (<https://www.ga.gov.au/about/projects/resources/national-geochemical-survey>).

The Executive Committee of the International Union of Geological Sciences (<http://www.iugs.org/>) approved the publication of the “*International Union of Geological Sciences Manual of Standard Geochemical Methods for the Global Black Soil Project*” at its 74th meeting in Busan of South Korea on the 17th of January 2020. The Executive Committee members Qiuming Cheng (President), Kristine Asch (Vice President), William Cavazza (Vice President), Stanley C. Finney (Secretary-General), Hiroshi Kitazato (Treasurer), Roland Oberhänsli (Past President), Ben Mapani (Councillor), Edmund Nickless (Councillor), Silvia Peppoloni (Councillor) and Claudia Mora (Councillor) are thanked for approving the publication of this manual.

The Global Black Soil Project is carried out under the auspices of IGCP 665 “*Sustainable Use of Global Black Soil Critical Zone*” (http://globeblacksoils.org/news_en/; [UNESCO IGCP665](#)).

The generous assistance of Golden Software (<https://www.goldensoftware.com/>) is acknowledged for the greatly reduced rates in the update of its software packages. The Black Soil maps were plotted with MapViewerTM (v.8) and the boxplots and pie diagrams with GrapherTM (v.17).

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1. GENERAL INTRODUCTION

Alecos Demetriades^{1,2}, Dai Huimin³, Liu Kai³ and Igor Savin⁴

¹ IUGS Commission on Global Geochemical Baselines

² Institute of Geology and Mineral Exploration, Athens, Hellas (retired)

³ Shenyang Centre of China Geological Survey, Shenyang, Liaoning Province, P.R. China

⁴ V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation

'**Black Soil**' is the popular name used in many countries of the world for soil with a thick and dark coloured surface horizon (Figure 1; Appendix 1). This soil is among some of the most important and productive agricultural soil types in the world (FAO, 2003, 2015; Liu *et al.*, 2012). After several decades of intensive cultivation, Black Soil types are facing serious degradation problems such as erosion and salinisation (Xu *et al.*, 2010). It is, therefore, of paramount importance to survey and to study the world's Black Soil regions, and to develop sustainable land use plans for their protection.

Globally, Black Soil occupies approximately 7% of the ice-free land area (approx. 9,200,000 km²)¹. Black Soil primarily occurs in the middle latitudes under unique morpho-climatic conditions (Figure 2).

Black Soil is placed in categories depending on the soil classification system used. In the U.S. Department of Agriculture (USDA, 2014) classification system it belongs to Mollisols (from Latin *mollis*, 'soft'). Mollisols, according to USDA (2014) are divided into 8 suborders (Figure 3):-

- 1) Albolls (wet soil; aquic soil moisture regime with an eluvial horizon);
- 2) Aquolls (wet soil; aquic soil moisture regime);
- 3) Rendolls (lime parent material);
- 4) Gelolls (very cold climate; mean annual soil temperature <0°C);
- 5) Cryolls (cold climate; frigid or cryic soil temperature regime);
- 6) Xerolls (Mediterranean climate; xeric moisture regime);
- 7) Ustolls (subhumid climate; ustic moisture regime), and
- 8) Udolls (humid climate; udic moisture regime).

In the World Reference Base (WRB) soil classification system (FAO, 2015), Black Soil types belong to reference soil groups of Chernozems, and partly to Kastanozems and Phaeozems. These soil types are characterised by '*mollic*' and '*chernic*' diagnostic horizons.

The Global Soil Partnership (GSP)² defines 'Black Soil' as the different soil types that have:

- "A well-structured, dark coloured surface horizon due to their enrichment in high-quality humus down to a depth of more than 40 cm (mostly 60 to 80 cm);
- A high base saturation (i.e., a high percentage of the cation exchange capacity is occupied by the basic cations Ca²⁺, Mg²⁺ and K⁺), and
- A moderate to high content in organic matter (more than 1% of organic carbon)".

If the above GSP definition is observed, then many agricultural areas, covered with thinner Mollic or Chernic horizons, will not be sampled. Therefore, in this manual, **Black Soil** is defined

¹ <https://www.cals.uidaho.edu/soilorders/mollisols.htm>

² <http://www.fao.org/global-soil-partnership/intergovernmental-technical-panel-soils/gsoc17-implementation/internationalnetworkblacksoils/more-on-black-soils/what-is-a-black-soil/en/>

as a dark-coloured surface soil consisting of a well-structured humic horizon with a high base saturation (i.e., a high percentage of the cation exchange capacity is occupied by the basic cations Ca^{2+} , Mg^{2+} and K^{+}), and with a moderate to high content in organic matter (more than 1% organic carbon). As the Global Black Soil project's principle objective is the study, in a holistic approach, of the serious degradation that Black Soil is facing all over the World because of its intensive agricultural use, but also to its exposure to denudation agents, areas with even thinner mollic horizons should be sampled and documented.

1.1. Objectives

The overall objective of the geochemical survey of Black Soil regions of the World is the establishment of a global Geochemical Reference Network for Black Soil, which will be used for monitoring future changes, and to provide some of the basic data for global climate changes. It is stressed that the geochemical survey will provide some of the parameters for monitoring global climate changes.

The specific objectives of the geochemical survey of the Black Soil regions of the World are:

- To assess the current global geochemistry and chemical quality of Black Soil, and to define the global geochemical baseline at the beginning of the 21st century for both agricultural and non-agricultural Black Soil;
- To provide some data for monitoring global climate changes (e.g., soil moisture, carbon, and nitrogen contents), and
- To establish a global Geochemical Reference Network for agricultural and non-agricultural Black Soil, which will be used for monitoring future changes.

It is hereby noted that in the Global Geochemical Baselines project sampling of agricultural soil is strictly forbidden because of its influence by human activities. Samples of residual soil are collected from second order catchment basins, as the objective is to define the natural geochemical baseline. Black Soil is an exception because of its agricultural significance, and the necessity for its sustainable use.



Figure 1. Mollisols (Chernozems) have: (1) a mollic or chernic epipedon (thick, dark humic surface horizon), and (2) base saturation of at least 50 per cent throughout the subsoil (USDA-NRCS image). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

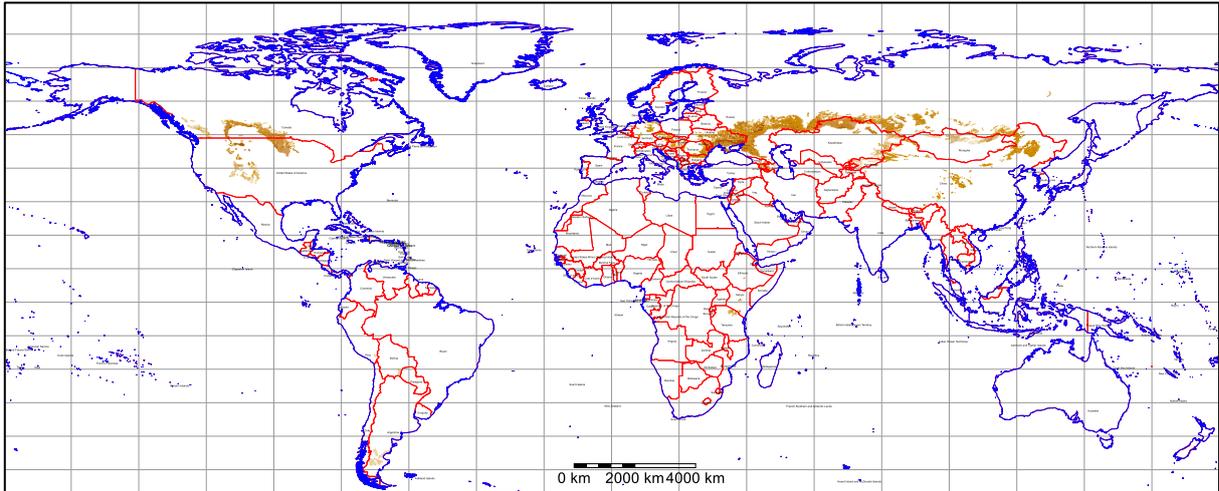


Figure 2. Map showing the occurrence of Black Soil in Asia (China, Mongolia, Kyrgyzstan, Kazakhstan, Azerbaijan, Armenia, Georgia, Russia), Europe (Ukraine, Moldova, Romania, Bulgaria, Hungary, Slovakia, Czechia, Germany), North America (Canada, United States of America), South America (Argentina, Peru, Bolivia, Paraguay), and Africa (Ethiopia, Tanzania, Kenya). Brown colour intensity on the map refers to the percentage of Black Soil (the darker – the greater is the Black Soil acreage). Refer to Appendix 2 for larger regional maps. Source: Google Earth kml file by Edith Haslinger & Robin Friedrich (Austrian Institute of Technology GmbH, Centre for Energy, Vienna, Austria), and Harald Loishandl-Weisz & Thomas Rosmann (Federal Environment Agency Austria, Department of Groundwater, Vienna, Austria). Map plotted with Golden Software’s MapViewer™ v.8 by Alecos Demetriades, Institute of Geology and Mineral Exploration (IGME), Athens, Hellas & IUGS Commission on Global Geochemical Baselines (IUGS CGGB).

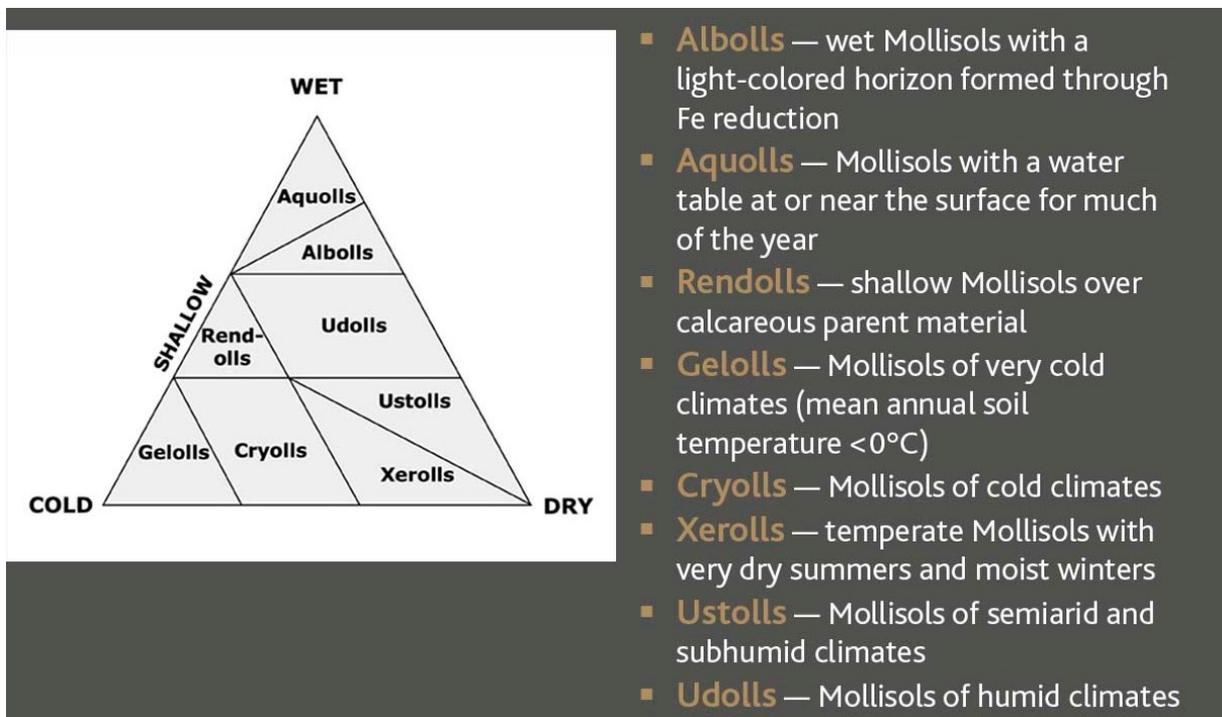


Figure 3. Ternary diagram showing the distribution of mollisols according to climatic conditions (Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>).

1.2. Black Soil landscapes and profiles

The following photographs (Figures 4 to 6) show Black Soil landscapes in China, and some typical profiles (Figures 7 to 12). In Appendix 1, additional photographs show Black Soil landscapes and profiles in other parts of the World.



Figure 4. Shuangya Mountain Black Soil wetland, China. Source: CAAC Inflight Magazine, 2017, Issue 12, No. 285, p.92-93.

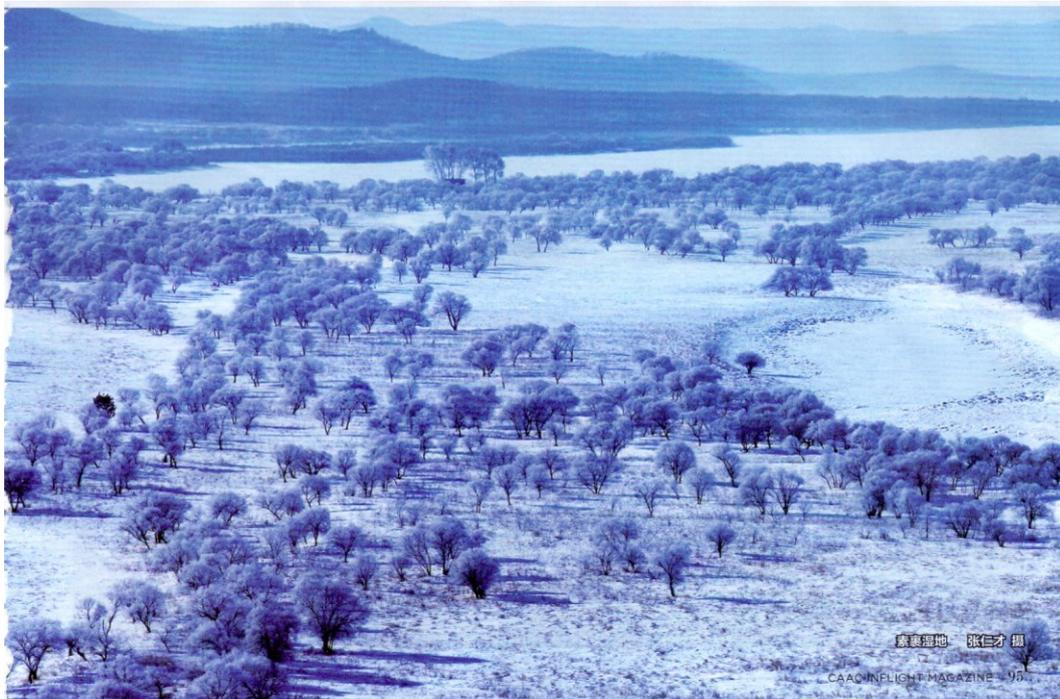


Figure 5. Shuangya Mountain Black Soil wetland, China. Source: CAAC Inflight Magazine, 2017, Issue 12, No. 285, p.95.



Figure 6. Shuangya Mountain Black Soil wetland, China. Source: CAAC Inflight Magazine, 2017, Issue 12, No. 285, p.96-97.



(a)



(b)

Figure 7. Black Soil landscape (a) and profile (b), Yijiadian Farm, Fuyu county, Songyuan city, Jilin Province. Longitude 125°33'33.81"E, Latitude 45°27'24.77"E. Photograph: Liu Kai, Shenyang Centre of CGS.



(a)



(b)

Figure 8. Black Soil landscape (a) and profile (b), Xiangfu Town, Fuyu County, Songyuan City, Jilin Province. Longitude 125°00'09.40"E, Latitude 45°17'57.44"E. Photograph: Liu Kai, Shenyang Centre of CGS.



(a)



(b)

Figure 9. Black Soil landscape (a) and profile (b), Wukeshu Town, Yushu County, Changchun City, Jilin Province. Longitude 126°07'42.27"E, Latitude 44°49'24.29"E. Photograph: Liu Kai, Shenyang Centre of CGS.



(a)

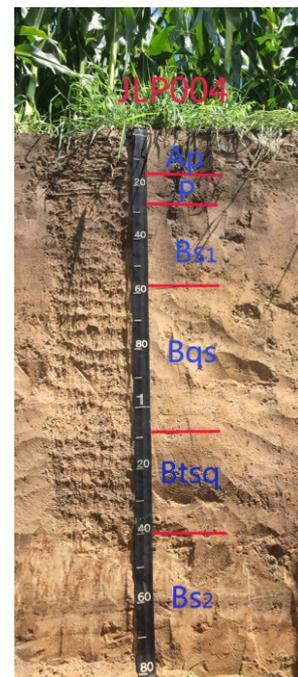


(b)

Figure 10. Black Soil landscape (a) and profile (b), Chengfa Town, Yushu country, Changchun city, Jilin Province. Longitude 126°44'58.55"E, Latitude 44°50'38.37"E. Photograph: Liu Kai, Shenyang Centre of CGS.



(a)



(b)

Figure 11. Black Soil landscape (a) and profile (b), Deshegn Town, Fuyu Country, Songyuan City, Jilin Province. Longitude 125°38'9.27"E, Latitude 45°28'50.5"E. The organic 'mollic' horizon is not well-developed. Photograph: Liu Kai, Shenyang Centre of CGS.



(a)



(b)

Figure 12. Black Soil landscape (a) and profile (b), Gongpengzi Town, Fuyu Country, Songyuan City, Jilin Province. Longitude 125°42'58.05"E, Latitude 45°05'29.00"E. The organic 'mollic' horizon is not well-developed. Photograph: Liu Kai, Shenyang Centre of CGS.

2. SAMPLING BLACK SOIL

Alecos Demetriades^{1,2}, Dai Huimin³, Liu Kai³ and Igor Savin⁴

¹ IUGS Commission on Global Geochemical Baselines

² Institute of Geology and Mineral Exploration, Athens, Hellas (retired)

³ Shenyang Centre of China Geological Survey, Shenyang, Liaoning Province, P.R. China

⁴ V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation

The Black Soil samples collected will serve (a) for the establishment of the current geochemical baseline, and (b) as future reference materials, so strict sampling procedures must be followed, and adequate quantities obtained and retained.

2.1. Survey design

2.1.1. Sample site selection

The primary Geochemical Terrestrial Network (GTN) is based on 7356 grid cells of 160x160 km, which cover the terrestrial surface of Earth (Figure 13). According to the procedure of the IUGS Commission on Global Geochemical Baselines, five random sites are selected in each 160x160 km grid cell (Figure 14). Point number 1 is located in the NE quadrant of the grid cell, number 2 in the NW quadrant, number 3 in the SW quadrant and number 4 in the SE quadrant, and point number 5 is randomly located in the grid (Darnley *et al.*, 1995; Salminen, Tarvainen *et al.*, 1998). This random sampling scheme is applied in the 160x160 km grid cells in which Black Soil occurs. The reason for generating random sample sites is to be quite objective in the selection of each sample site, as each point within the 160x160 km grid cell has an equal chance of being selected and, therefore, is not depended on subjective criteria.

During project planning, the generated random sites in the Geochemical Terrestrial Network (Figure 13) are plotted on 1:50,000 scale topographic maps, which have the Black Soil areas.

Figure 14 shows the random sites in GTN grid cell N31E63 within the Black Soil region of north-east China. One random site falls in each quadrant (80x80 km) and a fifth random site falls in this particular GTN grid cell in the north-east quadrant.

Figure 15 shows the random sites in GTN grid cell N36E55 in the Black Soil region of north-east China, where only two random sites fall within the Black Soil region, and the other three are outside. In such GTN grid cells that are near the border of the Black Soil region with other soil types, it is permissible to move the nearest sample site to fall within the Black Soil region. In fact, the selection of sampling sites is based on the Black Soil distribution and land use maps.

Special cases just for the global Black Soil geochemical mapping project: When Black Soil is dominant within the 160x160 km grid cell, the 5 random sample site scheme can be applied without any problem (Figure 14).

What happens, however, when Black Soil occurs in patches within the 160x160 km grid cell?

In such cases, the number of random points for sampling can be less than five. Figure 16 shows an example of how the Black Soil patches within the 160x160 km grid cell can be handled.

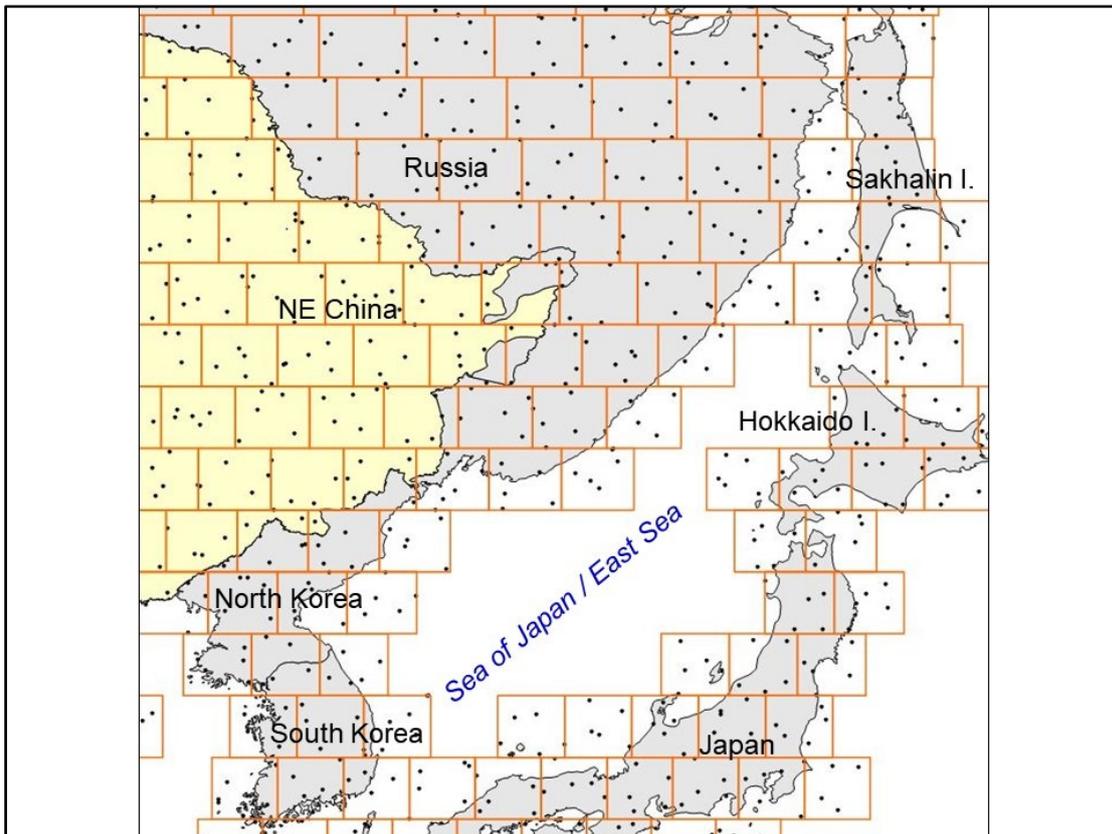


Figure 13. The map shows the 160x160 km GTN grid cells (orange line rectangles), and the black dots the five random sites within each grid cell. The yellow colour part indicates the Black Soil region in north-east China. Note: Coastal grid cells have random sites falling in the sea, which is a programming issue, and does not mean to collect samples from the seabed. In the cases where sample sites fall in the sea in coastal areas where the Black Soil occurs, they can be moved as indicated in Figure 16. Map plotted with Golden Software's MapViewer™ v.8 by Alecos Demetriades, IGME & IUGS CGGB.

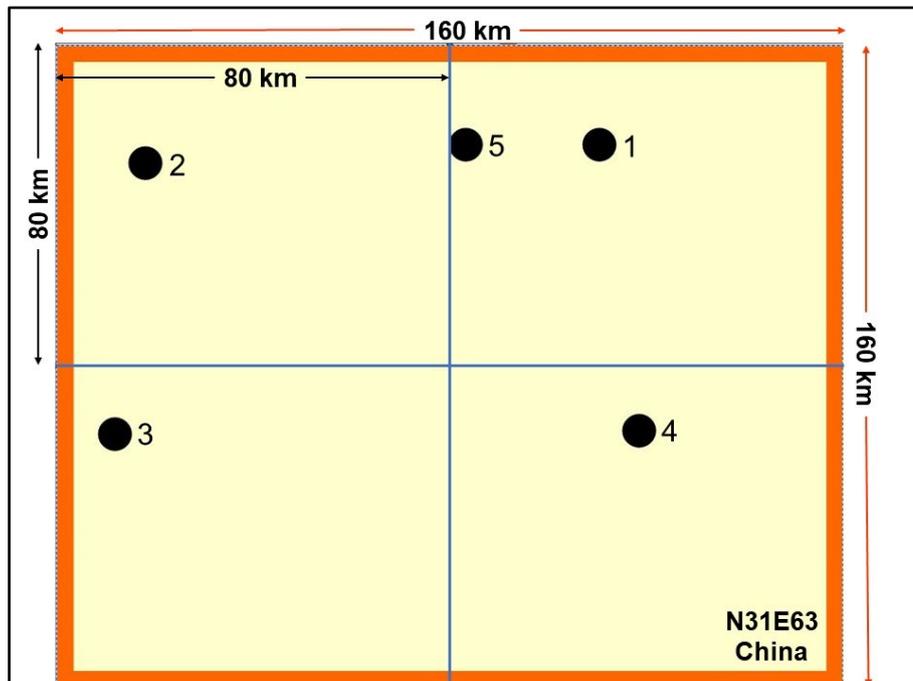


Figure 14. Yellow coloured GTN grid cell N31E63 is wholly within the Black Soil region of north-east China. The numbered black dots show the five random sites for the collection of Black Soil samples. Figure: Alecos Demetriades, IGME & IUGS CGGB.

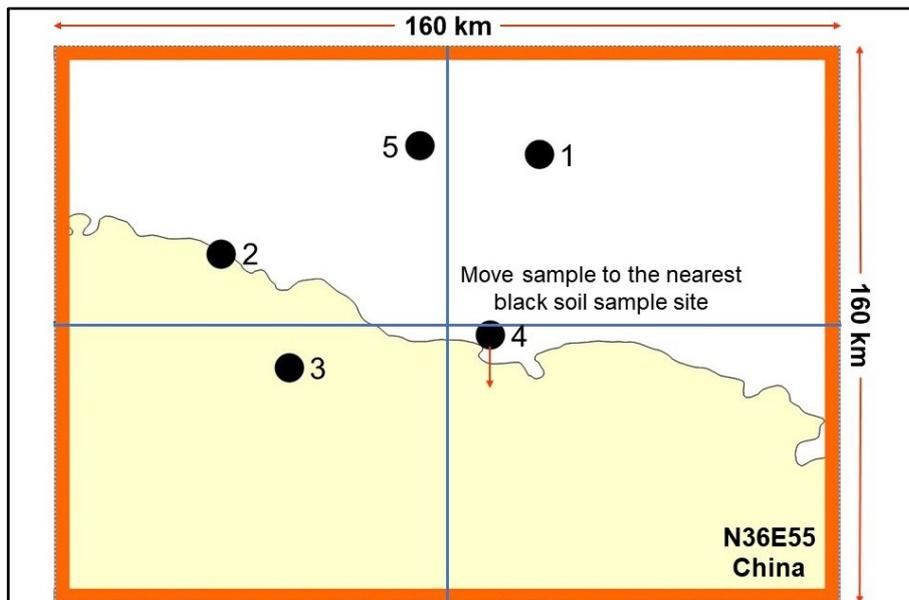


Figure 15. GTN grid cell N36E55 in the Black Soil region of north-east China shows that two of the random sites fall within the Black Soil region (yellow-coloured part). It is permissible to move random sites to the nearest Black Soil occurrence. Figure: Alecos Demetriades, IGME & IUGS CGGB.

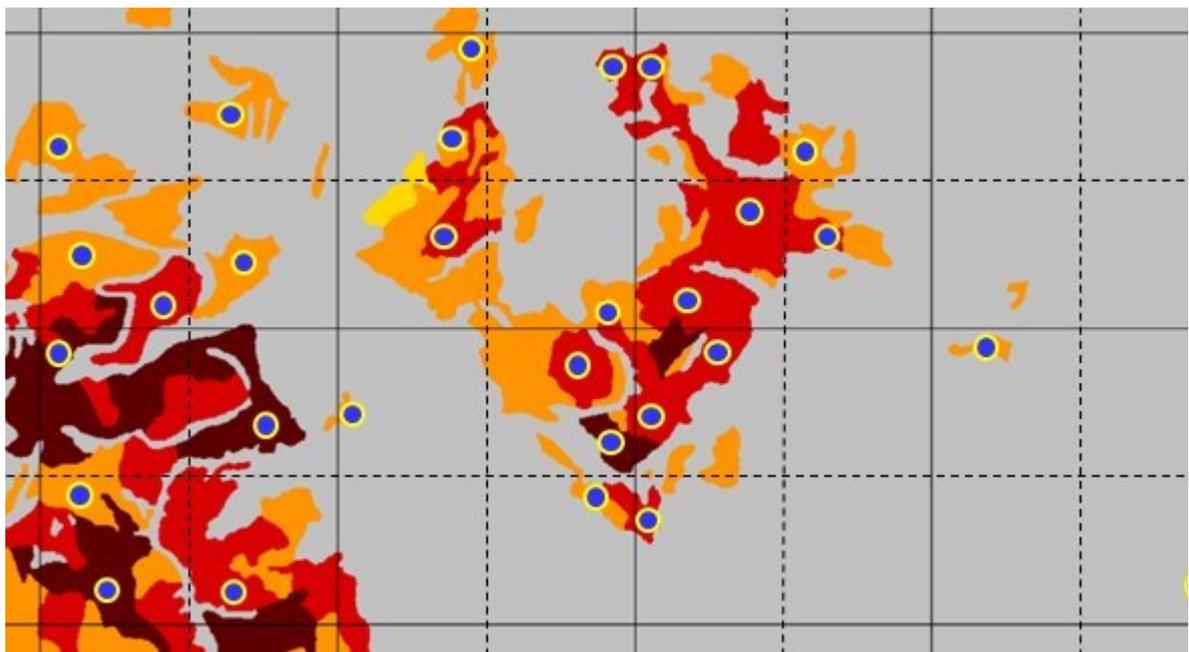


Figure 16. Example of five random sample sites located in 160x160 km GTN grid cells that cover almost the whole cell, and a smaller number of sample sites in grid cells with small Black Soil patches. Black lines define the 160x160 km grid cells, and the dotted lines the 80x80 km quadrants). Colour intensity (yellow to brown) on the map refers to the percentage of Black Soil (the darker the colour – the more is the Black Soil acreage). Figure: Igor Savin, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia.

The exact position of the sampling site is located, however, in the field, after a careful study of the Black Soil landscape.

The Black Soil sampling site is selected according to the following criteria:-

- Avoid possible contamination by selecting a sample site that is at least:
 - 100 m away from asphalted roads (particularly major roads/highways), railway lines, bridges, buildings, and dams;

- 50 m away from rural or dirt roads;
 - 50 m away from ditches;
 - 100 m away from buildings;
 - 25 m away from fences;
 - 100 m from high power electric lines, and
 - 2 km away from active major industrial activity, such as electric power plants or smelters.
- Avoid recently fertilised fields (*i.e.*, within the last few weeks prior to sampling); follow the general rule: if fertilisers can still be smelt, change sampling location.
 - Avoid sites that are disturbed by human activities other than agricultural practices, such as camping sites (*e.g.*, presence of fire-places, cans and/or bottles), graded areas, levelled fields (for irrigation), mines (disused or active), landfills, and rehabilitated sites. It is stressed that every single contaminated site will seriously influence the resulting geochemical results.
 - Avoid sites that are locally atypical.

Important note: As the purpose of the wide-spaced geochemical survey is the establishment of a Geochemical Reference Network and the 21st century geochemical baseline of Black Soil against which future changes will be referred to, it is important to collect samples from both agricultural and non-agricultural Black Soil (*i.e.*, cultivated and non-cultivated Black Soil). The ploughed agricultural Black Soil samples will provide data of the human impacted soil, and the non-agricultural Black Soil samples would best represent ‘*geochemical background*’ conditions.

2.2. Black Soil project samples to be taken

The following Black Soil project samples are taken:

- (a) Routine sample site of a normal 160x160 km grid cell:
 - 2–3 kg of Top Black Soil sample (0–20 cm); in areas of ploughed Black Soil, samples are collected down to a depth of 20 cm (ordinary ploughing depth); in natural Black Soil landscapes only the black ‘humic’ horizon is sampled, and if it is <20 cm thick, then the thinner horizon is sampled, and its thickness recorded on the field observations sheet.
 - 2–3 kg of Bottom Soil sample to be taken from the upper 20 cm thick section of the C horizon, which in some cases may be at a depth of more than 200 cm.
- (b) Duplicate field site of a duplicate grid cell (at least one in each country):
 - 2–3 kg of Top Black Soil sample (0–20 cm) + 2–3 kg of Top duplicate Black Soil sample.
 - 2–3 kg of Bottom Soil sample (C horizon – upper 20 cm thick section) + 2–3 kg of Bottom duplicate C horizon soil sample.

Enough material must be collected to yield a minimum of 1 kg of <2 mm grain-size Black Soil. Larger sample quantities can be taken and stored separately in each country.

2.2.1. Identifiers of Black Soil project samples

The identifiers of the Top and Bottom Soil samples are ‘A’ and ‘Z’, respectively:

(a) Routine sample site (*e.g.*, GTN grid cell N31E63 in NE China):

- Top Black Soil sample (A): N31E63A1
- Bottom Soil (C horizon) sample (Z): N31E63Z1

Note: Number ‘1’ represents the 1st sample site in GTN grid cell N31E63.

(b) Duplicate (D) field site (*e.g.*, GTN grid cell N33E15 in Ukraine):

- Top Black Soil sample: N33E15A3
- Top Black Soil sample – Duplicate: N33E15A3D
- Bottom Soil (C horizon) sample: N33E15Z3
- Bottom Soil (C horizon) sample – Duplicate: N33E15Z3D

Note: Number ‘3’ represents the 3rd sample site in GTN grid cell N33E15, and ‘D’ denotes the duplicate Top and Bottom Black Soil project samples.

2.3. Equipment for Black Soil sampling

2.3.1. Equipment to be provided by project Coordinator

The following equipment must be purchased or made centrally by the Coordinator³ of the Global Black Soil project, and provided to all sampling teams in each participating country:

- 30 x 60 cm x 0.04 mm strong certified trace-element-free plastic bags;
- Plastic strip locks (or cable ties) for securing the sample bags (attention: the locks cannot be opened once closed; this is a safety precaution for checking that the samples have not been tampered with from the time of sampling until they reach the sample preparation laboratory);
- 6 x 10 cm cardboard cards for writing the sample number on both sides;
- 7.5 x 11.5 cm zip-lock plastic bags for holding the 6 x 10 cm cards, and
- Black permanent drawing ink markers (ONLY black coloured allowed).

Instead of strong certified trace-element free plastic bags, another type of bag can be used, and purchased by project coordinator and distributed to all participating countries. This is:

- 30 x 60 cm white cotton (or caligo) bags with draw string (Note: They are not suitable for high moisture samples).

Whatever the decision, the same type of sample bags must be used throughout the duration of the Global Black Soil project.

The Coordinator of the Global Black Soil project must also purchase:

- Strong and durable trace-element-free sample containers for the storage of laboratory sample splits of 100 g weight;
- Strong and durable trace-element-free sample containers for the storage of two large Black Soil project archive sample splits of 500 g weight, and

³ Shenyang Centre of China Geological Survey, Shenyang, Liaoning Province, P.R. China

- The same strong and durable trace-element-free sample containers, used for the storage of laboratory sample splits of 100 g weight, for storing 100 g aliquots of the Black Soil project reference samples.

2.3.2. Equipment to be purchased by each participating country

The following equipment must be purchased by each participating country, and for all its sampling teams:

- Unpainted steel spade or stainless-steel spade (if the spade is painted, the paint must be removed by sand blasting prior to sampling); the wood handle must be unpainted (if varnished, it must be removed by sandpapering);
- Unpainted mattock cutter (if mattock cutter is painted, the paint must be removed by sand blasting prior to sampling); the wood handle must be unpainted (if varnished, it must be removed by sandpapering);
- Stainless steel knife;
- Metal free white plastic scoop or stainless-steel scoop;
- Stainless steel geological hammer either pointed-tip or chisel-end;
- Leather gloves;
- Hard bristle brush for cleaning plastic or stainless steel scoop, and geological hammer;
- Cotton-lint or cotton rags for cleaning sampling equipment;
- Wooden folding 2 m long measure (alternate colours) or plastic tape with alternate colours every 10 cm;
- 30 x 60 cm strong certified trace-element free plastic bags for packing, as a safety precaution during transportation to the sample preparation laboratory;
- Plastic strip locks (or plastic cable ties) for securing the outside plastic sample bags;
- Plastic or carton boxes for packing sample bags in the field, and subsequent transportation to sample preparation laboratory;
- Topographical maps, preferred scale 1:50,000 (a must in case electronic digital devices fail);
- Global Positioning System (GPS) for recording sample site coordinates, or a tablet with a GPS and digital topographical maps;
- Extra batteries for GPS;
- Orienteering compass (a must in case GPS fails);
- Field-ruggedised notebook or laptop computer with extra charger and spare batteries;
- Car adapter for charging notebook or laptop computer;
- Portable storage device (USB memory stick) for backup of field data and digital photographs;
- Digital camera for field documentation (minimum 5 megapixels);
- Extra batteries for digital camera;
- USB Cable to download photographs to laptop computer in the evening;
- Threshold scintillometer to measure natural radioactivity (Total, Th, U, K); the scintillometer must be calibrated at a certified national facility);
- Extra batteries for threshold scintillometer;
- Field observations sheets;

- Waterproof case to hold field observation sheets;
- Writing pens;
- HB pencils and pencil sharpener (back-up in case the pens fail to write in the field);
- First-aid kit, and
- Mobile telephone or other communication equipment like CB radios and satellite telephone (the latter may be needed in remote areas), or emergency position-indicating radio beacon (EPIRB).

Important Note: The use of an auger for sampling Black Soil samples is strongly not recommended, as each sampling site in the Global Black Soil project is unique and, thus, incredibly significant, and the three-dimensional pit information must be documented.

2.4. Black Soil project sampling procedure

2.4.1. Sampling procedure

2.4.1.1. Routine samples

In total, two soil samples are taken at each sampling site for the establishment of the Global Black Soil Geochemical Reference Network:

- A Top Black Soil sample 0-20 cm (Ap horizon – ploughed horizon from agricultural fields, and surface humic horizon from non-agricultural fields). In some cases, especially of Black Soil in non-agricultural areas (Figure A1.3), the thickness of the mollic horizon may be less than 20 cm (Figures A1.6, A1.8, A1.15); in these cases, the thinner mollic horizon is sampled, and the depth range recorded on the field observations sheet.
- A Bottom 20-cm thick C horizon soil sample. **Note:** The C horizon is especially important, and must be reached at all sampling sites because it is the reference horizon. It is anticipated that in most cases the C horizon will be reached at a depth of less than 200 cm. If it is deeper, then the pit should be dug until the C horizon is reached. The upper 20 cm thick section of the C horizon is sampled, and depth range noted on the field observations sheet. In case the C horizon has a thickness of less than 20 cm, then the thinner horizon is sampled, and the thickness range recorded on the field observations sheet.

Important note: The Top Black Soil and Bottom C horizon samples are collected from a SINGLE site, a SINGLE profile and a SINGLE horizon.

ATTENTION

As Black Soil samples will be analysed for Ag, Au and Pd:

***** All hand jewellery must be removed *****

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

Please pay great attention to this ‘little’, but very important, detail.

SMOKING is NOT PERMITTED during sampling.

At each Black Soil project sample site:

- (i) Switch on the GPS (Figure 17), or notebook or laptop computer with GPS, to obtain the WGS1984 decimal degree coordinates of the sample site.
- (ii) Write the sample numbers of Top and Bottom samples with a black permanent ink marker on the strong trace-element free plastic bag (or cotton bag; Figure 18).
- (iii) Write the sample numbers of Top and Bottom Black Soil samples on both sides of the small card, and place each card in the small plastic zip-lock bag and seal it (Figure 18).
- (iv) Clean the spade (Figure 19) and mattock cutter by inserting it several times into the soil at each new sample site.
- (v) Clear the surface litter to begin with a spade, and a mattock cutter if necessary.
- (vi) Dig a pit down to the C horizon with an unpainted steel or stainless-steel spade and mattock cutter, thus uncovering a clean vertical surface for sampling (Figure 20).
- (vii) Mark the soil horizons with the aid of a stainless-steel knife (Figure 20).
- (viii) Photographic documentation: At this stage, place an alternate coloured-section wooden measure on the face of the pit, and then take at least six digital photographs (see Section §2.4.1.3).
Additional photographs can be taken to show the textural characteristics of both the Top Black Soil horizon and bottom C horizon.
IMPORTANT: As a safety precaution, always photograph first the sample number of the Top Black Soil sample.
- (ix) Mark the location of the sample site on the 1:50,000 topographical map or digital map; this is a safety precaution to ensure that the GPS coordinates are correct.
- (x) Record the general observations on the field observations sheet (refer to Appendix 4), leaving the grain size to be completed after the collection of the Top and Bottom Black Soil samples.
- (xi) *First, collect the Bottom C horizon soil sample (Figure 21) using a geological hammer and a white plastic scoop, and store the sample in a strong certified trace-element free plastic bag (or cotton bag; Figure 22). This procedure avoids cleaning the surface of the bottom soil horizon from fallen Topsoil sample material, if the latter is taken first.*
- (xii) *Upon collecting the Bottom C soil horizon sample of about 2-3 kg weight, the numbered small card in the plastic zip-lock bag is placed on top of the sample (Figures 22b & 23).*
- (xiii) *Twist the top of the sample bag, and seal it securely with a plastic strip lock (Figure 24a).*
- (xiv) *For safety during transportation of the sample, place it in an ordinary plastic bag, and seal it securely with a plastic strip lock (Figure 24b).*
- (xv) *Clean thoroughly the sampling equipment with hard bristle brush and cotton lint.*
- (xvi) Second, collect the Top Black Soil sample using the same procedure as that for the Bottom sample (refer to steps xi to xv; Figures 25 to 28).
- (xvii) Store the two samples in different strong carton or plastic boxes.
- (xviii) Measure the natural radioactivity with a threshold scintillometer, which is held at knee height; record the measurements of Total, Th, U and K on the field observations sheet.
- (xix) Record the grain-size of the Bottom and Top Black Soil samples, and digital photograph numbers on the field observations sheet.

Grain-size estimation in the field: As a rule of thumb the grain-size of Black Soil project samples can be estimated in the field by the following practical method, after slightly wetting the soil sample (Haslinger *et al.*, 2014):

- *Clay*: soils fingers, is cohesive (sticky), is formable, has a high plasticity and a shiny surface after squeezing between fingers.
- *Silt*: soils fingers, is non-sticky, only weakly formable, has a rough and ripped surface after squeezing between fingers and feels very floury (like talcum powder).
- *Sand*: cannot be shaped, does not soil fingers and feels very grainy.

2.4.1.2. Duplicate field samples

Duplicate Top Black Soil and Bottom C horizon samples are collected randomly at least at every 30th sampling site (*i.e.*, $\approx 3\%$ duplication of the sample sites) in each country. However, countries with less than 30 GTN grid cells should collect Top Black Soil and Bottom C horizon samples from at least one random site. The duplicate sample site is selected at a distance from 5 to 50 metres away from the routine sampling site following the same procedure as for collecting the routine Top Black Soil and Bottom C horizon samples.

Important note: After collecting the Bottom C horizon and Top Black Soil samples, using the procedure described above, the dug-up soil is returned to the pit, the two samples placed on the surface together with the sample number (Figure 32) and GPS, and the last site digital photograph is taken to show that the pit was filled-in and the landscape returned to its original state.

2.4.1.3. Photographing

At each Black Soil project sampling site at least 6 digital photographs (>5 megapixels) are taken (Figures 29-32; and label photographs with the sample site number and suffix letters as indicated):

- First photograph: Top Black Soil sample site number (Figure 29; suffix letter ‘N’);
- Second photograph: General landscape photograph about the sampling site (Figure 30a; suffix letter ‘L’);
- Third photograph: Soil surface photograph taken by pointing downward from a height of about 1 m from ground surface (Figure 30b; suffix letter ‘S’);
- Fourth photograph: Close-up of sample pit with natural light. Before taking this photograph, mark with a knife the soil horizons, if they can be distinguished, and place an alternate coloured-section wooden measure on the face of the pit (Figure 31a; suffix letter ‘P’);
- Fifth photograph: Close-up of sample pit using fill-in flash for it is important to show the horizons and textural characteristics of the soil profile (Figure 31b; suffix letter ‘F’), and
- Sixth photograph: This is an important photograph as evidence that dug-up soil has been returned to the pit, and the landscape returned to its original state. Place on top of the fill-in pit (a) sample number, (b) sample bags and (c) GPS and then take the photograph (Figure 32; suffix letter ‘R’).

2.4.2. Photographic documentation of sampling procedure

The following set of photographs (Figures 17 to 33) show the sampling procedure at location Nehe Country, Qiqihaer City, Heilongjiang Province, China (48°37'29.91"N, 124°42'28.64"E), and photographs to be taken at each Black Soil project sampling site.



Figure 17. Photograph showing the GPS instrument for recording sample site coordinates - Step (i) of sampling procedure (see Section §2.4.1). Photograph: Liu Kai, Shenyang Centre of CGS.



Figure 18. Photograph shows steps (ii) and (iii) of sampling procedure (see Section §2.4.1): (ii) Write the sample numbers of Top and Bottom Black Soil samples with a black permanent ink marker on the strong trace-element free plastic bag, or in this case the cotton bag, and (iii) Write the sample numbers of Top and Bottom Black Soil samples on both sides of the small card, and place each card in the small plastic zip-lock bag and seal it. On the right hand side is the plastic bag for packing the cotton bags after sampling, and plastic strip lock for sealing it. Photograph: Liu Kai, Shenyang Centre of CGS.



Figure 19. Photograph showing spade and spatula, which need to be cleaned by inserting them several times into the soil at each new sample site. Step (iv) of sampling procedure (see Section §2.4.1). Photograph: Liu Kai, Shenyang Centre of CGS.



Figure 20. Photograph showing a close-up of vertical face of pit (natural light), which was dug in this case down to a depth of 170 cm, and soil horizons marked with a stainless-steel knife (steps vi & vii of sampling procedure – see Section §2.4.1). The depth is indicated by a plastic tape of alternate red and white colours at 10 cm intervals. Photograph: Liu Kai, Shenyang Centre of China Geological Survey (CGS).



Figure 21. Sampling of Bottom Black Soil project sample. In this case, instead of using a geological hammer and a white plastic scoop for collecting the sample, a spatula and a spade is used (step xi of sampling procedure – see Section §2.4.1). Photograph: Liu Kai, Shenyang Centre of CGS.



(a)



(b)

Figure 22. (a) First aliquot of Bottom Black Soil project sample to be placed in numbered cotton bag; (b) cotton bag filled with Bottom Black Soil sample (step xi of sampling procedure – see Section §2.4.1). Photographs: Liu Kai, Shenyang Centre of CGS.



(a)



(b)

Figure 23. Photographs showing (a) the numbered small card in the plastic zip-lock bag, and (b) its placement on top of the Bottom Black Soil project sample (step xii of sampling procedure – see Section §2.4.1). Photographs: Liu Kai, Shenyang Centre of CGS.



(a)



(b)

Figure 24. Photographs showing packing of Bottom Black Soil project sample: (a) sealing of cotton bag with a plastic strip lock, and (b) sealed cotton bag ready to be placed in plastic bag for safety during transportation (steps xiii & xiv of sampling procedure – see Section §2.4.1). Photographs: Liu Kai, Shenyang Centre of CGS.



Figure 25. Sampling of Top Black Soil sample. In this case, instead of using a geological hammer and a white plastic scoop for collecting the sample, a spatula and a spade was used (step xi of sampling procedure – see Section §2.4.1). Photograph: Liu Kai, Shenyang Centre of CGS.



(a)



(b)

Figure 26. (a) First aliquot of Top Black Soil sample to be placed in numbered cotton bag; (b) bag filled with Top Black Soil sample (step xi of sampling procedure – see Section §2.4.1). Photographs: Liu Kai, Shenyang Centre of CGS.



(a)



(b)

Figure 27. Photographs showing (a) the numbered small card in the plastic zip-lock bag, and (b) its placement on top of the Top Black Soil sample (step xii of sampling procedure – see Section §2.4.1). Photographs: Liu Kai, Shenyang Centre of CGS.



(a)



(b)

Figure 28. Photographs showing packing of Top Black Soil sample: (a) sealing of cotton bag with a plastic strip lock, and (b) sealed cotton bag placed in plastic bag for safety during transportation (steps xiii & xiv of sampling procedure – see Section §2.4.1). Photographs: Liu Kai, Shenyang Centre of CGS.



Figure 29. Photograph of Top Black Soil project sample site number (Photo No.: N33E60A4N). Photograph: Alecos Demetriades, IGME & IUGS CGGB.



Figure 30. (a) General landscape photograph about the Black Soil sample site (Photo No.: N33E60A4L), and (b) soil surface photograph taken from a height of about 1 metre (Photo No.: N33E60A4S). Photographs: (a) Liu Kai, Shenyang Centre of CGS, and (b) Alecos Demetriades, IGME & IUGS CGGB.

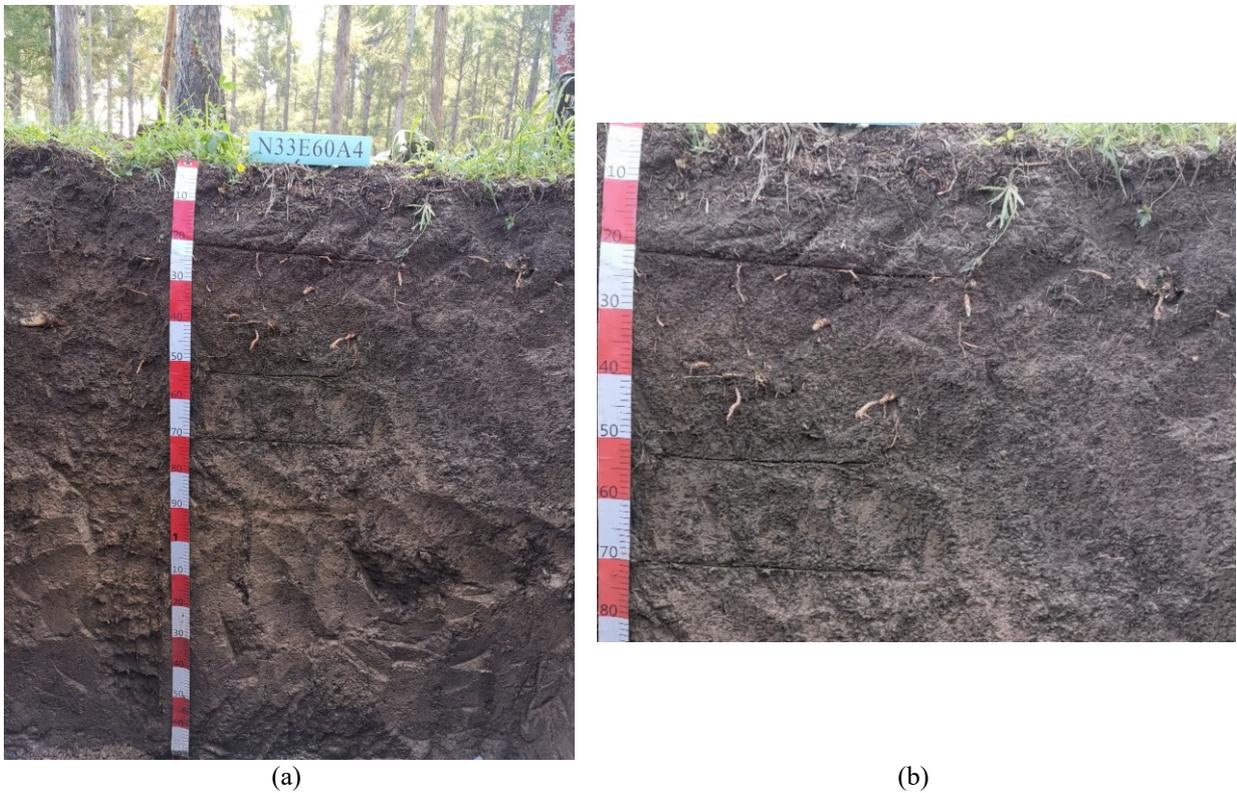


Figure 31. (a) Close-up of Black Soil profile with natural light (Photo No.: N33E60A4P), and (b) close-up with fill-in flash showing textural characteristics of soil horizons (Photo No.: N33E60A4F). Photographs: Liu Kai, Shenyang Centre of CGS.



Figure 32. Last photograph of bagged Top and Bottom Black Soil project samples with GPS on top of the fill-in pit, as evidence that dug-up soil has been returned to the pit, and the land to its original state (Photo No.: N33E60A4R). Photograph: Liu Kai, Shenyang Centre of CGS.



Figure 33. Landscape photograph of sample site showing the fill-in pit, and surrounding area. You are free to take additional photographs for documenting the environmental conditions near the sampling site. Photograph: Liu Kai, Shenyang Centre of CGS.

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3. LABORATORY WORK

Manfred Birke^{1,2}, Gwendy E.M. Hall^{1,3} and Alecos Demetriades^{1,4}

¹ IUGS Commission on Global Geochemical Baselines

² Federal Institute for Geosciences and Natural Resources, Hannover, Germany

³ Geological Survey of Canada, Ottawa, Ontario, Canada (retired)

⁴ Institute of Geology and Mineral Exploration, Athens, Hellas (retired)

3.1. Preparation of Black Soil project reference samples

Two large Black Soil project secondary reference materials (SRMs) of at least 1000 kg (<2 mm) each for external quality control should be prepared, their homogeneity tested and certified by undergoing a ring test with many participating laboratories (Reimann *et al.*, 2012; Reimann and Kriete, 2014). The two Black Soil project SRMs should have distinctly different major and trace element concentrations.

It is stressed that these are not the certified reference materials (CRMs) that the laboratory uses for its own internal quality control. These SRMs are prepared independently of the analytical laboratory, and inserted in the sample batches by the Black Soil Geochemistry Project Manager (BSGP Manager) for checking the quality of analytical data, and are unknown to the laboratory. They are inserted at a rate of one SRM to every 20 Black Soil project routine samples.

3.2. Preparation of solid blank reference sample

One large solid blank reference sample of 1000 kg should also be prepared. Schermann (1990) recommended such a solid blank reference sample of either quartz or kaolinite to be prepared for the Regional Geochemical Mapping of Europe (Western European Geological Surveys, WEGS, presently EuroGeoSurveys). Aliquots of this sample are placed in sample bags in the field, like any ordinary routine sample, and undergo the complete sample preparation procedure, *i.e.*, drying, disaggregation, homogenisation, sub-sample splitting, and analysis. This sample will serve to pin-point any potential cross-contamination of samples during their preparation and laboratory analysis stages. Of course, the preparation of such a sample should undergo homogeneity and ring testing, just like the two Black Soil secondary reference materials. Two aliquots of the solid blank project reference sample should be inserted randomly in every analytical batch of one hundred samples.

3.3. Sample preparation and storage

All collected Black Soil project samples should be sent to a central laboratory for sample preparation, homogenisation, and splitting into sub-samples for laboratory analysis, and safe storage for future use. The total number of splits depends on the analytical programme. However, it is recommended to make a minimum of twelve splits for the analytical programme. At least two large sample splits should be archived for future use.

Ideally, the samples should be air-dried on the same day that they were collected. If this is not possible, it is recommended that samples are stored at low temperatures (*e.g.*, in a refrigerator or cooling room) until air-drying can be carried out. It is noted that storage of soil samples in warm conditions may result in the loss of carbon due to on-going chemical and biochemical processes.

The following procedure is recommended for the preparation of Black Soil project samples on which inorganic elements are to be determined:

- Top and Bottom Black Soil project samples for the determination of inorganic trace element analysis are either air-dried at room temperature, or dried in a thermostatically controlled oven at a temperature not exceeding 25°C. **Caution:** Mercury (Hg) is known to escape even at 30°C.
- Each soil sample is transferred from the sample bag to an aluminium tray and spread into a thin layer.
- The small numbered card in the small plastic zip-lock bag accompanies each sample during sample preparation. It should be placed in a secure position in the drying tray.
- After drying, the samples are carefully disaggregated with a porcelain pestle in a porcelain mortar, taking care not to grind small pebbles.
- Following disaggregation, the soil samples are sieved through a 2 mm nylon screen.
- The entire <2 mm soil fraction is suitably homogenised, and split into sub-samples and placed in trace-element-free containers as detailed below. The process of homogenisation and sample splitting is an art if it is done by hand, *i.e.*, coning⁴ and quartering (Schumacher *et al.*, 1990; Gerlach *et al.*, 2002). Therefore, well-trained technicians should be given the task of homogenisation and sample splitting. Of course, there is an easier method by using a riffle splitter (Schumacher *et al.*, 1990); in this case, it is recommended to perform at least eight times riffle-splitting and recombining before the final splitting into sub-samples for laboratory analysis and storage. Whatever method is used, the splits or sub-samples should be representative of the whole sample.
- All utensils are carefully cleaned after preparation of each sample in order to avoid cross-contamination of samples. There are different cleaning methods, *e.g.*, washing up with tap water, then rinsing thoroughly with deionised water and oven-drying; using a temperature-controlled ultrasonic bath.
- Soil (Top and Bottom) sample splits for chemical and physico-chemical analyses, as well as determination of mineralogy, are sent to the selected laboratory or laboratories, *remembering that all samples must be analysed in the same laboratory for the same suite of determinands and by the same analytical method.*
- The remaining splits of <2 mm soil (Top and Bottom) should be archived in a dust free storeroom where the ambient temperature does not exceed 30°C. This is the reference collection for future use.

IMPORTANT: Global Black Soil project samples must be stored in appropriate and well-labelled containers at a curated sample store. If these samples are not stored correctly, this valuable asset will be lost in a short period of time.

The sample splits for archiving require careful attention regarding storage and collation. This is an extremely valuable asset that can be used in the future for reanalysis, monitoring and other research purposes. Sample splits should be:

1. *Stored and collated in a secure environment so that the samples are preserved long into the future. Ideally this would be a permanent national store for environmental samples.*
2. *Preserved in storage containers that are certified trace-element free [e.g., glass, High-density polyethylene (HDPE), Polyethylene (PE), colour (white or 'natural' recommended)], and*

⁴ **Coning:** The reduction in size of granular or powdered sample by forming a conical heap, which is spread out into a circular, flat cake. The cake is divided radially into quarters and two opposite quarters are combined. The other two quarters are discarded. <https://goldbook.inpac.org/terms/view/C01265>.

3. *Labelled with the original sample number in a secure and permanent manner (e.g., alphanumeric number and bar coding).*

3.4. Arrangement of samples for analysis

3.4.1. Systematic errors and randomisation of samples

Systematic errors may occur in the laboratory during sample preparation and analysis. Some of these systematic errors are (Plant, 1973; Fletcher, 1981, 1986):

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

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

Randomisation of samples is the method devised by applied geochemists to remove any systematic relationship between order of analysis and geographical location (Plant, 1973; Plant *et al.*, 1975; Thompson, 1983; Schermann, 1990; Darnley *et al.*, 1995; Reimann *et al.*, 2009, 2011, 2012; Demetriades *et al.*, 2014; Demetriades and Birke, 2015). By randomisation of samples, any systematic between batch variation is increased in the analytical data, meaning that any systematic errors are spread randomly over all samples. This converts data that would be reflected as areas of shifted geochemical background levels, and are artefacts of the lack of accuracy in the chemical analyses, into increased 'local noise'. Care should be taken, therefore, to include a sufficient number of control samples⁵, 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 should be submitted for re-analysis, and the new analytical results utilised, provided they are satisfactory according to fitness-for-purpose⁶. Furthermore, randomisation of samples has another advantage, because project and international reference samples, and project replicate samples can be hidden in the batches and, thus, not recognised by the laboratory.

3.4.2. Randomisation and insertion of control samples

Randomisation of samples can be done in two different ways:

- (1) During the planning of the field survey the total number of routine and duplicate field samples, and their replicated splits, is estimated, as well as the number of reference samples (SRMs and solid Blanks) that will be inserted for analysis. Then this number is randomised, and a list made of the random numbers generated. A

⁵ **Control samples** are an important part of the quality control and assurance (QC/QA) procedure because they assure that the chemical analyses are properly performed and the generated results are reliable. They include the field duplicate-replicate splits, project SRMs and solid Blank samples and certified reference materials (CRMs). The field duplicate-replicate splits and project SRMs are samples that are matrix-matched with the routine project samples, and are randomly inserted in the batches by the BSGP Manager. Certified reference materials are normally inserted in the analytical batches by the laboratory. However, it is recommended that CRMs, unknown to the laboratory, should be inserted too in the analytical batches by the BSGP Manager.

⁶ 'Fitness-for-purpose' implies that the analytical results are fit for their intended use.

computer software program can perform the randomisation of sample numbers, and an output produced (Appendix 3). During the field survey, each sample is assigned in turn a random number from the list. In the preparation laboratory, the samples are ordered in ascending numbers during sample preparation, and the project reference samples, and the routine and field duplicate-replicate sample splits, are inserted at the appropriate reserved places using the same coding, and a record kept.

- (2) As the samples are collected from the 160x160 km GTN grid cells, the randomisation of routine Global Black Soil project samples, and control samples (reference and analytical replicates) is done in the sample preparation laboratory, and project samples are assigned new numbers; again, quality control samples (reference samples and project replicate splits) are inserted. This procedure has a major disadvantage, because the samples lose, in fact, their identity, as completely new numbers are assigned. Hence, the procedure must be done very carefully, and a good record kept of the project sample numbers, and their corresponding new random numbers, because upon receiving the analytical results the original sample numbers must be reassigned.

3.4.3. Arrangement of samples for analysis

The Global Black Soil project samples, together with the external quality control samples, should be submitted to the analytical laboratory in a random order and in one large single batch. In order to arrange the project's external quality control samples in each analytical batch, the analytical laboratory must be asked to date and time stamp for every analysis and to provide the following information before the submission of the samples for analysis:

- (i) The number of samples analysed in each analytical batch;
- (ii) The number of laboratory blank samples in each analytical batch;
- (iii) The number of international and internal reference samples in each analytical batch, and
- (iv) The number of replicated determinations on project samples.

When this information is at hand, the randomised sequence can be arranged by inserting (*e.g.*, Table 1):

- One SRM per 20 routine Global Black Soil project samples;
- Two solid blank reference samples per 100 routine Global Black Soil project samples;
- The second split of the field routine Global Black Soil project sample, and
- The two splits of the field duplicate Global Black Soil project sample.

3.5. Laboratory analysis

As the objective is to establish a homogeneous and harmonised Global Geochemical Reference Network database for Black Soil, all analyses for each set of parameters **MUST** be carried out in only one laboratory. External quality control, independent of laboratories, and consisting of randomising all samples, insertion of field and analytical duplicates, project SRMs and solid Blanks, and some CRMs, all unrecognisable by the participating laboratories, are important parts of the project. All analyses will have to pass strict quality criteria, agreed upon by contract with the laboratories, before accepting the analytical results (and paid for). These conditions are especially important, otherwise the generated Global Black Soil project geochemical database will be of questionable quality.

Table 1. Example of a random number list for sample number allocation to be used in the Global Black Soil project: (a) Random number list showing the insertion of field duplicate-replicate sample splits, aliquots of two Black Soil project SRMs (SRM 1 & SRM 2), and two aliquots of the solid Blank sample (Blank 1A and 1B); the empty cells are filled with routine Global Black Soil project samples in a consecutive number order. (b) When this batch of 100 samples is sorted in order of smallest to largest number, the samples are randomised. Table modified from Johnson (2011, Fig. 5.3, p.65).

(a) Random number list					(b) Random number list sorted from smallest to largest number				
RANDOM NUMBER LIST 1				Project Code	RANDOM NUMBER LIST 1				Project Code
				Number Range					Number Range
59	8	37	64		1	26	51	76	
38	44	100	61		2	27	52	77	
10	91	73	99		3	28	Duplicate A	53	78
86	79	60	96		4	29		54	79
98	68	16	77		5	30		55	80
3	65	6	35		6	31		56	81
76	89	58	97		7	SRM 2B	32	57	Blank 1B
9	52	12	66		8		33	58	82
78	27	1	83		9		34	59	83
50	42	19	54		10		35	60	84
24	62	31	11		11		36	61	85
30	40	26	46		12		37	62	86
5	94	20	15		13	SRM 1A	38	63	87
67	70	29	49		14		39	64	Blank 1A
71	56	95	28	Duplicate A	15		40	65	88
85	25	22	17	Duplicate B	16		41	SRM 1B	89
32	84	92	21	Replicate A	17	Duplicate B	42	66	90
93	47	69	75	Replicate B	18		43	67	91
55	90	48	13	SRM 1A	19		44	68	92
72	53	39	41	SRM 1B	20		45	69	93
80	2	4	88	SRM 2A	21	Replicate A	46	70	94
34	45	81	7	SRM 2B	22		47	71	95
82	43	63	74	SRM 2C	23		48	72	96
14	51	18	87	Blank 1A	24		49	73	97
33	36	23	57	Blank 1B	25		50	74	98
								75	SRM 2C
									99
									Replicate B
									100

3.5.1. Analytical laboratory arrangements and obligations

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

For the analysis of all Global Black Soil project sample types, a reputable accredited laboratory should be selected, and the analytical method or methods agreed, as well as the digital format for reporting the results. In addition to the user-controlled QA/QC⁷ samples discussed above and presented ‘blind’ to the laboratory, the laboratory should:

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

⁷ QA/QC = Quality Assurance/Quality Control

All the aforementioned results should be made available to the Black Soil Geochemistry Project Manager (BSGP Manager) by the laboratory, together with:

- ❖ A concise description of the analytical method or methods used;
- ❖ Lower and upper detection limits of each determinand;
- ❖ Recommended certified values of CRMs and internal laboratory reference materials (and accepted uncertainty), and
- ❖ A report of any problems encountered during the analysis of Black Soil project samples, and solutions given.

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

It is particularly important for the BSGP Manager to have a good communication and cooperation with the laboratory.

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

- Upon receipt of the analytical results from the laboratory, the BSGP Manager must ensure that there is in the team a professional applied geochemist with the skills to carry out an exhaustive statistical analysis of their quality using the internal (laboratory) and external (project) quality control results.
- If analytical problems are located, the analytical batch or batches shall be reanalysed by the laboratory without any charge, and
- In the case that all the analytical results are of poor quality, then the laboratory shall be obliged to reanalyse all samples without any charge, subject again to the same conditions for verification of their quality (see the quality control about the determination of particle or grain size in Reimann *et al.*, 2011, p.10-11 and 28-31).

3.5.2. Determination of inorganic elements and other parameters

Ideally, a large suite of elements should be determined on the Black Soil samples by (i) a true 'total' method, (ii) an *aqua regia* and (iii) a weak leach, *e.g.*, Ag, Al, As, Au, B, Ba, Be, Bi, Br, C, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, N, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pm, Pr, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr (Allen *et al.*, 2011).

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

For the analytical programme, three informative publications that should be consulted are:

- *Analytical methods in geochemical prospecting* by W.K. Fletcher (1981); Volume 1 In: G.J.S. Govett (Editor), Handbook of Exploration Geochemistry. Elsevier Scientific Publishing Co., Amsterdam, 255 pp.
- *Summary of analytical procedures for soil characterization* (and references therein), Appendix 2 in FAO (2015), World reference base for soil resources 2014 (p.182-186);

- *Sample Preparation and Inorganic Analysis for Urban Geochemical Survey Soil and Sediment Samples* by Allen *et al.* (2011), Chapter 3 (p.28-46) in C.C. Johnson *et al.* (Editors), *Mapping the Chemical Environment of Urban Areas* (Published by Wiley-Blackwell, John Wiley & Sons Ltd., Chichester, U.K.).

Geochemistry textbooks by Rose *et al.* (1979, p.44-70) and Levinson (1974, p.241-315; 1980, p.721-746) should also be consulted as they have chapters explaining the principles of analytical methods.

In the following sections a concise description is given for some analytical methods.

3.5.2.1. Acid digestion methods

Hydrofluoric acid (HF) is most effective in breaking up the Si-O bond to form SiF₄ which volatilises upon heating. Fluorides of As, B, Ti, Nb, Ta, Ge and Sb may be lost to varying extents upon heating.

Hydrochloric acid (HCl), a strong acid, is effective for the dissolution of carbonates, phosphates, borates and sulphates (except baryte) and has become an almost universal solvent suitable for most techniques (possible exception of ICP-MS due to the formation of Cl-molecular species). Its ability to digest Fe and Mn oxides is superior to that of HNO₃ due to its reducing and complexing properties. Pyrite is only slightly soluble in HCl while pyrrhotite, sphalerite and marmatite dissolve completely.

Hot, concentrated nitric acid (HNO₃) is used to decompose sulphides, selenides, tellurides, arsenides, sulphoarsenides and phosphates through oxidative degradation (S oxidised to SO₄²⁻). Nitric acid (HNO₃) dissolves most metals that occur in nature, with the exception of Au and the platinum group elements (PGEs). Iron sulphides and molybdenite dissolve easily. Practically all O-containing primary U minerals are decomposed with concentrated HNO₃.

The powerful oxidising and dehydrating properties of hot, concentrated perchloric acid (HClO₄) are effective in decomposing sulphides and organic matter, but care must be taken to avoid an explosive hazard with samples high in organic matter. Its high boiling point makes it useful in driving off HF and more volatile acids. Although sulphuric acid (H₂SO₄) has similar properties, it has not found such widespread application probably due to the interference effects developed by SO₄²⁻ in atomic absorption spectroscopy (AAS), and to the low solubility of alkaline earth and Pb sulphates. Nitric acid (HNO₃) is added to moderate the action of HClO₄ on organic material which could be explosive. There are many variations on the procedure but normally the mixed acids are evaporated to dryness and the residue dissolved in HCl (0.5-1 M) for analysis.

Hydrofluoric acid (HF) is customarily used with mineral acids to decompose oxides and sulphides as well as silicates. Fluoride is usually removed by evaporation with HClO₄ thereby preventing the precipitation of insoluble fluorides (*e.g.*, Ca, REEs) later in the digestion. Teflon or Pt dishes are employed and the absence of HF in the analyte solution makes it suitable for passage through glass nebulisers, spray chambers and torches.

The less rigorous *aqua regia* digestion is employed more frequently than HF-HClO₄-HNO₃ in geochemical exploration and environmental surveys when the elements of interest (*e.g.*, Cu, Pb, Zn) are sorbed onto clay minerals or in other readily decomposed phases. Some laboratories also add HF to digest the silicates. The mixture of 3 parts HCl to 1 part HNO₃ (*aqua regia*) has a strong oxidising power due to the formation of nascent chlorine and nitrosyl chloride [*The Lefort digestion uses a 1 part HCl to 3 parts of HNO₃ mixture*]. Hot *aqua regia* is an efficient solvent for numerous sulphides (*e.g.*, those of As, Se, Te, Bi, Fe, Mo), arsenides, selenides, tellurides, sulphosalts, and native Au, Pt and Pd. The minerals belonging to the group of simple oxides and their hydrates (*e.g.*, Fe-Mn) are completely decomposed with *aqua regia*. Natural U oxides, Ca phosphates and most sulphates (except baryte) are solubilised, as are some silicates

such as the zeolites. The oxidising strength of *aqua regia* can be enhanced by adding bromine. In some laboratories, there has been a trend away from employing the HClO₄-HNO₃ digestion, which requires special fume hoods, for the decomposition of material containing sulphides and organic matter in favour of the simpler *aqua regia* procedure. Evaporation to dryness with concentrated HCl acid converts salts to chlorides, ready for final solubilisation in dilute (0.5-1 M) mineral acid, which is compatible with the analytical technique. *Aqua regia* digestion for As, Sb, Bi, Se and Te should not be taken to dryness to avoid loss of analytes via volatilisation. Strong oxidising acid mixtures are required to convert all forms of Hg to Hg²⁺.

The results of *aqua regia* extraction methods are normally used in environmental legislation of most countries. The *aqua regia* method should be able to analyse a sample aliquot of 15-gram, and element concentrations determined by an ICP-MS or a combination of ICP-AES and ICP-MS (Reimann *et al.*, 2009; Birke *et al.*, 2014). Commercial laboratories nowadays even have *aqua regia* methods using 25-gram sample aliquots. Some laboratories use methods with 0.5-gram sample aliquots; such methods should not be selected, because of the very small weight, which is not representative of the sample to be analysed. It is important, therefore, to be informed about the laboratory operationally defined *aqua regia* digestion because, apart from the weight of the sample aliquot analysed, they are other variables to consider such as temperature, length of time, hot water bath or hot plate or microwave, and open versus closed digestion.

As with *aqua regia*, the effectiveness of acid extraction naturally depends upon the temperature, pressure, and length of sample/acid contact. More complete decomposition is achieved by closed rather than open system digestion where elevated temperature and pressure conditions can be used. Various types of vessels are available such as Polytetrafluoroethylene (PTFE) crucibles encased in metal ('bombs') and all Teflon vessels of different shapes. Polypropylene and polycarbonate bottles can be used up to 130°C while PTFE-lined vessels can withstand temperatures of 150-250°C. Pressure decomposition with mixed acids may digest certain refractory minerals (*e.g.*, beryl, pyrite) that are not completely solubilised in open digestion. Unlike most of these vessels, screw-capped Teflon vials of 15 ml volume or greater are inexpensive enough to be used for large-scale decomposition schemes. Closed system digestion is increasingly used with the energy source being microwave radiation rather than heat. The advantages include more complete dissolution in much less time, lower volume of acids required and less exposure to toxic fumes. Adaptation to high production has been slow due to the manipulations involved but newer designs are addressing this issue.

3.5.2.2. X-ray Fluorescence Spectrometry

X-ray Fluorescence Spectrometry (XRF) was introduced in the 1960s for the routine analysis of rocks for major elements and a select suite of trace elements, namely Sr, Rb, Y, Nb and Zr. Samples are prepared as fused discs (fused beads) or pressed powder pellets. The availability of extremely stable high power X-ray tubes and the development of mathematical procedures to correct for absorption-enhancement effects have resulted in such excellent precision in silicate analysis that quality indices are essentially limited by the degree of sample inhomogeneity.

In summary, XRF can be used to determine elements from F to U at concentrations in the parts per million (ppm or mg/kg) to per cent (%) range but is limited in the variety of rock and other matrices studied, silicates being by far the most common.

Matrix corrections require special attention in unusual samples, and the lack of well characterised similar certified reference materials (CRMs) is a hindrance. The technique is easily adaptable to automation and sample preparation is simple, without problems associated with dissolution. Discs or pellets can be stored for repeat analysis. XRF is an exemplary technique in analysis for the major elements and the trace elements Rb, Sr, Y, Zr, Nb, Pb and Th, and performs well for Co, Ni, Cu and Zn. There has been a trend in some laboratories to replace this method by ICP-AES and ICP-MS, after suitable acid digestion, but the precision of XRF in the

above determinations is outstanding in silicate and carbonate matrices, and its capabilities are considerable for routine automated analysis. Elements that can be determined by this method are: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Sn, Sb, I, Ba, La, Ta, W, Tl, Pb, Bi, Th and U.

Analysis of silicates and carbonates by ICP-AES and ICP-MS, following LiBO₂, fusion does not yet rival the precision obtained by fused disc XRF for the major elements.

All XRF measurements on bulk samples are subject to non-linear effects resulting from attenuation, or infrequently enhancement, of fluorescence X-ray intensities by interaction with the sample matrix. These effects comprise mainly:

- attenuation as the beam penetrates the sample, dependent upon photon energy (less attenuation with low energy) and sample matrix composition (the higher the atomic number, the greater the attenuation), and
- attenuation of the fluorescence photons emerging from the sample.

Many mathematical models, based either on fundamental principles or empirically determined, have been developed to account for these matrix effects. There is a critical depth below the surface of a sample beyond which fluorescent X-ray photons are effectively absorbed. The magnitude of this critical penetration depth depends on the photon energy and on the mean mass attenuation coefficient of the sample. *For example*, for the K α lines of Na and La in a silicate powder they are estimated to be 0.005 mm and 10.6 mm, respectively. Thus, for a powder sieved to pass 60 μ m, the fluorescence signals from the lightest elements (Na K α to Ca K α) will be derived from a single monolayer. It is unlikely that this mass of sample would adequately represent the bulk, and distortions may arise from heterogeneity along the surface of a compressed powder. Heavier elements are much less affected, because the signal is from a greater thickness of material than from lighter elements. Hence, the heavier trace elements may be determined in samples prepared as pressed pellets, while for the major elements it is essential that the mineralogical constituents of the sample are broken down.

Powder pellets are prepared by mixing the sample [having been sieved to pass a 200 mesh screen (0.075 mm)] with a suitable binder, compressing and forming a disc. Most fluxes used to prepare glass discs (fused beads) are based on lithium tetraborate and/or metaborate, which are not normally detected by XRF. Problems arise in the fusion of mineralised samples. Elements such as, Sb, Se, Te, Hg, Cd and S as sulphide, are likely to be volatilised, but this can be partially overcome. The fusion based method is normally reserved for the 'whole rock' analysis of silicates, and to a lesser extent carbonates, chromite and baryte. It is general practice to calibrate with as many CRMs as possible, although other calibration schemes are also used.

For soil samples, the <2.0 mm grain-size fraction after sieving is milled with an agate ball mill to 0.063 mm for the preparation of fused beads and powder pellets.

3.5.2.3. Determination of other parameters

Other parameters to be determined are: pH, loss on ignition (LOI), grain-size, soil water retention, bulk density, total nitrogen, total carbon, total organic carbon (TOC), and cation exchange capacity (CEC).

3.5.3. Determination of pesticides and herbicides

Organic compounds, such as pesticides and herbicides are used in agriculture, and ideally should be determined. Each country participating in the Global Black Soil project should provide a list of pesticides and herbicides used in its Black Soil region in order to decide which ones to analyse.

Pesticide residues and their metabolites have been analysed in environmental samples using a variety of chromatographic methods such as gas chromatography (GC), high performance liquid chromatography (HPLC), and capillary electrophoresis (CE). Due to their high sensitivity and selectivity, GC and HPLC are the most frequently used methods for the detection of these compounds. However, because many pesticides exhibit thermal instability and low volatility, derivatisation reactions, tedious pre-treatment procedures, and a large amount of organic solvent are required for GC and HPLC. As a result, CE has become the preferred alternative method for the analysis of pesticides and their degradation products (Rojano-Delgado and de Castro, 2014; Elbashir and Aboul-Enein, 2015). Capillary electrophoresis is widely used for pesticide determination due to its high separation efficiency, short separation time, low reagent consumption, and ease of operation; however, its concentration sensitivity is low when coupled with Ultraviolet-visible (UV-Vis) detectors. The capillary electrophoresis can be used in combination with offline sample pre-treatment, or online preconcentration techniques with high enrichment factors.

For the analytical programme for organic compounds, informative publications that should be consulted are:

- *Organic Analysis for Urban Geochemical Survey Soil Samples* by Harrison and Reeder (2011), Chapter 4 (p.47-60) in C.C. Johnson *et al.* (Editors), *Mapping the Chemical Environment of Urban Areas* (Published by Wiley-Blackwell, John Wiley & Sons Ltd., Chichester, U.K.).
- *Analytical Methods for Pesticides and Herbicides* by Liu *et al.* (2018), *Water Environment Research*, Vol. 90, No. 10, 1323-1347.
- *Methods of Analysis-Determination of Pesticides in Sediment Using Gas Chromatography/Mass Spectrometry* by Hladik and McWayne (2012), U.S. Geological Survey Techniques and Methods 5-C3, 18 pp.; <http://pubs.usgs.gov/tm/tm5c3>.

3.5.4. Determination of mineralogy

The Global Black Soil project samples should be analysed by X-ray diffraction (XRD), and the percentages of major mineral phases calculated (Smith *et al.*, 2014). A split of the <2-mm fraction is used for the mineralogical analysis. All quantitative XRD analysis requires precise and accurate determination of the diffraction pattern for a sample, both in terms of peaks and intensities.

X-ray diffraction (XRD) is a powerful non-destructive technique for characterising all kinds of matter – ranging from fluids, to powders and crystals. It provides information on crystal structure, phase, preferred crystal orientation (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays diffracted at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice.

X-ray diffraction analysis is used, not only to identify the phase of unknown substance and to estimate the lattice parameters, but also to determine the concentration of that phase in the mixture. The peak profile is also employed to estimate the particle size of very small crystals (crystallites) in a powder sample. Powder diffraction is one of the principal research tools of mineralogists since many minerals are available in polycrystalline form (Dinnebier and Billinge, 2008; Pecharsky and Zavalij, 2009; Lavina *et al.*, 2014).

Qualitative XRD analysis usually involves the identification of phases in a specimen by comparison with ‘standard’ patterns (*e.g.*, ICDD database, International Centre for Diffraction

Data), and relative estimation of proportions of different phases in multiphase specimens by comparing peak intensities attributed to the identified phases.

Quantitative analysis of diffraction data usually involves the determination of amounts of different phases in multiphase samples (Ufer *et al.*, 2008a, b; 2012a, b; Waseda *et al.*, 2011; Lavina *et al.*, 2014). Quantitative XRD analysis is based on the fact that the intensity of the diffraction pattern of a crystalline substance depends on the concentration of that phase in a mixture. The relationship between intensity and concentration is not always linear, but it is found to be possible when a particular peak of the desired substance is focussed on relative to the case of that substance alone. Therefore, the diffraction peak corresponding to the specific plane of the desired crystalline substance of interest should be observed at a fully different angle from those of other ingredients, and its integrated intensity provides an indication of the amount. Numerous methods have been developed to use peak intensity for quantitative analysis of diffraction data. Jenkins and Snyder (1996) have introduced most of these methods.

All quantitative XRD analysis requires precise and accurate determination of the diffraction pattern for a sample both in terms of peak positions and intensities. While some kinds of quantitative analysis (*i.e.*, particle shape and clay structure) rely on the existence of preferred orientation, most require a uniformly sized, randomly oriented fine (ideally 1–2 μm) powder specimen to produce intensities which accurately reflect the structure and composition of phases analysed.

The most effective quantitative methods, particularly those involving pattern modelling, are computationally intensive, and can be only applied with powerful analytical software (*e.g.*, GSAS, FullProf, FULLPAT, RockJock, Rietveld-Software BGMN, AutoQuan). The methods with the greatest chance of producing successful results generally involve the addition of a known amount of an internal standard and the calculation of the ratios of the areas of the standard peaks to those of the phases being determined. Zinc oxide (ZnO, 10 weight per cent) is to be added to each sample as an internal standard, which allows calculation of the amorphous component (portion of sample that is not quantified by the diffraction technique). The sample-ZnO mixture is ground for 3 minutes in isopropyl alcohol using a micronising mill and agate beads. Dried samples are disaggregated by passing through a 400- μm sieve and lightly pressing them into back-loaded sample mounts.

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4. QUALITY CONTROL PROCEDURES

Alecos Demetriades^{1,2}, Christopher C. Johnson^{1,3} and Ariadne Argyraki^{1,4}

¹ IUGS Commission on Global Geochemical Baselines

² Institute of Geology and Mineral Exploration, Athens, Hellas (retired)

³ GeoElementary, Derby, United Kingdom

⁴ Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Hellas

4.1. Introduction

The analytical data that will be produced for the Global Black Soil project are environmentally sensitive, because they are directly related to the quality of our food products, and to human health. Consequently, the generated geochemical data must be of proven quality and integrity.

To ensure the quality of generated geochemical data, a rigorous quality control and assurance procedure (QC/QA) must be adopted from the start of the project. The quality control procedure should give an estimation of sampling, analytical, and geochemical variance, and measurement uncertainty (Ramsey, 1997, 1998; Ramsey and Argyraki, 1997; Ellison *et al.*, 2000; Ramsey and Ellison, 2007; Ellison and Williams, 2007, 2012; Demetriades, 2011a; Majcen *et al.*, 2011; Ramsey *et al.*, 2019).

4.1.1. Obligations of Global Black Soil Geochemistry Project Manager

At the present time, most commercial laboratories are accredited. It is very important to understand, however, the accreditation process. A laboratory is considered competent in the application of specific documented laboratory methods and standard operating procedures. Accreditation mandates to keep a record of all procedures that a batch of samples undergoes in the laboratory. Hence, any errors can be located by backtracking. Accreditation requires that quality control and quality assurance programmes be in place for all aspects of the laboratory operations. All facilities and equipment are tightly scrutinised to insure adequacy for intended applications, and the laboratory must be participating in a proficiency analytical testing programme. To put it simply, an accredited laboratory has the right '*internal*'⁸ quality control procedures in place to analyse samples. It is, therefore, the professional responsibility of the BSGP Manager of the Global Black Soil project to place his/her own '*external*' quality control procedures to ensure that results received are of a good standard and fit for the purposes of the project. Hence, the BSGP Manager must ensure that there is in the team a professional applied geochemist with the skills to check the quality and integrity of the data received from the laboratory, or to establish a Quality Control Team (QC Team) with such skills.

It is important to remember that the analytical results of the Global Black Soil geochemical mapping project must be of high quality and integrity, because they are related to the quality of our food products, as their quality affects our health. Therefore, the BSGP Manager must not rely on the '*element concentration numbers*' given by the laboratory. He/she must ensure that these '*numbers*' are meaningful, and are substantiated by independent external quality control results, which are project monitored. Consequently, the QC Team, upon receipt of the analytical results, must check them thoroughly to verify their quality and integrity.

To begin with, the analytical report of the laboratory must be studied, before proceeding to check the quality of analytical data. Directly afterwards, the arduous task of verification of the quality of the analytical data starts, using the external quality control results, and the laboratory

⁸ An accredited laboratory has its own '*internal*' quality control procedure installed. The BSGP Manager for the verification of the integrity and quality of the Global Black Soil project analytical data should install his/her independent '*external*' quality control procedure, which is unknown to the laboratory.

internal quality control results. If the QC Team is not satisfied with the quality of analytical results, then the laboratory shall be obliged to reanalyse the problematic batch or batches of samples, or even the whole sample suite. Verifying the quality of the generated analytical results is an important condition that should be included in the contract with the laboratory.

When satisfied with the quality of the analytical results, a procedure to estimate the geochemical, sampling and analytical variation, as well as measurement uncertainty, is done by using the robust statistical method proposed by Ramsey (1998; Lee and Ramsey, 2001; Lyn *et al.*, 2007, Boon, 2009; Demetriades, 2011a). Then and only then the BSGP Manager should sanction the second step, which is the processing of geochemical data leading to map plotting.

The results of robust analysis of variance show the contribution to measurement uncertainty that arises from the processes of primary sampling and chemical analysis. In the geochemical mapping survey of Black Soil, the estimation of measurement uncertainty of the analytical results of each determinand is of paramount importance, because it is an important parameter that describes quantitatively the quality of geochemical results. Some laboratories nowadays report measurement uncertainty, but it is prudent for the QC Team to estimate measurement uncertainty using the Global Black Soil project's independent quality control results.

As the geochemical data generated by the Global Black Soil project are important for the quality of food products produced, it is important to write a detailed quality control report. Hence, the statement that *the generated Global Black Soil geochemical project data must be of high quality and integrity*. In fact, *the first and foremost obligation of the Black Soil Geochemistry Project Manager is the delivery of good quality geochemical data for multipurpose use*. Finally, when the BSGP Manager is satisfied that the quality and integrity of survey results is up to the standard required for the investigation (fitness-for-purpose), only then should proceed with data processing and map plotting.

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

4.2. Quality control report

Upon receiving the analytical results from the laboratory the quality and integrity of the data should be verified, using various statistical techniques (see Section 4.3; Johnson 2011; Demetriades, 2011a), as it has been done in the GEMAS project, and a quality report written (Reimann *et al.*, 2009, 2011, 2012; Demetriades *et al.*, 2014). The quality assessment report is an integral part of any geochemical project, and must be compiled and made available.

4.3. Data checking

4.3.1. Checking of raw analytical data

Johnson (2011) has written a well-documented chapter "*Understanding the Quality of Chemical Data from the Urban Environment – Part 1: Quality Control Procedures*" in the textbook "*Mapping the Chemical Environment of Urban Areas*" (Johnson *et al.*, 2011), which should be consulted. The procedure for checking the raw analytical data upon receipt from the laboratory is given below.

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

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

Answers to the above questions will give an immediate impression of the quality of the data, and it is at this stage where the most obvious problems with the data can be identified.

At this point, something should also be done with respect to missing, semi-quantitative and unreliable data (see Johnson *et al.*, 2018), as such data will affect the data analysis process (see Reimann *et al.*, 2008, Chapter 2, p.13-28). An archive of the original data file, as received from the laboratory, should always be saved before any changes are made.

A work analytical data file should be prepared. If the project samples have been given new random numbers, then the first task is to associate them with those in the original field database, where all control samples are characterised. For extracting all control sample analytical results, such as those of field duplicates, analytical replicates, SRMs, and project solid blanks, it is recommended that the samples should be suitably coded in the original database that is submitted to the laboratory as proposed by Johnson (2011), *i.e.*:

- field duplicate samples: DUPA and DUPB;
- field replicate samples: REPA and REPB;
- project SRM sample(s): REF1 and REF2, and
- project solid blank sample: BLK (refer to Section §3.2 in this manual).

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

4.3.1.1. Laboratory blank samples

First check the analytical results of the laboratory blank samples, which should be all below the laboratory's lower detection limit for all determined elements. The reagent blank is made-up of the same acids (plus deionised water), which are added to the solid⁹ samples for bringing into solution the chemical elements (Johnson, 2011; Magnusson and Örnemark, 2014; Cantwell, 2019). The primary purpose of the reagent blank samples is to trace any interferences or contamination introduced during any part of the measurement procedure in the laboratory. Therefore, if elevated values are observed for any element, then laboratory contamination is suspected, and it should be checked by reanalysis of the sample batches analysed during that particular period. Once satisfied with this particular visual test, the verification of the quality of the analytical results can proceed.

4.3.1.2. Project solid blank sample

Second in line is the check of the project solid blank sample analytical results, which should be within the accepted limits, as estimated by the standardisation procedure. It is noted that the solid

⁹ 'Solid' samples are the analysed aliquots of the collected Black Soil project samples.

blank sample is packed in the field, and goes through the sample preparation procedure as the routine project samples, and its main purpose is to indicate contamination during the course of sample preparation and analysis (Schermann, 1990).

If the solid blank sample is pure silica, then the concentration of all elements, except Si, should be below the laboratory's lower detection limit. However, if the solid blank sample is kaolinite (Schermann, 1990), then the analytical results should be within the accepted limits, as estimated by the standardisation procedure. If the results deviate from the accepted limits, then most likely the solid blank sample aliquots have been contaminated either during sample preparation or laboratory analysis. If the laboratory blank samples (*e.g.*, pure silica sand) are above the lower detection limit in that particular analytical batch or batches, then the project solid blank sample has been contaminated during sample preparation or laboratory analysis.

It should be noted that the duplicate-replicate splits or secondary reference materials (SRMs) can be used also to indicate introduced contamination. A duplicate-replicate split would only indicate '*within batch*' contamination, whereas a secondary reference material could give an indication of '*between batch*' contamination.

The results of the suspected batch or batches of contaminated routine Black Soil samples should be studied carefully in order to assess the extent of contamination, and if it can be corrected by applying a correction factor, otherwise new samples should be collected.

4.3.1.3. Control charts

According to Johnson (2011, p.67-71), the results for reference materials can be plotted on a control chart (also referred to as a Shewhart plot or X-Chart), which is a time sequenced graph with fixed defining limits (Miller and Miller, 2005). An example of such a chart is given in Figure 34. The X-axis shows the date of analysis or the laboratory batch if batch numbers are

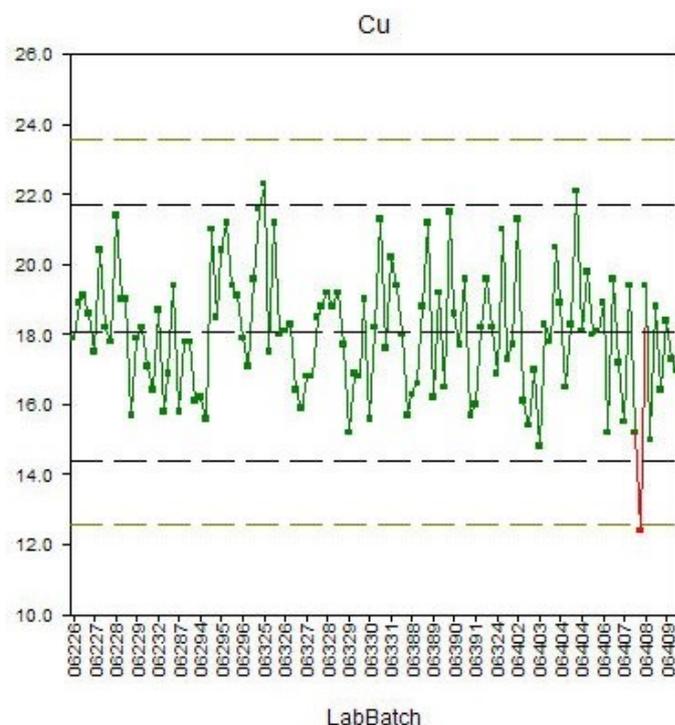


Figure 34. Example of a control chart plot of Cu using QI Analyst software for the BGS Moroccan secondary reference material MB1 (after Johnson *et al.*, 2001, Figure 2.4, p.10). Central solid line represents accepted value (AV); outer dashed lines are at $AV \pm 2SD$ and $AV \pm 3SD$. Symbol plotted in red represents a batch that fails QC criteria. Source: Johnson, 2011, Figure 5.4, p.68.

assigned sequentially. The Y-axis displays the element concentration and the accepted value (AV) for the reference material, a value calculated from previous repeated analyses of the certified reference materials (CRMs). The AV used on the control chart must be that which has been determined by exactly the same analytical method as the one used for the sample analyses undergoing the quality control procedures. It is impossible to know what the ‘true’ value is, but the AV should be a good approximation of it. Defining limits are also plotted on the chart; in Figure 34, these are calculated as the AV \pm 2 and 3 standard deviations (SD). The AV \pm 2SD threshold is normally used as an alert to possible analytical problems, and exceeding the AV \pm 3SD requires an explanation, and a possible indication that the batch of samples needs reanalysis, particularly if this is a trend, observed for more than one element. This process of plotting a control chart is something that is usually done by the laboratory itself with its own reference materials. Using the secondary reference materials (SRMs) inserted in each sample batch, the BSGP Manager or QC Team can check accuracy by visual inspection of these plots. *Accuracy* is a measurement of how close to a ‘true’ or ‘accepted’ value a result is. A scattering of results about the AV line is to be expected, though a consistent trend to a higher or lower value would be referred to as *analytical bias*.

Control charts are invaluable in detecting analytical shifts that can occur over time, as, *for example*, after the installation of a new X-ray tube in X-ray fluorescence spectrometry (XRFS) or when any analytical instrument has been recalibrated. This can be used to identify levelling factors, required to level chemical results collected over a long period of time (Johnson *et al.*, 2018).

The second example is a control chart of a project reference sample (Figure 35), which does not show the expected random variation of the individual sub-sample results about the mean. It has many outliers, and even time trends. Such data cannot be accepted when the objective is to

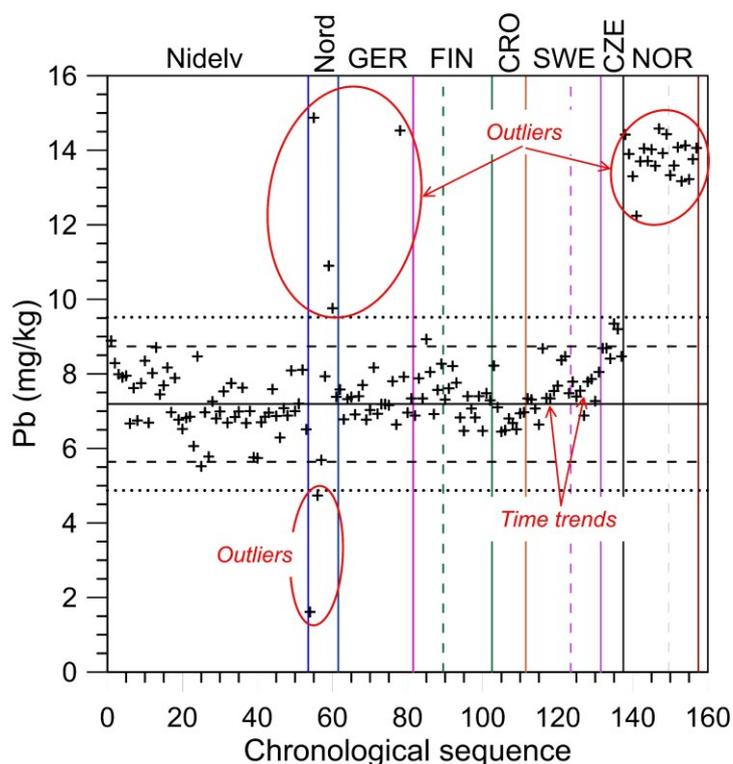


Figure 35. Example of a control chart for a secondary reference sample (SRM) used in the EuroGeoSurveys URGE I project. Central solid line represents the mean value; outer dashed lines are at mean \pm 2SD and stippled lines at mean \pm 3SD. The secondary reference sample was used in the urban geochemical mapping projects in different European cities, the results of which are separated by solid coloured lines. In some cases, the city samples were analysed in two different batches and at different time, and dashed lines separate the two batches. Plotted by Alecos Demetriades (IGME & IUGS CGGB) with Golden Software’s Grapher™ v.17.

compare the analytical results among different countries (in this example, different cities); in this plot, problems are shown even between two analytical batches of the same city.

4.3.1.4. Precision

Analytical precision can be calculated by different statistical methods as described by Johnson (2011) and Demetriades (2011a).

Precision is a measurement of how closely the analytical results can be reproduced, and is independent of the true value (*i.e.*, results can all show close agreement, but they may be a long way from the accepted value, AV). A visual impression of precision can be gained from the control chart (Figure 34), since data will plot in a much narrower band if the method has good precision. Similar visual impressions of precision can be given by X-Y plots (Figure 36) and Thompson and Howarth plots (see Section §4.3.1.8), which are described below. Overall precision at the 95% confidence level can be also estimated quantitatively, based on the mean (μ) and standard deviation (SD) expressed as a percentage:

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

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

Substituting CV in Equation 1:

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

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

4.3.1.5. Duplicate-Replicate X-Y plot

According to Johnson (2011, p.69-70), a simple X-Y plot of duplicate-replicate pair results for an element gives an immediate visual appreciation of the laboratory precision for that particular element (Figure 36). If in these plots the cluster of points does not follow closely the line of gradient 1, but instead forms a dispersed scatter of points, then data for that element should either be rejected or used with caution. A random scatter would indicate that variability in the results is most likely generated in the laboratory (for replicate samples) or includes significant within-site variability (if seen in the duplicate plots). Figure 36 displays some example plots from the British Geological Survey G-BASE soil samples for East Midlands urban samples. The Cu plot shows that the sampling and analytical variances are low, so there is confidence that Cu results reflect actual between site variability. The Ni plot exhibits a number of outlying DUPA versus DUPB points, indicating that when a site is sampled for a second time there are occasional significant within-site variations, a feature displayed for the same duplicate pairs by other elements (*e.g.*, Fe, V, Cr and Co - not illustrated herein). This is to be expected in urban areas, where there is greater inhomogeneity in soil over short distances due to anthropogenic contamination.

This method is only applicable if there is a sufficient number of duplicate-replicate pairs with a range of element concentrations that can produce a meaningful plot. When only single or a small number of duplicate-replicate pairs are available the Thompson-Howarth plots

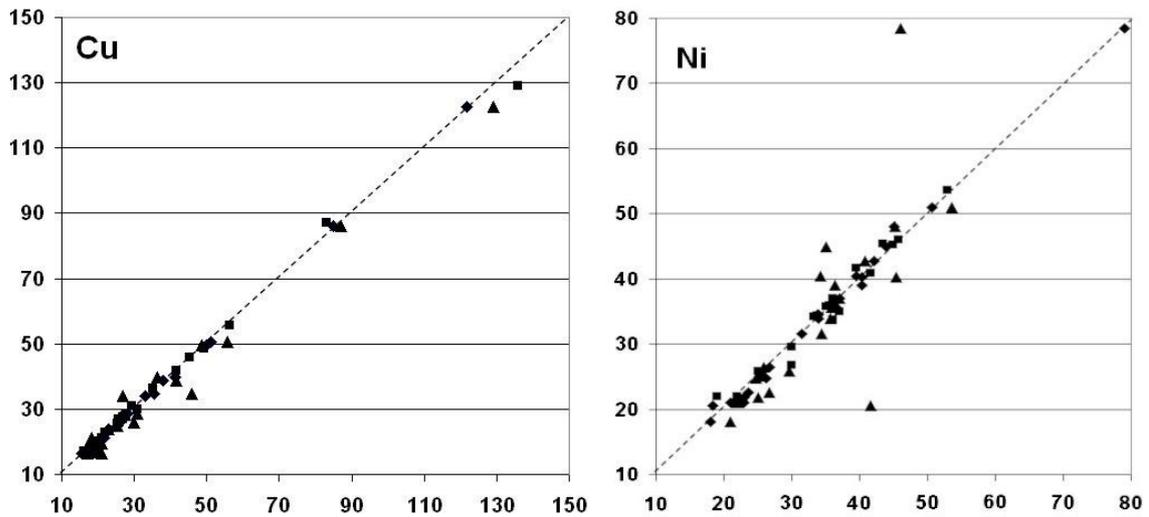


Figure 36. Duplicate-replicate plots for Cu and Ni for G-BASE urban soil (35-50 cm) from United Kingdom East Midlands. Axis units in mg/kg. Triangle = DUPA versus DUPB; Square= REPA versus DUPA; and Diamond = REPB versus DUPB (all x-axis versus y-axis); dashed line has 1:1 slope. Source: Johnson, 2011, Figure 5.6, p.69.

(Thompson and Howarth, 1976, 1978; Thompson, 1983; AMC, 2002) described below, can be used.

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

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

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

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

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

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

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

$$\text{Precision, P (\%)} = 1.96 * \frac{\sqrt{\text{Var}}}{\mu} * 100 \quad \text{at the 95\% confidence level} \quad (7)$$

Software for X-Y plots is readily available and Microsoft Excel or R routines provide adequate graphs (Reimann *et al.*, 2008). The G-BASE project uses the macro facility of Microsoft Excel rapidly to plot duplicate-replicate graphs for some 50 elements simultaneously. Charts of interest can be subsequently extracted and formatted in a suitable manner for publication. A Microsoft Excel workbook (DUPREPLOT) can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines' website (<http://www.globalgeochemicalbaselines.eu>).

4.3.1.6. Practical detection limit and analytical precision

The analytical precision can be calculated by another method as described below (Demetriades 2011a, p.81-83).

The practical detection limit and analytical precision can be estimated by using the method proposed by Howarth and Thompson (1976) and Thompson and Howarth (1976, 1978), with modifications made by Demetriades and Karamanos (2003) and Demetriades (2011a) at a particular step of the procedure. Replicated analyses are performed on at least 55 randomly selected samples. The steps followed are:

1. Calculate the mean values of the 55 pairs $[(X_1+X_2)/2]$. According to Thompson and Howarth (1978), this mean value is an estimate of true concentration of an element for the particular analytical method used.
2. Calculate the absolute differences between each pair $|X_1-X_2|$. The absolute difference is an estimate of the standard deviation, σ_c , at that particular concentration. $|X_1-X_2|$ is normally distributed and relates to the parent population, with a standard deviation σ_c , such that:

$$\sigma_d = \sqrt{1.96 * \sigma_c} \quad (8)$$

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

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

where d is the mean value for the difference; and

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

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

3. Arrange list in increasing order of concentration means.
4. From the first 11 results, calculate the mean concentration (*Group mean*) and the median difference (*Group median*).
5. Repeat step 4 for each successive group of 11 samples, ignoring any remainder less than 11. *Hence, the reason for suggesting that replicated analyses should be performed on at least 55 randomly selected samples, which gives 5 groups of 11 samples.*
6. Calculate the linear regression of the median difference (*Y-axis, dependent variable*) on the means (*X-axis, independent variable*). At this point, the first author introduced a modification. In classical regression, ($Y = a + bX$), a linear relationship is quantified by fulfilling the following requirements of (a) dependency and (b) knowing one variable without error. Thompson and Howarth (1978) assumed that the group means are the independent variable or predictor (X), by which the group median difference (Y) is estimated. The question posed is the following: *which is really the dependent variable?* Since, both variables are derived from the grouping of the same analytical data set, they are subject to errors of the same order of magnitude. It is concluded, therefore, that the requirements of classical regression cannot be met. To overcome this situation Kermack and Haldane (1950) developed the reduced major axis line, which is the line of best-fit

between a set of points (Figure 37; Till, 1974). Essentially, is the best-fit line between the two regression lines of $(Y = a + bX)$ and $(X = a + bY)$. Hence, errors of estimation are minimised.

7. Obtain from the major axis regression line of the group median differences, $|X_1 - X_2|$, on the group means, $(X_1 + X_2)/2$, the intercept, a , and coefficient, b .
8. Multiply by 1.048 (*i.e.*, $1/0.954$) the intercept, a , and coefficient, b , to obtain σ_o and k , respectively; from the regression $\sigma_c = \sigma_o + kc$, so that the precision, P_c , is given by

$$P_c = \frac{1.96 * \sigma_o}{X_{ci}} + 1.96 * k \quad (11)$$

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

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

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

$$= \frac{196.0 * \sigma_o}{X_{ci}} + 196.0 * k \quad (13)$$

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

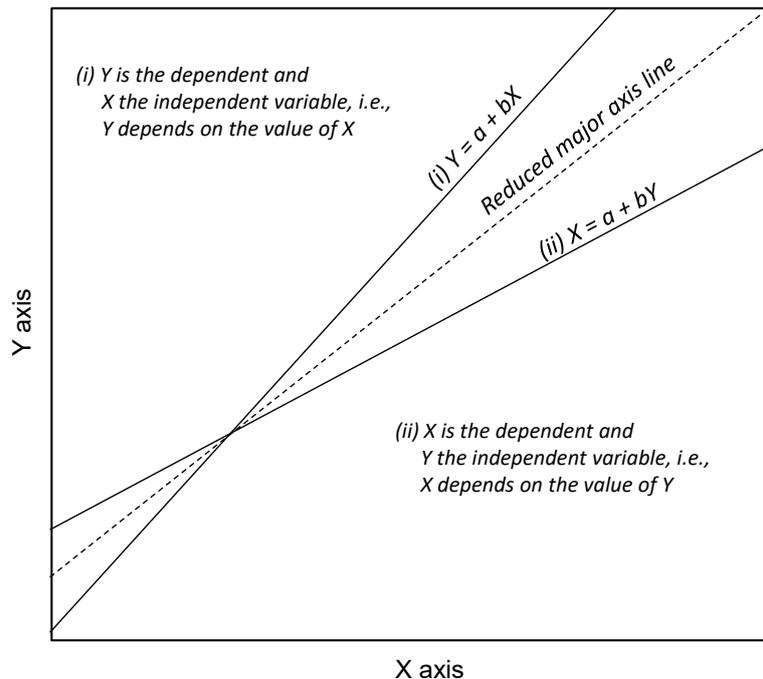


Figure 37. The reduced major axis line is the best fit line of Y on X and X on Y . Source: Demetriades, 2011a, Figure 6.2, p.82.

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

precision falls asymptotically towards the value of 1.96k as defined in the expression $P_c = (1.96\sigma_o / X_{ci}) + 1.96k$ (Equation 11). For further information, and the implications involved in the estimation of these quality control parameters, Thompson and Howarth (1976) should be consulted. It is important to understand the asymptotic nature of precision, and that it is wrong to quote a single value for precision, *i.e.*, at concentrations higher than the detection limit, precision falls asymptotically towards the value of 1.96k or 196.0k in the above expressions (refer to Fletcher, 1981, Figure 2-5, p.32; see Figure 38 below). On the geochemical distribution maps the relative precision equation should be given, so that the reader can estimate precision at any specific concentration.

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

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

For the estimation of precision by the above method, a Microsoft Excel workbook (PDLPRECIS) is available, which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines' website (<http://www.globalgeochemicalbaselines.eu>).

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

The asymptotic nature of precision is shown in Figure 38, using the Be duplicate-replicate results from the *aqua regia* GEMAS grazing land soil data set. In this case, the laboratory provided uncensored data, and even sub-zero (negative) values. Using the procedure described above, two different estimations were made, with and without the negative values. The precision in both cases falls asymptotically towards the value of 1.96k or 196.0k in the above expressions. Beyond this limit, the curve reaches a plateau, and this is considered to be the overall precision. The practical detection limit (PDL), as already mentioned above, is defined as the concentration that gives rise to a signal equal to twice the standard deviation of blank fluctuations, *i.e.*, at a value of $P_c = 100\%$ and $X_{ci} = 1.96\sigma_o$. On the graph, it is the tangent to the curve leading to $P_c = 100\%$. As expected, there are differences in the estimation, even by removing a single pair of negative values:-

- (a) PDL = 0.072 mg Be/kg (with negative and N=94 pairs), and an overall precision of 18.4% at the 95% confidence level, and a precision equation (Figure 38a):

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

- (b) PDL = 0.046 mg Be/kg (without negative value and N=93 pairs), and an overall precision of 24.5% at the 95% confidence level, and a precision equation (Figure 38b):

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

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

The laboratory's lower detection limit is 0.1 mg Be/kg, which is higher than the values estimated for the practical detection limit, *i.e.*, 0.072 and 0.046 mg Be/kg, respectively (see Figure 38). For elements, such as Be, where most of the values are exceptionally low, and near to the method's lower detection limit, it is an advantage to estimate the practical detection limit, using actual project data. Otherwise, if the laboratory provided censored analytical data at the laboratory's detection limit of 0.1 mg Be/kg, all values below this limit would have been given half the value of the lower detection limit (LDL), *i.e.*, 0.05 mg Be/kg, if chosen imputation method is to replace values <LDL by 0.5*LDL (of course there are other imputation techniques). Thus, losing many actual background values.

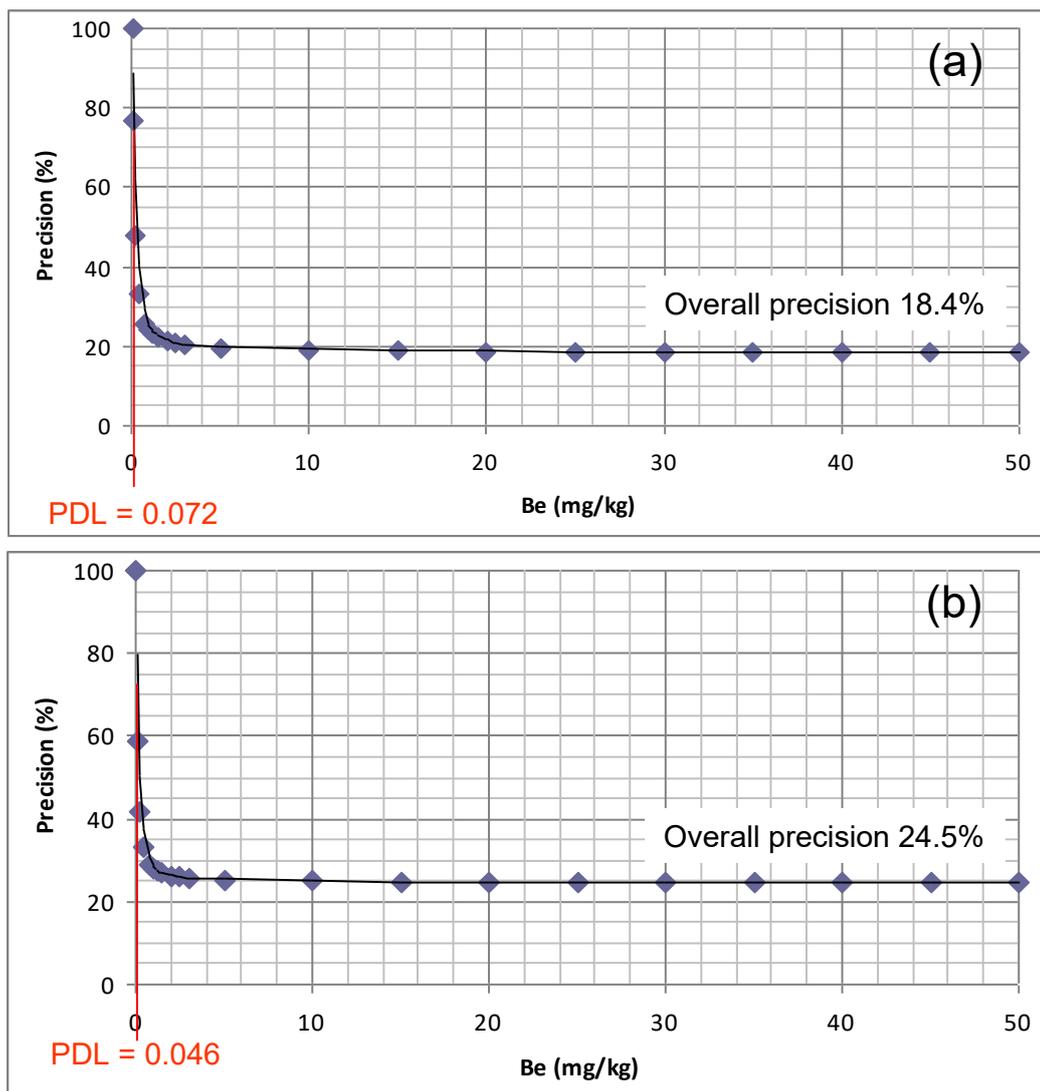


Figure 38. Variation of precision with concentration. Two examples of Be from the *aqua regia* GEMAS grazing land soil data set (Reimann *et al.*, 2014) plotted with Microsoft Excel: (a) with negative values (N=94 pairs), and (b) with negative values removed (N=93 pairs). The former gives an overall precision of 18.4% at the 95% confidence level, and the latter an overall precision of 24.5% at concentrations beyond 50 mg Be/kg. Plotted by Alecos Demetriades, IGME & IUGS CGGB.

4.3.1.7. Cumulative probability plot

According to Johnson (2011, p.68-69), replacing the below lower detection limit (LDL) value with an arbitrary value (usually half the cited detection limit) will introduce a distortion in the data distribution at low concentrations, and this will have an impact on both descriptive and multivariate statistics. Analysts tend to be conservative with their LDLs and, furthermore, many results reported as below detection have recordable useful values that show structure in the data distribution below the laboratory's cited LDL. This is illustrated in Figure 39 by a cumulative probability plot, where the flattening of the graph indicates a more realistic limit of detection, which is much lower than that cited by the analyst. Cumulative probability plots have long been used by applied geochemists to partition analytical results into a combination of different populations (Tennant and White, 1959; Lepeltier, 1969; Sinclair, 1976, 1983, 1986), and their usefulness in establishing more realistic detection limits is shown herein. A procedure for estimating practical detection limits for chemical elements determined on project samples according to Thompson and Howarth (1978) has already been described in Section §4.3.1.6.

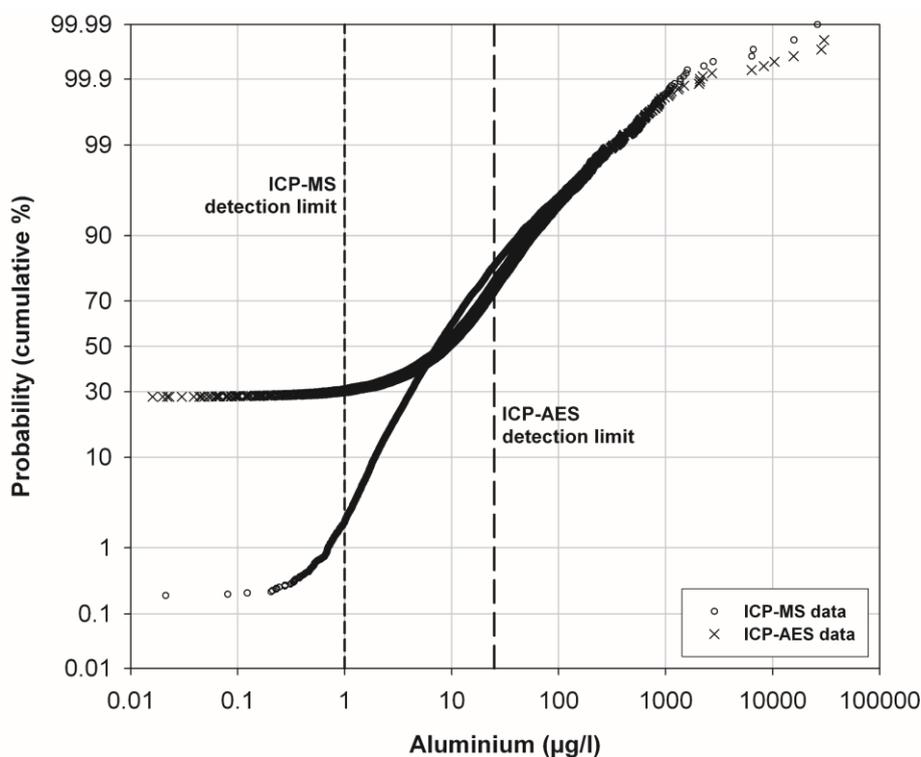


Figure 39. Cumulative probability plot indicating true detection limits for water samples determined by two different analytical methods. This was plotted using SigmaPlot v.10 software by E.L. Ander (BGS). Source: Johnson, 2011, Figure 5.5, p.69.

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

Another example of cumulative frequency is displayed in Figure 40, using the uncensored As and Tl analytical results from the EuroGeoSurveys project of Geochemical Mapping of Agricultural and grazing land soil of Europe (GEMAS). It is quite evident that the lower detection limits of As and Tl are lower than those given by the laboratory.

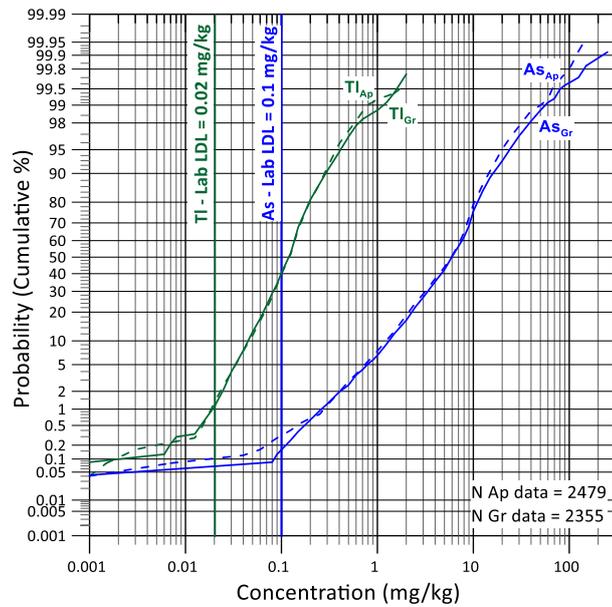


Figure 40. Cumulative probability plots indicating that the conservative laboratory lower detection limits (LDL) of aqua regia extractable As and Tl for the agricultural (Ap) and grazing land (Gr) soil samples of the EuroGeoSurveys project of Geochemical Mapping of Agricultural and grazing land Soil (GEMAS) of Europe, using uncensored data (Reimann *et al.*, 2014), are higher than the true detection limits. In this case, the practical detection limit can be as low as 0.005 and 0.00009 mg/kg for As and Tl, respectively (Reimann *et al.*, 2009). Plotted by Alecos Demetriades (IGME & IUGS CGGB) with Golden Software's Grapher™ v.17.

4.3.1.8. Thompson-Howarth plot

Thompson and Howarth (1978) and Thompson (1983) describe a method of estimating analytical precision using duplicate-replicate sample pairs (Johnson, 2011, p.70). This is a graphical method, which can be used even for a single replicate pair that gives an immediate visual impression of the precision of the analytical method (see Figure 41). The absolute difference

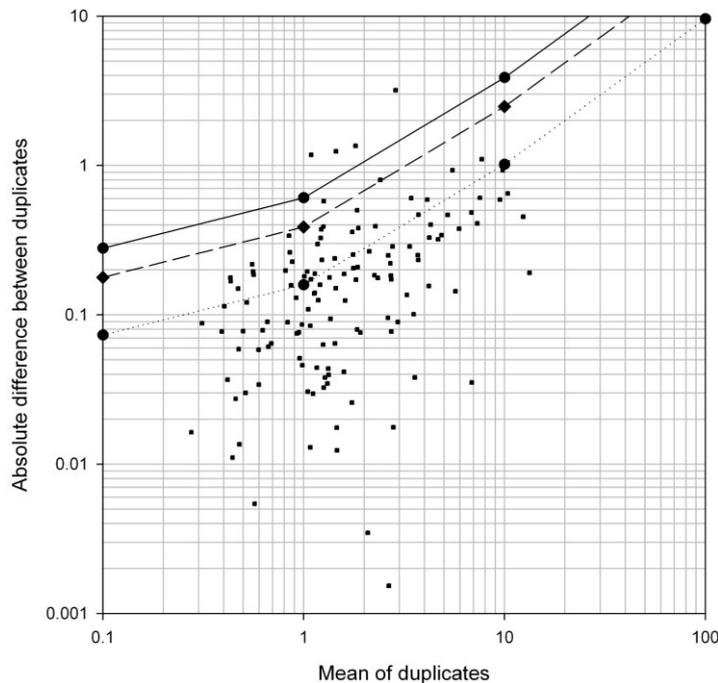


Figure 41. A logarithmic scale Thompson-Howarth plot used for visualising analytical precision. This is a plot of G-BASE stream water duplicates for As with probabilities calculated at 0.2 µg/l detection limit using SigmaPlot v.10 software by E.L. Ander (BGS). See AMC (2002) for rationale behind the Thompson-Howarth plot. Solid, dashed, and dotted lines represent 99, 90, and 50 per cent confidence levels. Source: Johnson, 2011, Figure 5.7, p.71.

between the two replicate analyses is plotted against the mean of the replicate results. On the graph, the fit-for-purpose criteria are defined by the detection limit (herein $0.2 \mu\text{g/l As}$) and 99, 90, and 50 percentile lines. In Figure 41, precision is generally good with only a small percentage of duplicate-replicate pairs plotting above the 90th percentile line. Reimann *et al.* (2008, 2009, 2011, 2012) give examples of Thompson-Howarth plots generated using R routines.

The second Thompson and Howarth plot (Figure 42) is a variant using normal linear axes. In this case, the 10% precision at the 95% confidence level is generally good at the 99th percentile, as only 4 duplicate-replicate pairs plot above the 99th percentile line.

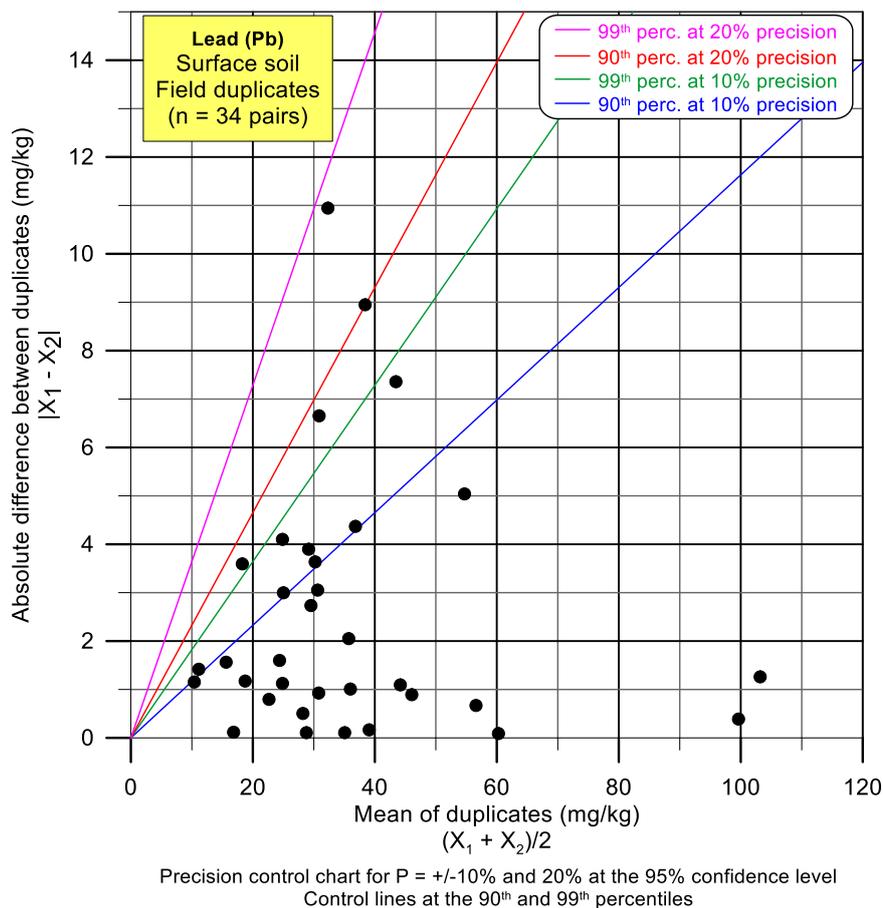


Figure 42. A normal linear scale Thompson and Howarth plot used for visualising the precision of Pb. This is a plot from the results of the Hellenic Institute of Geology and Mineral Exploration's urban soil geochemistry project at Thrakomakædônæs, a suburb of Athens. Colour lines represent 10% and 20% precision at the 95% confidence level, and at the 90th and 99th percentiles. Plotted by Alecos Demetriades (IGME & IUGS CGGB) with Golden Software's Grapher™ v.17.

4.3.1.9. Robust ANOVA for the estimation of uncertainty due to sampling and analysis

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

The balanced RANOVA method proposed by Ramsey (1998), apart from estimating the geochemical, sampling and analytical variances, calculates measurement uncertainty, which is an

essential parameter for the qualification of the Black Soil geochemical data set. According to Ramsey *et al.* (2019, p.1) “*Uncertainty of measurement is the most important single parameter that describes the quality of measurements. This is because uncertainty fundamentally affects the decisions that are based upon the measurement result*”. *Uncertainty of measurement, or measurement uncertainty*, is defined in metrological terminology as:

“*Parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand*¹⁰” (ISO/IEC, 1993; Ramsey and Argyraki, 1997, p.244; Ramsey *et al.*, 2019, p. 6).

Uncertainties in the measurement process arise from a variety of sources, which are discussed in detail by Ellison and Williams (2012) and Ramsey *et al.* (2019). In their simplest form, the sources of measurement uncertainty can be categorised in two groups: (i) sampling and (ii) laboratory treatment of samples (*i.e.*, sample preparation and analysis). Hence, the two categories of measurement uncertainty discussed are ‘*sampling uncertainty*’ and ‘*analytical uncertainty*’, as well as the geochemical or spatial variance.

For the estimation of measurement uncertainty two different methodologies have been proposed, *i.e.*, (i) the ‘*bottom up*’ (or ‘modelling’, ‘theoretical’, ‘predictive’), and (ii) the ‘*top down*’ (or ‘empirical’, ‘experimental’, ‘retrospective’) (Ramsey, 1998; Ramsey and Ellison, 2007). Whichever approach is followed, the general objective is to obtain a sufficiently reliable estimate of the overall measurement uncertainty. The ‘*top down*’ approach does not require all the individual sources of uncertainty to be quantified, but only the combined effect to be assessed. If, however, the overall level of uncertainty is found to be unacceptable, according to the requirements of the project, *i.e.*, the measurements are not ‘*fit-for-purpose*’, then actions should be taken to reduce the uncertainty. Alternatively, the estimated measurement uncertainty may be unnecessarily small, and in such a case there may be justification for increasing the analytical uncertainty, and thereby decreasing the cost of analysis.

In the ‘*bottom-up*’ approach the random error from each individual component of a method is quantified separately as a standard deviation s , and then a model is used to combine them (Ramsey, 1998; Ellison *et al.*, 2000; Ellison and Williams, 2012; Ramsey *et al.*, 2019). Its limitation is the requirement to identify all sources of uncertainty. However, it is relatively easy to consider the obvious sources of error, which are explicit parts of a method, *e.g.*, weighing, volumetric additions.

The ‘*top-down*’ approach is intended to obtain a reliable estimate of uncertainty, without necessarily knowing any of the sources individually, and has the widest applicability in measurement systems and applications (Ramsey *et al.*, 2019). It relies on overall precision measurements from either in-house or inter-organisational measurement trials. The latter are more difficult to use, comparatively impractical and somewhat costly for a project, because for the estimation of the total uncertainty of a measurement sampling proficiency tests or collaborative trials are required (Argyraki *et al.*, 1995). Thus, in this case many laboratories ($n > 8$) are involved in the sampling and analysis by using exactly the same protocol (collaborative trial in sampling – CTS, or by applying different protocols that are selected to be the most appropriate for the tested objective (sampling proficiency test – SPT). The scatter of measurements reported by all laboratories is then used to derive an overall estimate of uncertainty.

The duplicate method is the simplest and probably most cost-effective of the ‘empirical methods’ for estimating combined uncertainty including sampling. It is based upon a single sampler duplicating a small proportion of the primary project samples. The field duplicate samples are taken from a minimum number of eight sampling target sites, selected at random to

¹⁰ Measurand = quantity intended to be measured; a synonymous term is ‘determinand’

represent the typical composition of the target sites. To collect the field duplicated samples, a sampler is repeating the same sampling protocol with permitted variations that reflect the ambiguity in the protocol and the effect of small-scale heterogeneity of the determinand or measurand. Worked examples of the duplicate method can be found in the Eurachem Guide on measurement uncertainty arising from sampling (Ramsey *et al.*, 2019). Note that this method does not include any contribution from sampling bias, which in most instances is assumed to be negligible.

A balanced hierarchical sampling and analytical scheme should be used for the estimation of *geochemical, sampling, and analytical variance* and *random components of measurement uncertainty* (Figure 43). Robust analysis of variance (RANOVA) is preferred, because it accommodates outlying values that exceed a certain distance from the mean (usually 1.5 times the standard deviation) by down-weighting them rather than rejecting them (Ramsey, 1998; Lee and Ramsey, 2001; Boon, 2009). The RANOVA method was proposed by Ramsey (1998), and subsequently verified by Lyn *et al.* (2007). In case, for some reason, the routine and duplicate samples from the same location cannot be split into two sub-samples for analysis, then two different aliquots of each routine and duplicate sample should be analysed randomly within the sample suite of the project.

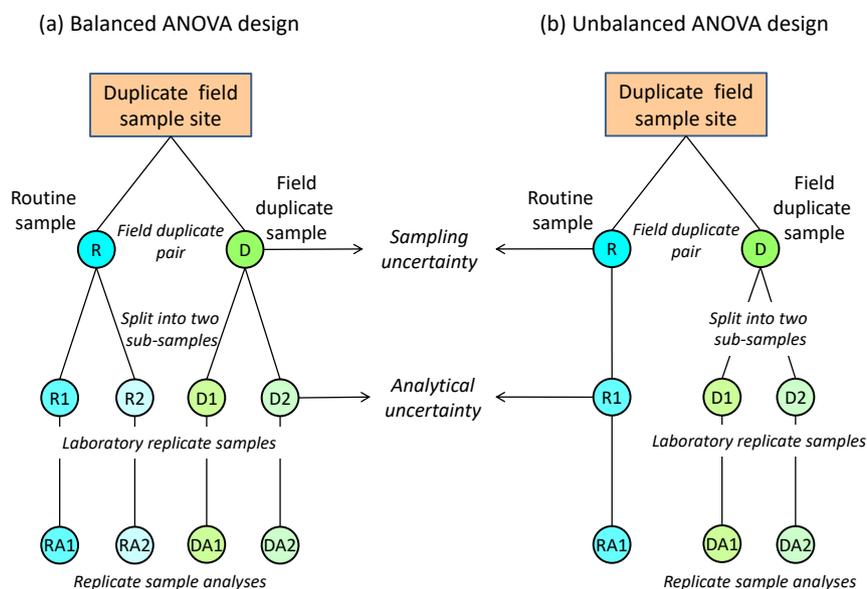


Figure 43. (a) Balanced and (b) unbalanced hierarchical geochemical sampling and analytical schemes for the estimation of geochemical, sampling, and analytical variance and random components of measurement uncertainty. Source: Demetriades *et al.*, 2014, Figure 6.4, p.56, slightly modified.

Collection of field duplicate samples is an inherent part of the *field geochemical investigation* itself, because the different types of variation of a parameter in the study area must be known. As pointed out by Ramsey (1998) two of the component variances can be classed as *measurement uncertainty*, and these are the *sampling* s^2_{samp} and *analytical variance* s^2_{anal} . The third component is the between location variance, the spatial variance, due to real variation of the determinand or measurand across the investigated area. This is called the *geochemical variance* s^2_{geoch} , in this particular case of a geochemical investigation. According to Ramsey *et al.* (1992) and Ramsey (1998), the ‘*sampling & analytical noise*’, the ‘*measurement uncertainty*’, should satisfy the following conditions:

Sampling + Analytical variance must be <20% of the total variance in the project area for each determinand studied. In fact, the analytical variance should not exceed 4% of the total variance (Garrett 1969; Ramsey et al., 1992; Ramsey, 1998). Thus, the maximum sampling variance should not exceed 16% of the total variance.

As pointed by Ramsey (1998), if the measurement uncertainty is >20%, it does not mean that the analytical results are unusable. In such cases, emphasis must be placed on the interpretation of apparent differences between concentrations at different sampling sites, which means that the quality control raw data should be visually inspected.

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

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

$$s^2_{total} = s^2_{geoch} + s^2_{samp} + s^2_{anal} \quad (16)$$

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

$$s^2_{meas} = s^2_{samp} + s^2_{anal} \quad (17)$$

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

$$s^2_{total} = s^2_{geoch} + s^2_{meas} \quad (18)$$

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

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

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

$$\text{expanded uncertainty, } U = k * u = 1.96 * s_{meas} \quad (20)$$

Ramsey (1998) used 2 as the coverage factor, but this represents a confidence level at 95.44%. Since, computers perform nowadays all calculations, it is recommended to use the coverage factor of 1.96, representing the 95% confidence level. However, the choice of coverage factor is discussed in detail in other publications that should be consulted (Ellison and Williams, 2012; ISO/IEC, 2008; JCGM 100, 2008).

The *expanded or extended uncertainty* U , expressed as a percentage in relation to the mean (μ) concentration of a particular determinand, gives the *relative measurement uncertainty* $U' \%$:

$$\text{relative expanded uncertainty, } U' \% = \frac{(100 * 1.96) * s_{meas}}{\mu} \quad (21)$$

where:

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

Similarly, the relative expanded uncertainty for sampling and/or analysis can be expressed (Ramsey *et al.*, 2019):

$$\text{relative sampling uncertainty, } U'_{\text{samp}} \% = \frac{(100 * 1.96) * S_{\text{samp}}}{\mu} \quad (22)$$

$$\text{relative analytical uncertainty, } U'_{\text{anal}} \% = \frac{(100 * 1.96) * S_{\text{anal}}}{\mu} \quad (23)$$

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

$$\text{relative expanded uncertainty, } U' \% = \left(\frac{(100 * 1.96) * S_{\text{meas}}}{\mu} \right) \div \sqrt{2} \quad (24)$$

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

$$X + U = X \left(1 + \frac{U' \%}{100} \right) \quad (25)$$

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

$$X - U = X \left(1 - \frac{U' \%}{100} \right) \quad (26)$$

where:

X = the concentration of the determinand or measurand in the sample medium

U = the expanded uncertainty at the 95% confidence level

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

The above Equations 25 and 26 may be refined if the *analytical bias* B_a is estimated using certified reference samples, CRMs (Ramsey and Argyraki, 1997; Ramsey, 1998; Ramsey *et al.*, 2019), which is a procedure employed by conventional accredited laboratories. The *upper limit of expanded uncertainty* U at the 95% confidence level is estimated by:

$$X + U = X \left(1 + \frac{U' \%}{100} \right) \left(1 - \frac{B_a}{100} \right) \quad (27)$$

and the *lower limiy of expanded uncertainty* by:

$$X - U = X \left(1 - \frac{U' \%}{100} \right) \left(1 - \frac{B_a}{100} \right) \quad (28)$$

where:

- X = the concentration of the determinand or measurand in the sample medium
 U = the expanded uncertainty at the 95% confidence level
 $U' \%$ = the relative expanded uncertainty at the 95% confidence level
 B_a = the analytical bias estimated as a percentage by regression.

Ramsey and Argyraki (1997) pointed out that the interpretation of *relative uncertainty* in the measurements of a particular determinand or measurand in soil assumes that it does not vary with concentration. Such a case has been observed in determinands, the analytical precision of which is considerably higher than the detection limit (Thompson and Howarth, 1976, 1978). Since the *relative analytical precision* $P_c\%$ varies according to the concentration of the determinand, the above equations 25 and 26 may be improved, by incorporating precision, estimated on survey samples (Ramsey 1997, 1998; Ramsey and Argyraki, 1997). The *upper limit of expanded uncertainty* U at the 95% confidence level can be calculated, therefore, by:

$$X + U = X \left(1 + \frac{U' \%}{100} \right) \left(1 - \frac{P_c \%}{100} \right) \quad (29)$$

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

$$X - U = X \left(1 - \frac{U' \%}{100} \right) \left(1 - \frac{P_c \%}{100} \right) \quad (30)$$

where:

- X = the concentration of the determinand or measurand in the sample medium
 U = the expanded uncertainty at the 95% confidence level
 $U' \%$ = the relative expanded uncertainty at the 95% confidence level
 $P_c \%$ = the analytical precision at the 95% confidence level

The practical detection limit, and analytical precision, can easily be estimated using the method described above (see Section §4.3.1.6).

4.4. ANOVA Software

4.4.1. Estimation of classical and robust ANOVA

The following two programs are freely available for downloading from the website of the Royal Society of Chemistry

(<https://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/>):

- **ROBAN** is a stand-alone program, running in Windows, to execute robust analysis of variance with nested balanced data (Figure 43a).

- **RANOVA2** is a stand-alone program, running in Microsoft™ Excel and executes robust and classical analysis of variance with nested data. It is suitable for both balanced (Figure 33a) and unbalanced (Figure 43b) designs.

The drawback of both programs is that the data of only one element can be processed each time, which means many runs of the two programs for processing of multi-element data sets.

Ramsey with his 1998 paper made available the ROBCOOP4.EXE program, which runs on 32-bit computers, and processes multi-element data sets. This program has been updated to ROBCOOP5.EXE to run on both 32-bit and 64-bit computers. It is available for downloading, together with instructions, from the Publications web page of the IUGS Commission on Global Geochemical Baselines' website (<http://www.globalgeochemicalbaselines.eu>).

4.4.2. Classical and robust balanced ANOVA example

According to Ramsey (1998, p.102) the ROBCOOP4.EXE and, consequently the new version ROBCOOP5.EXE, program is “adjusted for a specified maximum incidence of outlying values, in this case 10% of the total population. If there is a higher proportion of outlying values, then this would be expected to lead to somewhat erroneous estimates of the component variances.” Therefore, the first step is to check if there are more than 10% outlying values of the total population for each determinand in the duplicate-replicate data set. This can be done by plotting boxplots in order to see if there are any outlying values (Tukey, 1977; Hoaglin *et al.*, 1983; Kürzl, 1988). The FOREGS XRF duplicate-replicate data set of topsoil is used as example.

Figures 44 and 45 are multiple-boxplots of the major and trace element XRF duplicate-replicate topsoil data sets, respectively.

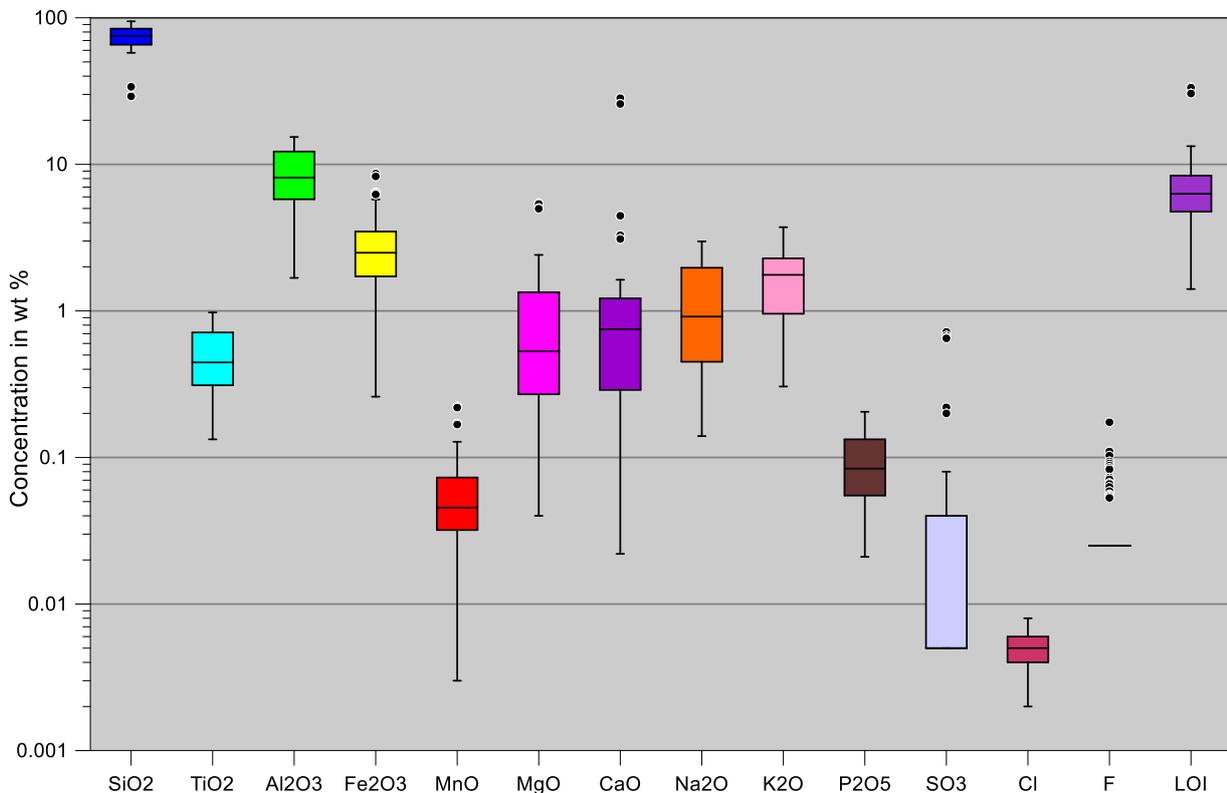


Figure 44. Multiple-boxplot of major element quality control data in European topsoil (N=23 duplicated sites). Plotted by Alecos Demetriades (IGME & IUGS CGGB) with Golden Software's Grapher™ v.17.

The major elements multiple boxplot plot displays outliers for Fe₂O₃, MnO, MgO, CaO, SO₃, F and LOI (Figure 44), and the trace element multiple-box plot shows outliers for As, Bi, Ce, Co, Cr, Cu, Hf, Mo, Pb, Rb, Sb, Sc, Sn, Sr, Ta, U, V, Zn and Zr (Figure 45). Hence, these elements must be closely examined by either plotting boxplots for each element or studying visually the table of duplicate-replicate results or both. It is quite apparent that F in Figure 44, and Bi, Co, Cu, Mo, Sb, Ta and U in Figure 45 have more than 10% outlying values, which means that the classical and robust ANOVA will most likely give erroneous results with the ROBCOOP software. The reason is that most of the values of these elements are below the analytical method's detection limit.

Let us select CaO and Zn for a more detailed study. The multiple-boxplots (Figure 46) and tabulated concentrations (Table 2) of CaO and Zn, show that there are 10 outlying values for CaO and 8 for Zn above the upper whisker at 1.63% and 95 mg/kg, respectively. Their corresponding percentages out of the total number of sample splits (N=92) are 10.9% for CaO and 8.69% for Zn. From this evaluation, CaO exceeds slightly the upper limit of 10%.

The other elements with outliers should be subjected to the same rigorous treatment before running the ROBCOOP5.EXE program.

The output results of the ROBCOOP5.EXE program for CaO and Zn are shown in Tables 3 and 4, respectively, and the pie charts in Figure 47 display the proportion of geochemical (spatial), sampling, and analytical robust analysis of variance results.

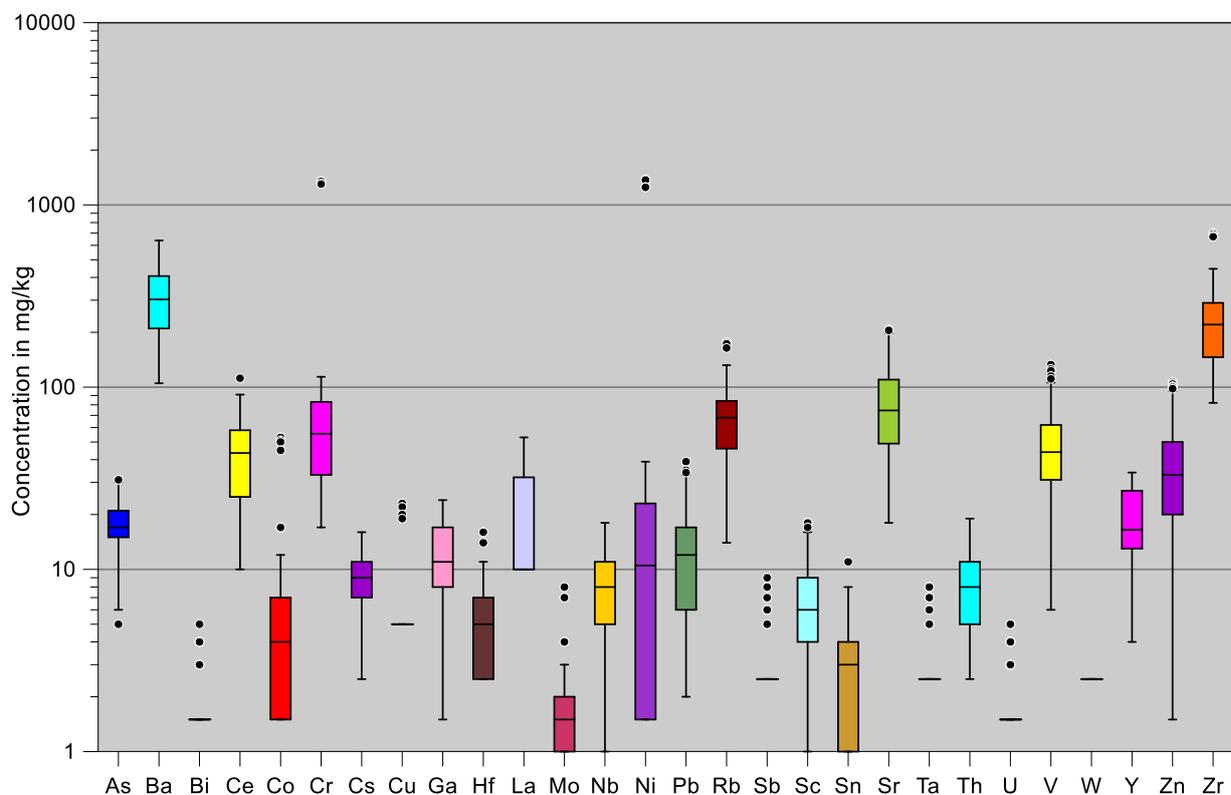


Figure 45. Multiple-boxplot of trace element quality control data in European topsoil (N=23 duplicated sites). Plotted by Alecos Demetriades (IGME & IUGS CGGB) with Golden Software's Grapher™ v.17.

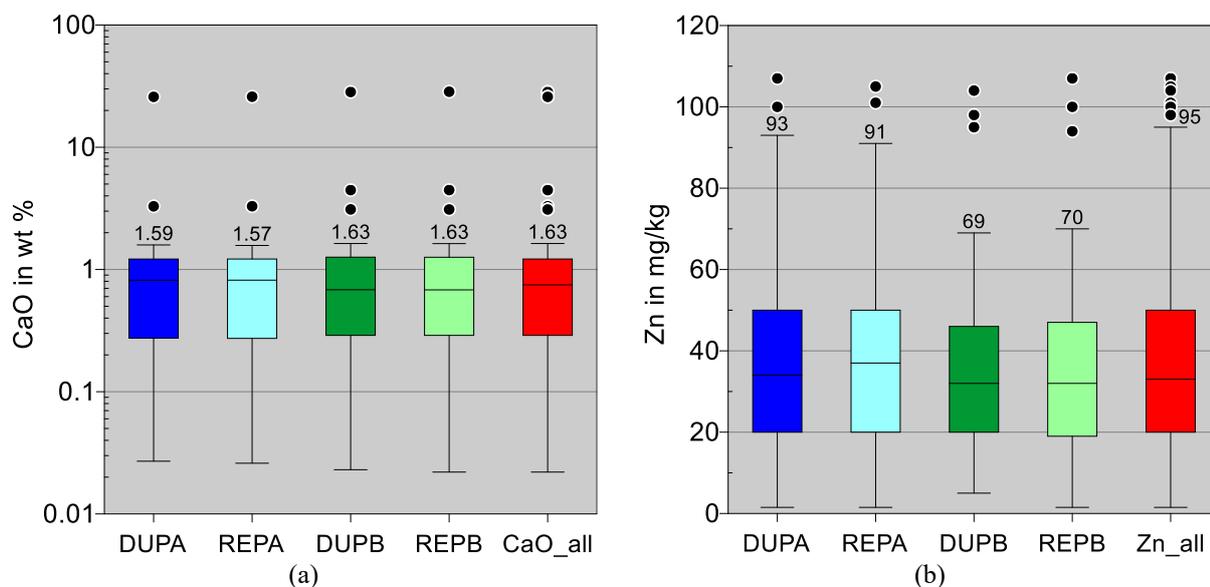


Figure 46. Multiple-boxplots of duplicate-rotate sample splits of (a) CaO and (b) Zn, FOREGS Topsoil QC data set. The value of the upper whisker of all duplicate-rotate splits (N=92) is 1.63 wt% CaO, and 95 mg/kg Zn. Samples with values greater than these limits are considered as outliers (see Table 2). Notation: DUPA = Routine sample; REPA = Replicate split of routine sample; DUPB = Field duplicate sample; REPB = Replicate split of field duplicate sample. Plotted by Alecos Demetriades (IGME & IUGS CGGB) with Golden Software's Grapher™ v.17.

Table 2. CaO (wt%) and Zn (mg/kg) XRF results of routine and duplicate sample splits of FOREGS Topsoil samples. According to the results of the total number of samples (N=92), the outlying values for CaO are >1.63%, and for Zn >95 mg/kg. The outlying values are indicated by bold red numbers. For notation of duplicate-rotate samples refer to Figure 46.

Sample Number	Cao in wt%				Zn in mg/kg			
	DUPA	DUPB	REPA	REPB	DUPA	DUPB	REPA	REPB
N31E05T2	0.655	0.654	0.683	0.681	67	62	60	60
N37W04T4	0.128	0.129	0.119	0.121	11	10	15	12
N32E04T5	0.363	0.363	0.36	0.355	40	41	41	42
N34E07T3	0.963	0.964	0.976	0.981	93	91	95	94
N35E01T1	0.896	0.888	1.01	0.997	40	40	38	40
N37W01T4	0.027	0.026	0.023	0.022	1.5	1.5	5	1.5
N42E10T2	1.29	1.28	1.26	1.26	20	21	20	19
N43E09T4	1.22	1.22	1.34	1.33	13	9	15	13
N34E03T3	0.489	0.489	0.486	0.484	100	101	98	100
N32E01T1	0.337	0.337	0.257	0.256	30	31	32	34
N40E10T5	1.38	1.37	1.63	1.63	48	48	41	41
N33E08T5	0.23	0.232	0.234	0.232	22	23	23	26
N42E04T5	0.816	0.818	0.954	0.961	20	20	20	21
N43E04T5	3.29	3.29	3.10	3.10	50	49	37	31
N30E06T1	0.275	0.273	0.289	0.289	46	47	46	47
N38E04T4	0.549	0.55	0.539	0.548	27	26	24	25
N28E11T1	1.03	1.02	0.815	0.829	107	105	104	107
N34E10T5	0.147	0.149	0.11	0.110	17	19	19	19
N36E08T3	0.142	0.143	0.303	0.302	7	6	18	18
N31E03T4	1.59	1.57	4.46	4.47	50	50	46	47
N33E02T3	25.8	25.9	28.3	28.5	30	29	29	28
N34E01T1	1.03	1.04	0.566	0.57	34	37	30	32
N32E10T1	0.953	0.952	1.02	1.02	70	74	69	70

Table 3. Classical and robust analysis of variance results of CaO from the FOREGS Topsoil XRF data set. Output of ROBCOOP5.EXE program.

Element	CaO			
Number of duplicated sample sites	23			
CLASSICAL ANALYSIS OF VARIANCE (ANOVA)				
	Geochemical	Sampling	Analytical	Measurement
Sum of Squares	2697.573	15.11987	0.013085	
Standard deviation (+/-)	5.521766	0.573193	0.016866	0.573441
Variance	30.4899	0.328551	0.000285	0.328835
% of total variance	98.93301	1.066074	0.000923	1.066997
Expanded relative uncertainty at the 95% confidence level		55.82796	1.642727	55.85212
Expanded uncertainty factor at the 95% confidence level		1.556413	1.015386	1.556825
Mean	2.012359			
Total standard deviation (+/-)	5.551462			
ROBUST ANALYSIS OF VARIANCE (RANOVA)				
	Geochemical	Sampling	Analytical	Measurement
Standard deviation (+/-)	0.608722	0.095392	0.002858	0.095435
Variance	0.370543	0.0091	8.2E-06	0.0091078
% of total variance	97.60101	2.396848	0.002152	2.399
Expanded relative uncertainty at the 95% confidence level		23.92172	0.71675	23.93246
Mean	0.781585			
Total standard deviation (+/-)	0.616158			
Uncertainty, u, for one sample	0.095435			
Expanded uncertainty, eu, for one sample at the 95% confidence level	0.187052			
Expanded relative uncertainty, eu%, for one sample at the 95% confidence level	23.93246			
Uncertainty, U, for four measurements at each duplicated sample site	0.067483			
Overall expanded relative uncertainty, eU%, at the 95% confidence level	16.9228			

Table 4. Classical and robust analysis of variance results of Zn from the FOREGS Topsoil XRF data set. Output of ROBCOOP5.EXE program.

Element	Zn			
Number of duplicated sample sites	23			
CLASSICAL ANALYSIS OF VARIANCE (ANOVA)				
	Geochemical	Sampling	Analytical	Measurement
Sum of Squares	71963.6094	529.8125	96.625	
Standard deviation (+/-)	28.495779	3.235335	1.449325	3.545129
Variance	812.009399	10.46739	2.100544	12.5679359
% of total variance	98.47583	1.269425	0.254742	1.524167
Expanded relative uncertainty at the 95% confidence level		15.61342	6.994308	17.108459
Expanded uncertainty factor at the 95% confidence level		1.392159	1.314888	1.536373
Mean	40.614132			
Total standard deviation (+/-)	28.715454			
ROBUST ANALYSIS OF VARIANCE (RANOVA)				
	Geochemical	Sampling	Analytical	Measurement
Standard deviation (+/-)	24.64397	2.004806	1.292611	2.385391
Variance	607.325256	4.019245	1.670843	5.6900878
% of total variance	99.071793	0.655652	0.272561	0.928213
Expanded relative uncertainty at the 95% confidence level		10.56222	6.810056	12.567313
Mean	37.202587			
Total standard deviation (+/-)	24.759146			
Uncertainty, u, for one sample	2.385391			
Expanded uncertainty, eu, for one sample at the 95% confidence level	4.675365			
Expanded relative uncertainty, eu%, for one sample at the 95% confidence level	12.567312			
Uncertainty, U, for four measurements at each duplicated sample site	1.686726			
Overall expanded relative uncertainty, eU%, at the 95% confidence level	8.886432			

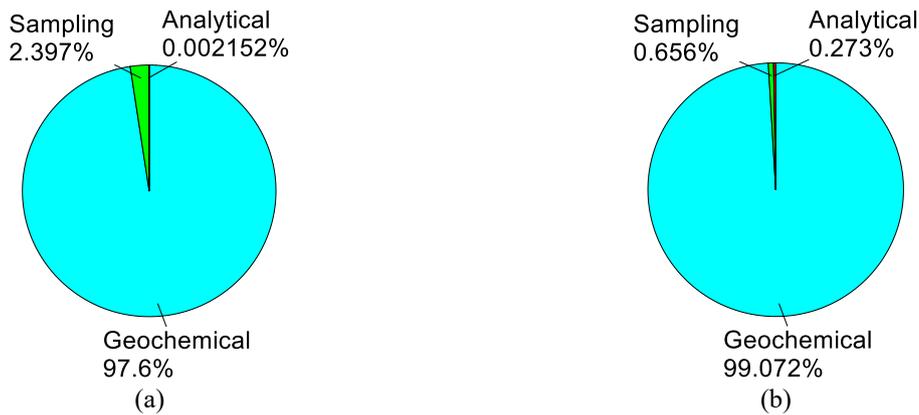


Figure 47. Pie charts of robust ANOVA results for (a) CaO and (b) Zn in topsoil samples of the FOREGS Geochemical Atlas of Europe, determined by XRF. Plotted by Alecos Demetriades (IGME & IUGS CGGB) with Golden Software's Grapher™ v.17.

Tables 3 and 4 show distinct differences in the expanded relative uncertainty at the 95% confidence level between classical and robust ANOVA results, especially for CaO; the overall measurement uncertainty of classical ANOVA is 55.9% compared to 23.9% in robust ANOVA. In both cases, the greatest contribution to measurement uncertainty is due to sampling, as there is a small within sample site variation of CaO, which is shown in the pie chart (Figure 47a).

For Zn again, the greatest contribution to measurement uncertainty in both classical and robust ANOVA results is due to sampling (Table 4; Figure 47b).

In both cases, the robust measurement variance out of the total is comparatively small, 2.402% for CaO and 0.929% for Zn. Consequently, the robust geochemical variance for both CaO (97.6%) and Zn (99.1%) has the greatest contribution to the total variance. The results are, therefore, considered to be fit-for-purpose and the maps can be plotted (Figure 48).

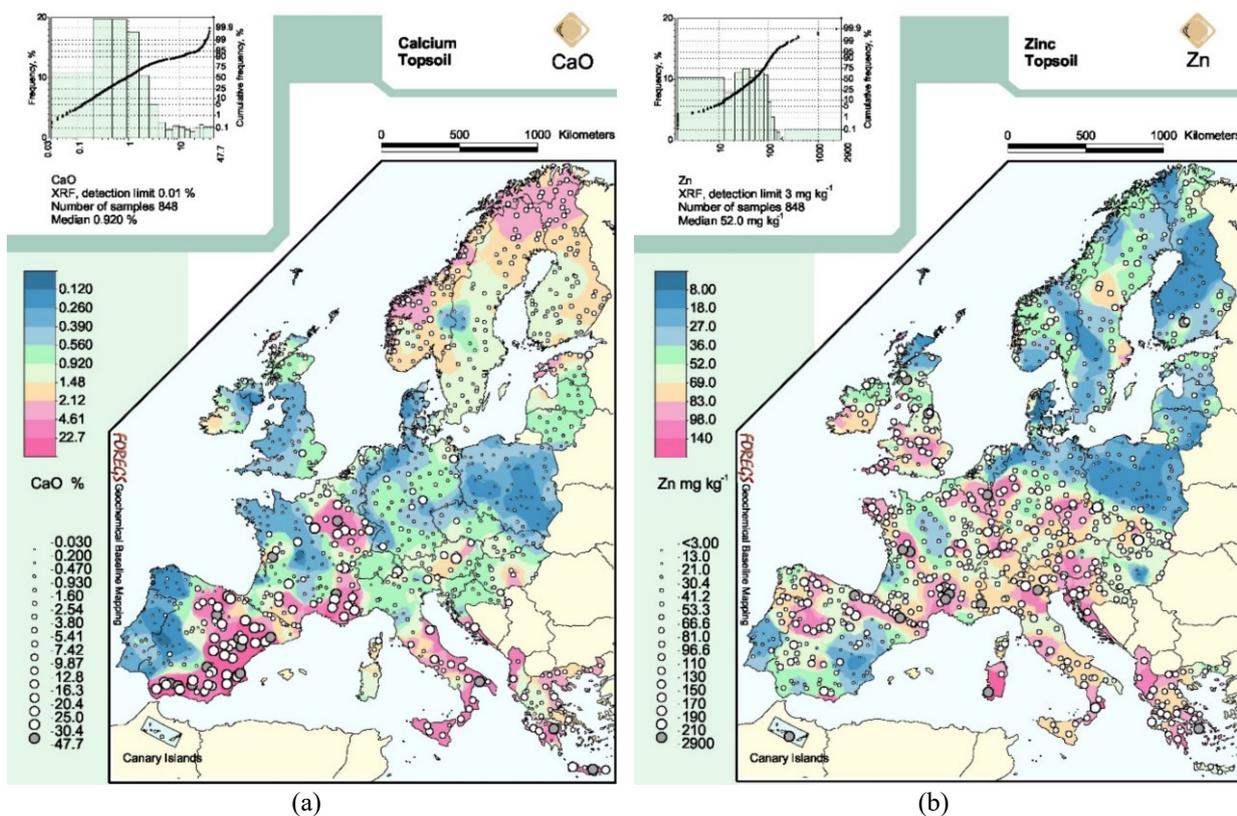


Figure 48. FOREGS Geochemical Atlas of Europe maps of topsoil (a) CaO and (b) Zn determined by XRF. Source: Salminen *et al.* (2005, p.158 CaO; p.513 Zn).

5. SUPPORTING INFORMATION AND GUIDELINE VALUES

Alecos Demetriades^{1,2}, Dai Huimin³, Liu Kai³ and Igor Savin⁴

¹ IUGS Commission on Global Geochemical Baselines

² Institute of Geology and Mineral Exploration, Athens, Hellas (retired)

³ Shenyang Centre of China Geological Survey, Shenyang, Liaoning Province, P.R. China

⁴ V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russia

5.1. Supporting information

For the interpretation of Global Black Soil geochemical data, the following information is required:

- A lithological (parent material) map as well as any lithochemical data;
- A geological map;
- A soil map;
- A record of the different land uses at different periods;
- A land use map with the location of all recent potential contaminating activities and petrol stations;
- Historical record of past industrial activities, and
- Climatic data, *i.e.*, records of rainfall and temperature as far back as possible.

5.2. Guideline values

A *guideline* or *intervention value* refers to a legislated contaminant concentration in a sample medium below which no harm to human health will occur. Of course, there is the reverse definition: a *guideline* or *intervention value* refers to a legislated contaminant concentration above which there is a potential unacceptable chronic risk (long term) to human health. To our knowledge, no guideline values exist for Black Soil *sensu stricto*.

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

Most European countries have set their own national soil guideline values (*e.g.*, APAT, 2006; EA, 2009; VROM, 2000; FME, 2002; Carlon, 2007). It is particularly important to understand that each country derives its SGVs according to different criteria and, therefore, these guideline values cannot be used in other countries. To understand the futility of such attempts two maps of the *aqua regia* extractable Ni in the <2 mm soil fraction from the FOREGS 'Geochemical Atlas of Europe' (Salminen *et al.*, 2005) and the EuroGeoSurveys 'Geochemical Mapping of Agricultural and Grazing land' (GEMAS) in Europe (Reimann *et al.*, 2014) are presented (Figure 49). As it can be observed, there are distinct differences from northern to southern Europe, with the Balkans having the highest Ni concentrations in topsoil, and the countries north of the Pleistocene glacial limit the lowest.

Let us consider the Finnish soil guideline value of Ni, which is set at 50 mg/kg, and determined by an *aqua regia* extraction (Tarvainen and Jarva, 2011). Nickel values in Finnish soil samples vary from <2 to 36 mg/kg, with a median of 6 mg/kg. Hence, the aforementioned guideline value of Ni is appropriate for soil in Finland. If the Hellenic Ni results are studied, it is found that these vary from 2 to 1812 mg/kg, with a median of 72 mg/kg; the high Ni values are

geogenic and are mainly due to the mafic-ultramafic (ophiolite) complexes, and their erosion products. Therefore, if someone attempts to use in Hellas the Finnish soil guideline value of Ni, these naturally elevated values will be considered hazardous. This is, of course, absurd, but it could have happened in the early part of the twentieth century, during the Technical Working Group discussions, established under the European Commission's Thematic Strategy for Soil Protection in 2003-4 (Van-Camp, 2004), as some officers were considering to propose a single soil guideline for the whole of Europe. Fortunately, the results of the FOREGS 'Geochemical Atlas of Europe' (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006) averted this proposal, as there was sound evidence about the variable natural chemical variation in Europe.

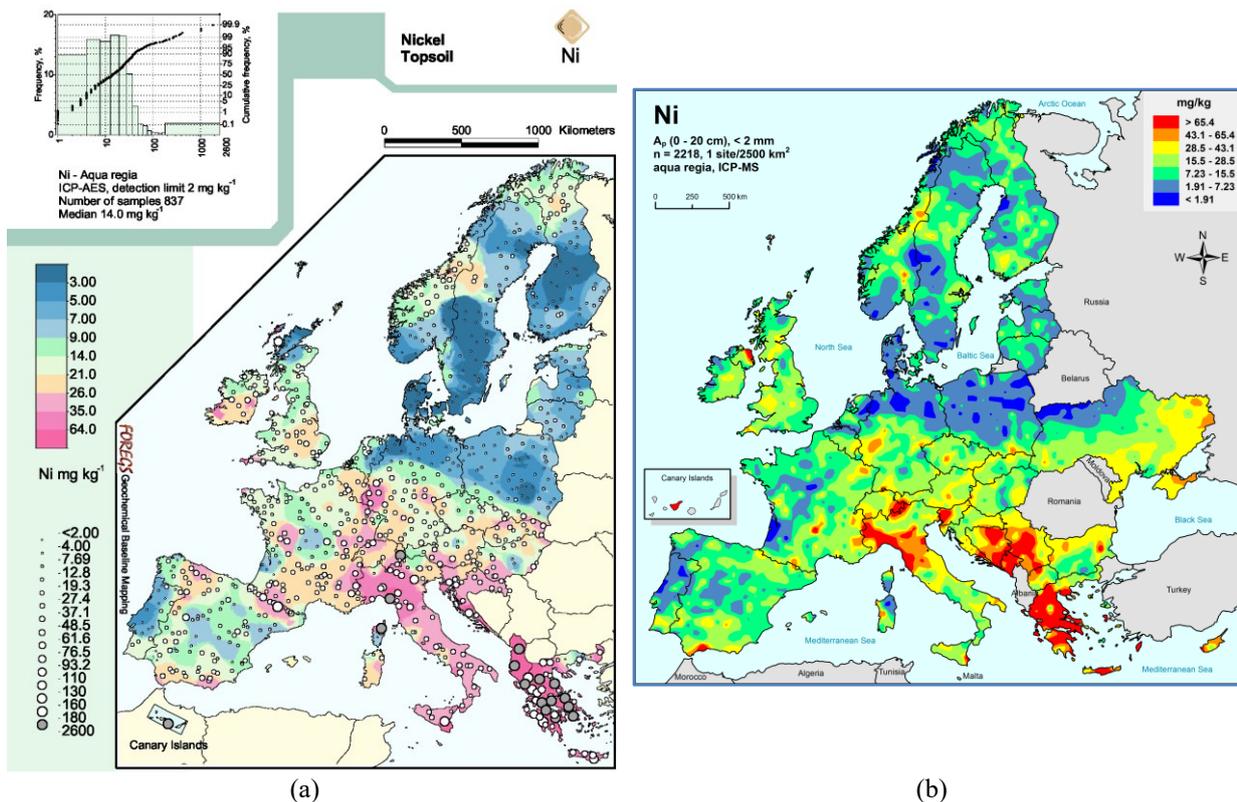


Figure 49. Geochemical distribution of *aqua regia* extractable Ni in Europe (a) topsoil (Salminen *et al.*, 2005, p.360), and (b) agricultural soil (Reimann *et al.*, 2014, Figure 11.39.5, p.329).

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

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Note: All website links checked on the 1st of January 2020.

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APPENDIX 1: PHOTOGRAPHS OF BLACK SOIL LANDSCAPES AND VERTICAL PROFILES

A1.1. United States of America

Table A1. Explanation of soil profile descriptions of Figures A1.2 to A1.21.

<i>Soil horizons</i>	<i>Subdivisions</i>	<i>Explanation of letter notation</i>
A	Ap	Ploughed portion of the A horizon
	A1	Mineral horizons, formed or forming at or adjacent to the surface.
	A2	Mineral horizons in which the feature emphasised is loss of clay (similar to E).
	AB	Transitional horizon between the A and B horizons. A horizon features more dominant.
E	E	Mineral horizons in which the feature emphasised is loss of clay (similar to A2)
B	BA	Transitional horizon between the B and A horizons. B horizon features more dominant.
	BE	Transitional horizon between the B and E horizons. B horizon features more dominant.
	Bk	'k' indicates an accumulation of visible pedogenic calcium carbonate (<50% by volume). Carbonate accumulations occur as carbonate filaments, coatings, masses, nodules, disseminated carbonate, or other forms.
	Bk1	
	Bk2	
	Bkk	
	Bkkm	'kk' indicates major accumulations of pedogenic calcium carbonate, and 'm' indicates occurrence of marl.
	Bt	't' indicates an accumulation of silicate clay that either has formed within a horizon and subsequently has been translocated within the horizon or that has been moved into the horizon by illuviation, or both. At least some part of the horizon shows evidence of clay accumulation, either as coatings on surfaces of peds or in pores, as lamellae, or as bridges between mineral grains.
	Bt1	
	Bt1	
	Bt1	
	Bt2	
	Bt2	
	Bt2	
	Btb	For 't' see above. 'b' denotes a buried genetic horizon
	Btg1	For 't' see above. 'g' denotes strong gleying.
	Btg2	
	Btk	See above explanation for 'k' and 't' notation.
	Btn1	'n' indicates accumulation of exchangeable sodium. For 't' notation see above.
	Btn2	
Bw	'w' indicates the development of colour or structure, or both, with little or no apparent illuvial accumulation of material.	
Byz	'y' indicates an accumulation of gypsum, and 'z' accumulation of salts that are more soluble than gypsum.	
BC	Transitional horizon between the B and C horizons.	
C	C	Mineral horizons or layers, excluding strongly cemented and harder bedrock. Their material may be either like or unlike that from which the solum presumably formed. The C horizon may have been modified, even if there is no evidence of pedogenesis.
	Cg1	'g' indicates strong gleying with a chroma of 1.
	Cg2	'g' indicates strong gleying with a chroma of 2.
	2Cg	'g' indicates strong gleying with a chroma of 2.
	Cr	'r' indicates weathered or soft bedrock.
R	R	Underlying consolidated bedrock.

Source: https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/ref/?cid=nrcs142p2_054253

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A1.1.1. Aquolls



Figure A1.1. Aquoll/Udoll Landscape, central Illinois. This University of Illinois research farm is representative of the relatively low relief, glaciated till plain landscapes of Illinois and Iowa, United States of America (U.S.A.). Loess of varying thickness overlies glacial drift, and these serve as the dominant soil parent materials. Mean annual precipitation ranges from approximately 890 to 1090 mm (35-43 inches). Native prairie vegetation and scattered upland hardwood forests have largely been replaced by cropland with corn, soybeans and small grains among the major crops (Image from Google Maps). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

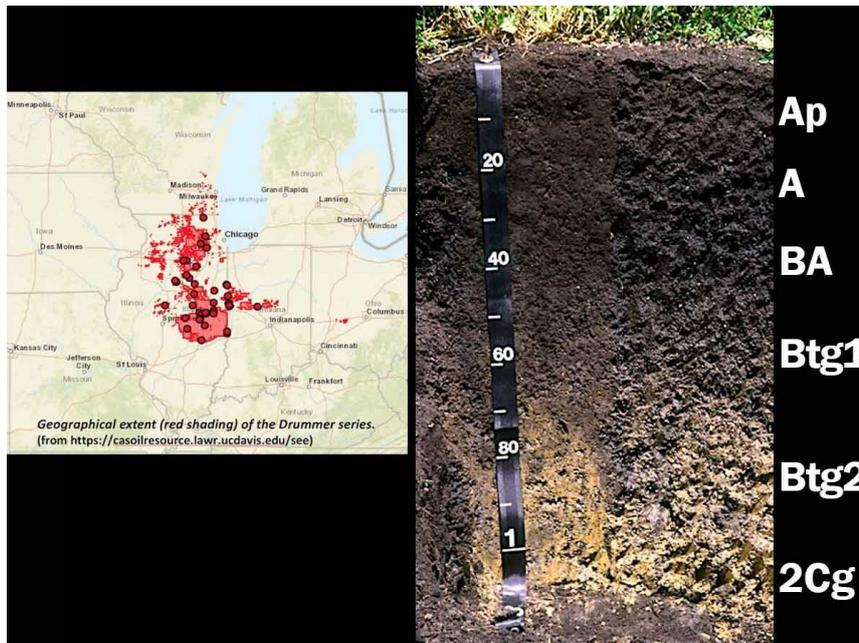


Figure A1.2. Typical Endoaquoll (fine-silty, mixed, superactive, mesic), Illinois. This very deep, poorly drained soil belongs to the Drummer series and is in the state soil of Illinois, (U.S.A.). Drummer soil types are the most extensive in the state and have formed on loess, silty sediments and glacial drift on nearly level outwash plains, terraces and till plains. Subsurface tile drainage is used to lower a seasonal water table and reduce the amount of time the upper root zone is saturated, thereby facilitating the use of these soil types for crop production. Under native conditions Drummer type soil supports hydrophytic grasses, sedges and reeds. Scale is in centimetres (Image from P. Buck, USDA-NRCS). The red dots are sampling sites. Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

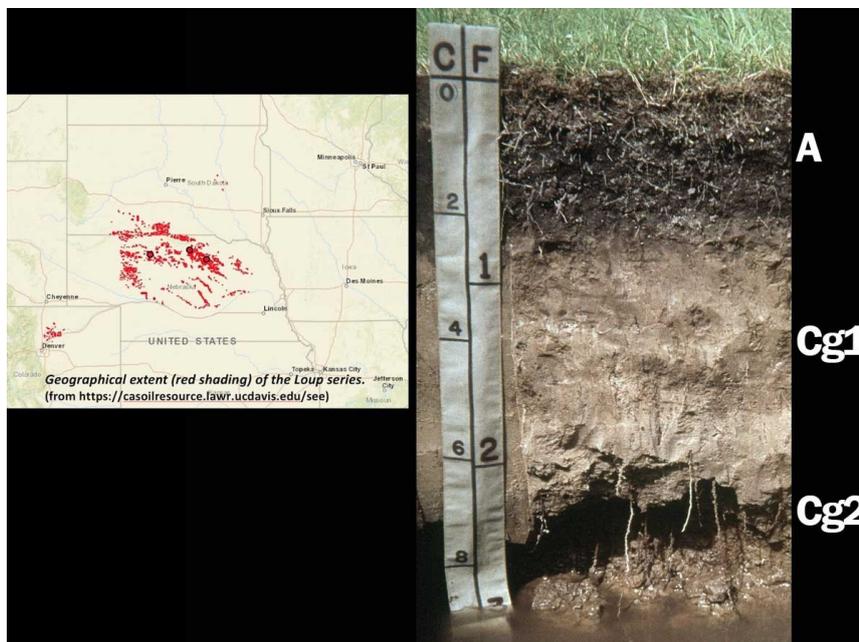


Figure A1.3. Typical Endoaquoll (sandy, mixed, mesic), Nebraska (U.S.A.). This very deep, poorly drained soil is a member of the Loup series. This soil type has formed on loamy and sandy alluvium and has a water table at or near the surface for much of the year. Because of the high water table, most of this soil remains in native grasses and is used for hay production and grazing. The dull colours of the Cg horizons result from prolonged periods of saturation in which Fe is reduced to more mobile, colourless forms. (Image reproduced from *Soils of the Great Plains: Land Use, Crops and Grasses* by Andrew R. Aandahl by permission of the University of Nebraska Press. Copyright 1982 by the University of Nebraska Press). *Such soil is good for the estimation of the Black Soil geochemical background.* The red dots are sampling sites. Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

A1.1.2. Albolls, Rendolls

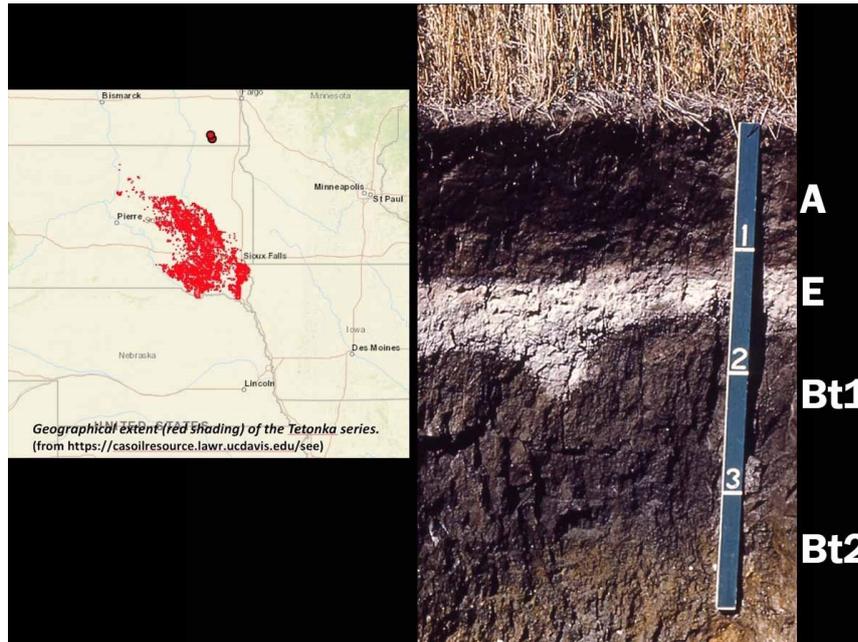


Figure A1.4. Argialboll, South Dakota (U.S.A). This poorly drained soil belongs to the Tetonka series and has formed on alluvium overlying glacial till in upland depressions and wide drainageways. Permeability is slow, and water ponds on the surface after heavy rain and snow melt. Argialboll is typically wet except in late summer and autumn unless it has been drained. This striking profile consists of a clayey argillic Bt horizon that is overlain by a white albic E horizon. Where drained, this type of soil is commonly used for cultivated crops, including corn, soybeans, small grains and sorghum. Mean annual precipitation is approximately 510 mm (20 inches). Scale is in feet. (Image from the Soil Science Society of America Marbut Memorial Slide Set). The red dots are sampling sites. Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

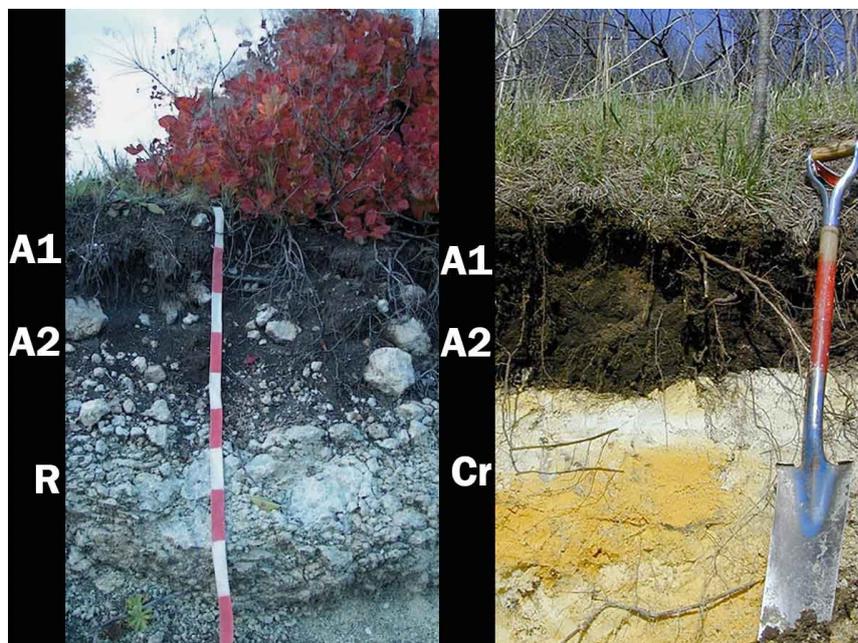


Figure A1.5. Rendolls. This shallow soil type occurs in humid climates and consists of very dark A horizons (mollic epipedons) directly overlying CaCO₃-rich parent material. Left: This Rendoll from Europe has formed on limestone (Image from Soil Atlas of Europe, European Soil Bureau Network). Right: This Rendoll from south-eastern Minnesota (U.S.A.) has formed on calcareous sedimentary deposits with mean annual precipitation of approximately 890 mm (35 inches). Rendolls are not extensive in the U.S.A. (Image from University of Idaho). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

A1.1.3. Gelolls, Cryolls



Figure A1.6. Geloll, interior Alaska (U.S.A.). This landscape and soil are in the Interior Alaska Highlands approximately 80 km (50 miles) east of Fort Yukon. Mean annual precipitation is approximately 380-510 mm (15-20 inches) and mean annual temperature is approximately -5°C (23°F). Vegetation is a mosaic of alpine dwarf scrub and lichen. This rocky soil type has a gelic temperature regime (mean annual soil temperature less than 0°C). However, the Geloll area warms up enough in summer such that permafrost is deeper than 2 m below the surface and, therefore, they are not classified as Gelisols. This soil has formed on loess over gravelly cryoturbated deposits. Diagnostic features are limited to a mollic epipedon (A horizon). Scale is in decimetres (Images from USDA-NRCS, Wasilla, AK). *Such soil is good for the estimation of the Black Soil geochemical background.* Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

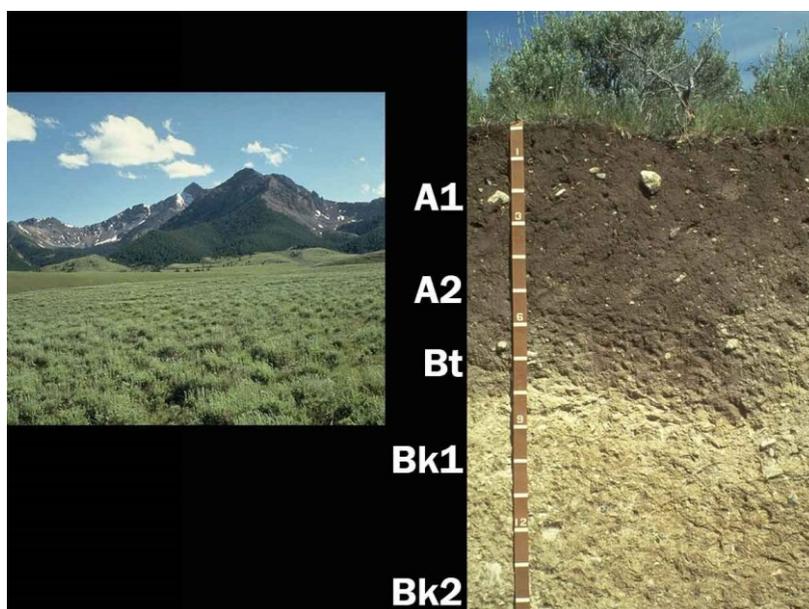


Figure A1.7. Pachic Argicryoll, eastern Idaho (U.S.A.). This landscape and soil are found at elevations ranging from approximately 2,100-2,500 m (6,900-8,200 ft). Parent material is limestone colluvium and glacial outwash. Cold temperatures have slowed the decomposition of organic matter, resulting in a thick, dark mollic epipedon (A horizons) and classification in a Pachic subgroup. Some clay translocation and accumulation in the upper profile has occurred following the downward movement of carbonates. Wavy horizon boundaries can be seen on the right side of the profile. These are the result of extensive animal burrowing, possibly badger in this case. Scale is in decimetres (Images from University of Idaho). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

A1.1.4. Xerolls

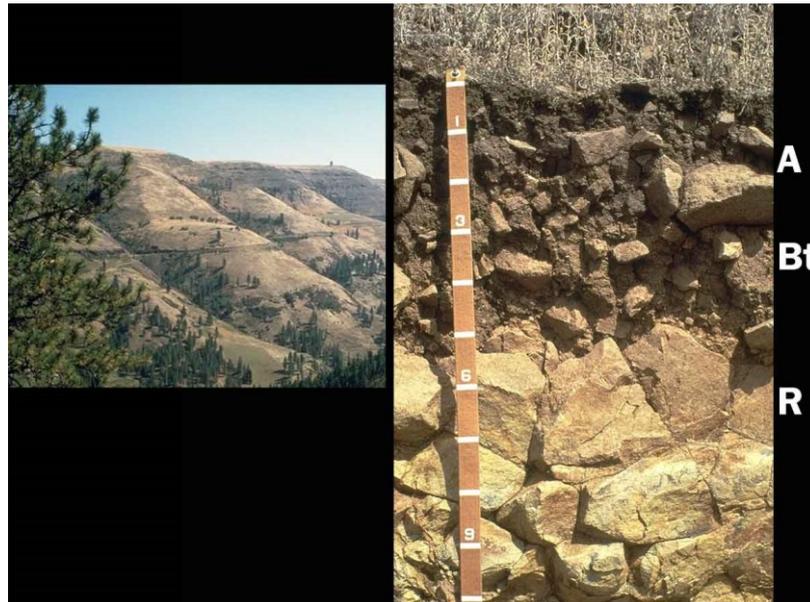


Figure A1.8. Lithic Argixeroll (loamy-skeletal, mixed, superactive, mesic), Nez Perce County, Idaho (U.S.A.). This shallow soil is a member of the Gwin series and has formed in loess mixed with basalt colluvium. Mean annual precipitation is approximately 510 mm (20 inches). Gwin soil occupies the more stable bench positions seen in the landscape image allowing an argillic Bt horizon with 27-35 per cent clay to form. The high percentage of rock fragments and shallow profile severely limit the total available-water-holding capacity of this soil. Primary land use is grazing and wildlife habitat. Scale is in decimetres (Images from University of Idaho). *Such soil is good for the estimation of the Black Soil geochemical background.* Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.



Figure A1.9. Pachic Ultic Haploxeroll (fine-silty, mixed, superactive, mesic), Latah County, Idaho (U.S.A.). This soil belongs to the Palouse series and is typical of the deep loess soil type found in the Palouse region of eastern Washington and northern Idaho. Mean annual precipitation is approximately 530 mm (21 inches). This soil type has formed under native grassland vegetation including Idaho fescue (*Festuca idahoensis*) and bluebunch wheatgrass (*Pseudoroegneria spicata*); however, very few areas of native vegetation remain due to the soil's high agricultural productivity. The Bt horizons do not qualify as an argillic horizon because the increase in clay is too gradual. The mollic epipedon is quite thick, extending from the surface to an average depth of approximately 60 cm. Crops grown on Palouse soil include winter wheat, barley, dry peas and lentils. Erosion is a major concern for the use and management of this soil type. Scale is in decimetres (Images from University of Idaho). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.



Figure A1.10. Calcic Haploxeroll (coarse-silty, mixed, superactive, frigid), Madison County, Idaho (U.S.A.). This very deep soil belongs to the Rexburg series and has developed on loess-mantled fans, foothills and basalt plains. This soil type is used extensively for both irrigated and non-irrigated crop production. The landscape on the left shows some irrigated ‘famous’ Idaho potatoes. Calcium carbonate has been leached deeper in the profile, forming a calcic (Bk) horizon. The relatively cold, dry climate has slowed soil development and very little neoformation or subsoil accumulation of clay has taken place – the Bw horizon only contains 8-18 per cent clay. CaCO₃ content of the calcic horizon typically ranges from approximately 15-30 per cent. Mean annual precipitation is approximately 360 mm (14 inches). Scale is in decimetres (Images from University of Idaho). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.



Figure A1.11. Oxyaquic Argixeroll (fine-silty, mixed, superactive, mesic), Latah County, Idaho (U.S.A.). This soil type is a member of the Southwick series and has developed on loess under ponderosa pine (*Pinus ponderosa*) forest. Mean annual precipitation is approximately 610 mm (24 inches). The significant grass/shrub understory associated with ponderosa pine forest in this area contributes to the development of a mollic epipedon. The A-Bw horizon sequence has formed mostly on Holocene loess while the Btb horizon represents the upper part of a Middle to Late Wisconsin palaeosol. The Btb horizon is hydraulically restrictive with a saturated hydraulic conductivity of approximately 0.1 cm/day. Water is perched above this horizon for a period extending from late November through May. Scale is in decimetres (Images from University of Idaho). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

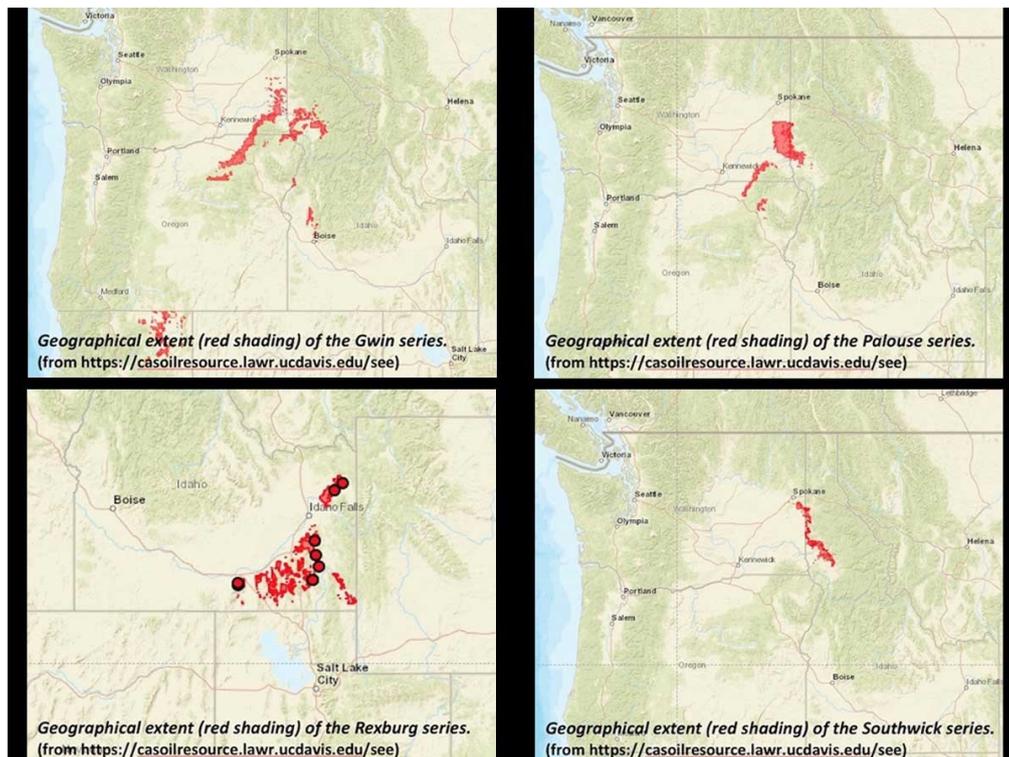


Figure A1.12. Geographical extent of Gwin, Palouse, Rexburg and Southwick series in the United States of America. The red dots are sampling sites. Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

A1.1.5. Ustolls

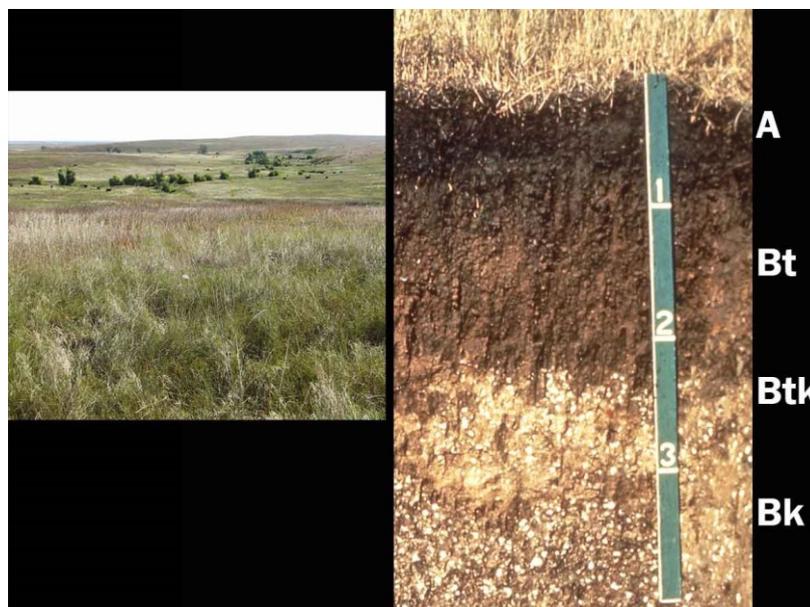


Figure A1.13. Typical Argiustoll, South Dakota (U.S.A.). This profile illustrates the typical morphology associated with soil formed under grassland vegetation in the drier areas of the Great Plains region, such as seen in the landscape image from the Fort Pierre National Grassland. The thick, dark A horizon has developed because of the proliferation and subsequent decomposition of fine and very fine roots. This process is known as melanisation. Secondary carbonates are clearly visible as the white nodules in the subsoil, indicating that they have been translocated in the profile and re-precipitated. As CaCO_3 has been leached from the upper part of the soil, clay movement and accumulation has resulted in the formation of an argillic Bt horizon. Scale is in feet (Landscape image from USDA-Forest Service; soil profile image from the Soil Science Society of America Marbut Memorial Slide Set). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.



Figure A1.14. Udic Argiustoll (clayey-skeletal, smectitic, mesic), eastern Kansas (U.S.A.). This deep, rocky soil is a member of the Florence series and has formed On cherty limestone. This soil type receives approximately 810 mm (32 inches) of annual precipitation and represents the moister end of the Ustolls. Significant accumulation of clay has occurred in the argillic Bt horizon, which typically contains 50-80 per cent clay. Hard cherty limestone bedrock (R) can be seen at the bottom of the profile. (Images reproduced from *Soils of the Great Plains: Land Use, Crops and Grasses* by Andrew R. Aandahl by permission of the University of Nebraska Press. Copyright 1982 by the University of Nebraska Press). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

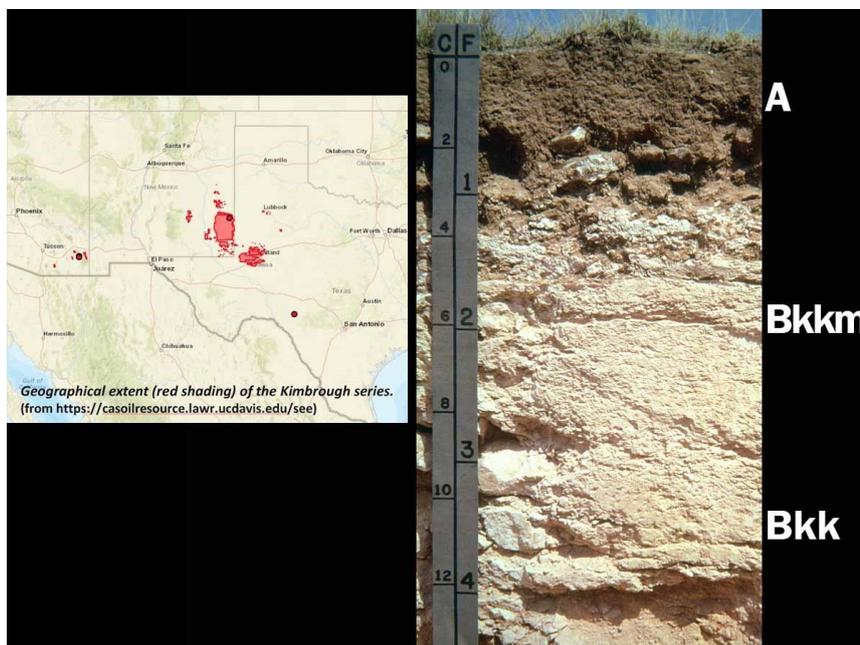


Figure A1.15. Petrocalcic Calcicustoll (loamy, siliceous, superactive, thermic, shallow), New Mexico (U.S.A.). This shallow soil belongs to the Kimbrough series. This soil only receives approximately 405 mm (16 inches) of annual precipitation and represent the dry end of the Ustolls. The thick CaCO_3 -cemented petrocalcic (Bkkm) horizon is also referred to as caliche, and has likely taken a few hundred thousand years to achieve this degree of development. Because of the low rainfall and shallow depth to the petrocalcic horizon, most of this soil type is used for rangeland. (Image reproduced from *Soils of the Great Plains: Land Use, Crops and Grasses* by Andrew R. Aandahl by permission of the University of Nebraska Press. Copyright 1982 by the University of Nebraska Press). *Such soil is good for the estimation of the Black Soil geochemical background.* The red dots are sampling sites. Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

A1.1.6. Udolls



Figure A1.16. Argiudoll Landscape, Central Great Plains (U.S.A.). This landscape is typical of loess-mantled till plains of southern Iowa and north-western Missouri. Mean annual precipitation ranges from approximately 700-1,100 mm (28-43 inches). Although now mostly in agricultural production, this soil type once supported tall grass prairie, including big bluestem (*Andropogon gerardii*) and western wheatgrass (*Pascopyrum smithii*). (Image reproduced from *Soils of the Great Plains: Land Use, Crops and Grasses* by Andrew R. Aandahl by permission of the University of Nebraska Press. Copyright 1982 by the University of Nebraska Press). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

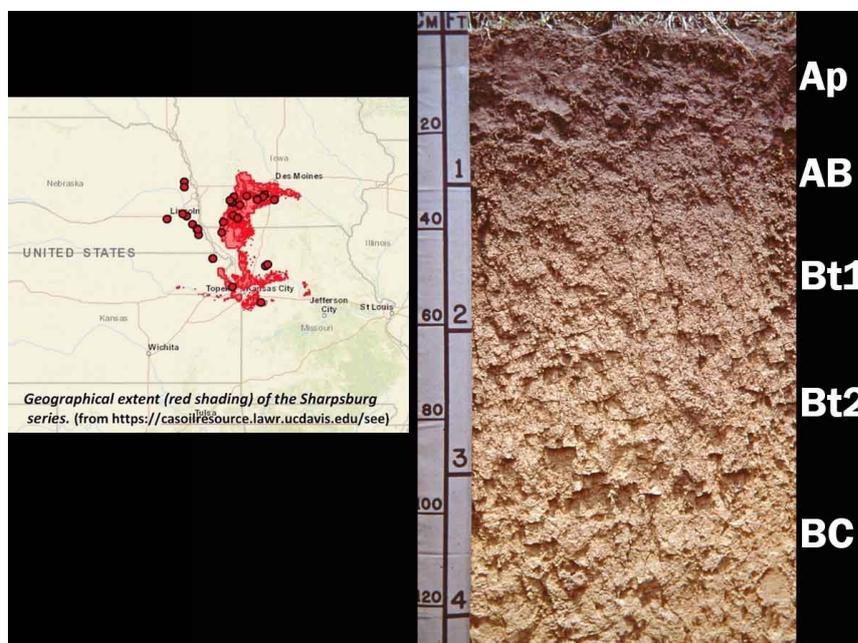


Figure A1.17. Typic Argiudoll (fine, smectitic, mesic). This very deep soil is a member of the Sharpsburg series. This soil type has formed on deep loess under tall grass prairie. Mean annual precipitation is approximately 900 mm (35 inches), which has been sufficient to leach CaCO_3 from the profile. This has allowed clay movement and the formation of an argillic horizon (Bt horizons) with textures of silty clay loam or silty clay. (Image reproduced from *Soils of the Great Plains: Land Use, Crops and Grasses* by Andrew R. Aandahl by permission of the University of Nebraska Press. Copyright 1982 by the University of Nebraska Press). The red dots are sampling sites. Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.



Figure A1.18. Argiudoll Landscape, south-eastern Nebraska (U.S.A.). This landscape is typical of till plains of south-eastern Nebraska and north-eastern Kansas. Mean annual precipitation ranges from approximately 740-990 mm (29-39 inches). Soil has developed under tall and mid grass prairie. Grasses such as big bluestem (*Andropogon gerardii*) shown here have extensive root systems, which contribute to the formation of a mollic epipedon. (Image reproduced from *Soils of the Great Plains: Land Use, Crops and Grasses* by Andrew R. Aandahl by permission of the University of Nebraska Press. Copyright 1982 by the University of Nebraska Press). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

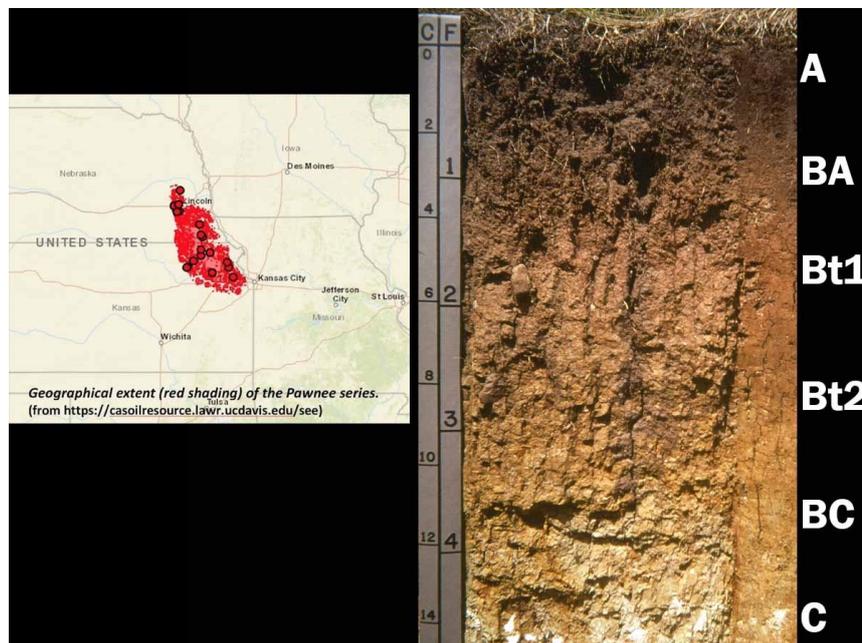


Figure A1.19. Oxyaquic Vertic Argiudoll (fine, smectitic, mesic), south-eastern Nebraska (U.S.A.). This very deep soil belongs to the Pawnee series. This soil type has formed under tall grass prairie on dissected till plains. Mean annual precipitation is approximately 860 mm (34 inches). The argillic Bt horizon in this soil is well developed — it typically has strongly expressed prismatic structure, extends to a depth of 1 m or more, and has clay textures. This horizon perches water above it during late winter/early spring. (Image reproduced from *Soils of the Great Plains: Land Use, Crops and Grasses* by Andrew R. Aandahl by permission of the University of Nebraska Press. Copyright 1982 by the University of Nebraska Press). The red dots are sampling sites. Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.



Figure A1.20. Natrudoll Landscape, North Dakota (U.S.A.). This nearly level till plain receives approximately 530 mm (21 inches) of annual precipitation and is dominated by Mollisols. The areas of poorer plant growth that are visible occur on soil with a natric (Na-affected) horizon, which is classified as Natrudolls. (Image reproduced from *Soils of the Great Plains: Land Use, Crops and Grasses* by Andrew R. Aandahl by permission of the University of Nebraska Press. Copyright 1982 by the University of Nebraska Press). Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

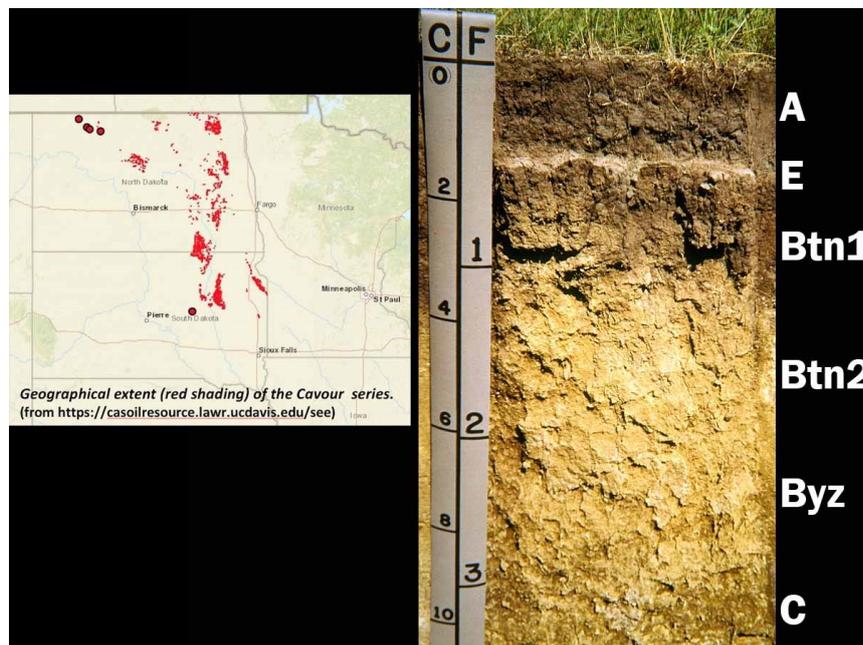


Figure A1.21. Calcic Natrudoll (fine, smectitic, frigid), North Dakota (U.S.A.). This very deep soil is a member of the Cavour series and has formed on glacial till. A major feature of this soil is the presence of a natric (Btn) diagnostic horizon. A natric horizon is characterised by the accumulation of clays from overlying horizons and high Na^+ content. The high Na^+ content results in slow to very slow permeability, which has prevented the leaching of gypsum and soluble salts (Byz horizon) from the soil profile. (Image reproduced from *Soils of the Great Plains: Land Use, Crops and Grasses* by Andrew R. Aandahl by permission of the University of Nebraska Press. Copyright 1982 by the University of Nebraska Press). The red dots are sampling sites. Source: <https://www.uidaho.edu/cals/soil-orders/mollisols#gallery-a2872e8f-1029-4734-b8ff-1eff284545d0--slideshow>.

A1.2. Russian Federation



(a) Chernozems on the slope of a gully

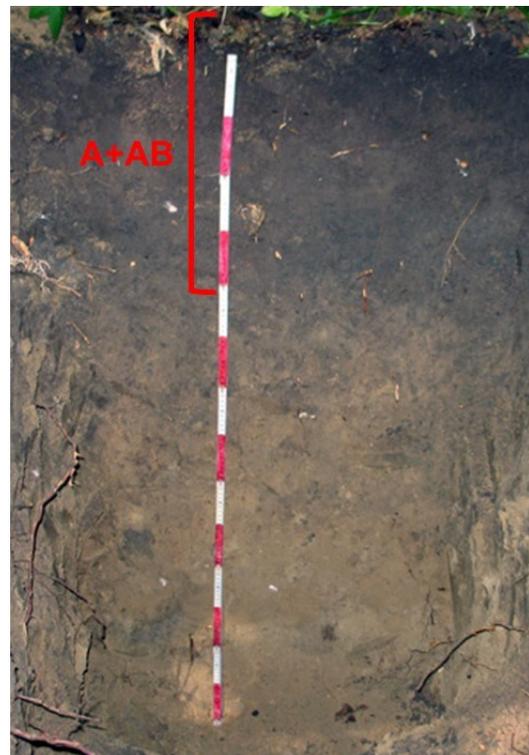


(b) Chernozems moderately eroded

Figure A1.22. Chernozemic soil on the slopes of the Middle-Russian Upland (Tula region of Russia). Photograph: Igor Savin, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation.



(a) Phaeozems Luvic

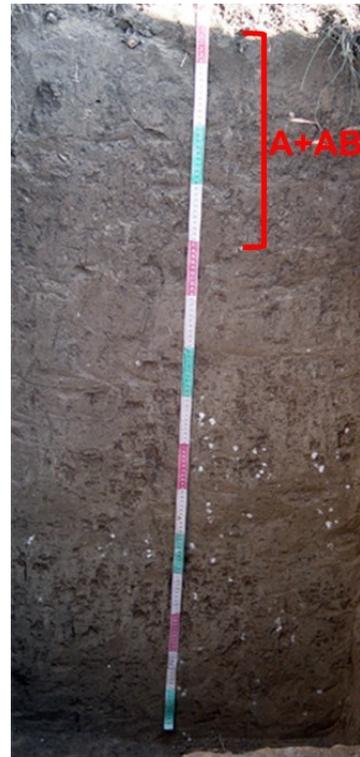


(b) Chernozems Chernic

Figure A1.23. Chernozems (European part of Russia). Photograph: Igor Savin, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation.



(a) Chernozems Luvic

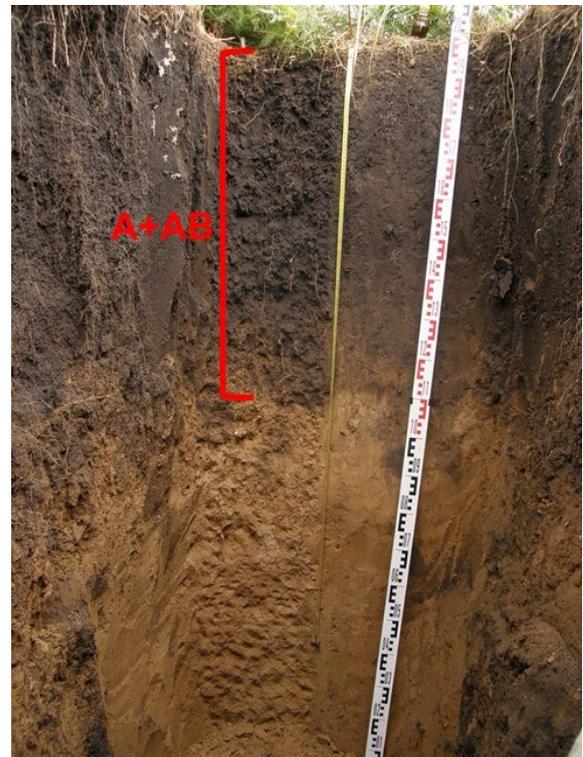


(b) Chernozems Calcic

Figure A1.24. Chernozems (North Caucasus region of Russia). Photograph: Igor Savin, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation.

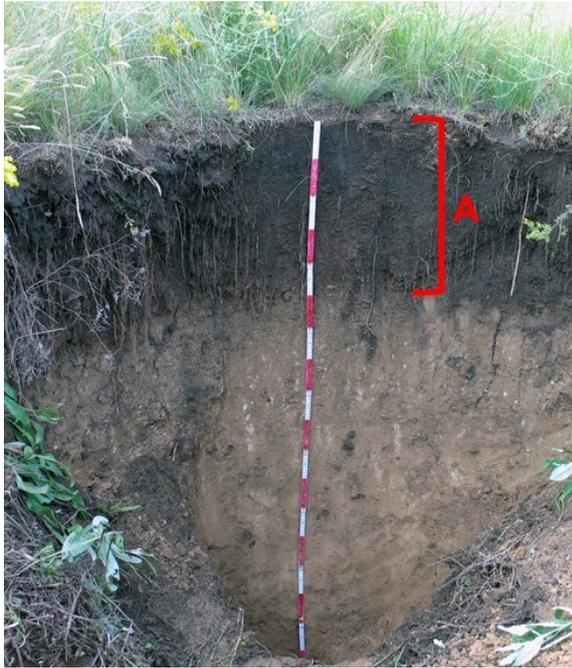


(a) Chernozems Chernic rummaged

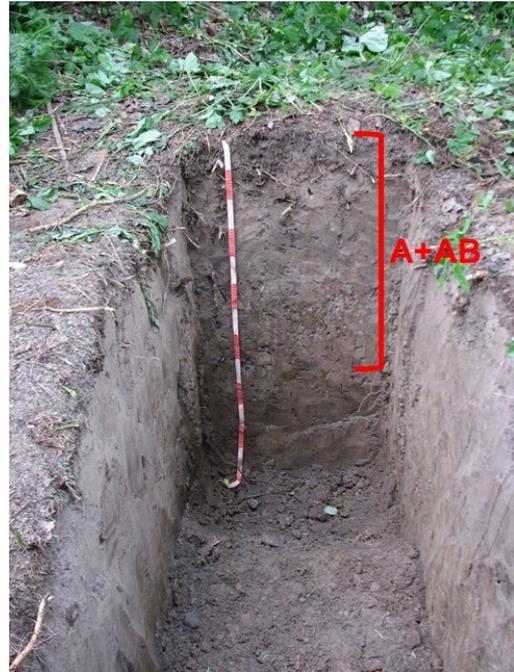


(b) Chernozems Luvic

Figure A1.25. Chernozems (Belgorod region, Russia). Photograph: Igor Savin, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation.



(a) Chernozems Calcic



(b) Chernozems Calcic

Figure A1.26. Chernozems (Volgograd region, Russia). Photograph: Igor Savin, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation.

APPENDIX 2: MAPS OF GLOBAL BLACK SOIL REGIONS

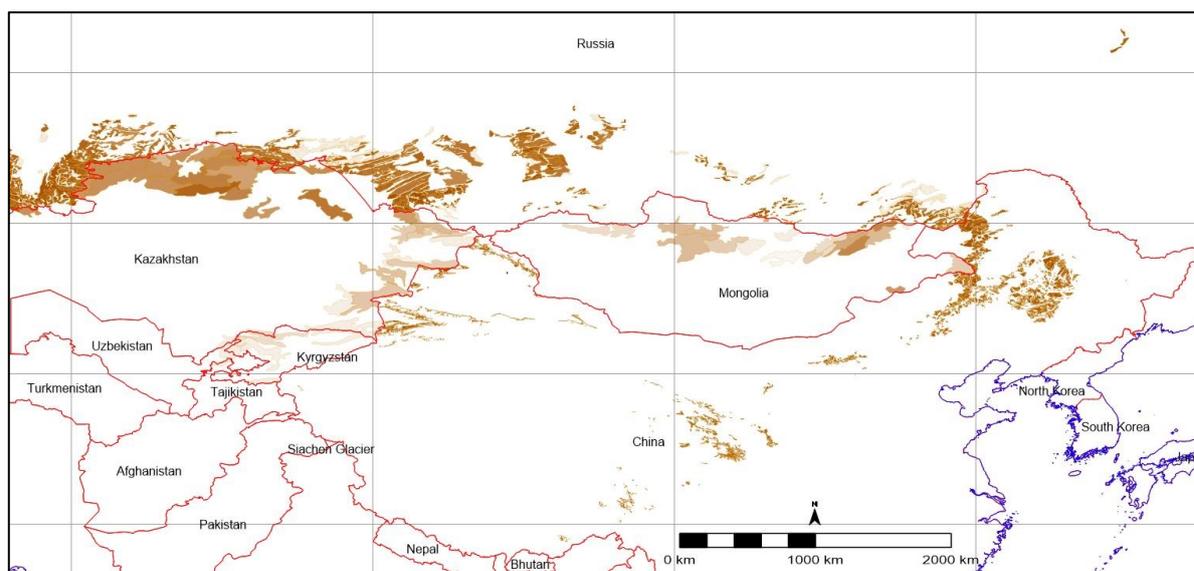


Figure A2.1. Map showing the occurrence of Black Soil in China, Mongolia, Kyrgyzstan, Kazakhstan, and Russia. Brown colour intensity on the map refers to the percentage of Black Soil (the darker – the greater is the Black Soil acreage). Source: Google Earth kml file by Edith Haslinger & Robin Friedrich (Austrian Institute of Technology GmbH, Centre for Energy, Vienna, Austria), and Harald Loishandl-Weisz & Thomas Rosmann (Federal Environment Agency Austria, Department of Groundwater, Vienna, Austria). Map plotted with Golden Software's MapViewer v.8 by Alecos Demetriades, Institute of Geology and Mineral Exploration, Athens, Hellas & IUGS Commission on Global Geochemical Baselines.

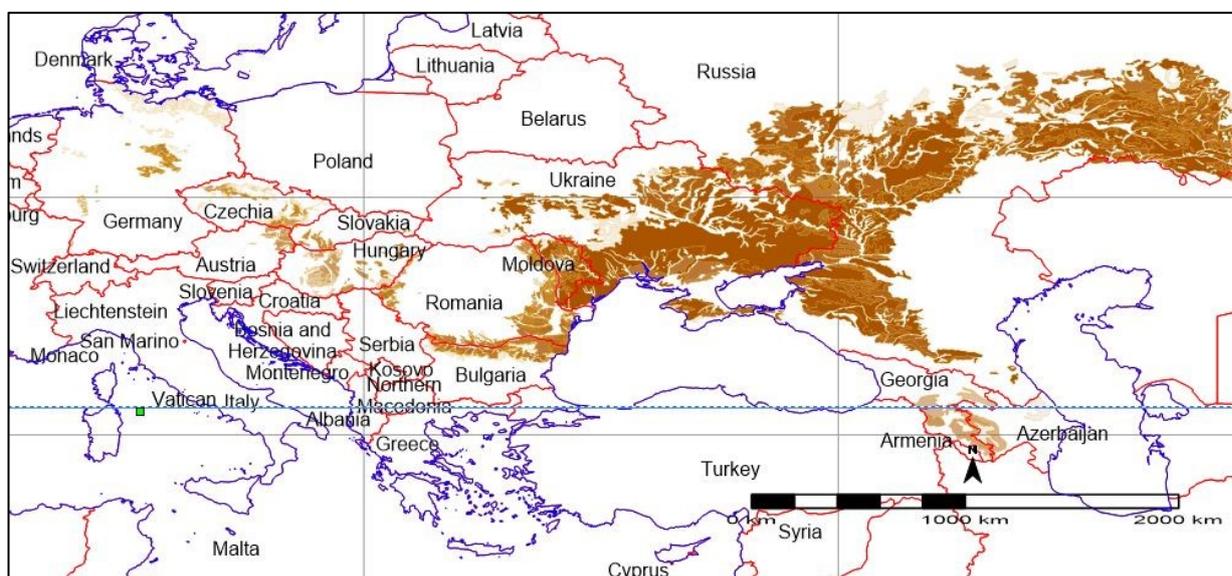


Figure A2.2. Map showing the occurrence of Black Soil in Russia, Azerbaijan, Armenia, Georgia, Ukraine, Moldova, Romania, Bulgaria, Hungary, Slovakia, Czechia, and Germany. Brown colour intensity on the map refers to the percentage of Black Soil (the darker – the greater is the Black Soil acreage). Source: Google Earth kml file by Edith Haslinger & Robin Friedrich (Austrian Institute of Technology GmbH, Centre for Energy, Vienna, Austria), and Harald Loishandl-Weisz & Thomas Rosmann (Federal Environment Agency Austria, Department of Groundwater, Vienna, Austria). Map plotted with Golden Software's MapViewer v.8 by Alecos Demetriades, Institute of Geology and Mineral Exploration, Athens, Hellas & IUGS Commission on Global Geochemical Baselines.

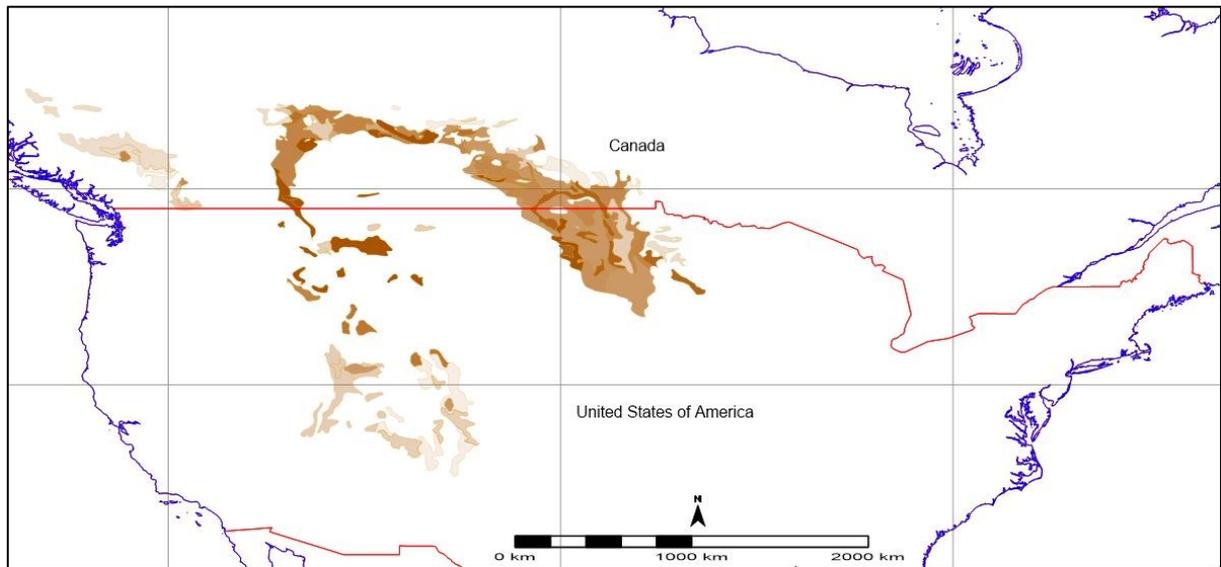


Figure A2.3. Map showing the occurrence of Black Soil in Canada and the United States of America. Brown colour intensity on the map refers to the percentage of Black Soil (the darker – the greater is the Black Soil acreage). Source: Google Earth kml file by Edith Haslinger & Robin Friedrich (Austrian Institute of Technology GmbH, Centre for Energy, Vienna, Austria), and Harald Loishandl-Weisz & Thomas Rosmann (Federal Environment Agency Austria, Department of Groundwater, Vienna, Austria). Map plotted with Golden Software’s MapViewer v.8 by Alecos Demetriades, Institute of Geology and Mineral Exploration, Athens, Hellas & IUGS Commission on Global Geochemical Baselines.

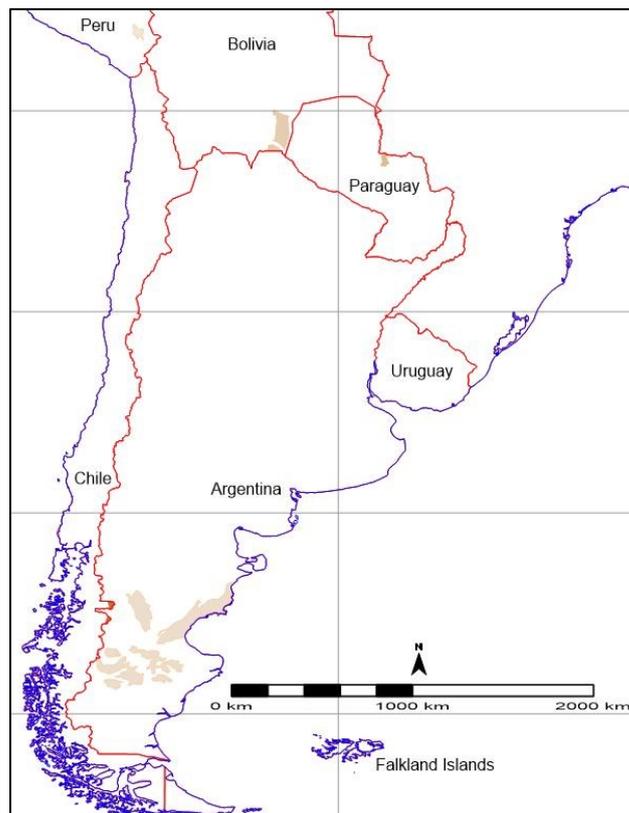


Figure A2.4. Map showing the occurrence of Black Soil in Argentina, Peru, Bolivia, and Paraguay. Brown colour intensity on the map refers to the percentage of Black Soil (the darker – the greater is the Black Soil acreage). Source: Google Earth kml file by Edith Haslinger & Robin Friedrich (Austrian Institute of Technology GmbH, Centre for Energy, Vienna, Austria), and Harald Loishandl-Weisz & Thomas Rosmann (Federal Environment Agency Austria, Department of Groundwater, Vienna, Austria). Map plotted with Golden Software’s MapViewer v.8 by Alecos Demetriades, Institute of Geology and Mineral Exploration, Athens, Hellas & IUGS Commission on Global Geochemical Baselines.

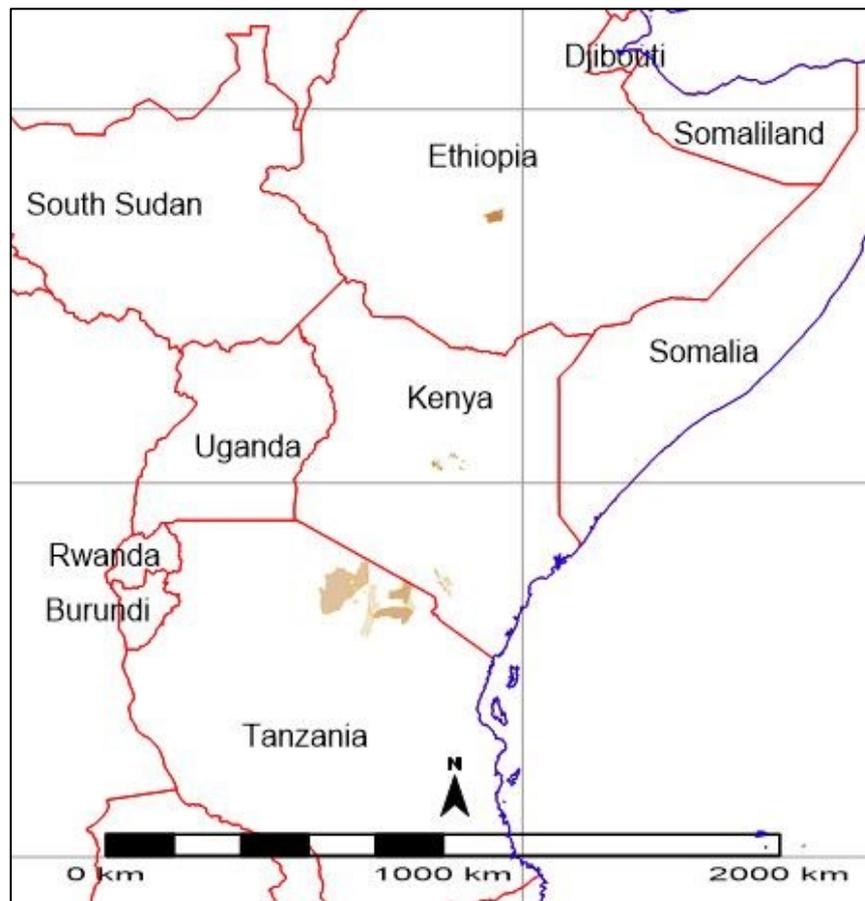


Figure A2.5. Map showing the occurrence of Black Soil in Ethiopia, Tanzania, and Kenya. Brown colour intensity on the map refers to the percentage of Black Soil (the darker – the greater is the Black Soil acreage). Source: Google Earth kml file by Edith Haslinger & Robin Friedrich (Austrian Institute of Technology GmbH, Centre for Energy, Vienna, Austria), and Harald Loishandl-Weisz & Thomas Rosmann (Federal Environment Agency Austria, Department of Groundwater, Vienna, Austria). Map plotted with Golden Software’s MapViewer v.8 by Alecos Demetriades, Institute of Geology and Mineral Exploration, Athens, Hellas & IUGS Commission on Global Geochemical Baselines.

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APPENDIX 3: GENERATION OF RANDOM SAMPLE NUMBERS

Random numbers can be generated quite easily using tools from the Web as, *for example*, the facility provided by the Random Organisation. Since, most random number functions usually generate duplicates the ‘Random Sequence Generator’ should be used at <http://www.random.org/sequences/>, because it generates a sequence of unique numbers. The case of Ajka (Hungary) is used as an example (see Figures A3.1 and A3.2):

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

Random Sequence Generator

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

Part 1: Sequence Boundaries

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

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

Format in column(s)

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

Part 2: Go!

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

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

Figure A3.1. Random number sequence generator input page from 1 to 100 (<http://www.random.org/sequences/>).

Random Sequence Generator

Here is your sequence:

69	87	83	46	63	82	73	5	6	22	55	14
36	58	15	45	96	66	12	71	98	35	90	79
34	28	47	100	72	30	88	26	7	19	16	48
60	29	31	56	95	8	4	64	41	52	17	78
92	13	99	70	77	11	23	85	67	54	80	39
40	33	94	50	21	20	9	38	59	89	3	53
74	43	76	57	24	37	44	25	91	97	42	68
93	65	84	32	27	18	10	81	49	61	51	86
2	75	62	1								

Figure A3.2. Output of random number sequence from 1 to 100. In the above case, the random numbers were output into twelve columns to include in this figure.

APPENDIX 4: FIELD OBSERVATIONS SHEET

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Field Observation Sheet**GLOBAL BLACK SOIL GEOCHEMISTRY PROJECT**

TOP Sample ID : _____ Date: _____

BOTTOM Sample ID: _____ Country: _____

Organisation: _____ Sampler: _____

GTN Coordinator if different from above: _____

SAMPLE SITE LOCATION Region: _____ Map sheet: _____

COORDINATES (Use Geographical coordinates WGS84 ONLY in decimal degrees):

 East West: _____° North South: _____°

Altitude: _____ metres above mean sea level

SAMPLE SITE DESCRIPTION

Approximate size of field selected for sampling: X = _____ m Y = _____ m

Landscape / topography: Level; Sloping; SteepLast crop: Wheat; Barley; Oat; Rye; Maize; Rice; Rapeseed; Sunflower; Sugar beet; Potato; Wetland Non-cultivated, moorland, *etc.*; Other, specify _____

Predominant parent lithology: _____

Depth of observed ground water table (cm): _____

Grain size range of TOP sample: sand-silt; silt-clay; clay

Abundance of organic matter in % (Top sample): _____ %

Abundance of clasts >2 mm in % (Top sample): _____ %

Soil moisture on day of sampling: Dry; Medium; WetGrain size range of BOTTOM sample: sand-silt; silt-clay; clayAbundance of organic matter in % (Bottom sample): %Abundance of clasts >2 mm in % (Bottom sample): %Soil moisture on day of sampling: Dry; Medium; Wet**Sampling interval** (Note: Sample single horizons only)TOP sample: 0-20 cm; Other, specify: from _____ to _____ cm

BOTTOM sample: from _____ to _____ cm

Possible sources of contamination, specify: _____

Distance to minor road: _____ m; Distance to major road: _____ m

GAMMA RADIATION (cps) Total: _____ Th: _____ U: _____ K: _____

Instrument type: _____

REMARKS (any unusual observations)

Photographs: _____

International Union of Geological Sciences Manual of Standard Geochemical Methods for the Global Black Soil Project

edited by

Alecos Demetriades, Dai Huimin, Liu Kai, Igor Savin,
Manfred Birke, Christopher C. Johnson and Ariadne Argyraki

The aims of the International Union of Geological Sciences Commission on Global Geochemical Baselines are:

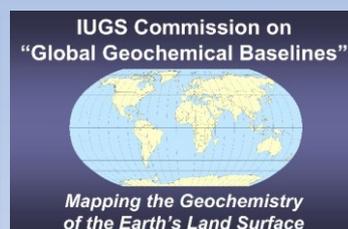
- To provide high quality geochemical baseline data for the terrestrial part of our home planet Earth;
- To establish a Geochemical Reference Network for levelling data sets of existing regional geochemical projects, and
- To provide reference samples and sites for future monitoring of the chemical state of the World's terrestrial surface.

Hence, the generated geochemical data must be of high quality, integrity and consistency.

Sampling of Black Soil (chernozems), *sensu stricto*, is not included in the programme of the International Union of Geological Sciences (IUGS) Commission on Global Geochemical Baselines, because it is an agricultural soil impacted by human activities. However, it is an important agricultural soil, and as is considered to be among some of the most productive soil types in the World, it should quite rightly be studied separately from other agricultural soil types.

The aim of the Global Black Soil Critical Zone Geo-ecological Survey (BASGES) is to study, in a holistic approach, the serious degradation problems that Black Soil types are facing all over the world because of several decades of intensive cultivation. Their present chemical state shall be studied by following the principles of the IUGS Commission on Global Geochemical Baselines for producing an internally consistent high quality geochemical database. The requirements are to use standardised sampling and sample preparation methods, and all samples must be analysed in the same laboratory for the same suite of determinands/parameters, following a strict quality control protocol.

The present manual contains comprehensive instructions for sample site selection, sample collection and preparation, recommendations for preparation of project reference samples, laboratory analysis, quality control procedures that should be implemented, checking the quality of analytical data, required supporting information for interpretation of geochemical data, and need for the establishment of site-specific guideline values for Black Soil in the different regions of its occurrence.



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