

International Union of Geological Sciences

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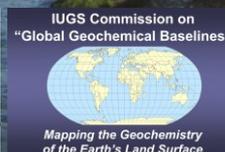
Standard Methods for Establishing the Global Geochemical Reference Network

edited by

Alecos Demetriades, Christopher C. Johnson, David B. Smith,
Anna Ladenberger, Paula Adánez Sanjuan, Ariadne Argyraki,
Christina Stouraiti, Patrice de Caritat, Kate V. Knights,
Gloria Prieto Rincón and Gloria Namwi Simubali

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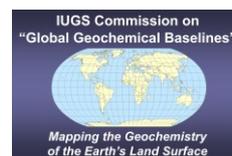
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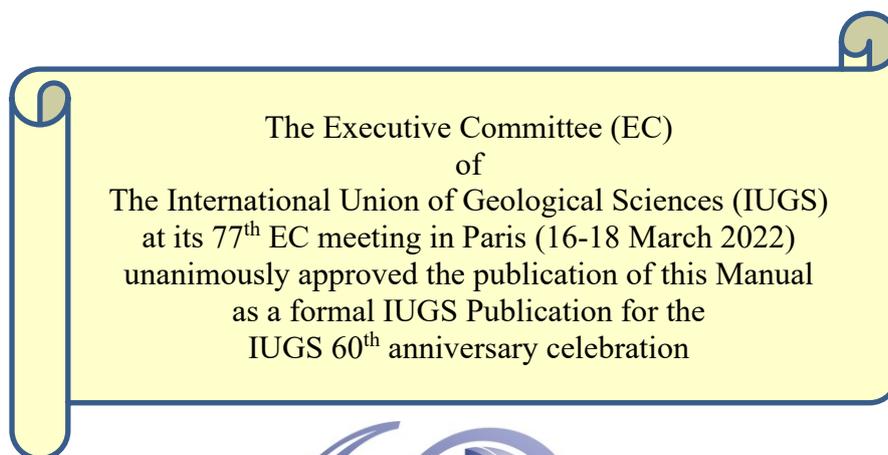
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Taken by Juan Pablo Lacassie Reyes, Servicio Nacional de Geología y Minería, Chile



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This Manual presents, for the first time a comprehensive overview of the standardised methods that should be employed across the land surface of the Earth to map the distribution of chemical elements in rock, soil, sediment and water.

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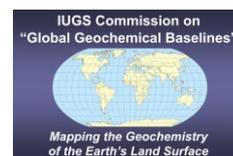
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International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network



Aims

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.

Synopsis

“Everything in and on the Earth - mineral, animal and vegetable - is made from one, or generally some combination of, the natural chemical elements occurring in the rocks of the Earth's crust and the surficial materials derived from them. Everything that is grown, or made, depends upon the availability of the appropriate elements. The existence, quality and survival of life depends upon the availability of elements in the correct proportions and combinations. Because natural processes and human activities are continuously modifying the chemical composition of our environment, it is important to determine the present abundance and spatial distribution of the elements across the Earth's surface in a much more systematic manner than has been attempted hitherto” (Darnley *et al.*, 1995, p.x). Although such a global database is urgently needed for multi-purpose use, the systematic attempt is still in its infancy because of the non-existence of a manual of comprehensive and standardised methods of sampling and other supporting procedures. The current ‘*International Union of Geological Sciences Manual of Standard Methods for Establishing the Global Geochemical Reference Network*’ fills this gap. The Manual follows the concept of 7356 Global Terrestrial Network grid cells of 160x160 km, covering the land surface of Earth, with five random sites within each grid cell for the collection of samples. This allows the establishment of the *standardised Global Geochemical Reference Network* with respect to rock, residual soil, humus, overbank sediment, stream water, stream sediment and floodplain sediment. Apart from the instructions for the collection of samples, the Manual covers sample preparation and storage, development of reference materials, geoanalytical methods, quality control procedures, geodetic and parametric levelling of existing geochemical data sets, data conditioning for the generation of time-independent geochemical data, management of data and map production, and finally project management. The methods described herein, apart from their use for *Establishing the Global Geochemical Reference Network*, can be used in other geochemical surveys at any mapping scale.

Keywords: geochemical surveys; baseline studies; sampling; rock; residual soil; humus; stream water; stream sediment; overbank sediment; floodplain sediment; sample preparation; sample storage; reference materials; analytical methods; quality control; data management; data conditioning; map production; project management

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Foreword

by

John Ludden, Qiuming Cheng, Roland Oberhänsli

IUGS PRESIDENTS

2020-2024



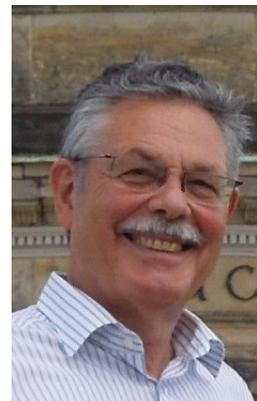
Prof. John LUDDEN, CBE

2016-2020



Prof. Qiuming CHENG

2012-2016



Prof. Roland OBERHÄNSLI

One of the current great challenges in applied geochemistry is defining and understanding, at a global scale, the concentration and spatial distribution of chemical elements in the Earth's surface materials such as rocks, soils, sediments, and stream water. These data are needed by agencies and specialists involved in activities such as environmental protection, risk assessment, remediation of contaminated land, public health, agriculture, food safety, and natural resource development and management. It is impossible to estimate the human-caused input of potentially harmful chemicals into the environment without first having a good understanding of the natural variation of those chemicals at the Earth's surface. The means to address this challenge lies in low-sampling density geochemical mapping conducted across the entire land surface of the Earth.

Creating a global-scale geochemical database and the resulting maps has been discussed within the geochemical community at least since the 1980s. An event that stimulated interest in global-scale geochemistry was the Chernobyl accident in Ukraine on 26 April 1986. The accident released large quantities of radioactive substances into the atmosphere for about 10 days. Most of the released material was deposited nearby, but the lighter material was carried by wind over Ukraine, Belarus, Russia, and to some extent over Scandinavia and Europe. Geoscientists quickly recognised that no global-scale geochemical baseline data existed to assess the impact of such human-caused accidents that affect large areas of the Earth's surface.

Shortly after the Chernobyl accident, discussions were initiated within the Western European Geological Surveys (WEGS; later renamed the Forum of European Geological Surveys (FOREGS) and presently called EuroGeoSurveys), that led to the submission of a proposal titled *International Geochemical Mapping* to the International Geological Correlation

Program (IGCP), now called the International Geoscience Program. IGCP is a cooperative enterprise of the United Nations Educational, Scientific and Cultural Organization (UNESCO) and the International Union of Geological Sciences (IUGS). The proposal was accepted by IGCP in 1988 as IGCP Project 259, and operated until 1992. From 1993 to 1997, IGCP 259 continued under IGCP as Project 360, *Global Geochemical Baselines*. The objectives of these projects were to (1) conduct a comprehensive review of methods being used at that time for regional-, national- and international-scale geochemical mapping studies; (2) develop recommendations for producing a global-scale geochemical database; and (3) establish a worldwide network of applied geochemists with an interest in conducting global-scale geochemical mapping studies. The project's final report, [*A global geochemical database for environmental and resource management*](#) was published by the Earth Sciences Division of UNESCO in 1995.

This report introduced the concept of a global geochemical reference network (GRN). The GRN is a grid-based sampling scheme comprised of 19,833 cells covering the whole globe. Of these, 7356 cells cover the land surface of the Earth, and are known as the [*Global Terrestrial Network*](#) (GTN). These cells, approximately 160x160 km in size, would form the basis for conducting multi-media sampling (stream sediment, soil, humus, overbank/floodplain sediment, surface water) at a global scale. The authors of the report envisioned that the resulting geochemical database and samples would provide:

- data from which a global-scale geochemical atlas may be prepared;
- an archive of samples for use by future researchers;
- documentation of the composition of a variety of surficial materials at locations with a relatively uniform spatial distribution over the land surface of the Earth;
- a supply of locally relevant standard reference materials for use in more detailed geochemical surveys in the region of origin;
- reference points for normalising national-scale geochemical databases; and
- sites for recurrent monitoring in the future to facilitate the recognition and quantification of change caused by natural processes or anthropogenic activities.

Directly after the publication in 1995 of the IGCP 259 final report, the Directors of FOREGS approved the first multi-national continental-scale geochemical mapping of Europe, according to IGCP 259 specifications. The project started in June 1997 and published a field sampling manual in 1998. The final product was the two-volume [*Geochemical Atlas of Europe*](#) published in 2005 and 2006. Twenty-six European countries participated in the project and collected stream sediment, stream water, topsoil, subsoil, humus, and floodplain sediment samples at an average sampling density of 1 site per 4600 km².

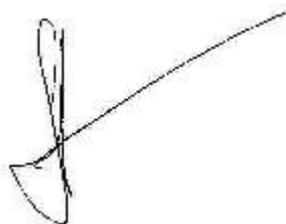
Over the next ten years, several countries conducted national-scale geochemical mapping projects at a similar sampling density, but usually only focussed on one or two of the recommended sample media from IGCP 259. Such studies have been conducted in Australia, China, India, Mexico, a second European-wide study, and the USA. It is also noted that these studies were generally not conducted according to standardised sampling and analytical protocols. In 2016, two events occurred that greatly advanced the cause of global-scale geochemical mapping. In May 2016, the UNESCO International Centre on Global-Scale Geochemistry opened in Langfang, People's Republic of China. This was followed in August by IUGS establishing the *Commission on Global Geochemical Baselines* (hereafter referred to as 'the Commission'). The Commission is essentially a continuation of the Task Group on Global Geochemical Baselines, which operated from 1997 to 2016 under the auspices of both IUGS and the International Association of GeoChemistry. The Task Group, in turn, was a follow-on of IGCP Projects 259 and 360.

According to IUGS By Laws, one of the primary objectives of IUGS Commissions is to "coordinate long-term international cooperative investigations to establish standards in

appropriate fields.” In pursuit of the goal to establish standards for global-scale geochemical mapping, the Commission worked with applied geoscientists throughout the world to produce this book titled *International Union of Geological Sciences Manual of Standard Methods for Establishing the Global Geochemical Reference Network*. Using the [FOREGS field sampling manual](#) as a starting point, this book provides in much greater detail the methods that should be employed for mapping the abundance and spatial distribution of chemical elements in rocks, soils, sediments, and water across the entire land surface of the Earth based on sampling according to the GTN.

The book contains separate chapters providing extensive information on sampling protocols for rocks, residual soil, humus, stream water, stream sediments, and overbank and floodplain sediments. There are also chapters discussing sample site selection; sample preparation; quality control procedures, including development of project reference materials; data management; map preparation; project management; and information on how to level existing geochemical data sets. Any applied geochemist contemplating carrying out a geochemical mapping project at a global scale, or any other scale, should find a wealth of useful information within these pages. It is hoped, and anticipated, that a long-term outcome from the publication of this book will be more geochemical mapping projects conducted to these standardised protocols. This will allow much easier comparison of data and maps among the various individual projects. Worldwide multi-media sampling based on the GTN to produce a true global-scale geochemical database is a long-range goal that will require the cooperation of all countries.

This sampling manual is another accomplishment of the IUGS Commission on Global Geochemical Baselines. A manual of this complexity would not have been possible without the hard work of all the authors, reviewers, and editors of the volume. We extend our sincere gratitude to them all. In particular, we would like to recognise the long-term dedication of Alecos Demetriades to the completion of this manual. Alecos is the Chair of the Commission’s Sampling Committee, the lead editor for this sampling manual, and the lead author or co-author for most of its chapters. This manual has been his vision for many years, and its publication would have been impossible without his tireless work.



John Ludden



Qiuming Cheng



Roland Oberhänsli

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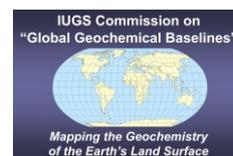
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Acknowledgements

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The IUGS Executive Committee members John Ludden (President), Hassina Mouri (Vice President), Daekyo Cheong (Vice President), Stanley C. Finney (Secretary-General), Hiroshi Kitazato (Treasurer), Qiuming Cheng (Past President), Silvia Peppoloni (Councillor), Claudia Inés Mora (Councillor), Jennifer McKinley (Councillor), and Ludwig Stroink (Councillor) are thanked for approving the publication of this Manual.

Chapter reviewers

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Chapter 1. General Introduction

Chapter 2. Global Terrestrial Network Grid Cells, Selection of Sample Sites, and Sample Types to be Collected

Annex A2.1. Geodetic Levelling of Existing Geochemical Data Sets

Annex A2.2. Parametric Levelling of Existing Geochemical Data Sets

Chapter 3. Sampling Methods: An Introduction

Evgenia Kontogianni

Academic Librarian

Hellenic Survey of Geology and Mineral Exploration

1 Spyrou Louis, Olympic Village, Entrance C

GR-13677 Acharnai, Athens, Hellenic Republic

E-mail address: evgekont@gmail.com

Chapter reviewers

Paraskevi-Maria Kourgia

Chemist and Environmental Technologist
National and Kapodistrian University of Athens
Faculty of Geology and Geoenvironment
Department of Economic Geology and Geochemistry
Panepistimiopolis, GR-157 84 Zographou
Athens, Hellenic Republic
E-mail address: b.kourgia@gmail.com

Zacharenia Kypridou

Geologist-Geochemist
Faculty of Geology and Geoenvironment
Department of Economic Geology and Geochemistry
Panepistimiopolis, GR-157 84 Zographou
Athens, Hellenic Republic
E-mail address: zach-kyp@geol.uoa.gr

3.1. Rock sampling

Helen Karamanos

Geologist-Applied Geochemist
Institute of Geology and Mineral Exploration, Central Macedonia Branch (retired)
Karidhias Street 3
Oræokastro,
Thessaloniki 570 73, Hellenic Republic
E-mail address: elemano@otenet.gr

Martiya Sadeghi

Economic Geologist
Economic Geology Unit, Department of Mineral Resources
Geological Survey of Sweden
Box 670
SE-751 28 Uppsala, Sweden
E-mail address: martiya.sadeghi@sgu.se

3.2. Residual soil sampling

[Annex A3.2.1. Residual Soil and Humus Sampling: World Soil Profiles](#)

[Annex A3.2.2. Residual Soil and Humus Sampling: Soil Profiles](#)

Josip Halamić

Professor for geochemical and geological mapping
Croatian Geological Survey
Sachsova 2, 10 000 Zagreb
Croatia
E-mail address: josip.halamic@gmail.com

Laurel Woodruff

Research Geologist
U.S. Geological Survey
Geology, Energy, and Minerals Science Centre
St. Paul, Minnesota 55112
United States of America
E-mail address: woodruff@usgs.gov

3.3. Stream water sampling

Raymond E. Lett

Emeritus scientist
British Columbia Geological Survey Branch
British Columbia Ministry of Energy
Mines and Petroleum Resources
Victoria, British Columbia, Canada
E-mail address: Raylett@shaw.ca

Jörg Matschullat

Professor of Geochemistry and Geoecology
Technical University Bergakademie Freiberg
Interdisciplinary Environmental Research Centre
Brennhausgasse 14D-09599 Freiberg, Germany
E-mail address: matschul@tu-freiberg.de

Alexei S. Rukhlov

Provincial Geochemist
British Columbia Geological Survey Branch
British Columbia Ministry of Energy
Mines and Low Carbon Innovation
1810 Blanshard Street, Victoria, British Columbia, Canada
E-mail address: Alexei.Rukhlov@gov.bc.ca

3.4. Stream sediment sampling

Helen Karamanos

Geologist-Applied Geochemist
Institute of Geology and Mineral Exploration, Central Macedonia Branch (retired)
Karidhias Street 3, Oræokastro
Thessaloniki 570 73, Hellenic Republic
E-mail address: elemano@otenet.gr

Xin Lin

Associate Professor of Applied Geochemistry
Chang'an University, School of Earth Sciences and Resources
2nd Ring Road South East, Beilin, Xi'an
Shaanxi Province, People's Republic of China
E-mail address: xinlin@chd.edu.cn

3.5. Overbank and Floodplain Sediment Sampling

Annex A3.5.1. Overbank and Floodplain Sediment Sampling: Profiles

Marianne Langedal

Applied Geochemist
Trondheim Municipality
Environmental Department
P.O.Box 2300 Torgarden
N-7004 Trondheim, Norway
E-mail address: marianne.langedal@trondheim.kommune.no

Paula Adánez Sanjuan

Engineering Geologist-Applied Geochemist
Instituto Geológico y Minero de España
23, Rios Rosas
ES-28003 Madrid, Spain
E-mail address: p.adanez@igme.es

Chapter 4. Sample Preparation and Storage

Belinda Flem

Analytical chemist-Geochemist
Geological Survey of Norway
Pb 6315 Torgarden
NO-7491 Trondheim, Norway
E-mail address: Belinda.Flem@ngu.no

George Morris

Senior Geologist-Geochemist
Geological Survey of Sweden
Box 670, SE-751 28 Uppsala, Sweden
E-mail address: George.Morris@sgu.se

Chapter 5. Development of Reference Materials for External Quality Control

Belinda Flem

Analytical chemist-Geochemist
Geological Survey of Norway
Pb 6315 Torgarden
NO-7491 Trondheim, Norway
E-mail address: Belinda.Flem@ngu.no

George Morris

Senior Geologist-Geochemist
Geological Survey of Sweden
Box 670
SE-751 28 Uppsala, Sweden
E-mail address: George.Morris@sgu.se

Chapter 6. Geoanalytical Methods and Requirements

Belinda Flem

Analytical chemist-Geochemist
Geological Survey of Norway
Pb 6315 Torgarden
NO-7491 Trondheim, Norway
E-mail address: Belinda.Flem@ngu.no

Philippe Négrel

Isotope Geochemist
BRGM, Water Environment Process Development and Analysis Division
3 Avenue Claude-Guillemin, BP 36009
F-45060 Orléans-Cedex 2, France
E-mail address: p.negrel@brgm.fr

Chapter 7. Quality Control Procedures

Michael H. Ramsey

Emeritus Professor
School of Life Sciences
University of Sussex
Falmer
BN1 9QG, Brighton, United Kingdom
E-mail address: m.h.ramsey@sussex.ac.uk

Peter Rostron

Consultant geochemist
44 Dyke Road
BN1 3JB Brighton, United Kingdom
E-mail address: pr52@outlook.com

Chapter 8. Data conditioning methods: Generating time independent geochemical data

Robert G. Garrett

Applied Geochemist, Emeritus Scientist
Northern Canada Division
Geological Survey of Canada
Natural Resources Canada
601 Booth Street
Ottawa, ON K1A 0E8, Canada
E-mail address: rgg.gx@bell.net

Chapter reviewers

Kate Knights

Consultant geochemist
20 Sullivan Street
Stoneybatter
Dublin, D07 C650, Ireland
E-mail address: kknights@hotmail.com

Chapter 9. Data Management and Map Production

Robert G. Garrett

Applied Geochemist, Emeritus Scientist
Northern Canada Division
Geological Survey of Canada
Natural Resources Canada
601 Booth Street, Ottawa, ON K1A 0E8, Canada
E-mail address: rgg.gx@bell.net

Federico Solano

Research Geologist
Geology, Energy & Minerals Science Center
U.S. Geological Survey
12201 Sunrise Valley Drive
Reston, VA 22042, United States of America
E-mail address: fsolanoc@usgs.gov

Chapter 10. Project Management

Clemens Reimann

Geologist-Applied Geochemist
Geological Survey of Norway (retired)

- Project Leader of the Kola Ecogeochemistry Project
- Project Leader of the Baltic Soil Survey (BSS)
- Project Leader of the European Groundwater Geochemistry project (EGG)
- Project Leader of the Geochemistry of European Agricultural Soils project (GEMAS)

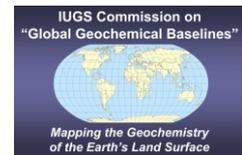
E-mail: clemensreimann@yahoo.co.uk

Reijo Salminen

Research Professor
Geological Survey of Finland (retired)

- Project Leader of the FOREGS Geochemical Atlas of Europe
- Project Leader of the Barents Ecogeochemistry project
- Leader of Geochemistry Subprojects in Tanzania and Uganda

E-mail: reijo.salminen@seutuposti.fi



Provision of soil photographs

Ochirbat Batkhishig

Soil Scientist
Institute Geography-Geoecology
Mongolian Academy of Science
Erkhuu Street 11r Horoolol
Sukhbaatar district, Ulaanbaatar-14192, Mongolia
E-mail address: batkhishig@gmail.com

Ochirbat Batkhishig provided high resolution photographs of Mongolian soil profiles, which are in Annex A3.2.2 of Chapter 3.2.

Antti-Jussi Lindroos

Senior Scientist
Natural Resources Institute Finland (Luke)
Latokartanonkaari 9, FI-00790 Helsinki, Finland
E-mail address: antti.lindroos@luke.fi

Antti-Jussi Lindroos provided the description of Finnish soil profiles, which are in Annex A3.2.2 of Chapter 3.2.

Peter Schad

Soil Scientist
Technical University of Munich
TUM School of Life Sciences
Emil-Ramann-Str. 2, 85354 Freising, Germany
<https://www3.ls.tum.de/en/boku/>
E-mail address: peter.schad@tum.de

Peter Schad provided the high-resolution photographs of soil profiles in Annex A3.2.1 according to the World Reference Base for Soil Resources of Chapter 3.2.

Provision of Global Reference Network Grid file

The original file of the Global Reference Network grid cells of 160x160 km covering the whole globe was generated in 1994 by Nils Gustavsson (Geological Survey of Finland), and consisted of 19,833 grid cells of 160x160 km. The file used in the FOREGS Geochemical Atlas of Europe project comprised 5711 grid cells covering only the terrestrial part of the Earth, and with many coastal grid cells missing, namely the coastal grid cells with their centre falling in water (ocean, sea, lake). The problem was discovered in 1997 during the planning of the [FOREGS Geochemical Atlas of Europe](#) project, and at that time it was corrected only for the European part. As we are presently discussing to cover not only the terrestrial part of the Earth but also the marine realm, it was important to correct this mistake of missing coastal and island grid cells,

and also to have the grid cells covering the oceans and seas. The original file generated by Nils Gustavsson could not be found in the Geological Survey of Finland. Fortunately, Robert G. Garrett from the Geological Survey of Canada, who worked with Nils Gustavsson and Arthur G. Darnley had the original Microsoft Access file with the 19,833 grid cells. Words cannot express our gratitude and appreciation to Robert G. Garrett for keeping safely this very valuable file, which enable us to compile (a) the Global Terrestrial Network file with 7356 grid cells of 160x160 km, and (b) the Global Marine Network file with 12,477 grid cells of 160x160 km.

Robert G. Garrett

Applied Geochemist, Emeritus Scientist
Northern Canada Division
Geological Survey of Canada
Natural Resources Canada
601 Booth Street, Ottawa, ON K1A 0E8, Canada
E-mail address: rgg.gx@bell.net

Provision of geochemical data

The Finnish and United Kingdom data used in Annexe A2.2 of Chapter 2 for the parametric levelling were provided by the Geological Survey of Finland (Maija Pennanen) and the British Geological Survey (Michael Watts, Paul Everett, James North), respectively.

Maija Pennanen
Geological Survey of Finland
P.O. Box 96 (Vuorimiehentie 5), FI-02151 Espoo, Finland
E-mail address: majja.pennanen@gtk.fi

Michael Watts, Paul Everett, James North
British Geological Survey
Keyworth, Nottingham NG12 5GG, United Kingdom
E-mail addresses: mwatts@bgs.ac.uk; paer@bgs.ac.uk; iprdigital@bgs.ac.uk

Generation of random points within the 160x160 km grid cells

Juanxia He and Xiaoyuan Geng are thanked for generating the 5 and 8 random points within each GTN grid cell of 160x160 km. The reason for generating two different files, with 5 and 8 random points in each 160x160 km grid cell, is that these two options are given in the the "[Blue Book](#)" (Darnley *et al.*, 1995), and countries are free to select which sampling density will be using. They also generated a 16 random points file, which can be used for wide-spaced regional geochemical mapping.

Juanxia He and Xiaoyuan Geng

Canadian Soil Information Service
Science and Technology Branch
Agriculture and Agri-Food Canada (<http://sis.agr.gc.ca/>)
Room 1136, 960 Carling Avenue, Ottawa, Canada K1A 0C6
E-mail addresses: Juanxia.he@agr.gc.ca and Xiaoyuan.geng@agr.gc.ca

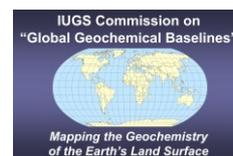
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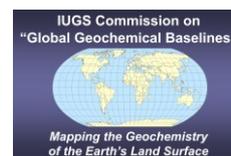


Editors

<i>Editor name</i>	<i>Affiliation and E-mail address</i>
Alecos Demetriades	Institute of Geology and Mineral Exploration*, Athens, Hellenic Republic; alecos.demetriades@gmail.com
Christopher C. Johnson	GeoElementary, Derby, United Kingdom; drccjohnson@gmail.com
David B. Smith	United States Geological Survey, Denver, USA; dbsmith13@gmail.com
Anna Ladenberger	Geological Survey of Sweden, Uppsala, Sweden; anna.ladenberger@sgu.se
Paula Adánez Sanjuan	Instituto Geológico y Minero de España, Madrid, Spain; p.adanez@igme.es
Ariadne Argyraki	Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Hellenic Republic; argyraki@geol.uoa.gr
Christina Stouraiti	Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Hellenic Republic; chstouraiti@geol.uoa.gr
Patrice de Caritat	Geoscience Australia, Canberra, Australia; Patrice.deCaritat@ga.gov.au
Kate V. Knights	Dublin, Ireland; kknights@hotmail.com
Gloria Prieto Rincón	Servicio Geológico Colombiano, Bogotá, Columbia; gprieto@sgc.gov.co
Gloria Namwi Simubali	Geological Survey of Namibia, Windhoek, Namibia; Gloria.Simubali@mme.gov.na

*Presently the Hellenic Survey of Geology and Mineral Exploration

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Contributors

<i>Contributor name</i>	<i>Affiliation and E-mail address</i>	<i>Chapter</i>
Stefano Albanese	University of Napoli Federico II, Naples, Italy; stefano.albanese@unina.it	9
Ariadne Argyraki	Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Hellas; argyraki@geol.uoa.gr	7, 10
Felipe Astudillo	Servicio Nacional de Geología y Minería, Valdivia, Chile; felipe.astudillo@sernageomin.cl	3.2, A3.2.2, 3.5, A3.5.1
Adrián Pérez Avila	Servicio Geológico Colombiano, Bogotá, Columbia; adperez@sgc.gov.co	A3.5.1
Maria João Batista	Laboratório Nacional de Energia e Geologia, Amadora, Portugal; mjoao.batista@lneg.pt	2, A2.2, 3, 3.1, 3.2,
Alejandro Bel-Ian	Instituto Geológico y Minero de España, Madrid, Spain; alexbellan@telefonica.net	3.4, 3.5
Manfred Birke	Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany; manfred-birke@web.de	A2.2, 6
Igor Bogatyrev	IUGS Commission on Global Geochemical Baselines; igor.bogatyrev@scmin.spb.ru	9
Jim Bogen	Norwegian Water Resources and Energy Directorate, Oslo, Norway; jbo.bogen@gmail.com	3.5
Laura Cecilia Tristán Capetillo	Servicio Geológico Mexicano, San Luis Potosi, México; lauratristan@sgm.gob.mx	3.4
César De La Cruz Poma	Instituto Geológico Minero y Metallúrgico, Lima, Perú; cdelacruz@ingemmet.gob.pe	3.4
Alecos Demetriades	Institute of Geology and Mineral Exploration, Athens, Hellas; alecos.demetriades@gmail.com	1, 2, A2.2, 3, 3.1, 3.2, A3.2.2, 3.3, 3.4, 3.5, A3.5.1, 4, 6, 7, 9, 10
Mikael Eklund	Geological Survey of Finland, Espoo, Finland; mikael.eklund@gtk.fi	3.3, 3.4
Peter Filzmoser	Institute for Statistics and Probability Theory, Vienna University of Technology, Vienna, Austria; P.Filzmoser@tuwien.ac.at	9
Fiona Fordyce	British Geological Survey Scotland, Edinburgh, United Kingdom	3.4
Robin Friedrich	Federal Environment Agency Austria, Department of Groundwater, Vienna, Austria; robin.friedrich@ait.ac.at	A3.2.1

<i>Contributor name</i>	<i>Affiliation and E-mail address</i>	<i>Chapter</i>
Virgilija Gregorauskien	Geological Survey of Lithuania, Vilnius, Lithuania; virgilija.gregorauskiene@lgt.lt	3.2, A3.2.2
Karina Maribel Cerna Guillen	Instituto Hondureño de Geología y Minas, Tegucigalpa, Honduras; kcerna@inhgeomin.gob.hn	3.1
Gwendy E.M. Hall	Geological Survey of Canada, Ottawa, Ontario, Canada; gwendyhall@gmail.com	6
Edith Haslinger	Austrian Institute of Technology GmbH, Centre for Energy, Vienna, Austria; Edith.Haslinger@ait.ac.at	3.2, A3.2.1, A3.2.2
Tarja Hatakka	Geological Survey of Finland, Espoo, Finland; tarja.hatakka@gtk.fi	3.3
Christopher C. Johnson	GeoElementary, Derby, United Kingdom; drccjohnson@gmail.com	1, 2, A2.2, 3, 3.2, 3.3, 3.4, 7, 8, 10
Kate V. Knights	Dublin, Ireland; kknights@hotmail.com	10
Juan Pablo Lacassie Reyes	Servicio Nacional de Geología y Minería, Valdivia, Chile; juan.lacassie@sernageomin.cl	3.2, A3.2.2, 3.5, A3.5.1
Anna Ladenberger	Geological Survey of Sweden, Uppsala, Sweden; anna.ladenberger@sgu.se	3.1, 6, 10
T. Robert Lister	British Geological Survey, Keyworth, Nottingham, United Kingdom; bob_lister@btinternet.com	8
Juan Locutura	Instituto Geológico y Minero de España, Madrid, Spain; juanlocuturaruperez@gmail.com	3.4, 3.5
Harald Loishandl-Weisz	Federal Environment Agency Austria, Department of Groundwater, Vienna, Austria; harald.loishandl-weisz@umweltbundesamt.at	A3.2.1
Pavol Lučivjanský	State Geological Institute of Dionyz Stur, Regional Centre, Spiska Nova Ves, Slovakia; pavol.lucivjansky@geology.sk	4, 5
Daniela Mackovych	State Geological Institute of Dionyz Stur, Regional Centre, Spiska Nova Ves, Slovakia; daniela.mackovych@geology.sk	4, 5
Iván Martín	Instituto Geológico y Minero de España, Madrid, Spain; i.martin@igme.es	3.4, 3.5
Francy Michell Medina	Instituto Hondureño de Geología y Minas, Tegucigalpa, Honduras; fmedina@inhgeomin.gob.hn	3.1
George Morris	Geological Survey of Sweden, Uppsala, Sweden; george.morris@sgu.se	6
Rolf Tore Ottesen	Geological Survey of Norway, Trondheim, Norway	3.5
Gloria Prieto Rincón	Servicio Geológico Colombiano, Bogotá, Columbia; gprieto@sgc.gov.co	A3.5.1, 10
Luis Vargas Rodriguez	Instituto Geológico Minero y Metallúrgico, Lima, Perú; lvargasr@ingemmet.gob.pe	3.4

<i>Contributor name</i>	<i>Affiliation and E-mail address</i>	<i>Chapter</i>
Thomas Rosmann	Federal Environment Agency Austria, Department of Groundwater, Vienna, Austria; thomas.rosmann@umweltbundesamt.at	A3.2.1
Michalis Salahoris	GeoSet Ltd., Papagos-Cholargos, Attiki, Hellas; michael.salahoris@gmail.com	A2.1
Reijo Salminen	Geological Survey of Finland, Espoo, Finland; reijo.salminen@seutuposti.fi	1, 3.2, 3.3, 3.4,
Ignace Salpeteur	Bureau de Recherches Géologiques et Minières, Orléans, France; ignace.salpeteur@gmail.com	3.4, 3.5
Paula Adánez Sanjuan	Instituto Geológico y Minero de España, Madrid, Spain; p.adanez@igme.es	A3.5.1, 10
Igor Savin	V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation; savigory@gmail.com	3.2, A3.2.2
Gloria Namwi Simubali	Geological Survey of Namibia, Windhoek, Namibia; Gloria.Simubali@mme.gov.na	10
David B. Smith	IUGS Commission on Global Geochemical Baselines; dbsmith13@gmail.com	1, 2, A2.2, 3, 3.2, 10
Steven M. Smith	IUGS Commission on Global Geochemical Baselines; smsmith@usgs.gov	9
Christina Stouraiti	Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Hellas; chstouraiti@geol.uoa.gr	10
Timo Tarvainen	Geological Survey of Finland, Espoo, Finland; Timo.Tarvainen@gtk.fi	1, 2, A2.2, 3, 3.2, A3.2.2, 3.3, 3.4, 9
Pablo Sebastian Oliva Vicentelo	Servicio Nacional de Geología y Minería, Valdivia, Chile; pablo.oliva@sernageomin.cl	3.2, 3.5, A3.5.1
Xueqiu Wang	UNESCO International Centre on Global- Scale Geochemistry, Langfang, Hebei, China; wangxueqiu@unesco-icgg.org	3.5
Zomenia Zomeni	Geological Survey Department, Lefkosia, Cyprus; zzomeni@gsd.moa.gov.cy	3.2

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Abbreviations and Acronyms

It is noted that a few abbreviations are the same but are used in a different context. *For example*, AR is the abbreviation used by soil scientists for Arenosols, and the same abbreviation is used by geologists for *aqua regia* extraction.

A	intercept on the Y-axis in the linear equation $Y = B \cdot X + A$
AAS	atomic absorption spectrometry
AC	Acrisols
AES	atomic emission spectrometry
AFC	Alkaline Fusion Spectrophotometry
AFS	Atomic Fluorescence Spectrometry
AIT	Austrian Institute of Technology GmbH
Al	aluminium
AL	Alisols
alr	additive log ratio
AMA	advanced mercury analyser
AMC	Analytical Methods Committee (Royal Society of Chemistry, London)
AN	Andosols
ANOVA	analysis of variance
AR	Arenosols
AR	<i>aqua regia</i>
ASTM	American Society for Testing and Materials
ASV	anodic stripping voltammetry
AT	Anthrosols
AV	accepted value
B	slope of the linear regression line of equation $Y = B \cdot X + A$
BC	Before Christ
BGR	Bundesanstalt für Geowissenschaften und Rohstoffe (Institute of Geosciences and Natural Resources, Germany)
BGS	British Geological Survey
BRGM	Bureau de Recherches Géologiques et Minières (France)
C	Celsius or centigrade temperature
CAL	calculated
CANMET	CANMET Materials Technology Laboratory (CANMET-MTL) is a division of Natural Resources Canada (NRCan)
CB	citizens band radio
CEC	cation exchange capacity
CGGB	Commission on Global Geochemical Baselines
CH	Chernozems
CI	confidence interval
CL	Calcisols
clr	centred log ratio
cm	centimetres, a common metric unit of distance
CM	Cambisols
cmol/kg	centimole per kilogram
COMB	combustion
C/N	carbon/nitrogen ratio
<i>conc.</i>	concentrated

Abbreviations and Acronyms

CP	cumulative probability
CRM	certified reference material
CSV	comma separated variable
CTS	collaborative trial in sampling
CV	coefficient of variation
CV-AAS	cold vapour atomic absorption spectrometry
DCA	Direct Current Arc; Emission Spectrometry
DC-OES	direct current optical emission spectroscopy
DL	detection limit
DOC	Dissolved Organic Carbon (It is defined as the organic matter that is able to pass through a filter ranging in size between 0.7 and 0.22 μm)
DS	sand dunes
DUPA	first routine duplicate field sample split
DUPB	second routine duplicate field sample split
EA	elemental analyser
EC	electrical conductivity
ED	energy dispersive
EDA	exploratory data analysis
ED(P)XRFS	energy dispersive polarised X-ray fluorescence spectrometry
ED-XRF	energy dispersive X-ray spectrometry
<i>e.g.</i>	Latin <i>exempli gratia</i> ; for example
EGS	EuroGeoSurveys (Geological Surveys of Europe)
EPIRB	emergency position-indicating radio beacon
ESDAC	European Soil Data Centre
ESDB	European Soil Database
ESRI	Environmental Systems Research Institute
<i>et al.</i>	Latin <i>et alii, et alia</i> ; and others
<i>etc.</i>	Latin <i>et cetera</i> ; and the rest; and similar things; and so on
EuroGeoSurveys	Geological Surveys of Europe
FA	fire assay
F-AAS	flame atomic absorption spectrometry
FAO	Food and Agriculture Organization of the United Nations
FEP	fluorinated ethylene propylene
FL	Fluvisols
FME	feature manipulation engine
FOREGS	Forum of European Geological Surveys (now EuroGeoSurveys)
FR	Ferralsols
g	gram
G-BASE	Geochemical Baseline Survey of the Environment (United Kingdom Geochemical Mapping programme)
GEMAS	GEochemical Mapping of Agricultural and grazing land Soils (project of EuroGeoSurveys' Geochemistry Expert Group)
GF-AAS	graphite furnace atomic absorption spectrometry
GG	glaciers
GGRN	Global Geochemical Reference Network

Abbreviations and Acronyms

GIS	geographical information system
GL	Gleysols
GMN	Global Marine Network
GPS	global positioning system
GR	Greyzems
GRAV	gravimetry
GRN	Global Reference Network
GSC	Geological Survey of Canada
GTK	Geologian Tutkimuskeskuksen (Geological Survey of Finland)
GTK	Geologian Tutkimuskeskuksen (Geological Survey of Finland)
GTN	Global Terrestrial Network
GY	Gypsisols
h	hour
HB	degree of pencil hardness (hard black pencil)
HCl	hydrochloric acid
HClO ₄	perchloric acid
HF	hydrofluoric acid
HG-AFS	hydride generation atomic fluorescence spectrometry
HNO ₃	nitric acid
HR-ICP-MS	high-resolution inductively coupled plasma atomic mass spectrometry
HS	Histosols
HWSD	Harmonised World Soil Database
IC	ion chromatography
IC	interlaboratory comparison
ICDD	International Centre for Diffraction Data
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectrometry (similar to ICP-OES)
ICP-ES	inductively coupled plasma emission spectrometry
ICP-MS	inductively coupled plasma atomic mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry (similar to ICP-AES)
ICP-SFMS	inductively coupled plasma - sector field mass spectrometry
ICP-TOF-MS	inductively coupled plasma-mass spectrometry (ICP-MS) instrument equipped with a time of flight (TOF) mass analyzer
ID	identifier; it uniquely identifies an object or a record
IDL	instrument detection limit
ID-TIMS	isotope dilution thermal ionisation mass spectrometry
IDW	inverse distance weighting
IGME	Instituto Geológico y Minero de España
IGME	Institute of Geology and Mineral Exploration (Hellenic Republic), presently the Hellenic Survey of Geology and Mineral Exploration
IIASA	International Institute for Applied Systems Analysis
ilr	isometric log ratio
INAA	instrumental neutron activation analysis
IR	infra-red
IR	non-dispersive infrared carbon analyser

Abbreviations and Acronyms

IS	island
ISE	ion selective electrode
ISO	International Organization for Standardization
ISO - BS EN	International Organization for Standardization - British Standards European Norm
ISRIC	International Soil Reference and Information Centre
ISSCAS	Institute of Soil Science of the Chinese Academy of Sciences
IUGS	International Union of Geological Sciences
JRC	Joint Research Centre of the European Commission
K	potassium
KCl	potassium chloride
kg	kilogram or kilogramme, a common metric unit of mass, equivalent to 1000 grams
km	kilometre, a common metric unit of distance, equivalent to 1000 metres
KML	see kml
kml	keyhole markup language (it is a file format used to display geographical data in an Earth browser, such as Google Earth)
KClO ₃	potassium chlorate
KNO ₃	potassium nitrate
KS	Kastanozems
LA	laser ablation
LA-ICP-MS	laser ablation inductively coupled plasma atomic mass spectrometry
LCL	lower confidence limit
LDA	laser diffraction analysis
LDL	lower detection limit
LiBO ₂	lithium metaborate
Li ₂ B ₄ O ₇	lithium borate
LIF	laser-induced fluorescence
LMCR	linear model of coregionalisation
LOI	loss-on-ignition
LoQ	limit of quantification
LP	Leptosols
LPS	laser particle sizer
LPSA	laser particle size analyser
LV	Luvisols
LX	Lixisols
M	the symbol for 'molar' in chemistry, <i>i.e.</i> , it describes the concentration of a chemical solution in moles per litre (mol/l)
MA	multi-acid digestion (it is a four-acid digestion that includes HF)
MAD	median absolute deviation
MBGSZ	Mining and Geological Survey of Hungary
MC-ICP-MS	magnetic sector multicollector inductively coupled plasma mass spectrometer
µg/g	micrograms per gram
µg/kg	micrograms per kilogram

Abbreviations and Acronyms

µg/l	micrograms per litre
µm	micrometre or micron, a unit of length equal to one millionth of a metre (1 x 10 ⁻⁶ metre)
mg	milligram(s); equivalent to one millionth of a gram (10 ⁻³ gram)
mg/kg	milligrams per kilogram
mg/l	milligrams per litre
MIDW	multifractal inverse distance weighting
MIRS	mid infrared spectroscopy
mm	millimetre
MMI	Mobile Metal Ion [®]
mol/l	moles per litre
mS/m	millisiemens per metre
ml	millilitre, common metric unit of volume; one litre has 1000 millilitres
ml/g	millilitres per gram
min	minute, common metric unit of time; one hour has sixty minutes
MS	MicroSoft
MWM	moving weighted median
MΩ	one million (10 ⁶) ohms, the metric unit of electrical impedance
N/A	not assigned
Na	sodium
Na ₂ CO ₃	sodium carbonate
NaNO ₃	sodium nitrate
Na ₂ O ₂	sodium peroxide
NDIR	non-dispersive infra-red
NE	north-east
ng	nanogram(s), a metric unit of mass equal to 10 ⁻⁹ gram, or one millionth of a milligram
ng/ml	nanograms per millilitre
NGU	Norges geologiske undersøkelse (Geological Survey of Norway)
NH ₄ I	ammonium iodide
NI	no data
NIST	National Institute of Standards and Technology (USA)
NT	Nitisols
NW	north-west
OGC	Open Geospatial Consortium
P	analytical precision at the 95% confidence level
PD	Podzoluvisols
PDL	practical detection limit
PE	polyethylene
PGE	platinum group element
PGEs	platinum group elements
PGI	Polish Geological Institute
pH	German 'potenz' meaning 'power' plus the symbol for hydrogen (H); a logarithm of the reciprocal of the hydrogen ion concentration in moles per litre of a solution, giving a measure of its acidity or alkalinity
PH	Phaeozems

Abbreviations and Acronyms

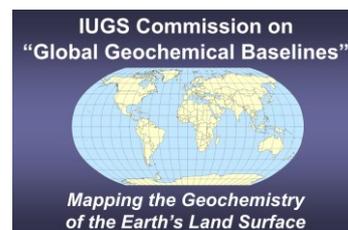
PL	Planosols
POL	Polarography
POT	Potentiometry
PP	polypropylene
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PRM	primary reference material
PRMs	primary reference materials
PSD	particle size distribution
PT	Plinthosols
PTFE	polytetrafluoroethene
PVC	polyvinyl chloride
PZ	Podzols
QA	quality assurance
QC	quality control
Q-ICP-MS	quadrupole inductively coupled plasma atomic mass spectrometry
QL	quantification limit
QR	quick response (code)
R	linear correlation coefficient
R	is a free software environment for statistical and graphical applications
RANOVA	robust analysis of variance
RDL	reported detection limit
REE	rare earth element
REEs	rare earth elements
REPA	first field replicate control sample split
REPB	second field replicate control sample split
RG	Regosols
RGB	red, green, blue
RK	rock outcrops
RM	reference material
RMA	reduced major axis
RNAA	radiochemical neutron activation analysis
rpm	revolutions per minute
RSD	relative standard deviation
SC	Solonchaks
SD	standard deviation
SGUDS	State Geological Institute of Dionyz Stur (Slovakia)
SIMS	secondary ion mass spectroscopy
SMU	soil mapping unit
SN	Solonetz
SnCl ₂	stannous chloride
SOP	standard operating procedure
SOPs	standard operating procedures
SOTER	soil and terrain databases
SOTWIS	SOTER-derived databases

Abbreviations and Acronyms

SPT	sampling proficiency test
SQ-ICP-MS	single quadrupole inductively coupled plasma atomic mass spectrometry
SRM	secondary reference material
SRMs	secondary reference materials
ST	salt flats
STU	silver-thiourea extraction
SUS	susceptibility meter
S _w	within-unit standard deviation
SW	south-west
TDS	total dissolved solids
TNO	Geological Survey of The Netherlands
TOC	total organic carbon
TOT	total digestion (fusion then digestion by HF + HNO ₃ after fusion)
TIT	titrimetry
TQ-ICP-MS	triple quadrupole inductively coupled plasma atomic mass spectrometry
UCL	upper confidence limit
UK	United Kingdom
UKAS	United Kingdom Accreditation Service
UN	United Nations
UNESCO	United Nations Educational, Scientific and Cultural Organization
UR	urban, mining, <i>etc.</i>
USA	United States of America
USB	Universal Serial Bus
US EPA or USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USN-ICP-MS	ultrasonic nebuliser inductively coupled plasma emission spectrometry
UTM	Universal Transverse Mercator
UV	ultra-violet
VNIRS	Visible Near InfraRed Spectroscopy
VR	Vertisols
v/v	volume concentration of a solution is expressed as % v/v, which stands for 'volume per volume'
W	watt
WD	wave dispersive
WD-XRFS	wave dispersive X-ray fluorescence spectrometry
WGS84	World Geodetic System is a standard for use in cartography, geodesy, and navigation (dating from 1984 and last revised in 2004)
WR	Water bodies
WRB	World Reference Base for Soil Resources
wt%	weight per cent
X	the independent variable in the linear equation $Y = B * X + A$
\bar{x}	arithmetic mean
XRD	X-ray diffraction
XRF	X-ray fluorescence used when referring to the instrument

Abbreviations and Acronyms

XRFS	X-ray fluorescence spectrometry used when referring to method
XRFDW	see WD-XRFS
Y	the dependent variable in the linear equation $Y = B \cdot X + A$



**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 1

General Introduction

Alecos Demetriades^{1,4}, Christopher C. Johnson^{2,4}, David B. Smith⁴,
Timo Tarvainen^{3,4}, Reijo Salminen³

¹ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

² GeoElementary, Derby, United Kingdom

³ Geological Survey of Finland, Espoo, Finland

⁴ IUGS Commission on Global Geochemical Baselines

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1.1. Introduction

Development of a global-scale geochemical database has been an active topic of discussion among applied geochemists for over four decades (Darnley, 1990, 1997; Darnley *et al.*, 1995; Bølviken *et al.*, 1996; Smith *et al.*, 2018). This is a database involving multiple sample media covering the entire land surface of the Earth that requires consistent and standardised methods for sampling, sample preparation, analysis and quality control. The data sets shall be based on the systematic collection and analysis of random samples of rock, residual soil, organic material (humus), stream water, stream sediment, overbank sediment and floodplain sediment from all countries. High quality and consistency of the generated data sets shall be achieved by using standardised sampling and sample preparation methods, and by analysing all collected samples in the same laboratories for the same suite of determinands as has already been done in the geochemical mapping of Europe (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006).

The present Manual contains comprehensive instructions for selecting random sample sites (Chapter 2) and for collecting each sample medium (Chapters 3.1 to 3.5). Further, it includes methods for sample preparation and storage (Chapter 4), development of reference materials (Chapter 5), geoanalytical methods (Chapter 6), quality control procedures (Chapter 7), data conditioning (Chapter 8), database management and map plotting (Chapter 9), and project management (Chapter 10).

The methods described in this Manual should prove useful to applied geochemists designing and implementing systematic geochemical surveys at any mapping scale.

1.2. Need for global geochemical baseline data

There is worldwide concern over the potentially damaging effects of chemicals in the environment on the health of humans, animals, and ecosystems (*e.g.*, Nriagu, 1979; Thornton, 1983, 1988; Nriagu and Pacyna, 1988; Plant *et al.*, 2001, 2005; Plant and Smith, 2003; Skinner and Berger, 2003; Selinus *et al.*, 2005, 2010, 2013; Hester and Harrison, 2006; Gaans *et al.*, 2007; CDC, 2009, 2021; Chen *et al.*, 2021). Economic development and population growth are exacerbating such problems as land degradation and contamination from uncontrolled urbanisation, industrialisation, deforestation, intensive agricultural practices, and overexploitation of aquifers. These human activities, together with natural processes (*e.g.*, volcanic eruptions, weathering, erosion, flooding, desertification, devastating forest fires and extremes of weather-driven by changing climate) are having an impact on the geochemistry of the Earth's land surface and the sustainability of its life-support systems from the local to the global scale (FAO and ITPS, 2015; FAO and UNEP, 2021). There is also concern about the need to meet worldwide future demands for mineral and energy resources (EC, 2020). This requires the discovery of new resources and their development in an environmentally responsible manner (Nickless *et al.*, 2015; Ali *et al.*, 2017).

Defining and understanding the current abundance and spatial distribution of chemicals in the Earth's surface or near-surface environmental compartments such as soil, sediment, surface and groundwater, and vegetation, the so-called 'critical zone' (Brantley *et al.*, 2007), are essential first steps in being able to recognise, quantify, and ultimately address natural or human-induced changes in the future. Darnley *et al.* (1995, p.x) summarised the need for a harmonised global geochemical database with the following timeless statements:

“Everything in and on the earth - mineral, animal and vegetable - is made from one, or generally, some combination of, the naturally occurring chemical elements (Fig. 1.1). Everything that is grown, or made, depends upon the availability of the appropriate elements. The existence, quality and survival of life depends upon the availability of elements in the correct proportions and combinations.

Because natural processes and human activities are continuously modifying the chemical composition of our environment, it is important to determine the present abundance and spatial distribution of the elements across the Earth's surface in a much more systematic manner than has been attempted hitherto”.

Five years later, Dr. Mary Lou Zoback, former President of the Geological Society of America, condensed the same issue eloquently in her Geological Society of America's 2000 Presidential address:

“Documenting and understanding natural variability is a vexing topic in almost every environmental problem: How do we recognize and understand changes in natural systems if we don't understand the range of baseline levels?” (Zoback, 2001, p.41).

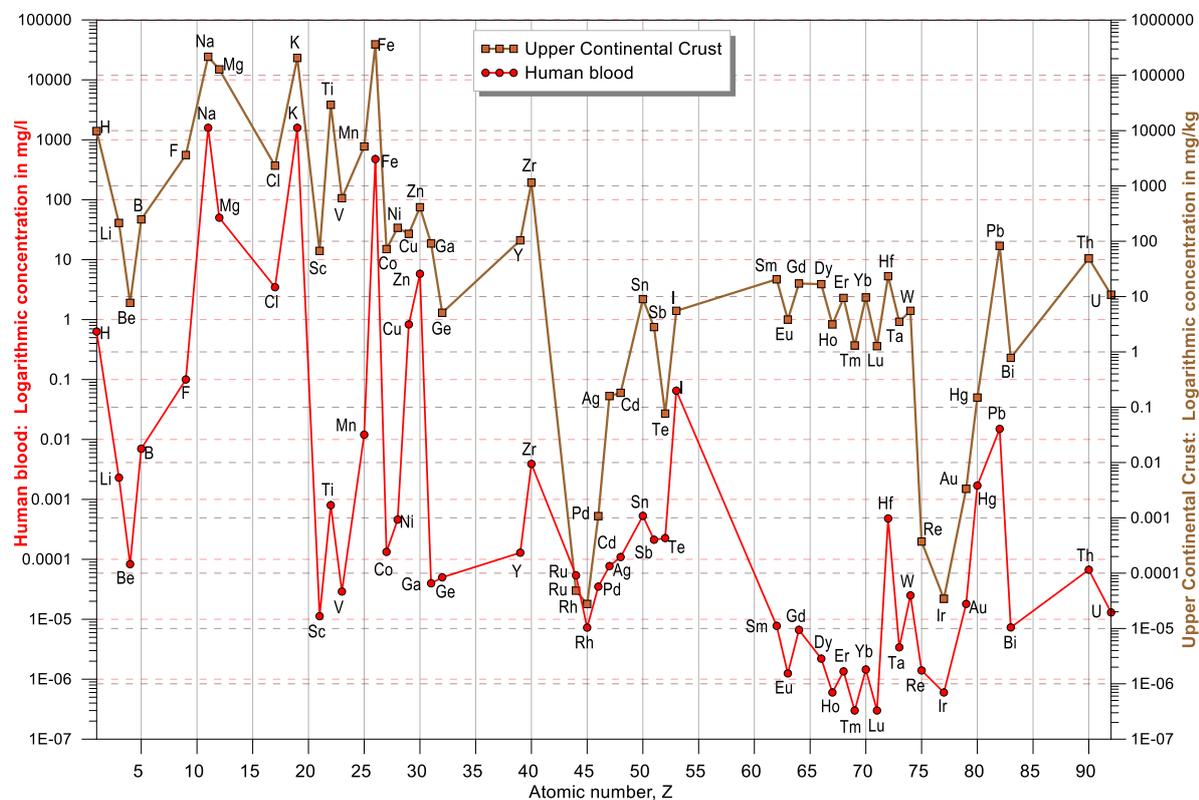


Figure 1.1. Graph showing the relationship between selected major and trace element mean concentrations in the upper continental crust and human blood. Their similar trend indicates that there is a close relationship between the chemical composition of human blood and the materials of the upper continental crust, although there is a significant difference in magnitude. Data sources: Upper Continental Crust (Reimann *et al.*, 2004, Table 11.1, p.105); Human blood (ALS Global, 2021). Drawn with Golden Software's Grapher™ v20 by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) & IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).

Systematic geochemical mapping is the best method available to assess and provide a baseline for monitoring changes in the levels of chemical elements at the Earth's surface (*e.g.*, Reimann and Caritat, 2005; Reimann *et al.*, 2018). Geochemical maps have traditionally been valuable in addressing a range of environmental problems at the local to national scale (*e.g.*, Thornton and Howarth, 1986; Birke *et al.*, 2015; Demetriades *et al.*, 2018; Levitan *et al.*, 2018; Lich, 2018), as well as for identifying areas with potential mineral resources (*e.g.*, Reimann and Caritat, 2005; Reimann *et al.*, 2007; Rapant *et al.*, 2008; Demetriades, 2014, 2021; Birke *et al.*, 2016; Reimann *et al.*, 2016; Caritat, 2018).

Several decades of geochemical mapping by national geological surveys and related organisations throughout the world have resulted in a wealth of valuable information (*e.g.*, Plant and Ridgway, 1990; Plant *et al.*, 1996, 1997; Darnley *et al.*, 1995; Garrett *et al.*, 2008). However, these data do not provide global coverage and cannot readily be applied to broader-scale regional or global studies because they have been generated by different sampling, sample preparation, and analytical methods. Part of the reason for this inconsistency is that there are no internationally accepted standards for geochemical surveys.

To be useful and authoritative, particularly at the global scale, geochemical baselines must be derived from data generated according to well-defined protocols that are applicable across a wide range of geomorphological landscapes, climatic zones, and ecological regions. It is possible that incompatible regional geochemical data sets could be more effectively used if normalised to a Global Geochemical Reference Network data set, *that is*, data generated from a worldwide suite of geochemical samples collected, prepared, and analysed using a universally consistent set of protocols. The purpose of this Manual of standard geochemical methods is to provide detailed instructions for establishing this global reference data set.

According to Darnley *et al.* (1995), the Global Geochemical Reference Network multi-media samples and the ensuing databases are intended to serve several purposes by providing:

- (1) Authoritative documentation concerning the chemical and mineralogical composition of a variety of surficial materials at locations evenly spaced over the land surface of the globe.
- (2) A supply of locally relevant standard reference materials for ongoing use in the region of origin.
- (3) A random set of global reference network points for normalising national and international geochemical databases.
- (4) A framework of systematic baseline data will make possible the preparation of a World Geochemical Baseline Atlas.
- (5) Samples on which further work can be undertaken, *e.g.*, to undertake isotopic analysis, speciation studies, determine organic pollutants, *etc.*, and
- (6) Sites for recurrent monitoring in the future, to facilitate the recognition and measurement of 'change', from whatever cause, natural or human-induced.

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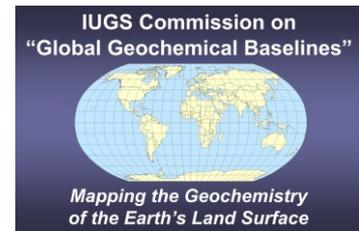
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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 2

**Global Terrestrial Network Grid Cells,
Selection of Sample Sites, and
Sample Types to be Collected**

Alecos Demetriades^{1,5}, Christopher C. Johnson^{2,5}, David B. Smith⁵,
Timo Tarvainen^{3,5}, Maria João Batista^{4,5}

¹ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

² GeoElementary, Derby, United Kingdom

³ Geological Survey of Finland, Espoo, Finland

⁴ Laboratório Nacional de Energia e Geologia, Amadora, Portugal

⁵ IUGS Commission on Global Geochemical Baselines

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2.1. Introduction

Production of coherent and quantitative geochemical maps to portray the chemical composition of the world's land surface is necessary, and requires the establishment of a suitable multi-media sample reference framework. One may ask the question: *How can such a geochemical reference framework of multi-media samples be developed?*

To answer this question, let us go back in time, long before the advent of global navigation satellite systems in the 1980s, and consider an analogy with topographical map making. At that time producing accurate topographical maps required the establishment of a 3-dimensional ground geodetic network. The core of this geodetic network was the 'triangulation point or trig point'¹, which was a reference point on the land surface with precise longitude and latitude coordinates and elevation above the datum. The corners of the trig point network were usually located on hilltops, each visible from at least two others. The angles between the lines joining them were measured precisely, and this process was called triangulation (Higgins, 1974; Musseter, 1985; Britannica, 2012, 2016; Simmons, 2014). Mapping the morphology of the land surface, surveyors used triangulation surveying by generating a denser set of intermediate spot levels, depending on the mapping scale. Thus, surveying may be described as the art of making measurements upon the earth's surface to produce a topographical map. Levelling is combined with surveying when it is required to determine the differences in elevation of points on the earth's surface to portray the variation of the height of the topography surveyed with either contour lines, or in vertical sections (Strahler, 1969; Higgins, 1974). If this 3-dimensional Geodetic Reference Network on a topographical map is studied, it can be observed that the trig points are randomly distributed.

Similar to topographical mapping, a Global Geochemical Reference Network representing element concentrations generated on a set of multi-media samples collected from randomly selected sites fulfils a comparable function for the geochemical mapping of the Earth's terrestrial surface (Darnley, 1997). Each Global Geochemical Reference Network sample point has coordinates as the trig point in surveying, and the element concentration of each reference sample type is analogous to the elevation or height of the trig point. As with a geodetic network, a geochemical reference network is not concerned with local detail, but the latter, as it is acquired, should be tied into the fixed points of the network (Darnley *et al.*, 1995). Hence, what is required is the establishment of '*fixed point element concentrations*' across the earth's land surface, generated with a harmonised quality-controlled methodology from sampling and sample preparation to chemical analysis. The methodology for the many steps required to establish the global geochemical reference network is the subject of this Manual. With the establishment of such a multi-media 3-dimensional Global Geochemical Reference Network of '*fixed point element concentrations*' (the geochemical datum), it will be possible to level national geochemical data sets of each sample type, and produce detailed maps, as the surveyors do in the production of topographical maps.

In conclusion, just as the foundation for detailed topographical surveys is provided by a primary 3-dimensional geodetic network, a comparable 3-dimensional reference network of each sample type is required for geochemical surveys. Darnley *et al.* (1995) proposed that the highest order grid cell in the global geochemical mapping hierarchy should be 160x160 km, an area of 25,600 km². A collection of standard reference materials of each sample type is required from these grid cells over the entire land surface of the world as the first step in the technical implementation of the global geochemical project. This Global Geochemical Reference Network (GGRN), based on carefully controlled sampling and geoanalytical requirements, as detailed in

¹ Triangulation station or Trigonometrical point or Trig point or Trig pillar: A survey point with known coordinates and elevation, which is marked on the ground by a concrete pillar with an engraved brass plate on its top, providing a mounting base for a theodolite. Trig points are usually situated on hilltops for the purposes of visibility. On a topographical map trig points are indicated by a small triangle, and its precise elevation recorded besides it.

this Manual, will provide an inter-regional (and intercontinental) framework to which more detailed or more specialised local geochemical surveys can be related.

2.1.1. Levelling of existing data sets

Darnley *et al.* (1995, p.75) discuss the different methods for levelling and normalisation of existing data sets, namely (a) parametric levelling, and (b) non-parametric normalisation (fractile normalisation, Clarke normalisation, quantile regression), and pointed out that such procedures are ‘geochemically blind’ because they simply manipulate numbers. They also state the conditions for the selection of data sets for compilation. *For example*, data sets for levelling should be comparable, *e.g.*, stream sediment GGRN data with regional stream sediment, and soil GGRN data with regional and detailed soil survey data sets. Further, it is stressed that it would likely be inappropriate to attempt to level data sets of cold partial extraction and total element concentrations, and similarly stream sediment results with heavy mineral concentrate data (see Annexes A2.1 and A2.2 for worked levelling examples).

2.2. Global terrestrial network grid cells

To establish the Global Geochemical Reference Network, Darnley *et al.* (1995) proposed that a variety of sample media should be collected according to grid-based sampling over the entire land surface of the Earth. The computation of the Global Reference Network (GRN) grid cells, covering the whole globe, was carried out in 1994 by Nils Gustavsson (Geological Survey of Finland). In total, there are 19,833 grid cells of 160x160 km (Fig. 2.1). The original Microsoft™ Access file was provided to the IUGS Commission on Global Geochemical Baselines in August 2018 by Robert G. Garrett (Geological Survey of Canada). Both, the generated Microsoft™ Excel file with all 19,833 grid cells, and the Google Earth *.kml file, are available for downloading from the website of the [IUGS Commission on Global Geochemical Baselines](#) (refer to the Supplementary material for more details).

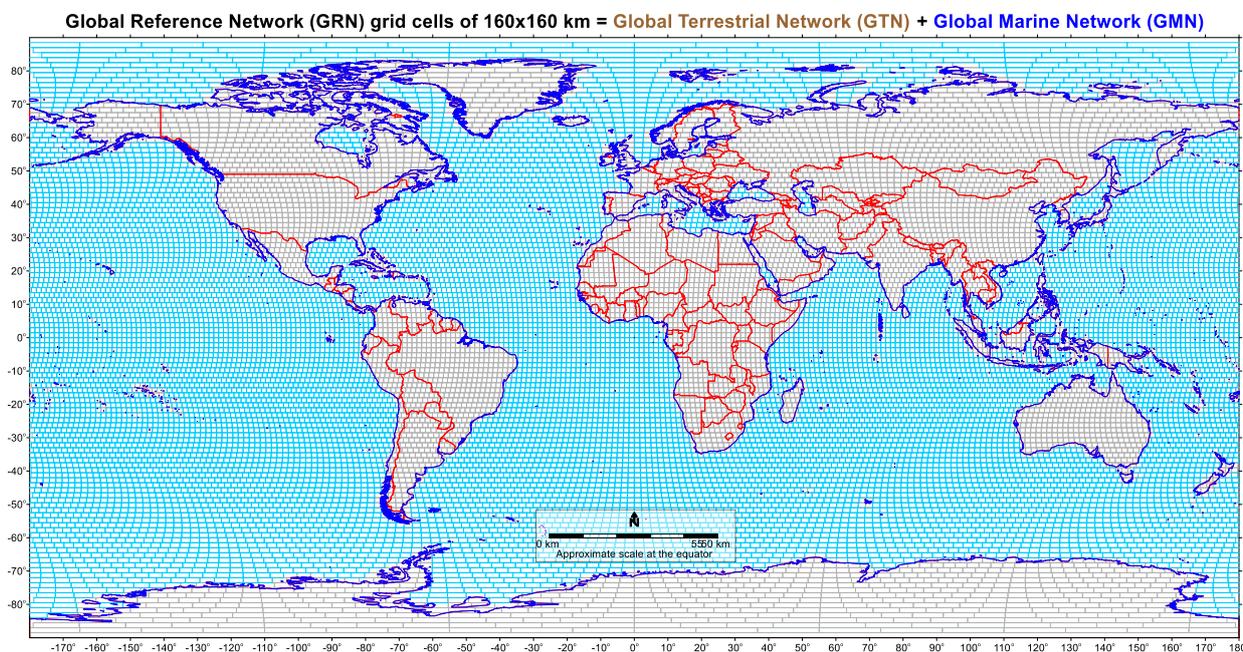


Figure 2.1. The Global Reference Network (GRN) grid cells consist of the Global Terrestrial Network (GTN) and Global Marine Network (GMN) grid cells. The nominal size of each 160x160 km grid cell is defined by two parallels of latitude $1\frac{1}{2}^\circ$ (approx. 166 km) apart, and two meridians. In order to retain a constant area, the grid cells are systematically displaced in longitude East and West in successive latitudinal bands. Drawn with Golden Software's Surfer™ v21 by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) & IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).

The 160x160 km grid cells (for the entire world) have their origin on the equator at the 0° (Greenwich) meridian and they are symmetrical North and South of the equator. For practical convenience, the cells are bounded by lines of latitude 1½° apart (approximately 166 km). To retain a constant area of 25,600 km² the meridians defining East and West boundaries are systematically displaced in longitude East and West in successive latitudinal bands. Overlap in the vicinity of the international dateline is ignored because it occurs over the Pacific Ocean.

The original Global Terrestrial Network (GTN) grid cells file, covering the land surface of the Earth, used in 1997 for planning the FOREGS Geochemical Atlas of Europe project, comprised 5711 grid cells (Salminen, Tarvainen *et al.*, 1998). Upon plotting the grid cells on a world map, it was discovered that many grid cells near coastal areas and over islands were missing. The reason for the missing grid cells was that their centre fell over a water body (ocean, sea, lake), and were thus deleted because each 160x160 km grid cell is required to have within it a minimum of three random sites for sampling. This is an important requisite of triangulation and levelling the data sets of regional and detailed geochemical surveys to their respective Global Geochemical Reference Network data sets (see Section §2.1 above). Of course, this was discovered during the FOREGS Geochemical Atlas of Europe project and was corrected for countries that started their sampling campaign a little later than the June 1997 kick-off. The reason for making this correction is that geochemical data are required from all grid cells for the compilation of global geochemical baseline maps.

For planning the Global Geochemical Reference Network project for the entire terrestrial surface of the Earth, a new file was generated by adding all the missing coastal grid cells and over islands. This new Microsoft™ Excel file, covering the terrestrial surface of the Earth, consists of 7356 grid cells of 160x160 km (Fig. 2.2), and is available, together with the Google Earth *.kml file, from the website of the [IUGS Commission on Global Geochemical Baselines](#).

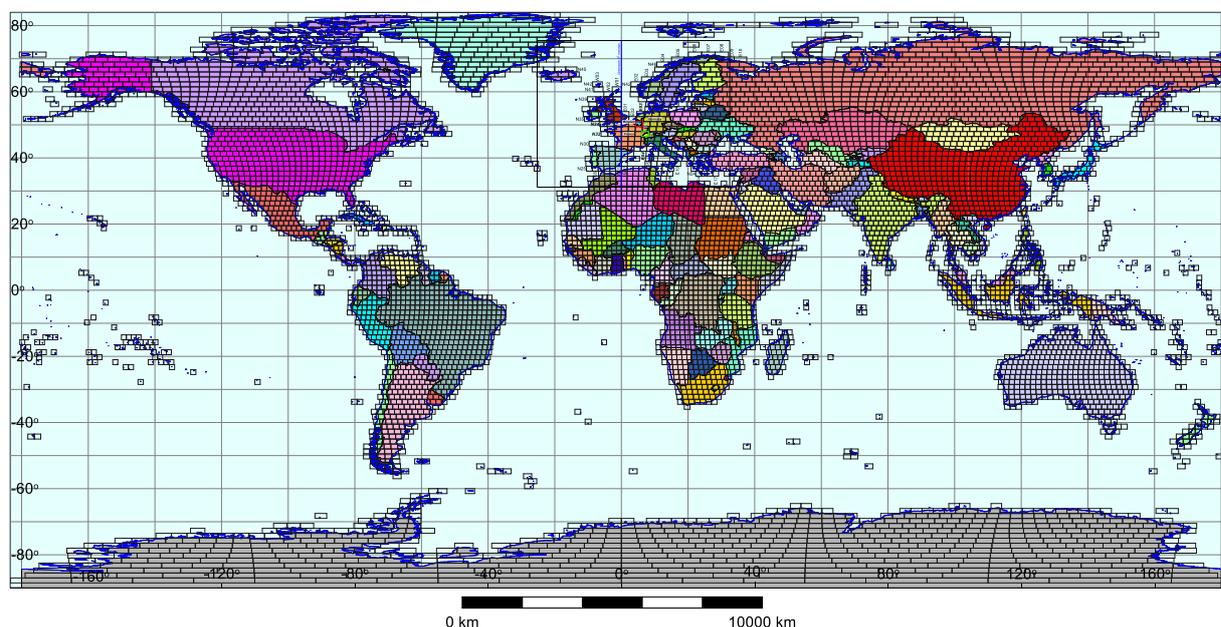


Figure 2.2. The 7356 Global Terrestrial Network (GTN) grid cells cover the entire land surface of the Earth, including islands. The nominal size of each 160x160 km grid cell is defined by two parallels of latitude 1½° (approx. 166 km) apart, and two meridians. For keeping a constant area, the grid cells are systematically displaced in longitude East and West in successive latitudinal bands. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8.

2.2.1. Identifiers of GTN grid cells

The identifiers of GTN 160x160 km grid cells consist of a four-part label:

- The latitude letter code ‘N’ and ‘S’, representing North and South from the equator, respectively.
- The longitude letter code ‘E’ and ‘W’, representing East and West from the 0° Greenwich meridian, respectively.
- A two-digit number after the latitude letter code (N or S), representing the position of the grid cell North or South from the equator, and
- A two-digit number after the longitude letter code (E or W), representing the position of the grid cell East or West from the 0° Greenwich meridian.

For example, the identifier N34E03 denotes that this 160x160 km GTN grid cell is the 34th cell to the North of the equator, and the 3rd cell to the East of the 0° Greenwich meridian, and covers parts of Belgium, France, Luxemburg and Germany (Fig. 2.3).

2.2.2. GTN grid cell coordination

The coordination of sampling within the 160x160 km grid cells falling completely within a country is coordinated by its national organisation. Some grid cells are located in more than one country. In these cases, sampling of that particular cell is coordinated by the national organisation of the country in which the centre of the grid cell is located. For example, grid cell N32E04 falls in Switzerland, France and Germany, and its centre is in Switzerland (Fig. 2.3).

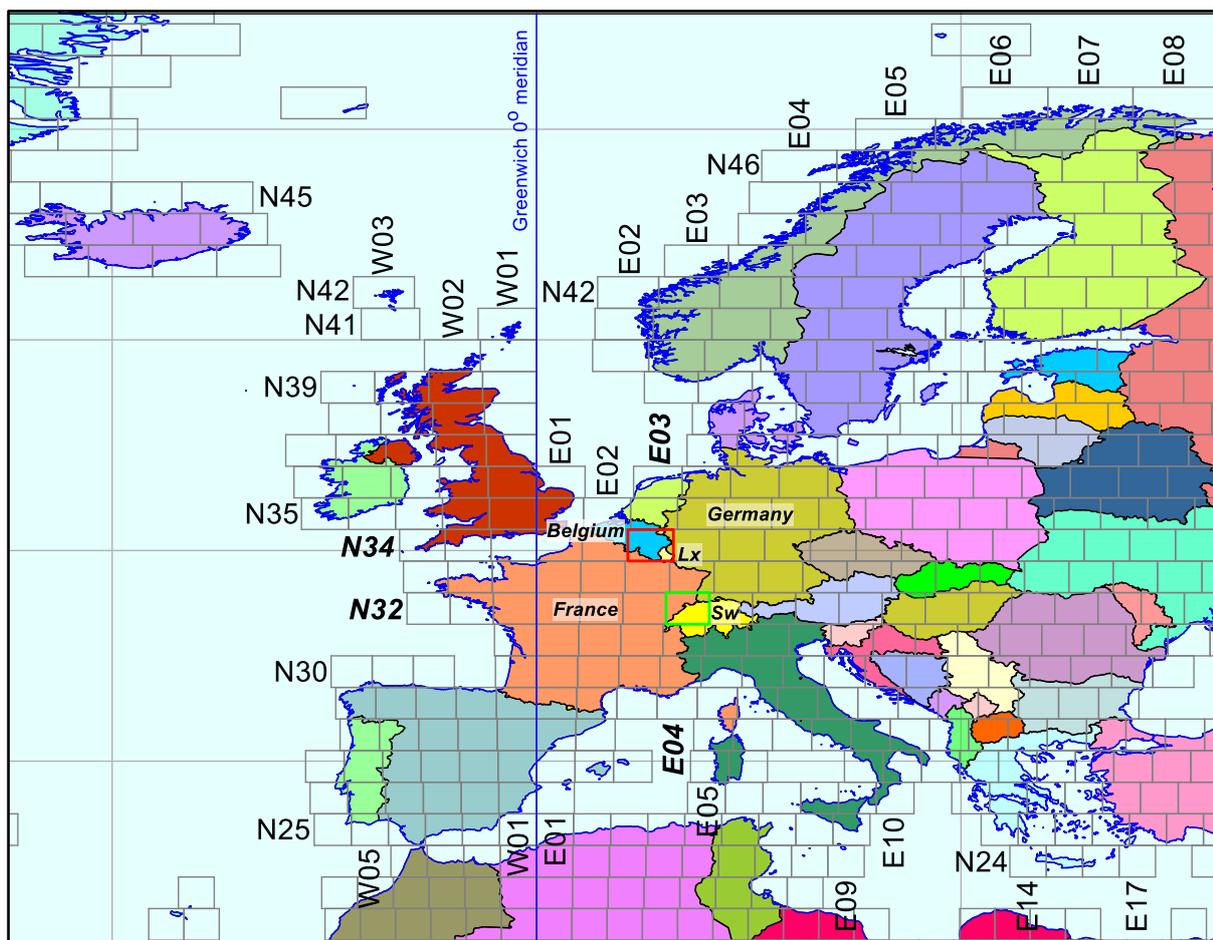


Figure 2.3. Map showing the FOREGS Geochemical Atlas of Europe area and adjacent countries. The coded numbers indicate the North-South and East-West GTN grid cell numbering system used in the Global Geochemical Reference Network project. The red colour lined GTN grid cell N34E03 covers Belgium, Luxembourg (Lx), France and Germany, and the green colour lined GTN grid cell N32E04 covers Switzerland (Sw), France and Germany. In the former case, Belgium is the coordinating country, and in the latter case is Switzerland. Refer to the text for an explanation. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8.

Therefore, the sampling in this particular grid cell is coordinated by Switzerland, and the Swiss organisation, responsible for its sampling, should get in touch with the French and German organisations for the sampling of catchment basins falling in their countries.

It is noted that the coordinating countries for the sampling of each 160x160 km grid cell are indicated in the relevant Microsoft™ Excel file, which can be downloaded from the website of the [IUGS Commission on Global Geochemical Baselines](#) (refer to the Supplementary material). Hence, the first task of each national organisation is to find out all grid cells that are coordinated by its country, and are its responsibility for their sampling. It is recommended to plot the 160x160 km grid cells on 1:50,000 scale topographical maps, and on a smaller scale topographical map, depending on the size of the country. The latter map provides an overview, and is used for planning purposes.

Important note: A condition that must be observed in the Global Geochemical Reference Network project is that the participating national organisations must not carry out any sampling on the territory of any other country without a previous written agreement with the organisation responsible for sampling in that particular territory. If one or more of the randomly selected catchments are located in a neighbouring country, it is important to contact the organisation responsible for the coordination, and to reach an agreement on their sampling.

2.3. Sample types to be collected

All sample types, mentioned below, are mandatory and must be collected from each randomly selected second- and third-order catchment basin, as this is the only way to establish reference sample suites of permanent value with the objective for their results to be used for (a) levelling to a common geochemical datum the results of more detailed geochemical mapping projects, and (b) compilation of a multi-media Global Geochemical Baselines atlas.

The following sample types must be collected from second-order catchment basins of an area of <100 km²:

- Rock
- Residual soil (Top and Bottom)
- Humus (where present)
- Stream water (where present)
- Stream sediment, and
- Overbank sediment (Top and Bottom).

The following sample type must be collected from third-order catchment basins of an area between 1000 and 6000 km², except for the cases mentioned above:

- Floodplain sediment (Top and Bottom).

2.3.1. Sample identifiers

The codes tabulated in Table 2.1 characterise the sample types to be collected from the second- and third-order catchment basins, according to the Strahler (1957, 1969) stream magnitude order classification, and a topographical map scale of 1:50,000.

The following identifier N26E14S3 clarifies the sample identification system where:

N26E14	= GTN grid cell identification code
S	= Sample medium code (in this case is Stream sediment)
3	= Random catchment (drainage) basin number

This grid cell is explained in greater detail and presented graphically in Section §2.6.

The field duplicate sample code for all sample types is ‘D’. In this case, for the stream sediment sample it would be N26E14S3D.

The identifier for the blank water (W) and blank solid (T) samples is zero (0), *i.e.*,

- GTN grid cell/random point number/W/0 (zero), *e.g.*, N26E14W30, and
- GTN grid cell/random point number/T/0 (zero), *e.g.*, and N26E14T30.

Table 2.1. Sample identifier codes, and example using GTN grid cell N26E14 and random site number 3 (see Section §2.6 where there is a detailed explanation).

<i>Catchment basin</i>	<i>Sample type</i>	<i>Code</i>	<i>Example</i>
Second-order (<100 km ²)	Rock	R	N26E14R3
	Residual soil – Top	T	N26E14T3
	Residual soil – Bottom	C	N26E14C3
	Humus (where present)	H	N26E14H3
	Stream water (where present)	W	N26E14W3
	Stream sediment (mineral sediment)	S	N26E14S3
	Overbank sediment – Top	K	N26E14K3
Overbank sediment – Bottom	N	N26E14N3	
Third-order (1000-6000 km ²)	Floodplain sediment – Top	F	N26E14F3
	Floodplain sediment – Bottom	L	N26E14L3

2.4. Random sampling design

The catchment basins for sampling are represented by points in each Global Terrestrial Network (GTN) grid cell of 160x160 km, and are totally randomised. Darnley *et al.* (1995) recommended either a 5- or an 8-random point sampling scheme for the Global Geochemical Reference Network project (Fig. 2.4), and each country is free to select the scheme it will follow. Of course, the latter scheme, with an additional 3 random points, is better for both levelling the results of more detailed geochemical surveys, and for producing global geochemical baseline maps. However, the 5-random point scheme is more cost- and time-effective, and it has been used successfully for the FOREGS Geochemical Atlas of Europe project (Salminen, Tarvainen *et al.*, 1998; Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006).

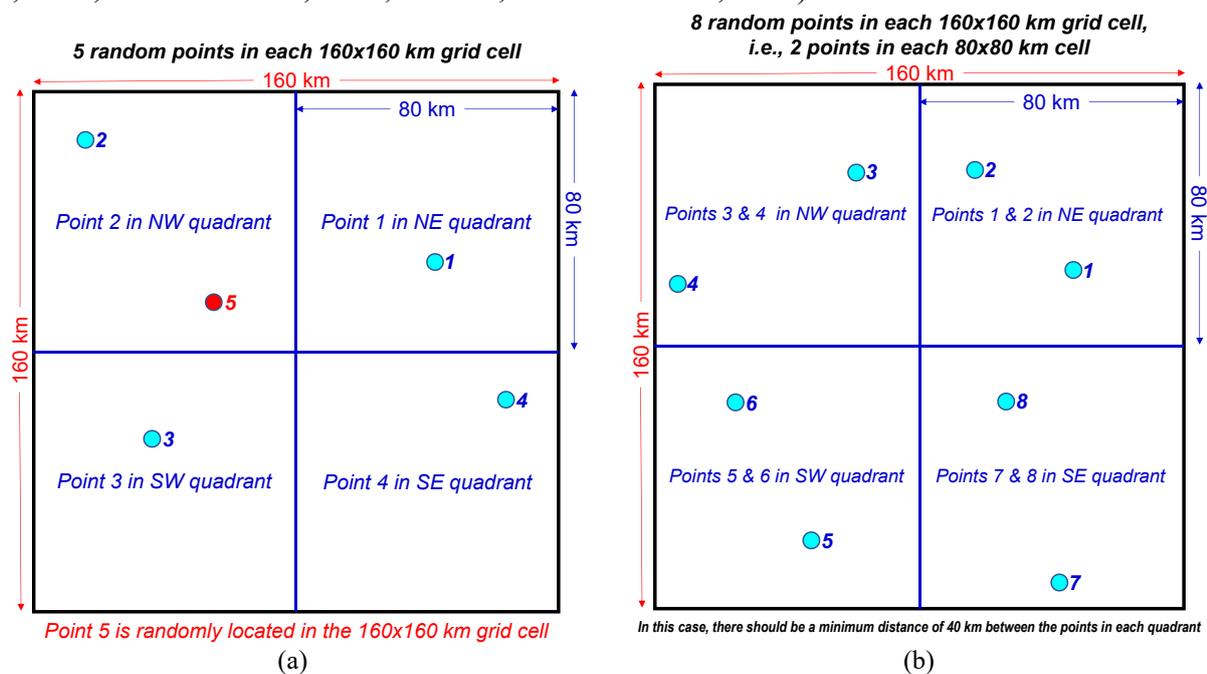


Figure 2.4. Random sampling schemes in each 160x160 km GTN grid cell: (a) 5-random point sampling scheme, and (b) 8-random point sampling scheme. Diagrams plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Microsoft™ PowerPoint.

The 5- and 8-random point sampling schemes were generated by R-scripts written and run by He and Geng (2022). The Microsoft™ Excel and Google Earth *.kml files of both schemes are available for downloading (refer to the Supplementary material). With respect to the 5-random sampling site scheme, point number 1 is located in the NE quadrant of the GTN grid cell, number 2 in the NW quadrant, number 3 in the SW quadrant and number 4 in the SE quadrant (Fig. 2.4a). Point number 5 is randomly located within the 160x160 km grid cell. If a national coordinator is not satisfied with the available random points for his/her country, the R-script, accompanied by instructions, is available and can be run for the generation of a new set of random points for planning the sampling campaign. The R-script for generating new random points can be run either for the GTN grid cells covering the whole country or for just a particular GTN grid cell.

2.5. Selection of catchment basins for sampling

The national set of 5-random points in each GTN 160x160 km grid cell should be plotted on 1:50,000 scale topographical maps for planning the sampling campaign. If the 1:50,000 scale topographical maps are not available in digital form, then the 5-random points should be plotted by hand by using the coordinates of each point.

2.5.1. Selection of small drainage basins in each GTN grid cell

The 5-random points in each 160x160 km GTN grid cell are used to select the five nearest small second-order drainage basins of <math><100\text{ km}^2</math> in area, according to the Strahler stream magnitude order classification system (Strahler, 1957, 1969). This is the smallest unit where pristine samples could be collected. The criteria that should be used for the selection of the small drainage basin for the collection of rock, residual soil (top and bottom), stream water, stream sediment and overbank sediment (top and bottom) (see Figs. 2.5, 2.6, 2.7 & 2.8) are:

- Rock samples should represent the dominant rock type, and
- Residual soil should represent the dominant soil type within the small catchment basin.

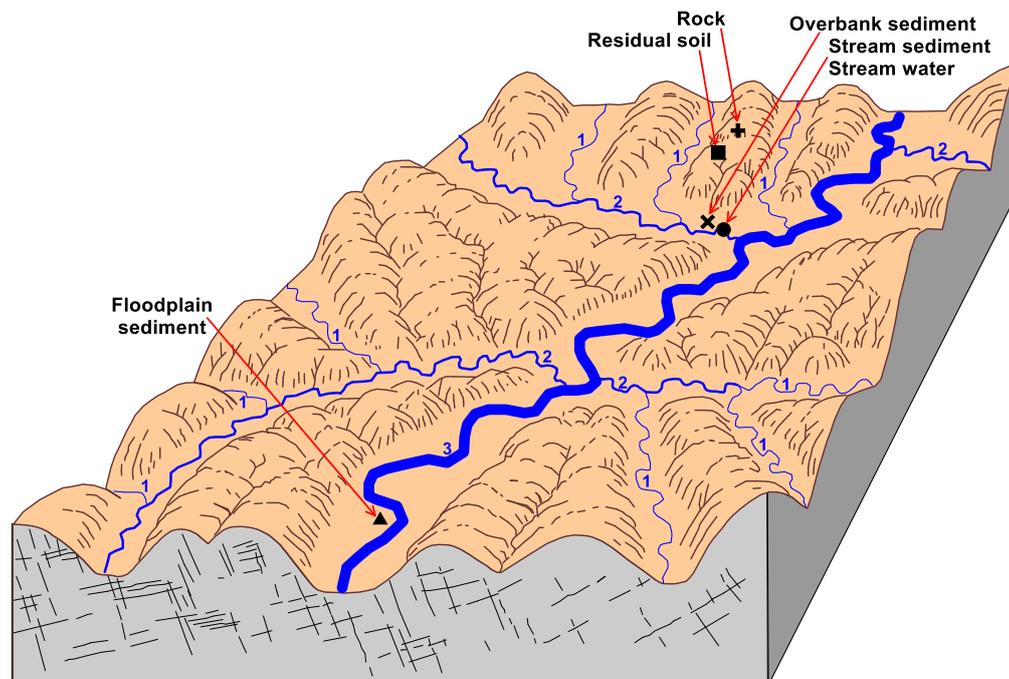


Figure 2.5. Block diagram showing possible sites of GTN sampling media in second- and third-order catchment basins at a mapping scale of 1:50,000. Notation: Numbers 1, 2 and 3 indicate catchment basin order according to the Strahler stream classification magnitude order (after Strahler, 1969, Fig. 27.1E, p.499, with minor modifications). Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8.

It is, therefore, recommended that geological and soil maps, if available, should be studied during the planning stage of the sampling campaign.

In case the random point happens to fall in the sea or a lake or an unreachable area, the nearest accessible small catchment basin should be used (see Fig. 2.8).

2.5.2. Selection of large drainage basins in each GTN grid cell

The large drainage basin with an area of 1000 to 6000 km² is easy to find because it is physically connected to the selected small catchment basin of <100 km² in area (see Figs. 2.5 & 2.8).

If no suitable size drainage basin is available, the top and bottom floodplain sediment samples can be taken from a smaller third-order drainage basin (>500 to 1000 km²). Justified exceptions to these specifications are the collection of samples from small countries and small islands, as in the case shown in Figure 2.8. What is important in such exceptional cases is the collection of floodplain sediment samples from third-order catchment basins at a map scale of 1:50,000.

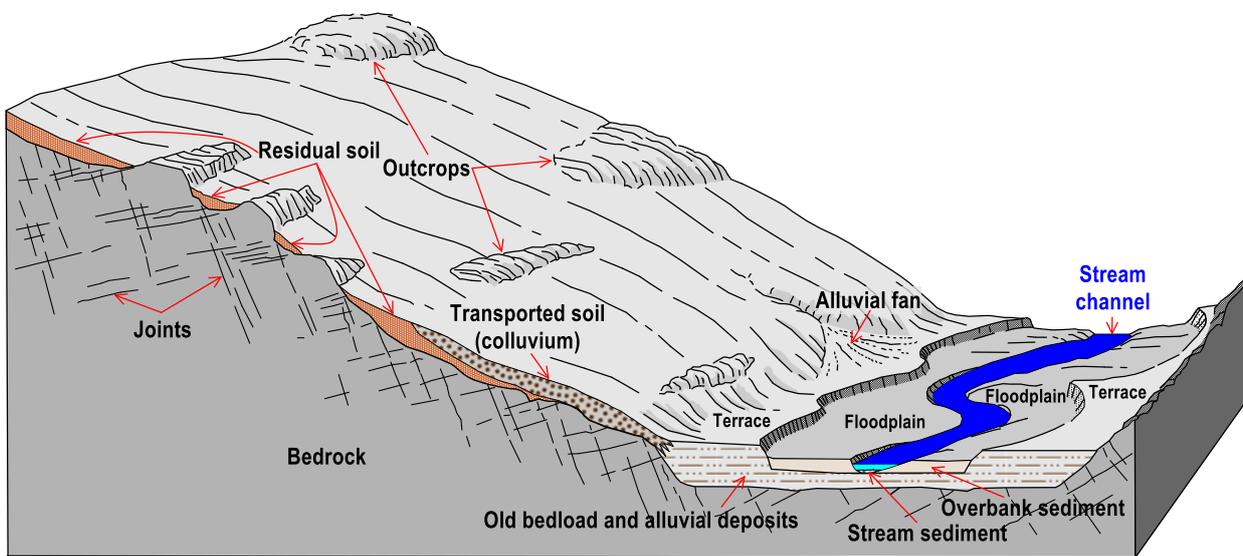


Figure 2.6. Block diagram showing possible sites of GTN sampling media in a second-order catchment basin at a mapping scale of 1:50,000 (after Strahler, 1969, Fig. 22.3, p.363, with minor modifications). Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8.

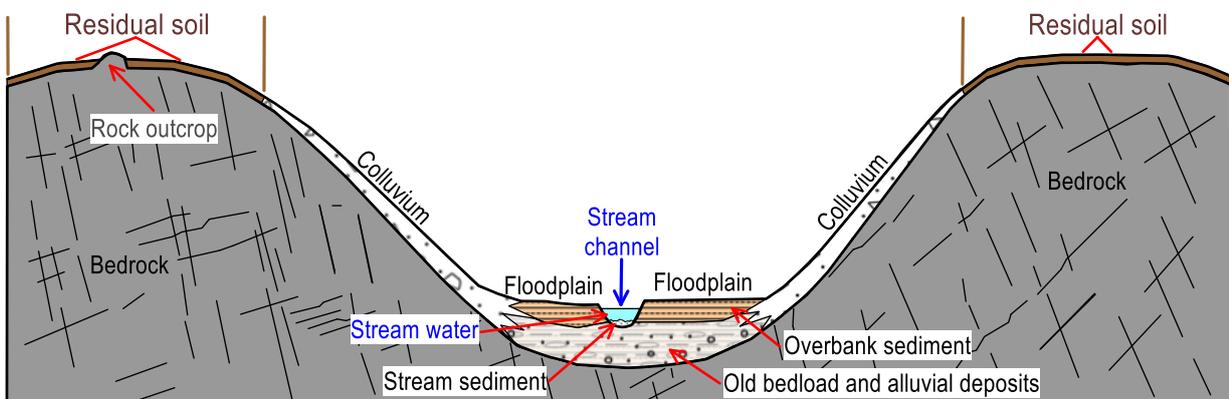


Figure 2.7. Cross-section of second-order stream valley showing different features and the sample sites for collecting rock, residual soil, stream water, stream and overbank sediment samples. Residual soil samples must not be collected from colluvium, as this is transported overburden. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

2.6. Example GTN grid cell N26E14

The samples to be collected from the second- and third-order catchment basins according to the Strahler (1957, 1969) stream magnitude order classification are indicated in Figure 2.8. The plan view shows random point number 3 second- and third-order catchment basins of GTN grid cell N26E14, and the possible sites for the collection of all specified sample types. This GTN grid cell was selected to show the problems of the random point generation algorithm, which generates random points indiscriminately whether they fall on land or water. During the planning stage of the sampling campaign, the random points are plotted on 1:50,000 topographical maps, and any problems such as random point 4 falling in the sea is moved to the nearest land. Possible sites for sampling are:

- On the island of Kea sample site 4a with an area of 132 km² where a second-order catchment basin with an area of <100 km² can be found.
- The second option is site 4b on the southern part of Euboea island, and
- The third option is site 4c on the island of Andros with an area of 380 km².

In all three cases, there are no third-order catchment basins with an area of 1000-6000 km². It is noted that there is no suitable catchment basin on mainland Hellas, and even if there was this will extend into the south-west quadrant of the N26E14 grid cell, which is covered by site number 3. Hence, a decision should be taken from which island the samples will be collected, with the knowledge that the large third-order catchment basin does not meet the specifications. However, in these special cases, it is more important to collect samples from each quadrant of the 160x160 km grid cell.

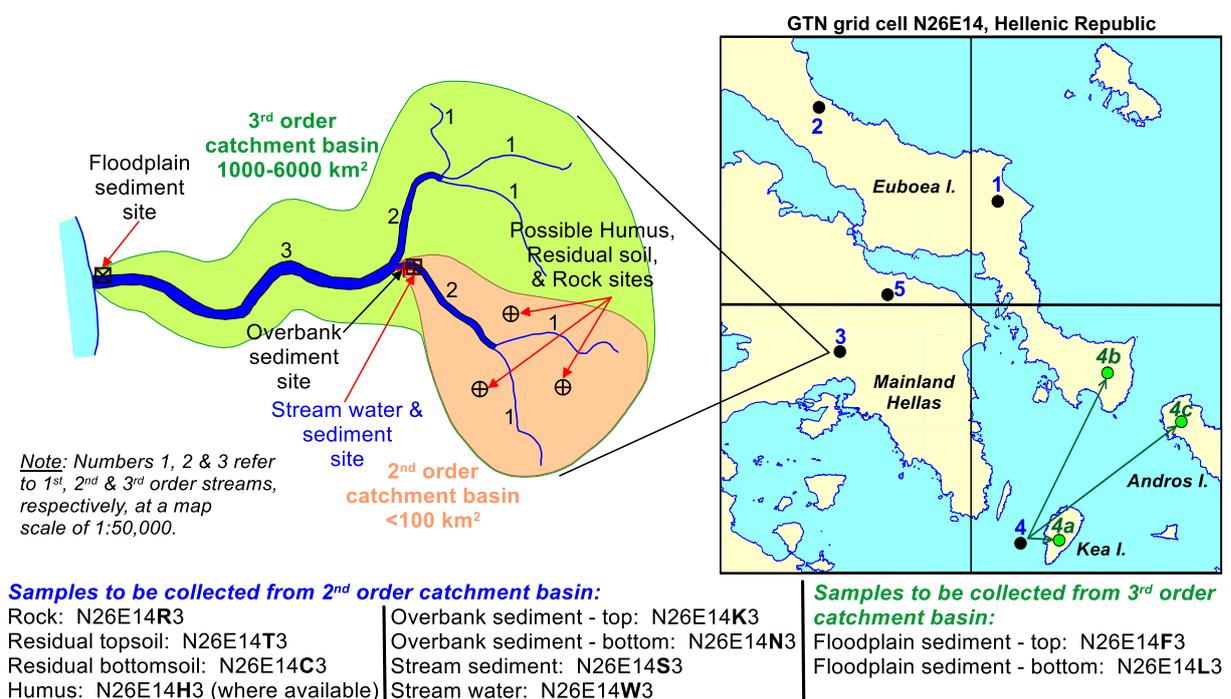


Figure 2.8. Example of a GTN grid cell N26E14 with 5 random points, and a schematic diagram showing the possible sample sites of rock, residual soil, humus, stream water and sediment, overbank sediment, and floodplain sediment from the catchment basin representing random point number 3. Two random points fall on mainland Hellas (3 & 5), two on Euboea Island (1 & 2), and one in the sea (4), which should be moved to a land site. See text for explanation. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8.

2.7. Differences from IGCP 259 recommendations

The differences between the IGCP 259 recommendations of Darnley *et al.* (1995), and this *Manual of Standard Methods for Establishing the Global Geochemical Reference Network* are:

- All sample types are mandatory because the purpose of the Global Geochemical Reference Network project is to provide sufficient reference data points to level geochemical mapping results at all scales.
- An important sample type that is now included is rock.
- The shorter sample identifiers of the FOREGS Geochemical Atlas of Europe project (Salminen, Tarvainen *et al.*, 1998) are used.
- Stream sediment is the only sample type that is collected as a composite from about 10 sub-sites along a stream stretch of 500 metres.
- Samples of residual soil are horizon-based, *i.e.*, A and C horizon samples. Similarly, overbank and floodplain sediments are collected from single top and bottom layers. They are all collected from a SINGLE pit or vertical section.
- No compositing of samples within each GTN grid cell for reducing analytical costs and, in fact, destroying the integrity and characteristics of individual samples, and the establishment of a primary Global Geochemical Reference Network similar to a geodetic grid (Darnley *et al.*, 1995; Darnley, 1997). This procedure is unacceptable and MUST NOT be used (see Demetriades *et al.*, 2018, p.167–170).
- The grain size fraction of residual soil and overbank sediment samples for analysis is <2 mm, and NOT the fine-grained fraction of <0.150 mm.

2.8. Differences from FOREGS project

The FOREGS Geochemical Atlas of Europe project was the first multinational and multi-media sampling project to follow closely the IGCP 259 recommendations of Darnley *et al.* (1995). The differences between the FOREGS Geochemical Atlas of Europe project (Salminen, Tarvainen *et al.*, 1998), and this *Manual of Standard Geochemical Methods* are:

- All sample types are mandatory.
- Rock is included as a mandatory sample medium.
- Samples of residual soil are horizon-based, *i.e.*, A and C horizon samples. Similarly, overbank and floodplain sediments are collected from a single top and a single bottom layer. They are all taken from a SINGLE pit or vertical section.
- The analysed grain size fraction for overbank sediment samples is <2 mm, and NOT the fine-grained fraction of <0.150 mm.

Supplementary material

1. The files described below can be downloaded from the '[Sampling/GTN 160x160 km](#)' web page of the [IUGS Commission on Global Geochemical Baselines](#).

(a) *Global Reference Network grid cells of 160x160 km files:*

- [IUGS-CGGB_19833_GRN_160x160km_grid_cells.xlsx](#) (Microsoft™ Excel workbook file with the 19,833 grid cells of the Global Reference Network each of 160x160 km).
- [IUGS-CGGB_19833_160x160km_grid_cells.zip](#) (same as above but in a Google Earth kml file format). When unzipped the file name is: *IUGS-CGGB_19833_GRN_160x160km_grid_cells.kml*.

(b) Global Terrestrial Network grid cells of 160x160 km files:

- [IUGS-CGGB_7356_GTN_160x160km_grid_cells.xlsx](#) (Microsoft™ Excel workbook file with the 7356 grid cells of the Global Terrestrial Network each of 160x160 km).
- [IUGS-CGGB_7356_GTN_grid_cells_160x160km.zip](#) (same as above but in a Google Earth kml file format). When unzipped the file name is: *IUGS-CGGB_7356_GTN_grid_cells_160x160km.kml*.

2. The following six files can be downloaded from the ‘[Sampling/Sampling Design](#)’ web page of the [IUGS Commission on Global Geochemical Baselines](#).

(c) Randomly selected points in each Global Terrestrial Network grid cell:

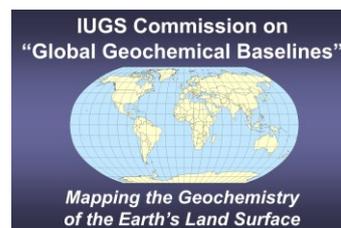
- [IUGS-CGGB_5-random-points_per_GTN_160x160km-grid-cell.xlsx](#) (Microsoft™ Excel workbook file with 5 random points in each of the 7356 grid cells of 160x160 km totalling 36,780 random sampling points).
- [IUGS-CGGB_5-random-points_per_GTN_160x160km-grid-cell.zip](#) (same as above but in a Google Earth kml file format). When unzipped the file name is: *IUGS-CGGB_5-random-points_per_GTN_160x160km-grid-cell.kml*.
- [IUGS-CGGB_8-random-points_per_GTN_160x160km-grid-cell.xlsx](#) (Microsoft™ Excel workbook file with 8 random points in each of the 7356 grid cells of 160x160 km totalling 58,848 random sampling points).
- [IUGS-CGGB_8-random-points_per_GTN_160x160km-grid-cell.zip](#) (same as above but in a Google Earth kml file format). When unzipped the file name is: *IUGS-CGGB_8-random-points_per_GTN_160x160km-grid-cell.kml*.
- [IUGS-CGGB_16-random-points_per_GTN_160x160km-grid-cell.xlsx](#) (Microsoft™ Excel workbook file with 16 random points in each of the 7356 grid cells of 160x160 km totalling 117,696 random sampling points). *It is noted that this sampling density is not recommended for the Global Geochemical Reference Network.*
- [IUGS-CGGB_16-random-points_per_GTN_160x160km-grid-cell.zip](#) (same as above but in a Google Earth kml file format). When unzipped the file name is: *IUGS-CGGB_16-random-points_per_GTN_160x160km-grid-cell.kml*.

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Note: All hyperlinks were checked on the 15th of December 2021.

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Annexe A2.1

Geodetic Levelling of Existing Geochemical Data Sets

Michalis Salahoris

GeoSet Ltd., 60 Cyprus Street, GR-156 69 Papagos-Cholargos, Attiki, Hellas

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A2.1.1. Geodetic levelling

The purpose of using this geodetic data processing methodology is the normalisation (or levelling) of the regional geochemical data set according to the reference values of the [five random points](#), as defined within each 160x160 km grid cell of the [Global Terrestrial Network \(GTN\)](#) and described in Chapter 2 (refer to the Supplementary material).

The basic concept behind the method is that the 5 random points in the GTN grid cell are at such a density that they form a comparatively smooth field, without local extrema within the area defined by the three neighbouring GTN points and, therefore, it can be approximated as a plane.

The Delaunay triangulation is used in digital terrain models to generate a TIN data structure (Okabe *et al.*, 2000) for levelling topographical survey measurements. This is the method that will be used for the geodetic levelling of regional geochemical data sets by using the GTN random point reference values.

A2.1.1.1. Main steps

The method consists of the following steps:

1. Define the triangulation irregular network from the points that cover the study area to define inclined planes. This is the network of 5 random points within each 160x160 km GTN grid cell.
2. Calculate the vertical distance of each regional geochemical data point to the triangulation plane defined by the 5 random points in each 160x160 km grid cell in order to estimate the normalised elemental concentration value of each data point.

A2.1.1.2. Example

The geodetic method is explained by using the Finnish regional geochemical nickel subsoil data and the FOREGS subsoil GTN reference data (Fig. A2.1.1; Salminen *et al.*, 2005). It has been performed using ESRI's ArcMap, v10.3.1¹ with active the 3D Analyst extension (FinlandExample.mxd; refer to Supplementary material).

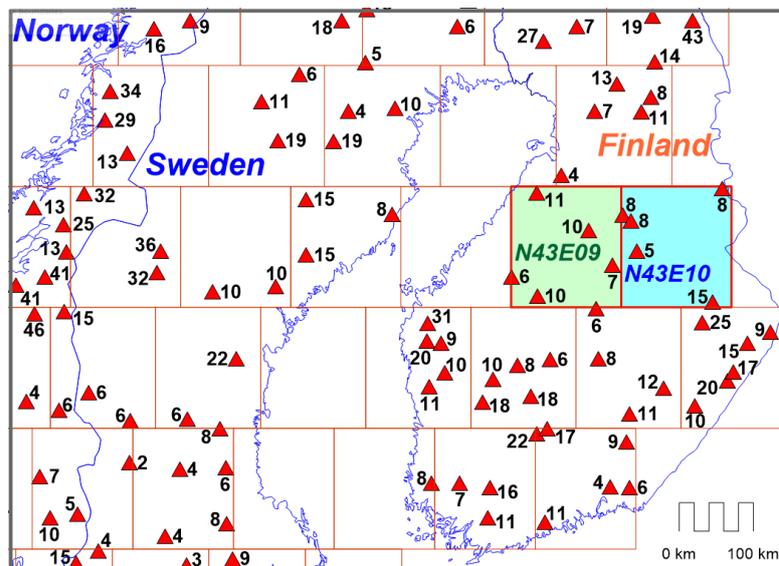


Figure A2.1.1. The map shows the two Finnish 160x160 km GTN grid cells N43E09 and N43E10, and all neighbouring grid cells in Sweden and Norway, displaying with red triangles the 5 random reference points within each grid cell and their Ni concentrations in subsoil samples (see Table A2.1.1).

¹ ESRI ArcGIS Pro: TIN surface <https://pro.arcgis.com/en/pro-app/2.7/help/data/tin/create-a-tin-surface.htm>; ESRI Desktop 10 <https://help.arcgis.com/en/arcgisdesktop/10.0/help/index.html#//00q900000016000000>

1. Input data (see Supplementary material):

- a. The file ‘*Finland_Subsoil_AR_data_GTN_N43E09_&_N43E10_Nickel.xlsx*’ with the Nickel *aqua regia* subsoil results of the 5 reference random sites within the GTN grid cells N43E09 and N43E10 (see Table A2.1.1).
- b. The file ‘*Finland_GTN_N43E09_&_N43E10_Nickel.xlsx*’ with the regional Nickel *aqua regia* subsoil or C horizon till results (Tarvainen, 1995, 1996; refer to Annexe A2.2 for additional information). For every observation point provided, *i.e.*, the PointID (field SampleNo), the following information is required: geographical coordinates in WGS 1984 (Easting and Northing – Longitude and Latitude), the GTN grid cell number that samples are within, the Sample Number, and the measurements of Ni concentrations (field Ni_511p in mg/kg), *e.g.*:

<i>Easting WGS1984</i>	<i>Northing WGS1984</i>	<i>GTN No</i>	<i>SampleNo</i>	<i>Ni_511p</i>
24.87842726	63.65765897	N43E09	68003	8.57
25.18322365	63.66680337	N43E09	68004	9.16
25.21949996	63.80274602	N43E09	68005	11.9

2. Data preparation:

- a. Select the GTN random point that overlaps the regional geochemical data (observations).
- b. Assign Ni values to each GTN random point of the above selection.
- c. Create one feature class with all the geochemical data points (observations) to be levelled.

3. Procedure:

- a. Open an ArcMap document and define a cartesian coordinate system of the data frame (in our case “*FinlanExample.mxd: EUREF FIN TM35FIN*”). This is recommended in order to effectively enforce the Delaunay triangulation rule during the next step (<https://desktop.arcgis.com/en/arcmap/latest/tools/3d-analyst-toolbox/create-tin.htm>)
- b. Build a TIN using the GTN reference sample points with the Ni concentrations as elevation values. In ArcMap: From toolboxes, 3D Analyst, Create Tin. In our example is the “*tinarsub tt tin*”.
- d. Visualise the TIN triangles (Fig. A2.1.2). In our case using the command “*TIN Edge*” tool (<https://desktop.arcgis.com/en/arcmap/latest/tools/3d-analyst-toolbox/tin-edge.htm>). Note that the triangles extend beyond the two grid cells.
- e. Add the feature classes with the observation points. In our case, the feature class is “*fingtnalp*”.
- f. Calculate the vertical distance of each observation point from the relevant tin plane. In our case, use the “*Add Surface Information Tool*” with Linear method, in field Z (Fig. A2.1.3; Tables A2.1.2 & A2.1.3).
- g. Create a new field (in our case dz) and calculate the difference between the measured values (field Ni_511p) and the calculated values (field Z).

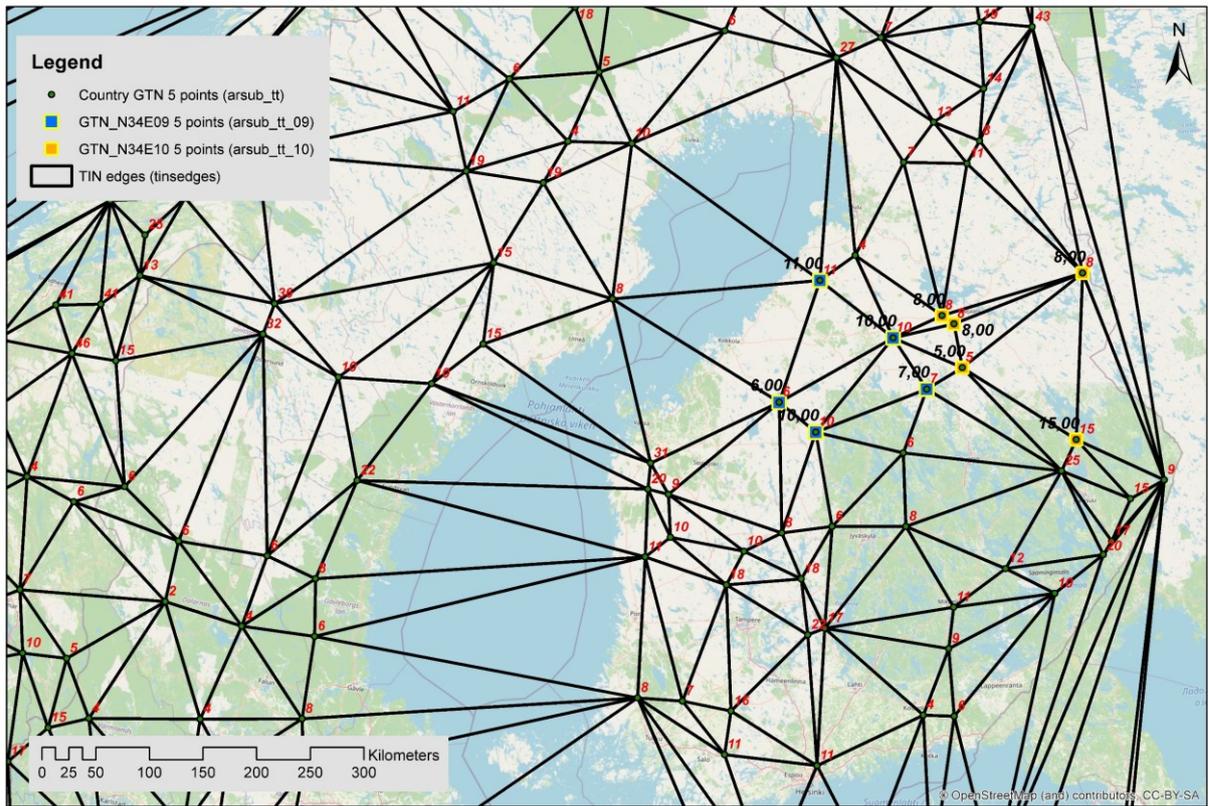


Figure A2.1.2. The map shows the TIN created using the 5 random points in GTN grid cells N34E09 and N34E10, Finland (see Tables A2.1.1 to A2.1.3).

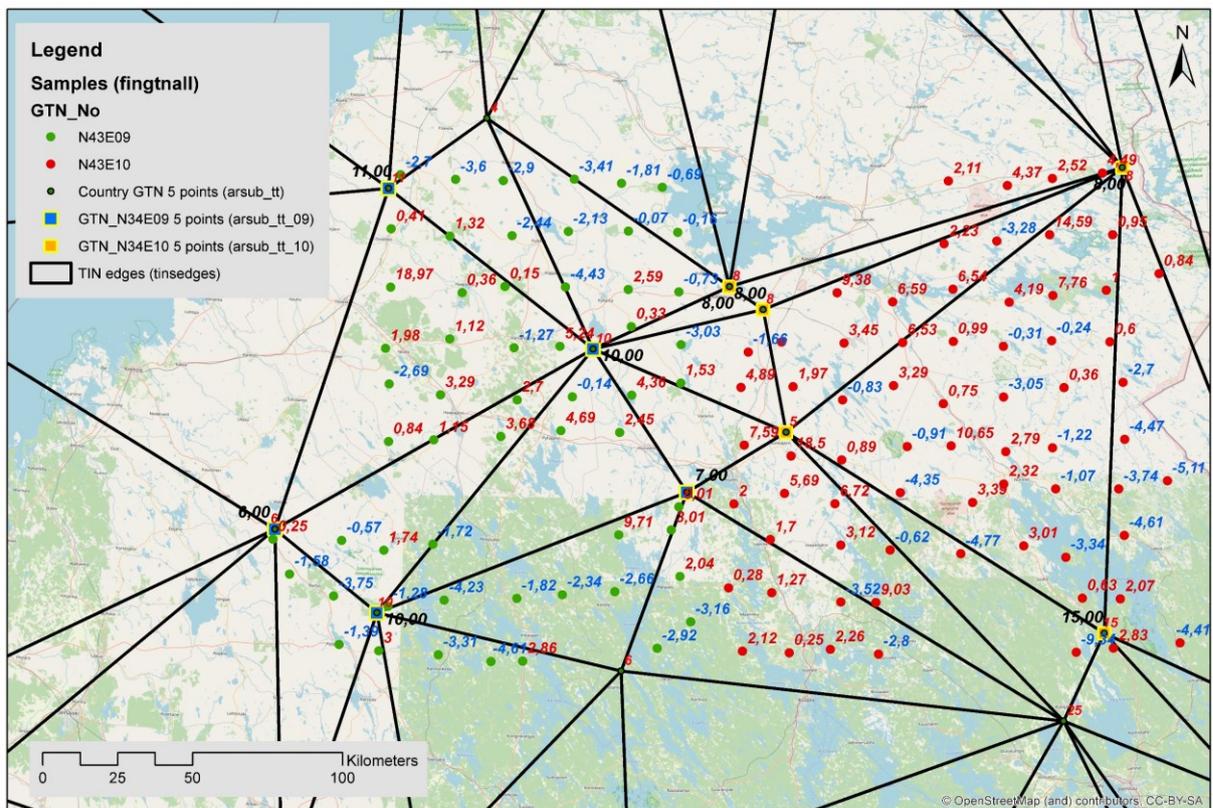


Figure A2.1.3. Sample points with levelled (normalised) values. Positive values (red) when the point regional geochemical survey Ni concentration values are greater than the reference plane elevation at each point, and negative values (blue) when they are smaller (see Tables A2.1.1 to A2.1.3).

Table A2.1.1. Nickel concentrations in subsoil samples from the FOREGS N43E09 and N43E10 GTN grid cells, Finland, are used as the reference data set for levelling the regional subsoil geochemical data (File: Finland_Subsoil_AR_data_GTN_N43E09_&_N43E10_Nickel.xlsx).

GTN: N43E09					
Longitude (°)	Latitude (°)	Sample No.	Country	Lab. No.	Ni (mg/kg)
26.25	63.95	N43E09C1	FI	99-000333	10.0
24.82	64.42	N43E09C2	FI	99-000334	11.0
24.14	63.38	N43E09C3	FI	99-000335	6.00
26.89	63.52	N43E09C4	FI	99-000336	7.00
24.84	63.14	N43E09C5	FI	99-000338	10.0

GTN: N43E10					
29.91	64.47	N43E10C1	FI	99-000339	8.00
27.18	64.14	N43E10C2	FI	99-000340	8.00
27.56	63.70	N43E10C3	FI	99-000341	5.00
29.65	63.07	N43E10C4	FI	99-000342	15.0
27.41	64.07	N43E10C5	FI	99-000343	8.00

Table A2.1.2. Nickel concentrations in subsoil samples from the regional geochemical survey, Finland, in N43E09 GTN grid cell, the estimated Ni levelled (Z) data and the difference (dz) between the original and levelled values.

Easting or Longitude (°)	Northing or Latitude (°)	GTN grid cell	Sample No.	Ni (mg/kg)	Ni (mg/kg) levelled (Z)	Ni (mg/kg) difference (dz)
24.88	63.66	N43E09	68003	8.57	7.73	0.84
25.18	63.67	N43E09	68004	9.16	8.01	1.15
25.22	63.80	N43E09	68005	11.9	8.61	3.29
24.87	63.83	N43E09	68006	5.79	8.48	-2.69
25.27	63.97	N43E09	68007	10.5	9.38	1.12
24.84	63.94	N43E09	68008	10.9	8.92	1.98
26.48	64.31	N43E09	68060	6.66	6.73	-0.07
26.43	64.45	N43E09	68061	4.47	6.28	-1.81
24.25	63.25	N43E09	68074	5.15	6.73	-1.58
24.55	63.19	N43E09	68075	4.64	8.39	-3.75
24.13	63.35	N43E09	68108	6.31	6.06	0.25
24.59	63.35	N43E09	68109	7.21	7.78	-0.57
26.52	63.81	N43E09	68256	13.2	8.84	4.36
26.85	63.85	N43E09	68257	9.34	7.81	1.53
26.85	63.96	N43E09	68258	5.59	8.62	-3.03
26.51	64.02	N43E09	68259	9.64	9.31	0.33
26.49	64.13	N43E09	68260	10.9	8.31	2.59
26.83	64.12	N43E09	68263	7.53	8.26	-0.73
26.82	64.30	N43E09	68264	7.03	7.19	-0.16
26.72	64.44	N43E09	68265	6.32	7.01	-0.69
25.28	63.18	N43E09	68408	4.98	9.21	-4.23
25.20	63.35	N43E09	68409	8.27	9.99	-1.72
24.87	63.33	N43E09	68410	10.7	8.96	1.74
24.91	63.16	N43E09	68411	8.64	9.92	-1.28
24.86	63.03	N43E09	68412	12.5	9.50	3.00
25.25	63.02	N43E09	68414	5.33	8.64	-3.31

<i>Easting or Longitude (°)</i>	<i>Northing or Latitude (°)</i>	<i>GTN grid cell</i>	<i>Sample No.</i>	<i>Ni (mg/kg)</i>	<i>Ni (mg/kg) levelled (Z)</i>	<i>Ni (mg/kg) difference (dz)</i>
24.60	63.04	N43E09	68722	7.42	8.81	-1.39
24.86	64.12	N43E09	68723	28.7	9.73	18.97
25.35	64.11	N43E09	68724	10.4	10.04	0.36
24.85	64.30	N43E09	68780	10.9	10.49	0.41
24.90	64.46	N43E09	68781	7.6	10.30	-2.70
25.25	64.28	N43E09	68782	12	10.68	1.32
25.28	64.45	N43E09	68783	4.35	7.95	-3.60
25.74	63.79	N43E09	68784	11.9	9.20	2.70
25.71	63.95	N43E09	68785	8.33	9.60	-1.27
26.11	63.81	N43E09	68786	9.6	9.74	-0.14
26.02	63.96	N43E09	68787	15.1	9.86	5.24
25.64	64.13	N43E09	68788	10.5	10.35	0.15
26.06	64.14	N43E09	68789	3.96	8.39	-4.43
25.68	64.29	N43E09	68790	5.76	8.20	-2.44
25.61	64.45	N43E09	68791	3.21	6.11	-2.90
26.07	64.30	N43E09	68792	4.75	6.88	-2.13
26.11	64.46	N43E09	68793	2.04	5.45	-3.41
25.60	63.00	N43E09	68794	3.25	7.86	-4.61
25.81	63.01	N43E09	68795	10.3	7.44	2.86
25.76	63.19	N43E09	68798	6.4	8.22	-1.82
26.07	63.21	N43E09	68800	5.29	7.63	-2.34
26.70	63.05	N43E09	68803	4.37	7.29	-2.92
26.92	63.13	N43E09	68805	5.27	8.43	-3.16
26.41	63.22	N43E09	68806	4.27	6.93	-2.66
26.44	63.39	N43E09	68807	17.2	7.49	9.71
26.85	63.27	N43E09	68808	9.57	7.53	2.04
26.79	63.41	N43E09	68809	9.82	6.81	3.01
25.63	63.68	N43E09	68811	13.2	9.52	3.68
26.04	63.70	N43E09	68813	14.2	9.51	4.69
26.44	63.70	N43E09	68815	11.1	8.65	2.45
26.84	63.48	N43E09	68816	6.97	6.96	0.01

Table A2.1.3. Nickel concentrations in subsoil samples from the regional geochemical survey, Finland, in N43E10 GTN grid cell, the estimated Ni levelled (Z) data and the difference (dz) between the original and levelled values.

<i>Easting or Longitude (°)</i>	<i>Northing or Latitude (°)</i>	<i>GTN grid cell</i>	<i>Sample No.</i>	<i>Ni (mg/kg)</i>	<i>Ni (mg/kg) levelled (Z)</i>	<i>Ni (mg/kg) difference (dz)</i>
27.21	63.48	N43E10	68251	10.3	8.30	2.00
27.28	63.66	N43E10	68252	13.5	5.91	7.59
27.55	63.52	N43E10	68253	14.1	8.41	5.69
27.59	63.63	N43E10	68254	24.9	6.40	18.50
27.26	63.84	N43E10	68255	11.6	6.71	4.89
27.53	63.97	N43E10	68261	6.45	7.10	-0.65
27.31	63.94	N43E10	68262	5.68	7.34	-1.66
27.92	64.12	N43E10	68268	17.1	7.72	9.38

<i>Easting or Longitude (°)</i>	<i>Northing or Latitude (°)</i>	<i>GTN grid cell</i>	<i>Sample No.</i>	<i>Ni (mg/kg)</i>	<i>Ni (mg/kg) levelled (Z)</i>	<i>Ni (mg/kg) difference (dz)</i>
27.96	63.97	N43E10	68269	9.96	6.51	3.45
27.94	63.80	N43E10	68270	4.87	5.70	-0.83
27.61	63.84	N43E10	68271	7.95	5.98	1.97
27.93	63.61	N43E10	68272	7.52	6.63	0.89
27.88	63.48	N43E10	68273	16.4	9.68	6.72
29.37	63.96	N43E10	68274	8.99	9.23	-0.24
29.04	63.95	N43E10	68275	7.98	8.29	-0.31
29.03	63.79	N43E10	68276	6.04	9.09	-3.05
28.63	63.78	N43E10	68277	8.66	7.91	0.75
28.37	63.65	N43E10	68278	6.91	7.82	-0.91
28.32	63.51	N43E10	68279	4.05	8.40	-4.35
28.67	63.65	N43E10	68280	19.4	8.75	10.65
29.02	63.53	N43E10	68281	12.8	10.48	2.32
28.81	63.48	N43E10	68282	13.5	10.11	3.39
29.04	63.63	N43E10	68283	12.8	10.01	2.79
29.35	63.63	N43E10	68284	9.73	10.95	-1.22
29.36	63.51	N43E10	68285	10.6	11.67	-1.07
29.79	63.50	N43E10	68286	8.82	12.56	-3.74
30.12	63.52	N43E10	68287	5.84	10.95	-5.11
29.84	63.65	N43E10	68288	7.22	11.69	-4.47
29.85	63.82	N43E10	68289	8.25	10.95	-2.70
29.77	63.95	N43E10	68290	11.1	10.50	0.60
30.13	64.15	N43E10	68293	9.18	8.34	0.84
29.76	64.10	N43E10	68294	10.6	9.60	1.00
29.39	64.09	N43E10	68295	16.3	8.54	7.76
29.09	64.08	N43E10	68296	11.9	7.71	4.19
29.45	63.81	N43E10	68297	10.6	10.24	0.36
28.70	63.96	N43E10	68298	8.13	7.14	0.99
28.29	63.84	N43E10	68299	9.85	6.56	3.29
28.36	63.97	N43E10	68300	12.6	6.07	6.53
28.30	64.09	N43E10	68301	13.6	7.01	6.59
28.71	64.12	N43E10	68302	13.3	6.76	6.54
29.02	64.26	N43E10	68303	4.18	7.46	-3.28
29.11	64.43	N43E10	68304	12.5	8.13	4.37
29.77	64.46	N43E10	68311	12.5	8.01	4.49
29.82	64.27	N43E10	68313	9.81	8.86	0.95
29.42	64.45	N43E10	68314	10.6	8.08	2.52
29.39	64.28	N43E10	68315	22.1	7.51	14.59
28.66	64.26	N43E10	68316	10.1	7.87	2.23
28.70	64.45	N43E10	68317	10.4	8.29	2.11
27.57	63.04	N43E10	68361	13.1	12.85	0.25
27.84	63.04	N43E10	68362	16.8	14.54	2.26
28.16	63.03	N43E10	68363	13.8	16.60	-2.80
29.71	63.02	N43E10	68367	18.2	15.37	2.83

<i>Easting or Longitude (°)</i>	<i>Northing or Latitude (°)</i>	<i>GTN grid cell</i>	<i>Sample No.</i>	<i>Ni (mg/kg)</i>	<i>Ni (mg/kg) levelled (Z)</i>	<i>Ni (mg/kg) difference (dz)</i>
30.15	63.03	N43E10	68373	8.39	12.80	-4.41
29.81	63.36	N43E10	68385	8.42	13.03	-4.61
29.14	63.34	N43E10	68386	14.9	11.89	3.01
29.46	63.02	N43E10	68387	8.43	17.77	-9.34
29.41	63.30	N43E10	68389	9.63	12.97	-3.34
29.51	63.18	N43E10	68390	14.6	13.97	0.63
29.77	63.17	N43E10	68391	16.1	14.03	2.07
28.72	63.32	N43E10	68392	6.82	11.59	-4.77
28.25	63.34	N43E10	68393	12.4	13.02	-0.62
28.15	63.18	N43E10	68394	24.8	15.77	9.03
27.91	63.19	N43E10	68395	11	14.52	-3.52
27.92	63.36	N43E10	68396	15.2	12.08	3.12
27.17	63.23	N43E10	68398	9.96	9.68	0.28
27.45	63.22	N43E10	68399	12.8	11.53	1.27
27.26	63.04	N43E10	68401	13	10.88	2.12
27.45	63.38	N43E10	68421	12.5	10.80	1.70

A2.1.1.3. Comments

The Ni concentrations of the Finnish FOREGS GTN reference data set are very low and, thus, negative values (dz) result when the levelled Ni (Z) concentrations are subtracted from the original values (Tables A2.1.2 & A2.1.3).

A2.1.2. Recommendations

During the “*Create TIN*” procedure the algorithm connects adjacent points to formulate the triangles, using the Delaunay triangulation method. *Which* adjacent points are connected, *which* results, and *which* Delaunay triangles are created, depends on the number of data points and their spatial distribution. In our example from Finland, we have used all the available data points. The triangles might be different if we could use points that are evenly distributed around the GTN grid cells N43E09 and N43E10, or a subset of them. Thus, the normalised values of the observations depend on how the Delaunay triangles are formed according to the spatial distribution of the 5 random reference sample GTN points. Therefore, it is necessary to study the sensitivity of the levelled results with respect to the changes in the definition of the Delaunay triangles. This recommendation is explained in Figure A2.1.4. It is obvious that different outside reference Delaunay triangles are created and, accordingly, different levelling values are possible. In order to address this issue, the following recommendations are made:

- a) To establish a permanent reference Delaunay triangle network to be utilised in all cases by all users, or if this is not possible
- b) To select reference points in the perimeter that are not at a long distance from the GTN grid cells where the regional geochemical survey values are to be levelled with the aim for the calculations not to be affected by distant random GTN reference values.

Finally, it is strongly recommended that in order to generate a better reference “*Tin*” plane is to select regional geochemical samples very near to the five random reference GTN points.

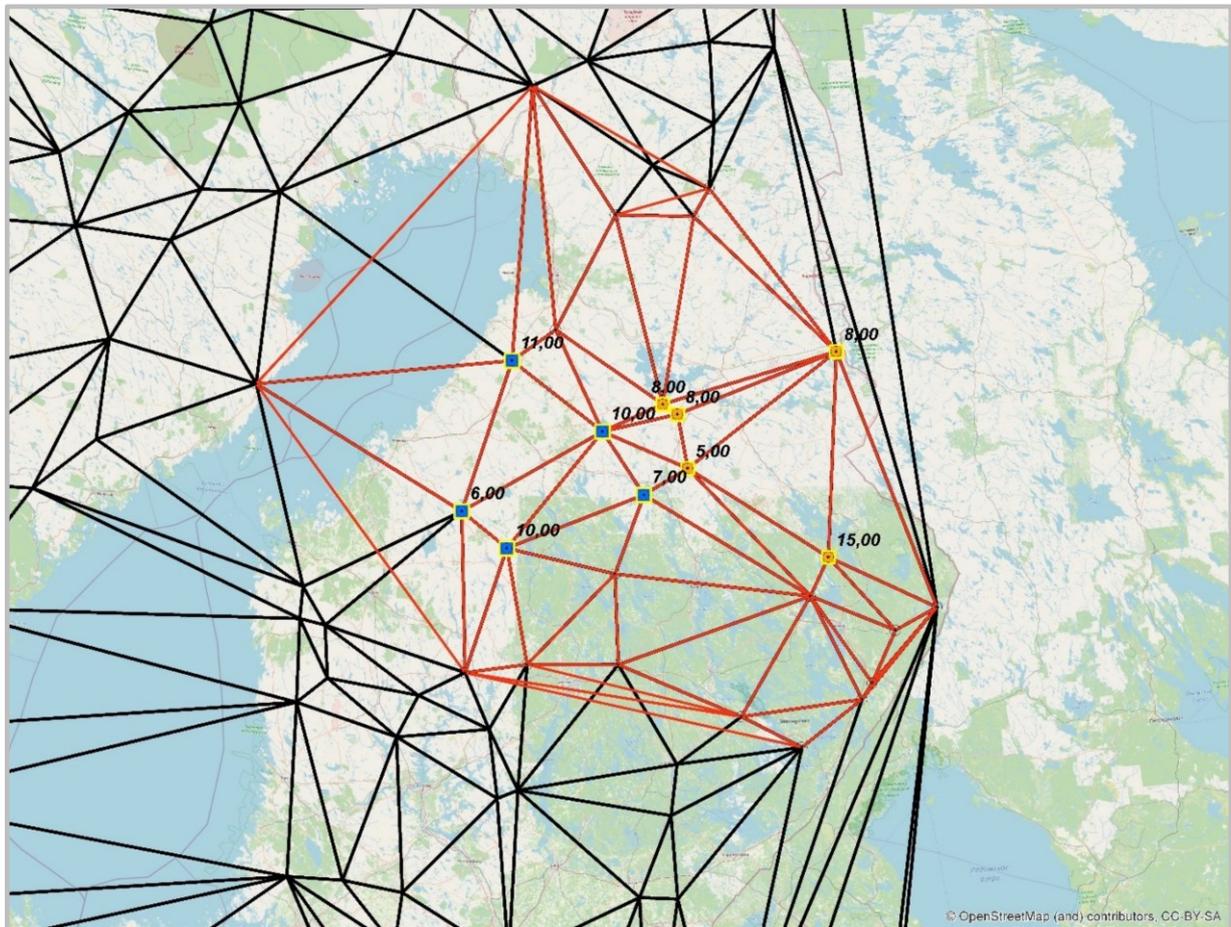


Figure A2.1.4. Delaunay triangles procedure for levelling existing geochemical results with respect to the values of a reference data set. The black and red lines show the Delaunay triangles formed when all 5 random points in the Finnish and adjoining Swedish GTN grid cells are used. The superimposed red lines show the selection of the 5 random points within GTN grid cells N43E09 and N43E10 and a few points in the perimeter. See also Figure A2.1.3.

Supplementary material

The following supplementary material is provided in the zip file ‘Annexe_A2.1_Supplementary_material.zip’, which can be downloaded from the [Publications](#) web page of the [IUGS Commission on Global Geochemical Baselines](#):

- Microsoft™ Excel file: ‘Finland_Subsoil_AR_data_GTN_N43E09_&_N43E10_Nickel.xlsx’ with the Nickel aqua regia subsoil values of the 5 reference random sites within the GTN grid cells N43E09 and N43E10 (extracted from the ‘C_AR_data_2v5_8Feb06.xlsx’ (see below).
- Microsoft™ Excel file: ‘Finland_GTN_N43E09_&_N43E10_Nickel.xlsx’ with the regional geochemistry Nickel aqua regia subsoil (C horizon till) results (from Tarvainen, 1995, 1996).
- Microsoft™ Excel file: ‘C_AR_data_2v5_8Feb06.xlsx’ with the values of Nickel for the 5 random points of the GTN grid cells in Europe (FOREGS GTN data set from Salminen *et al.*, 2005).

#	File name	Content
1.	FinlandExample.mxd	ESRI ArcMap 10.3.1 map document which contains all the original data and results. 3D Analyst is activated. All data references are relative to this document.
2.	Finland.mdb	ESRI, ver. 10.3.1, Personal Geodatabase (PGDB). Contains:

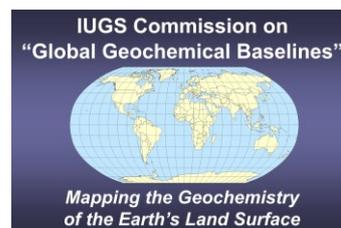
#	File name	Content
	a. fingtnall	Feature class with all the regional geochemical samples collected within GTN Grids N43E09 & N43E10. Fields Z and dz have been added during steps (e) and (f) of the process (see '3. Process' in Section §A2.1.1.2).
	b. arsub_tt	Feature class of all the GTN 5 random points. It contains columns of AS_AR_C_n and NI_AR_C_n values. The feature class has been created from Subsoil_1v0_21June2006\C_AR_data_2v5_8Feb06.xls using the Display X, Y data (ARSUB_TT\$Events) and save the results to the PGDB.
	c. Tinsedges	The edges of TIN data set created during step (c) of the procedure (see '3. Procedure' in Section §A2.1.1.2).
3.	tinarsub_tt	Tin Dataset created using arsub_tt.

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Note: All hyperlinks were checked on the 22nd of February 2022.

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Annexe A2.2

**Parametric Levelling of Existing
Geochemical Data Sets**

Alecos Demetriades^{1,6}, Christopher C. Johnson^{2,6}, Timo Tarvainen^{3,6},
Manfred Birke^{4,6}, David B. Smith⁶, Maria João Batista^{5,6}

¹ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

² GeoElementary, Derby, United Kingdom

³ Geological Survey of Finland, Espoo, Finland

⁴ Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany

⁵ Laboratório Nacional de Energia e Geologia, Amadora, Portugal

⁶ IUGS Commission on Global Geochemical Baselines

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A2.2.1. Levelling

Procedures of statistical levelling and normalisation of existing data sets with respect to GTN random site data, as pointed out by Darnley *et al.* (1995, p.75), are ‘*geochemically blind*’ because they simply manipulate numbers. The procedure used by surveyors, as envisaged by Arthur G. Darnley himself, to level elevations in relation to the reference values of trigonometric points is cumbersome and requires the assistance of an experienced ‘traditional’ surveyor (see Annexe A2.1 of Chapter 2 in this Manual).

In Darnley *et al.* (1995, p.75-78), there is a concise description of the following statistical levelling procedures:

- Parametric levelling (§8.4.2, p.75-76), which was abstracted, and modified for the purpose of this Manual.
- Non-parametric normalisation (§8.4.3, p.76).
- Fractile normalisation (§8.4.3.1, p.76).
- Clarke normalisation (§8.4.3.2, p.76-77), and
- Quantile regression (§8.4.3.3, p.77).

There is also a “Comparison of non-parametric methods” (p.77-78).

The examples that will be discussed are using parametric levelling, as this is the simplest procedure concerning the calculations involved. There are, however, certain conditions that must be observed by the applied geochemist, namely:

- The two data sets must be comparable: *for example*, stream sediment data with GTN stream sediment, soil C horizon data with GTN C horizon data, overbank sediment data with GTN overbank sediment data, *etc.* It is inappropriate to try to level stream sediment results with heavy mineral concentrate data.
- The grain size should be similar.
- The analytical method should be comparable. It is inappropriate to try to level data sets of cold partial extraction and total element concentrations, or *aqua regia* extraction results with total element concentrations.

Ideally, there should be no major problem in merging data from total determinations in like sample media.

A2.2.1.1. Parametric levelling method

Where geochemical data for the same sites or samples, or control samples, are available the following procedure and conditions should be followed:

- They should be displayed as simple X-Y plots with similar X- and Y-axis scaling; this condition is particularly important as the 45-degree diagonal should be plotted.
- The data that will be levelled should be plotted on the Y-axis.
- The user must decide if the data should be plotted with or without a logarithmic transformation. A good initial guide is, if when plotted without a logarithmic transformation the data ‘fan out’ at higher levels. Then, the data should be logarithmically transformed for reasons related to the homogeneity of variance and the subsequent numerical steps.

If the data plot close to the 45-degree diagonal, no further work is required and the data for that variable can be merged (Fig. A2.2.1a). The regression of X on Y may be computed by using the linear relationship equation, $Y = B \cdot X + A$, and a formal statistical test is undertaken to determine if the slope term (B) differs significantly from unity.

If the data points generally fall along a straight line but off the 45-degree diagonal, then it must be determined if the levelling:

- Involves a simple positive or negative shift.
- It is dependent on the absolute level, or
- It is a combination of both.

To do this the regression of X on Y is computed and the slope (B term) and intercept (A term) of the regression ($Y = B \cdot X + A$) are tested for being significantly different from one (1) and zero (0), respectively. The necessary linear corrections are carried out according to the following conditions:

- If only the intercept is significant, a simple positive or negative shift equal to the value of the intercept may be applied (Fig. A2.2.1b).
- If only the slope is significant, a multiplier equal to the slope is applied (Fig. A2.2.1c), and
- If both are significant both shift and multiplier terms must be applied (Fig. A2.2.1d).

If a logarithmic plot is required to obtain homogeneity of variance, then all calculations need to be completed in logarithms, with a final conversion back to the original scale.

If an inspection of the initial X-Y plots exhibits non-linearity, transformations may be investigated that linearise the plot. In selecting appropriate transformations, the user is well advised to consider the underlying physical processes involved in the chemical or physical measurement procedures. If a logarithmic rule or a Poisson counting process is involved a logarithmic or square-root transformation may be adequate.

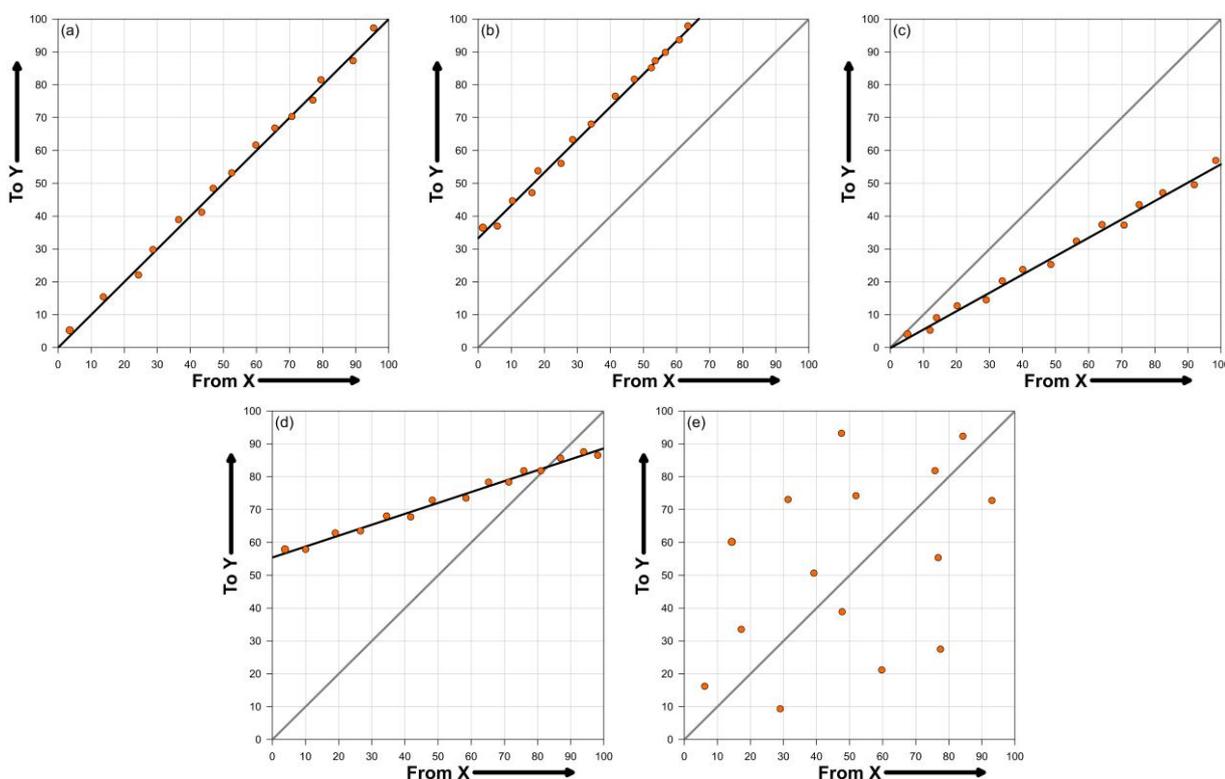


Figure A2.2.1. Various situations that may occur in parametric levelling: (a) No levelling needed. (b) Shift. (c) Multiplier. (d) Both shift and multiplier required, and (e) Parametric levelling impossible (From Darnley et al., 1995, Fig. 8-3, p.76; modified and redrawn by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) & IUGS Commission on Global Geochemical Baselines (IUGS-CGGB) with Golden Software's Grapher™ v20).

In the most serious cases of non-linearity, some form of polynomial or non-linear curve fitting might be considered. If it is necessary, however, to go to these lengths to merge data sets, it might be wise to reconsider the desirability of the act and the credibility of the results. Situations may arise where no correlation - linear nor non-linear - is shown between the data sets to be levelled (Fig. A2.2.1e). Then levelling with this procedure or any direct method must be considered impossible.

Field duplicate samples and analyses provide important data to be used in estimating the goodness-of-fit and the significance of the regression model.

A2.2.1.2. Parametric levelling examples

Parametric levelling was tested on regional data sets from (i) Finland (Tarvainen, 1995, 1996), (ii) Germany (Fauth *et al.*, 1985; Birke *et al.*, 2015), (iii) the Hellenic Republic (Demetriades, 2014, 2021) and (iv) the United Kingdom (Johnson *et al.*, 2005; Johnson, 2011; Everett *et al.*, 2019) with the corresponding GTN data sets from the FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005). In all cases studied, the geochemical results were plotted first on a map and the nearest national samples to the corresponding FOREGS GTN samples were selected (*e.g.*, Fig. A2.1.1 in Annexe 2.1). The parametric levelling method should work when dealing with the variability due to within-sample analytical variation. If, however, the between-site variability needs to be accommodated too, then the variability is too great to give meaningful results.

A2.2.1.2.1. Example from Finland

The analytical data set from Finland that was considered compatible with the corresponding results of the FOREGS GTN survey was the subsoil or C horizon till (Tarvainen, 1995, 1996). The determinations were made by ICP-AES following a hot *aqua regia* extraction on the <2 mm grain size fraction. Both sampling and analytical methods are similar to those of the FOREGS GTN survey (Salminen, Tarvainen *et al.*, 1998; Salminen *et al.*, 2005; Sandström *et al.*, 2005).

Distances between the two subsoil sample sets vary from about 975 to 13,305 metres (Table A2.2.1). The X-Y plot of FOREGS GTN subsoil vs. Finnish regional subsoil Ni results shows a small scatter about the 45-degree diagonal (Fig. A2.2.2a). This plot displays the between-site variability, which is unexpectedly small and may be explained by the glacial processes that transported and deposited the till. Such data may not require levelling.

Table A2.2.1. Nickel (mg/kg) concentrations in the nearest Finnish FOREGS GTN subsoil samples to the regional subsoil (till C horizon) samples, and the levelled Finnish results.

FOREGS GTN Sample No.	Longitude FOREGS	Latitude FOREGS	Distance (m)	Finland Sample No.	Longitude Finland	Latitude Finland	Ni FOREGS	Ni Finland	Ni Finland (Levelled)
N41E09C5	23.48	60.39	1105	68613	23.48	60.40	11	9.79	10.3
N41E10C3	25.05	60.33	7692	68499	25.12	60.39	11	10.8	11.4
N41E10C5	27.37	60.76	9175	68474	27.46	60.69	6	5.22	5.63
N42E08C3	21.88	62.01	8070	68159	21.86	62.08	11	9.38	9.90
N42E08C4	22.3	62.19	13,305	68087	22.21	62.30	10	11.1	11.7
N42E09C2	24.29	62.28	3802	68206	24.36	62.27	8	7.64	8.11
N42E10C1	28.3	62.00	10,065	68429	28.16	62.06	12	12.8	13.4
N42E10C4	29.16	61.78	975	68449	29.18	61.78	10	9.21	9.72
N42E11C3	30.05	62.09	3272	68454	30.11	62.08	20	18.5	19.3
N43E09C3	24.14	63.38	3475	68108	24.13	63.35	6	6.31	6.75
N43E09C4	26.89	63.52	5172	68816	26.84	63.48	7	6.97	7.42
N44E09C3	25.49	64.64	11,375	68065	25.68	64.58	4	2.16	2.49

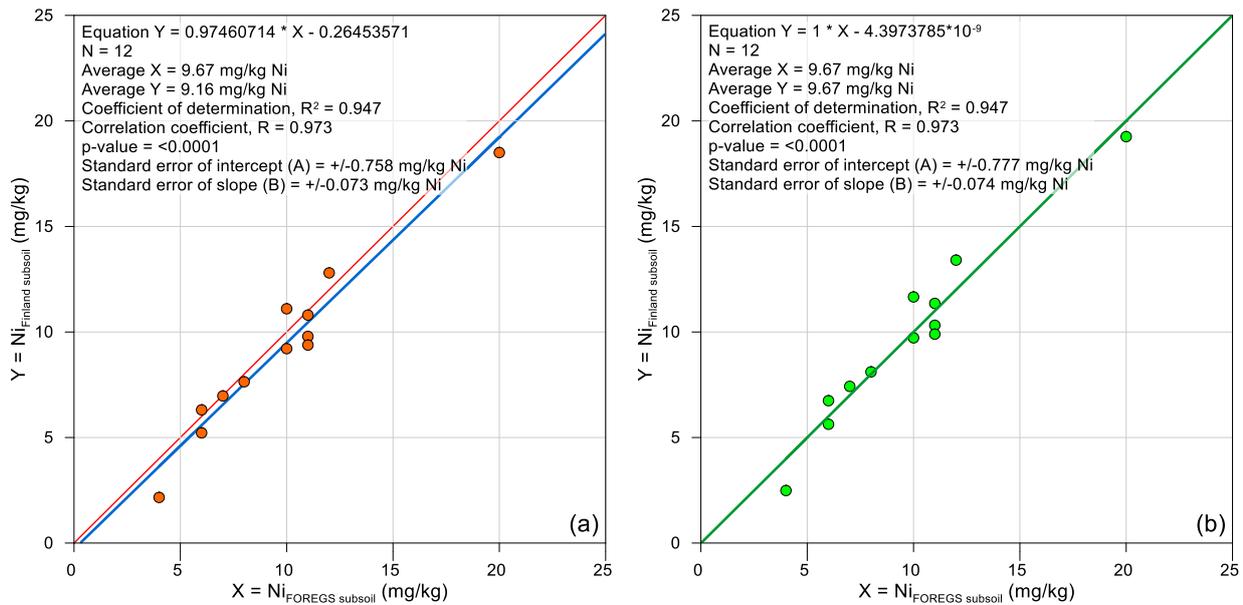


Figure A2.2.2. X-Y plots of hot aqua regia extractable Ni results of FOREGS Finland GTN subsoil versus regional subsoil (till) samples, determined in both cases by ICP-AES on the <2 mm grain size fraction. The red and blue lines in (a) indicate the 45 degree diagonal and the linear correlation, respectively, and the green line in (b) shows the linear correlation after levelling the Finnish Ni regional subsoil results. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

The Ni results have a high linear correlation coefficient ($R = 0.973$; $R^2 = 0.947$) with a minor deviation from the 45-degree diagonal (Fig. A2.2.2a). It is concluded that the Ni results, tabulated in Table A2.2.1, can be used for parametric levelling of the Finnish regional subsoil (till C horizon) results with regard to the corresponding FOREGS GTN data.

The linear correlation equation between Ni FOREGS GTN and Finnish subsoil samples is:

$$Y_{\text{Finland subsoil}} = 0.97460714 * X_{\text{FOREGS subsoil}} - 0.26453571$$

For levelling the Finnish subsoil data with respect to the FOREGS GTN subsoil results, the first correction to be carried out is to shift the intercept to the zero origin of the graph. As the value of the intercept is negative (-0.26453571 mg/kg Cr), the positive value is added to each Finnish subsoil Ni concentration in order to move the intercept to the zero origin of the graph. Subsequently, each Finnish subsoil result is divided by the slope at 0.97460714 to give the levelled Finnish subsoil Ni values, which are tabulated in Table A2.2.1. Upon plotting the Ni FOREGS GTN against the Ni Finnish levelled results, the calculated subsoil linear correlation line falls on the 45-degree diagonal (Fig. A2.2.2b). A shift to slightly higher Ni values is observed in the levelled Finnish Ni subsoil concentrations, and this is due to the higher FOREGS GTN subsoil concentrations (Table A2.2.1).

A2.2.1.2.2. Example from Germany

The German reconnaissance stream sediment data set at a density of 1 sample/3.65 km² (Fauth *et al.*, 1985; Birke *et al.*, 2015) was considered compatible with the FOREGS GTN survey. The nearest regional stream sediment samples to the corresponding FOREGS GTN stream sediment samples were selected for testing parametric levelling (Table A2.2.2). The distance between the neighbouring samples varied from 36 to 695 metres. Zinc was selected for this study. It was determined by flameless AAS following a hot aqua regia extraction on the <0.200 mm stream sediment grain size, while the FOREGS GTN results were obtained by hot aqua regia extraction on the <0.150 mm grain size and measured by ICP-AES. Figure A2.2.3a shows the X-Y plot of Zn distribution in the FOREGS GTN versus the German reconnaissance stream sediment

samples. The plot displays a small scatter of the sample values about the 45-degree diagonal. As the differences between the two data sets, in relation to the sample site distance and Zn concentrations between the two data sets, are comparatively small, it is assumed that the samples were collected from the same or nearby drainage basins.

Table A2.2.2. Zinc (mg/kg) concentrations in the nearest German FOREGS GTN and the German reconnaissance stream sediment samples, and the levelled German results.

FOREGS GTN Sample No.	Longitude FOREGS	Latitude FOREGS	Distance (m)	Germany Sample No.	Longitude Germany	Latitude Germany	Zn FOREGS	Zn Germany	Zn Germany (Levelled)
N33E05S5	8.97	49.28	695	6719	8.96	49.29	38	35	36.8
N33E06S5	11.62	48.98	194	7035	11.62	48.98	49	40	41.7
N33E07S2	13.73	48.58	584	7448	13.73	48.58	63	65	66.1
N33E07S3	13.60	48.91	229	7047	13.60	48.91	85	90	90.5
N33E07S4	13.09	49.16	36	6844	13.09	49.16	56	65	66.1
N34E04S2	7.17	50.29	244	5709	7.17	50.29	53	45	46.6
N34E05S4	10.25	49.81	392	6127	10.25	49.81	76	70	71.0
N35E04S5	8.14	51.29	539	4714	8.14	51.30	131	130	130
N36E05S1	10.41	52.61	218	3328	10.41	52.61	13	10	12.4
N36E05S4	9.77	54.01	105	1924	9.77	54.01	24	25	27.1

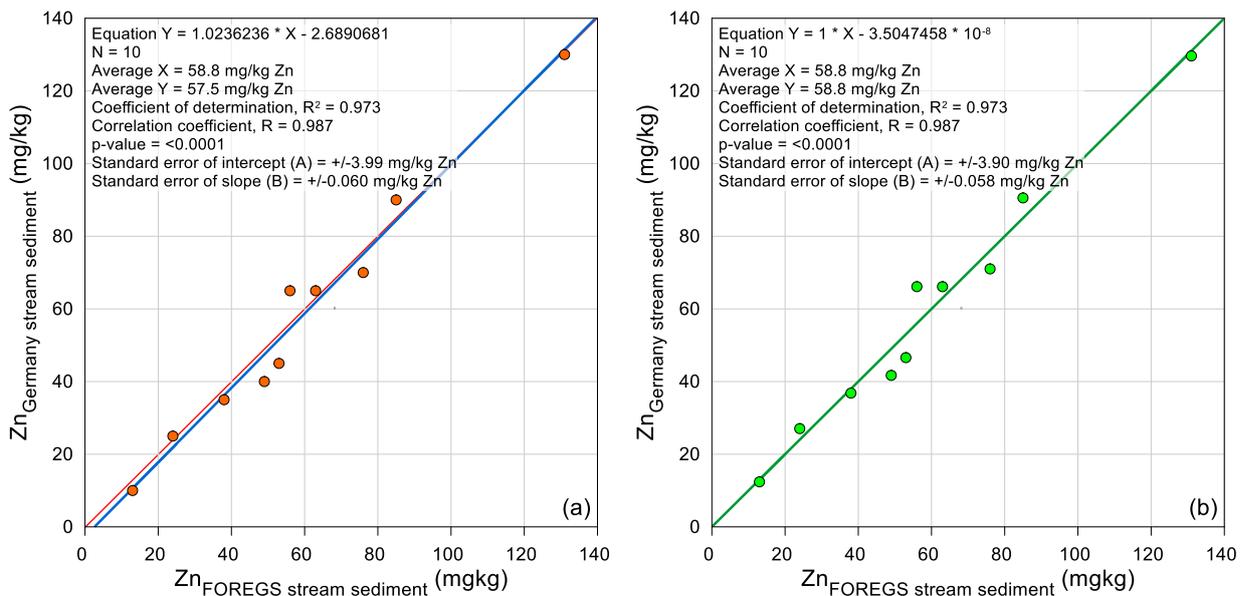


Figure A2.2.3. X-Y plots of hot aqua regia extractable Zn results of FOREGS GTN German versus German stream sediment samples, determined by ICP-AES and flameless AAS on the <0.150 and <0.200 mm grain size fractions, respectively. The red and blue lines in (a) indicate the 45-degree diagonal and the linear correlation, respectively, and the green line in (b) shows the linear correlation after levelling the German Zn stream sediment results. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

The Zn results display a high linear correlation coefficient ($R = 0.987$; $R^2 = 0.973$) with a minor deviation from the 45-degree diagonal (Fig. A2.2.3a). It is concluded that the Zn results, tabulated in Table A2.2.2, can be used for parametric levelling of the German reconnaissance stream sediment results with respect to the corresponding FOREGS GTN data.

The linear correlation equation between Zn FOREGS GTN and German stream sediment samples is:

$$Y_{\text{German stream sediment}} = 1.0236236 * X_{\text{FOREGS stream sediment}} - 2.6890681$$

Like the Finnish procedure, the levelling of the German reconnaissance stream sediment data with respect to the FOREGS GTN stream sediment, the first correction to be carried out is to shift the intercept to the zero origin of the graph. As the value of the intercept is negative (-2.6890681 mg/kg Zn), the positive value is added to each German stream sediment Ni concentration to move the intercept to the zero origin of the graph. Subsequently, each German stream sediment result is divided by the slope at 1.0236236 to give the levelled German stream sediment Zn values, which are tabulated in Table A2.2.2. After plotting the Zn FOREGS GTN against the Zn German stream sediment results, the calculated subsoil linear correlation line falls on the 45-degree diagonal (Fig. A2.2.3b). Again, there is an overall slight shift to higher values of the levelled German Zn stream sediment results (Table A2.2.2).

A2.2.1.2.3. Example from the Hellenic Republic

The Hellenic example, like the German one, comes from the reconnaissance stream sediment survey, which in this case has a much higher density at 2 to 3 samples/km². Thus, the Hellenic regional stream sediment samples selected are either from the same second-order catchment basins as those of the corresponding FOREGS GTN stream sediment survey or from a nearby catchment with similar lithology (Table A2.2.3). The FOREGS Hellenic GTN and Hellenic reconnaissance stream sediment sample suites were both brought into solution by hot *aqua regia*, and the elements were determined by ICP-AES and double-beam AAS, respectively, which means there are differences in the sensitivity and precision due to the analytical equipment used. There is also another minor difference, which is the grain size of the analysed samples, which was <0.150 mm for the FOREGS and <0.177 mm for the Hellenic stream sediment sample suites. The Hellenic stream sediment samples were collected from the early 1970s to the mid-1980s, while the corresponding FOREGS GTN samples were taken in 1998. The Hellenic reconnaissance stream sediment samples were analysed only for Ag, Co, Cu, Ni, Mn, Pb, U and Zn because the objective of the survey was to delineate polymetallic sulphide and uranium mineralisation (Smith *et al.*, 1976). Silver and U were not determined in the FOREGS *aqua regia* extraction (Sandström *et al.*, 2005).

Table A2.2.3. Cobalt (mg/kg) concentrations in the nearest Hellenic FOREGS GTN and the Hellenic reconnaissance stream sediment samples, and the levelled Hellenic results.

FOREGS GTN Sample No.	Longitude FOREGS	Latitude FOREGS	Distance (m)	Hellas sample No.	Longitude Hellas	Latitude Hellas	Co FOREGS	Co Hellas	Co Hellas (Levelled)
N25E13S1	22.43	37.09	86	807	22.43	37.10	9	10	7.27
N26E13S1	22.45	38.90	103	478	22.45	38.90	23	27	18.7
N28E12S4	21.92	40.96	1260	698	21.93	40.96	7	10	7.27
N28E13S4	23.61	41.10	1060	248	23.62	41.11	6	5	3.91
N28E13S5	23.01	41.07	800	25	23.02	41.08	14	14	9.96
N28E14S4	25.03	41.26	366	1531	25.04	41.26	8	8	5.92
N28E14S5	25.58	41.14	500	5228	25.58	41.15	15	15	10.6
N28E15S2	26.33	41.38	536	1151	26.34	41.38	15	16	11.3

The Co X-Y plot (Fig. A2.2.4) shows a small scatter of the sample values about the 45-degree diagonal. The Co stream sediment results display a high linear correlation ($R = 0.976$; $R^2 = 0.953$) with a minor deviation from the 45-degree diagonal (Fig. A2.2.4a). It is concluded that the Co results, tabulated in Table A2.2.3, can be used for parametric levelling of the Hellenic reconnaissance stream sediment results with reference to the corresponding FOREGS GTN data.

The linear correlation equation between Co FOREGS GTN and Hellenic stream sediment samples is:

$$Y_{\text{Hellenic stream sediment}} = 1.1485527 * X_{\text{FOREGS stream sediment}} - 0.80120153$$

Like the Finnish and German procedure, the levelling of the Hellenic reconnaissance stream sediment results, with respect to the FOREGS GTN stream sediment data, requires first to shift the intercept to the zero origin of the graph. Since the value of the intercept is negative (-0.80120153 mg/kg Co), the positive value is added to each Hellenic stream sediment Co concentration to move the intercept to the zero origin of the graph. Subsequently, each result is divided by the slope at 1.1485527 to give the levelled Hellenic stream sediment Co values, which are tabulated in Table A2.2.3. After plotting the Co FOREGS GTN against the levelled Co Hellenic stream sediment results, the linear correlation line falls on the 45-degree diagonal (Fig. A2.2.4b). The levelled Co Hellenic stream sediment results show a slight shift to lower values (Table A2.2.3) because the corresponding FOREGS GTN concentrations are lower.

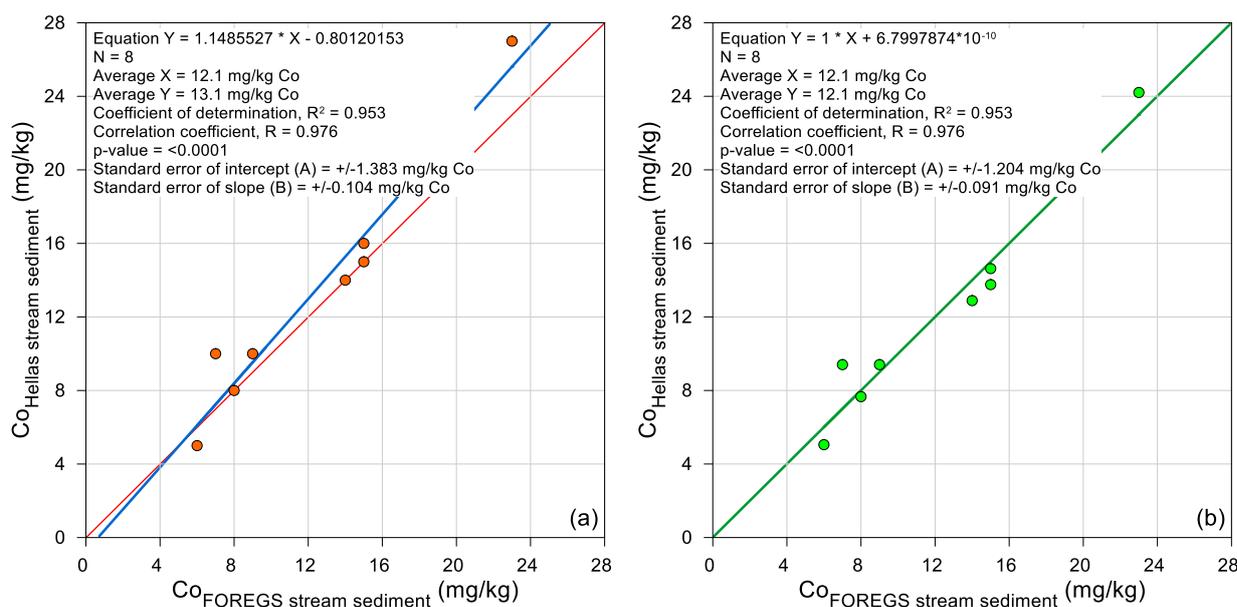


Figure A2.2.4. X-Y plots of hot aqua regia extractable Co concentrations of FOREGS GTN Hellenic versus Hellenic reconnaissance stream sediment results. The red and blue lines in (a) indicate the 45-degree diagonal and the linear correlation, respectively, and the green line in (b) shows the linear correlation after levelling the Hellenic Co stream sediment results. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

A2.2.1.2.4. Example from the United Kingdom

The United Kingdom has two data sets that may be considered compatible with the corresponding FOREGS GTN results, namely the regional soil (Johnson *et al.*, 2005) and stream sediment (Everett *et al.*, 2019) surveys. The analytical data used for both the United Kingdom (UK) and corresponding FOREGS are the total element concentrations determined by X-ray fluorescence (XRF) on the <2 mm and <0.150 mm grain size fractions of soil and stream sediment samples, respectively. Ideally, total element concentrations do not require any levelling. However, it was considered to be a good idea to discuss the comparability of the FOREGS GTN and United Kingdom XRF data sets.

Each data set was examined carefully and the nearest United Kingdom samples to the corresponding FOREGS GTN samples were selected for further treatment (Tables A2.2.4 & A2.2.5). In some cases, two different UK subsoil samples were selected as being close to the corresponding FOREGS GTN samples. The distance between the FOREGS GTN subsoil samples and those of the United Kingdom varies between 299 to 1046 m (Table A2.2.4), and the corresponding distance for the stream sediment samples varies between 146 to 735 m (Table A2.2.5). This is interesting because it shows the spatial variability between the sample sites.

The X-Y plots of Ba and Cr show a wide scatter, with Ba displaying the greatest variation and non-linear relationship (Figs. A2.2.5a, b). The Cr X-Y plots exhibit an overall linear relationship about the 45-degree diagonal (Figs. A2.2.5c, d). Nevertheless, all four plots show the between-sample site variability of the FOREGS GTN and United Kingdom samples, and this is reasonable because of the distance between them.

Although the Cr X-Y plots are NOT ideal because the values are scattered and the linear correlation coefficient is not high enough ($R = 0.770$; $R^2 = 0.592$; Fig. A2.2.5c), the results will be used for levelling.

Table A2.2.4. FOREGS GTN and United Kingdom G-BASE chromium (Cr) XRF subsoil results in mg/kg, distance between the sample sites, and levelled UK Cr results. FOREGS GTN subsoil samples that have two nearest UK samples are marked by pale yellow highlighting.

FOREGS GTN No.	Distance between (m)	UK G-BASE No.	Cr FOREGS	Cr UK	Cr UK (Levelled)
N35W01C1	719	432411S	126	115	104
N35W01C1	750	432420S	126	111	96.9
N35W01C2	321	425929S	65.0	87	54.0
N35W01C5	850	430895S	102	94	66.6
N35W01C5	1046	430884S	102	121	115
N35W02C1	341	368574S	144	159	183
N36W01C1	550	404336S	81.0	115	104
N36W01C1	831	404365S	81.0	99	75.5
N36W01C2	299	402814S	53.0	94	66.6
N36W01C3	471	421361S	90.0	112	98.7
N36W01C4	834	422690S	107	113	101
N36W01C5	560	401736S	109	149	165
N36W01C5	950	401786S	109	95	68.3
N36W02C5	302	350673S	14.0	63	11.1

Table A2.2.5. FOREGS GTN and BGS G-BASE chromium (Cr) XRF stream sediment results in mg/kg, distance between the sample sites, year of collection and levelled United Kingdom Cr results.

FOREGS GTN No.	FOREGS Year	Distance between (m)	UK G-BASE No.	BGS Year	Cr (FOREGS)	Cr (UK)	Cr UK (Levelled)
N35W01S1	1998	547	432442C	1999	121	122	112
N35W01S2	1998	171	425961C	1998	95.0	102	92
N35W01S5	1998	167	430840C	1999	114	109	99
N35W02S1	1998	405	369542C	1987	112	137	127
N36W01S1	1998	146	404551C	1995	100	105	95
N36W01S2	1998	671	402812C	1995	103	138	128
N36W01S3	1998	735	421191C	1997	88.0	92	82
N36W01S4	1998	659	422841C	1997	77.0	86	76
N36W01S5	1998	298	401754C	1994	78.0	89	79
N36W02S1	1998	323	401642C	1994	90.0	88	78
N36W02S4	1998	667	364325C	1987	61.0	46	35.8
N36W02S5	1998	600	350697C	1988	70.0	115	105

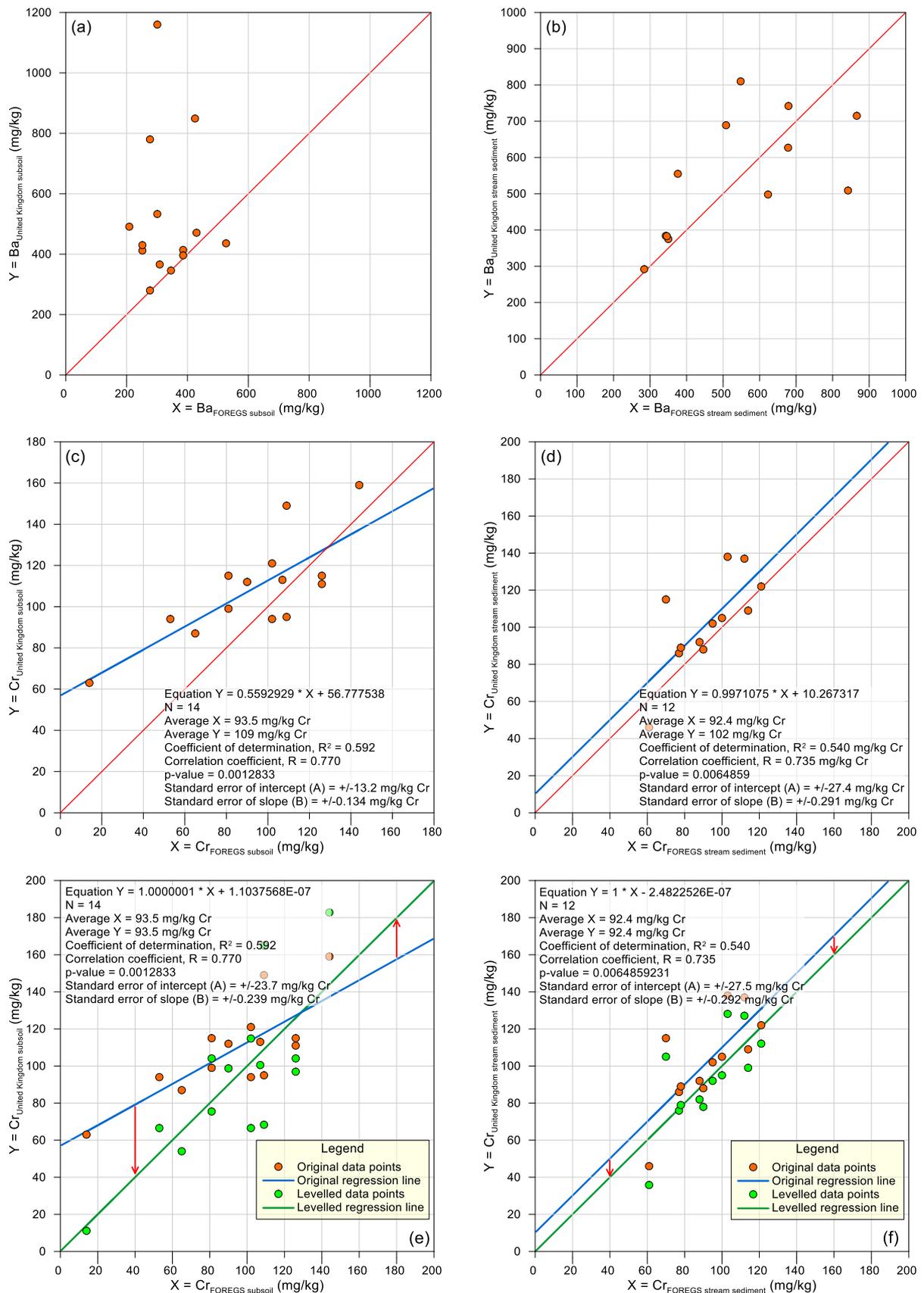


Figure A2.2.5. X-Y plots of total X-ray fluorescence results of (a) Ba & (c & e) Cr concentrations in subsoil samples ($N=14$), and (b) Ba & (d & f) Cr contents in stream sediment samples ($N=12$) of the FOREGS GTN and United Kingdom surveys, respectively. The red line indicates the 45-degree diagonal; the blue line in (c, d, e & f) displays the linear relationship; the green line in (e & f) the levelled linear correlation, and the red arrow lines in (e & f) indicate the direction of levelling with respect to the original linear correlation. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's GrapherTM v20.

The linear correlation equation between Cr FOREGS GTN and United Kingdom subsoil samples is:

$$Y_{\text{United Kingdom subsoil}} = 0.55929295 * X_{\text{FOREGS subsoil}} + 56.777538$$

The first correction to be carried out is to shift the intercept to the zero origin of the graph. Hence, from each United Kingdom subsoil Cr value, the intercept at 56.777538 mg/kg Cr is subtracted. Subsequently, each result is divided by the slope at 0.55929295 to give the levelled UK subsoil values, which are tabulated in Table A2.2.4. Upon plotting the Cr FOREGS GTN against the Cr UK subsoil levelled results, the linear correlation line falls on the 45-degree diagonal (Fig. A2.2.5e). An overall shift to lower values is observed in the UK subsoil levelled Cr concentrations (Table A2.2.4) because the FOREGS GTN subsoil concentrations are lower.

The linear correlation equation of the second example between Cr FOREGS GTN and United Kingdom stream sediment samples is:

$$Y_{\text{United Kingdom stream sediment}} = 0.99710748 * X_{\text{FOREGS stream sediment}} + 10.267317$$

The same procedure is followed as that of the first UK example, *i.e.*, the shift of the intercept to the zero origin of the graph. Thus, from each United Kingdom stream sediment value, the intercept at 10.267317 mg/kg Cr is subtracted. Then, each result is divided by the slope at 0.99710748 to give the levelled UK stream sediment values, which are given in Table A2.2.5. Subsequently, upon plotting the Cr FOREGS GTN against the Cr UK stream sediment levelled results, the linear correlation line of the calculated values falls on the 45-degree diagonal (Fig. A2.2.5f). Again, an overall shift to lower values is observed in the levelled Cr stream sediment concentrations (Table A2.2.5) because of the lower FOREGS GTN stream sediment values.

It is stressed that ideally, total element concentrations do not require levelling. Hence, the following statements are made in the case that the laboratory results were generated with a partial analytical method. In such a case, although the applied geochemist may think that the levelling of the United Kingdom subsoil and stream sediment concentrations with respect to the corresponding FOREGS GTN samples is satisfactory, the results should be examined more carefully. Apart from the comparatively wide scatter of the plotted values, which remains after levelling, the linear correlation, the coefficient of determination and the p-values have not improved at all. They are, in fact, the same (compare Figs. A2.2.5 c & e, and d & f). Consequently, the conclusion should be that the two United Kingdom data sets (if they were partial analytical results) cannot be levelled with reference to the corresponding FOREGS GTN data.

A2.2.1.3. Reduced major axis line method

The worked parametric levelling examples that have already been described from Finland, Germany, the Hellenic Republic and the United Kingdom use the linear regression equation. There is another statistical linear regression procedure worth describing. This is the reduced major axis line method, which was developed by Kermack and Haldane (1950) and popularised by Till (1974). It produces a unique best-fit linear regression line of organic correlation or isogonic growth line, as it is otherwise called:

$$Y = B * X \pm A$$

Where the slope $B = s_y/s_x$ and A represents the intercept.

s_y is the standard deviation of Y values (ordinate – vertical axis), and

s_x is the standard deviation of X values (abscissa – horizontal axis). This reduces to:

$$B = \sqrt{[CSSY/CSSX]}$$

And the linear correlation coefficient, R, is computed by:

$$R = \frac{CSCP}{\sqrt{(CSSX * CSSY)}}$$

Where:

CSSP = Corrected sum of cross products = $\sum X*Y - \sum X*\sum Y/N$

CSSY = Corrected sum of squares of Y = $\sum Y^2 - \sum Y*\sum Y/N$

CSSX = Corrected sum of squares of X = $\sum X^2 - \sum X*\sum X/N$

N = Number of sample pairs.

The value of the slope, C, gives the sign of the correlation coefficient, R.

To begin with, the parametric levelling procedure will be discussed in order to link the reduced major axis method with what has been described hitherto.

The Hellenic Ni FOREGS GTN and reconnaissance stream sediment results (Table A2.2.6) are used as an example for testing the reduced major axis method. The X-Y plot (Fig. A2.2.6a)

Table A2.2.6. Nickel (mg/kg) concentrations in the nearest Hellenic FOREGS GTN and the Hellenic reconnaissance stream sediment samples, distance between them and the levelled Hellenic results.

FOREGS GTN Sample No.	Longitude FOREGS	Latitude FOREGS	Distance (m)	Hellas sample No.	Longitude Hellas	Latitude Hellas	Ni FOREGS	Ni Hellas	Ni Hellas (Levelled)
N25E13S1	22.43	37.09	86	807	22.43	37.10	21	28	28.3
N26E13S1	22.45	38.90	103	478	22.45	38.90	63	73	63.0
N28E12S4	21.92	40.96	1260	698	21.93	40.96	22	20	22.2
N28E13S4	23.61	41.10	1060	248	23.62	41.11	12	5	10.6
N28E13S5	23.01	41.07	800	25	23.02	41.08	31	25	26.0
N28E14S4	25.03	41.26	366	1531	25.04	41.26	21	12	16.0
N28E14S5	25.58	41.14	500	5228	25.58	41.15	55	61	53.7
N28E15S2	26.33	41.38	536	1151	26.34	41.38	37	46	42.2

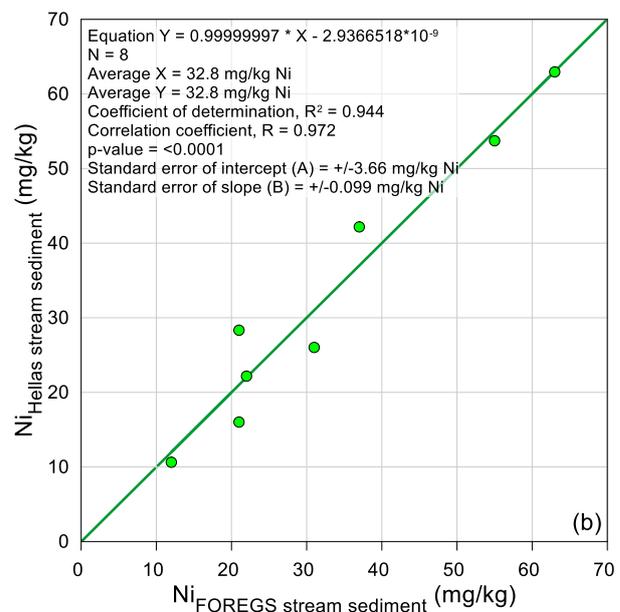
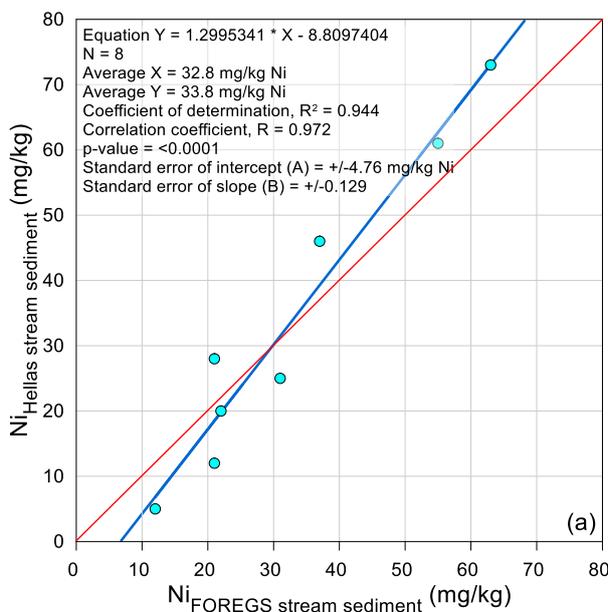


Figure A2.2.6. X-Y plots of hot aqua regia extractable Ni concentrations of FOREGS GTN Hellenic versus regional Hellenic regional stream sediment results. The red and blue lines in (a) Indicate the 45-degree diagonal and the linear correlation, respectively, and the green line in (b) Shows the linear correlation after levelling the Hellenic Ni stream sediment results. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

shows a moderate scatter of the sample values about the 45-degree diagonal. The Ni results display a high linear correlation coefficient ($R = 0.972$; $R^2 = 0.944$) with a minor deviation from the 45-degree diagonal.

The linear correlation equation between the Ni FOREGS GTN and Hellenic reconnaissance stream sediment samples is:

$$Y_{\text{Hellenic stream sediment}} = 1.2995341 * X_{\text{FOREGS stream sediment}} - 8.8097404$$

The parametric levelling of the Ni Hellenic reconnaissance stream sediment data, with respect to the FOREGS GTN stream sediment results, requires first the shift of the intercept to the zero origin of the graph. As the value of the intercept is negative (-8.8097404 mg/kg Ni), the positive value is added to each Hellenic stream sediment Ni concentration to move the intercept to the zero origin of the graph. Subsequently, each result is divided by the slope at 1.2995341 to give the levelled Hellenic stream sediment Ni values for plotting the linear correlation line, which coincides with the 45-degree diagonal (Fig. A2.2.6b).

The reduced major axis procedure is given in Table A2.2.7. The reduced major axis equation results are used in the same manner as the procedure described for the parametric levelling examples, *i.e.*, to each Hellenic stream sediment value the intercept at 10.05421029 mg/kg Ni is added, and each result is divided by the slope at 1.337533139 to give the reduced major axis Ni Hellenic stream sediment results (Table A2.2.8). It is noted that calculated parametric levelling and reduced major axis Ni results are overall similar.

For pictorial comparison, the results of the different statistical procedures used are plotted on the same graph (Fig. A2.2.7). The decision on which levelling procedure to use depends on the data. It is recommended, however, to test both the parametric and reduced major axis levelling, and to select the procedure that gives the optimum fit. In this case, the parametric levelling is better because the fitted regression line falls exactly on the 45-degree diagonal.

A2.2.2. Conclusions and recommendations

As already pointed out by Darnley *et al.* (1995, p.75), statistical levelling and normalisation procedures applied to existing data sets are '*geochemically blind*' because they simply manipulate numbers.

The parametric levelling method works exceptionally well when one is dealing with the variability due to within-sample analytical variation. If, however, the between-sample site variability must be considered, then the variability is too great to give meaningful results. Hence, the applied geochemist should be incredibly careful with the use of these statistical methods. Ideally, the parametric levelling should be done on samples collected from the same site, *i.e.*, in the way field duplicate samples are collected.

The examples that have been discussed selected national survey results that were overall similar to those used in the FOREGS GTN mapping, *i.e.*, same sample type, similar grain size analysed and analytical method. The attempt was to select the closest possible national samples to the corresponding FOREGS GTN samples to minimise the between-sample site variability. This approach is successful when the sampling density of the regional geochemical survey is high, as has been observed in the cases of the reconnaissance stream sediment surveys in Germany and the Hellenic Republic.

It is, therefore, strongly recommended during the planning stage of the Global Geochemical Reference Network sampling campaign in each country, apart from the collection of the random sample types that will be collected from each 160x160 km grid cell, to collect additional samples from the same sites of regional or detailed geochemical surveys. The analytical results of these 'field duplicate' samples could then be used effectively for levelling the analytical results of past geochemical surveys. A similar recommendation was given in Annex A2.1 for the geodetic levelling of existing regional geochemical data sets.

Table A2.2.7. The reduced major axis linear regression procedure calculations are shown below using the Ni concentrations in the FOREGS GTN and Hellenic reconnaissance stream sediment samples.

FOREGS GTN No.	Hellas Sample No.	FOREGS Ni (X)	Hellas Ni (Y)	FOREGS Ni (X²)	Hellas Ni (Y²)	X*Y
N25E13S1	807	21	28	441	784	588
N26E13S1	478	63	73	3969	5329	4599
N28E12S4	698	22	20	484	400	440
N28E13S4	248	12	5	144	25	60
N28E13S5	25	31	25	961	625	775
N28E14S4	1531	21	12	441	144	252
N28E14S5	5228	55	61	3025	3721	3355
N28E15S2	1151	37	46	1369	2116	1702
N pairs =	8					
Sum X =		262				
Sum Y =			270			
Sum X*Y =						11771
Mean X =		32.8				
Mean Y =			33.75			
Sum X ² =				10834		
Sum Y ² =					13144	

CSCP = 2928.5

CSSX = 2253.5

CSSY = 4031.5

Slope B = $\sqrt{(CSCY/CSSX)} = 1.337533139$

Intercept A = $\text{Sum Y/N} - (B * \text{Sum X/N}) = \text{Mean Y} - (B * \text{Mean X}) = -10.05421029$

Reduced Major Axis (RMA) regression line:

$$Y_{\text{Hellenic stream sediment}} = 1.337533139 * X_{\text{FOREGS stream sediment}} - 10.05421029$$

Table A2.2.8. Nickel (mg/kg) concentrations in the nearest Hellenic FOREGS GTN and the Hellenic reconnaissance stream sediment samples, the parametric levelled and reduced major axis linear regression Hellenic results.

FOREGS GTN Sample No.	Longitude FOREGS	Latitude FOREGS	Distance (m)	Hellas sample No.	Longitude Hellas	Latitude Hellas	Ni FOREGS	Ni Hellas	Ni Hellas (Levelled)	Ni Hellas (Reduced Major Axis)
N25E13S1	22.43	37.09	86	807	22.43	37.10	21	28	28.3	28.5
N26E13S1	22.45	38.90	103	478	22.45	38.90	63	73	63.0	62.1
N28E12S4	21.92	40.96	1260	698	21.93	40.96	22	20	22.2	22.5
N28E13S4	23.61	41.10	1060	248	23.62	41.11	12	5	10.6	11.3
N28E13S5	23.01	41.07	800	25	23.02	41.08	31	25	26.0	26.2
N28E14S4	25.03	41.26	366	1531	25.04	41.26	21	12	16.0	16.5
N28E14S5	25.58	41.14	500	5228	25.58	41.15	55	61	53.7	53.1
N28E15S2	26.33	41.38	536	1151	26.34	41.38	37	46	42.2	41.9

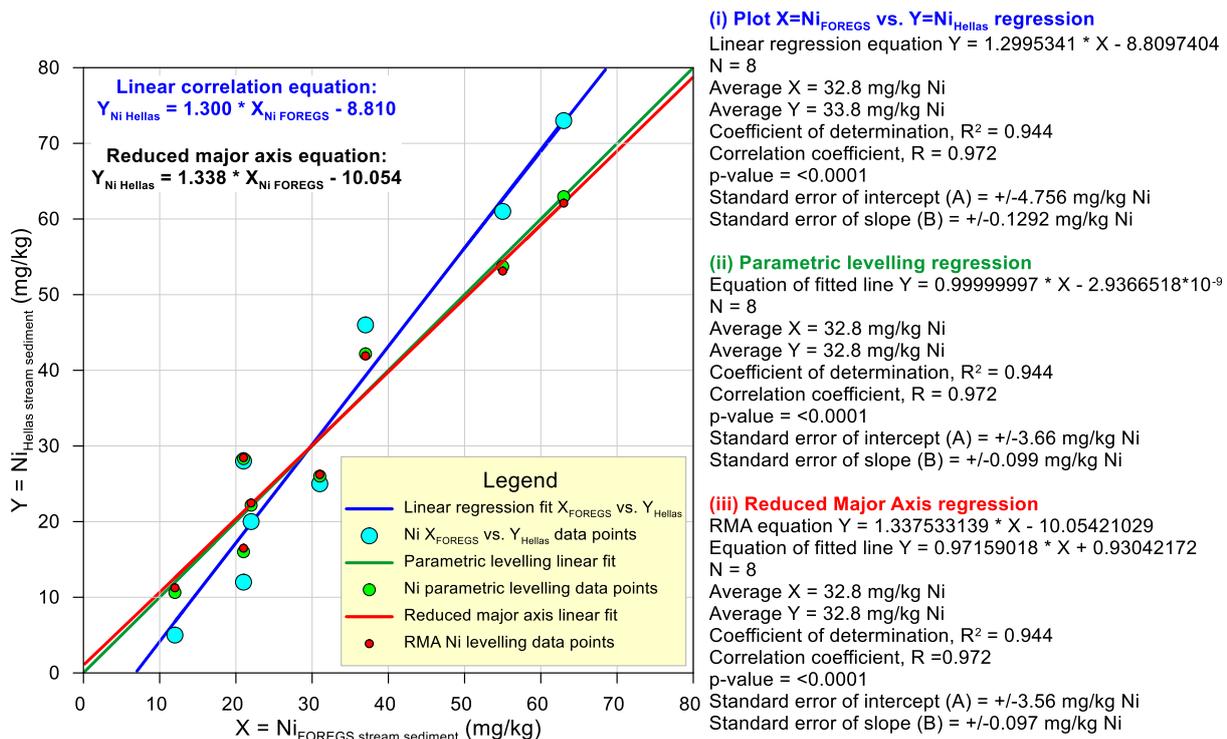


Figure A2.2.7. X-Y plot of aqua regia extractable Ni of FOREGS GTN versus Hellenic reconnaissance stream sediment results. The graph shows (i) The original Ni pair data points (cyan dots and blue regression line). (ii) The parametric levelling Ni pair data points (green dots and green regression line), and (iii) The reduced major axis pair data points (red dots and red regression line). Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

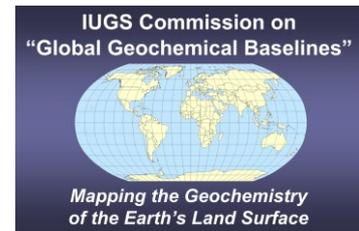
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Note: All hyperlinks were checked on the 25th of February 2022.

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 3

Sampling Methods: Introduction

Alecos Demetriades^{1,5}, Christopher C. Johnson^{2,5}, David B. Smith⁵,
Timo Tarvainen^{3,5}, Maria João Batista^{4,5}

¹ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

² GeoElementary, Derby, United Kingdom

³ Geological Survey of Finland, Espoo, Finland

⁴ Laboratório Nacional de Energia e Geologia, Amadora, Portugal

⁵ IUGS Commission on Global Geochemical Baselines

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3A. Introductory notes

In Chapter 2, the Global Terrestrial Network (GTN) grid cells of 160x160 km, and the selection of sample sites in second- and third-order catchment basins, according to the stream magnitude order classification system by Strahler (1957, 1969), are described. Further, identifiers of the different sample types are given. It is strongly recommended to read Chapter 2 a few times because it is important to understand the philosophy of the GTN sampling design, the selection of sample sites, and the use of sample identifiers before proceeding to study this Chapter where the sampling procedure is described in detail.

Sampling is the most important and costly stage of any geochemical mapping project, and it is the most difficult to repeat if not carried out properly (Demetriades, 2014, 2021; Demetriades *et al.*, 2018). Consequently, the applied geochemists involved in sampling must be well-trained in the collection of samples of:

- (i) Rock,
- (ii) Residual soil (Top and Bottom),
- (iii) Humus (where present),
- (iv) Stream water (where present),
- (v) Stream sediment, and
- (vi) Overbank sediment (Top and Bottom)

from second-order catchment basins with an area of <100 km², and

- (vii) Floodplain sediment (Top and Bottom)

from third-order catchment basins with an area between 1000 and 6000 km².

It is strongly stressed that untrained personnel must NOT be allowed to go out in the field for sampling, if not accompanied and supervised by an experienced field applied geochemist until they become proficient.

The stepwise sampling instructions are designed for novices but also experienced field applied geochemists for teaching purposes. They must be followed precisely because the aim of the project for 'Establishing the Global Geochemical Reference Network' is to collect all sample types from all countries with a standardised methodology. Further, the wide-spaced sampling density of 1 site/5120 km² in GTN grid cells of 160x160 km is exceedingly demanding because all collected samples will constitute the *Standardised Global Geochemical Reference Network* for each sample type.

The sampling of residual soil is the most difficult, even for experienced field applied geochemists. Therefore, *it is strongly recommended that all national sampling teams must be trained by an experienced soil scientist for the recognition of soil horizons.*

The sampling methods described in this Chapter can be applied also to regional geochemical surveys by changing the sampling density according to the area of the country and available funds.

3B. Equipment

In the following Chapters, describing the standardised methodology for sampling Rock, Residual soil, Humus, Stream water, Stream sediment, Overbank sediment and Floodplain sediment, there are two lists of equipment:

- (i) Equipment to be provided by the Project Coordinator, and
- (ii) Equipment to be purchased by each participating country.

The first list of equipment to be provided by the Project Coordinator is important because it secures the standardised methodology and, therefore, needs to be purchased centrally and

distributed to all participating countries. Thus, each national coordinator should inform the Project Coordinator of the number of sampling teams that will be involved in the sampling campaigns in each country.

The second list of equipment is, of course, just as important and could easily be purchased in each country. In this case, the national coordinator should ensure that all sampling teams in the country have the same equipment.

**Aluminium and Brass equipment and Coloured plastic scoops and buckets
must be avoided**

3C. Preparation of equipment for sampling

Most equipment that will be purchased by each participating country is ready for use. However, some equipment may require attention. New spades and mattock cutters are usually painted, and the wooden handle may be varnished or painted (Fig. 3.1a). Previously used spades and mattock cutters, such as those shown in Figure 3.1c, may be rusted and, in this case, the rust must be removed (Fig. 3.1d). Similarly, new sledgehammers and chisels are painted, and used geological hammers may be slightly dirty-rusted (Fig. 3.1e). The paint and rust must be removed before the equipment is used for sampling, and this can be achieved quite easily by sandblasting (Figs. 3.1b, d & f). The varnish and paint on wooden handles can be removed again by sandblasting.



(a)



(b)



(c)



(d)



(e)



(f)

Figure 3.1. (a) Painted spade and mattock cutter. (b) Paint removed by sandblasting. (c) Rusted spade and mattock cutter. (d) Rust removed by sandblasting. (e) Painted 2 and 5 kg sledgehammers and chisel, and slightly dirty-rusted geological hammers. (f) Paint and dirt-rust removed by sandblasting. Photographs by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) & IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).

3D. Sample number flip card system for photographs

It is recommended that each country makes a sample number flip card system, according to the GTN number code used in the Global Geochemical Reference Network project. This will be used to set up the sample site number, and sample type for taking the first photograph at each site. Figure 3.2 shows the sample number flip card system for a country situated in the northern (N) hemisphere and to the east (E) of the Greenwich meridian. Countries that are in the southern hemisphere and to the east of the Greenwich meridian should make a flip card system with 'S' and 'E', respectively. Accordingly, countries that are to the west of the Greenwich meridian should exchange the 'E' with 'W'. Countries that happen to be on both sides of the equator and the Greenwich meridian should have both 'N' and 'S', and 'E' and 'W', respectively.

Figure 3.2 shows the photographs with the site identification codes together with the letters and numbers that are necessary for making the sample number flip card system.

The letters and numbers should be printed on a thick paper or a thin card, cut into rectangles, then plasticised, perforated and mounted in a plastic or plasticised metal ring binder. The latter is preferred, if available.

It is strongly recommended that each national sampling team should have, as a safety precaution, at least two sample number flip card systems during the field sampling campaign.

<i>Site photograph identification code</i>								<i>Explanation of the first photograph at each site</i>	
								Identification code (ID) of a rock (R) sample site photograph.	
								Identification code of a field duplicate (D) rock sample site photograph. This is a special case for all sample types if the duplicate field site is very different from the routine sample site.	
								Identification code of a residual soil sample site photograph. The ID code of the Topsoil (T) sample is used.	
								Identification code of a humus (H) sample site photograph. This is for special cases, as normally the humus horizon is included in the residual soil photograph.	
								Identification code of a Stream water/Stream sediment sample site photograph, as these two samples are collected from the same site, the Stream water ID is used.	
								Identification code of an overbank sediment sample site photograph. The ID code of the top (K) overbank sediment sample is used.	
								Identification code of a floodplain sediment sample site photograph. The ID code of the top (F) floodplain sediment sample is used.	
N	0	0	E	0	0	R	1		
S	1	1	W	1	1	T	2	D	
	2	2		2	2	H	3		
	3	3		3	3	W	4		
	4	4		4	4	K	5		
	5	5		5	5	F			
	6	6		6	6				
	7	7		7	7				
	8	8		8	8				
	9	9		9	9				

- R = Rock
- T = Residual soil (Top)
- H = Humus
- W = Stream water/Stream sediment
- K = Overbank sediment (Top)
- F = Floodplain sediment (Top)

Figure 3.2. A sample number flip-card system is used to set up the sample number for taking the first photograph at each sample site. For an explanation see the text. Photographs by Alecos Demetriades (IGME/IUGS-CGGB).

3E. Plastic laminated scalebar for photographs

It is recommended to make a plastic laminated 12-cm scalebar to be used as a scale for photographs in cases where the two-metre measure is not displayed. Figure 3.3 shows such a scalebar.

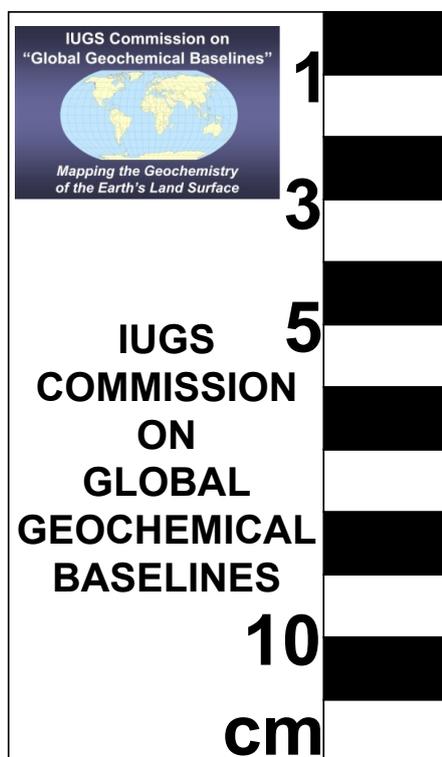


Figure 3.3. Scalebar for photographs: 12-cm scalebar with the logo and name of the IUGS Commission on Global Geochemical Baselines to be printed on both sides of a card and plasticised for protection. Designed by Alecos Demetriades (IGME/IUGS-CGGB) with Microsoft™ PowerPoint.

3F. Photographs to be taken

The minimum number of digital photographs, which should be taken at each rock, residual soil, stream water, stream sediment, overbank sediment and floodplain sediment sampling site, is given in each Chapter that describes the sampling procedure.

3G. Photograph identifiers

Table 3.1 provides the photograph codes that should be used for the digital photograph archive.

Table 3.1. Photograph identifier codes. Random site 3 of GTN grid cell N26E14 is used as an example (see Fig. 2.8 in Chapter 2). Notation: The star (*) refers to the random GTN point number 1, 2, 3, 4 or 5.

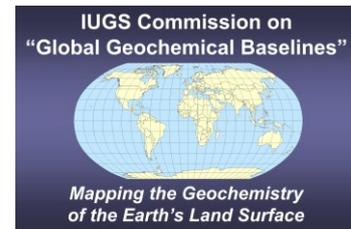
Catchment basin	Sample type photograph	Photograph code	Example
Second-order (<100 km ²)	Rock:	R	
	Sample number	R*N	N26E14R3N
	Landscape photograph	R*L	N26E14R3L
	Site photograph (natural light)	R*S	N26E14R3S
	Site photograph (fill-in flash)	R*F	N26E14R3F
	Close-up	R*C	N26E14R3C
	Residual soil:	T	
	Sample number	T*N	N26E14T3N
	Landscape photograph	T*L	N26E14T3L
	Ground surface	T*G	N26E14T3G
	Site photograph (natural light)	T*S	N26E14T3S
	Site photograph (fill-in flash)	T*F	N26E14T3F
	Close-up	T*C	N26E14T3C
	Photograph of the fill-up pit (a must at all sites)	T*P	N26E14T3P
	Humus (where present):	H	
	Site photograph (natural light)	H*S	N26E14H3S
	Site photograph (fill-in flash)	H*F	N26E14H3F
	Close-up	H*C	N26E14H3C
	Stream water/Stream sediment:	W	
	Sample number	W*N	N26E14W3N
	Landscape photograph	W*L	N26E14W3L
	Site photograph (natural light)	W*S	N26E14W3S
	Site photograph (fill-in flash)	W*F	N26E14W3F
	Close-up	W*C	N26E14W3C
	Overbank sediment:	K	
	Sample number	K*N	N26E14K3N
	Landscape photograph	K*L	N26E14K3L
Site photograph (natural light)	K*S	N26E14K3S	
Site photograph (fill-in flash)	K*F	N26E14K3F	
Close-up	K*C	N26E14K3C	
If a pit is dug, take a photograph of the fill-up pit	K*P	N26E14K3P	
Floodplain sediment:	F		
Sample number	F*N	N26E14F3N	
Landscape photograph	F*L	N26E14F3L	
Site photograph (natural light)	F*S	N26E14F3S	
Site photograph (fill-in flash)	F*F	N26E14F3F	
Close-up	F*C	N26E14F3C	
If a pit is dug, take a photograph of the fill-up pit	F*P	N26E14F3P	
Third-order (1000-6000 km ²)			

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Note: All hyperlinks were checked on the 12th of February 2022.

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 3.1

Rock Sampling

Maria João Batista^{1,5}, Alecos Demetriades^{2,5},
Karina Maribel Cerna Guillen^{3,5}, Francy Michell Medina^{3,5},
Anna Ladenberger^{4,5}

¹ Laboratório Nacional de Energia e Geologia, Amadora, Portugal

² Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

³ Instituto Hondureño de Geología y Minas, Tegucigalpa, Honduras

⁴ Geological Survey of Sweden, Uppsala, Sweden

⁵ IUGS Commission on Global Geochemical Baselines

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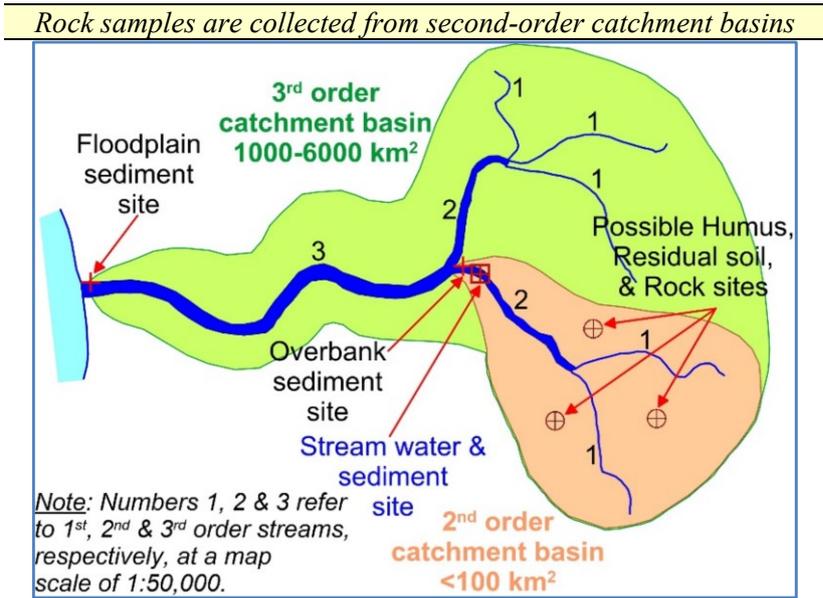
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3.1.1. Introduction

Rocks are in terms of geochemical processes the primary source of chemical elements in the natural materials at the Earth's surface (soil, sediment, water). In geoscience, rock geochemistry provides essential information about the variety of geological processes of rock formation such as magma crystallisation, hydrothermal alteration, ore formation, weathering style, depositional environment, redox conditions, geotectonic setting, and many others (Rollinson, 1993; Rollinson and Pease, 2021). The advantages of sampling rock lithotypes are well-documented in the literature and are widely used in the different stages of geological mapping and mineral exploration (Hawkes and Webb, 1962; Levinson, 1974, 1980; Beus and Grigorian, 1977; Rose *et al.*, 1979; Govett, 1983).

To identify the necessary interpretational procedures, it is essential to single out features of the geological framework or mineralisation system that have a bearing on multi-element primary geochemical dispersion. Geological events, including those that form mineral deposits, are detectable by litho-geochemistry. While a proper understanding of geological processes and the mechanisms of element migration and fixation are essential, they are beyond the scope of this Manual, and specialised texts should be consulted (Beus and Grigorian, 1977; Govett and Nichol, 1979; Govett, 1983; Rollinson, 1993; Rollinson and Pease, 2021).

There are many terrestrial whole-rock geochemical databases and repositories (*e.g.*, Lehnert *et al.*, 2000; Walker *et al.*, 2006; Strong *et al.*, 2016; Champion *et al.*, 2016; Haraguchi *et al.*, 2018; Gard *et al.*, 2019). However, they usually consist of published literature data, often at the local scale, and as they do not originate from systematic rock-geochemical mapping campaigns, none of them are truly internally consistent.

For the Global Geochemical Reference Network mapping project, as well as regional and detailed rock-geochemical surveys, the chemistry of fresh rock samples determines the primary background distribution of chemical elements, and anomalous patterns where these occur. In fact, the geochemical signatures of igneous, sedimentary, metamorphic and mineralisation processes can be identified using the most representative lithotypes.

The objective of rock sampling within the Global Geochemical Reference Network project is to collect the most representative rock type from the randomly selected second-order catchment basin with an area of <100 km² (refer to Sections §2.4 to 2.6 in Chapter 2). The representativeness of the rock sample depends on many factors, such as the availability and accessibility of the outcrop, its size, shape and internal structure, texture, homogeneity of the rock, the grain size of constituent minerals and the retrieved sample weight. In order to choose the optimal rock sample within the second-order catchment basin, it is particularly important to study before the sampling campaign the geological map of the region in conjunction with high-resolution satellite imagery to locate potential outcrops for sampling.

Taking a representative fresh rock sample from outcrops, meaning that there is no change in rock primary constituents and, thus, its original chemical composition is maintained, as pointed out by Levinson (1974) and Govett (1983), is a difficult task and debated for decades. The reasons are many, *i.e.*, most rock types are not homogeneous, their grain size and mineralogy in the outcrops usually vary from point to point. A particular rock face may outcrop preferentially because of its weathering characteristics, and the outcrop surface may be weathered and oxidised. As stated by Levinson (1974), there is no averaging effect such as it exists in the secondary environment and, thus, rock samples are often representative of only the material that is actually collected.

In rock sampling, the human factor and the sampler's preferences should not be underestimated. To eliminate all the bias, there is a need to follow a well-defined sampling procedure, which means that the personnel involved in rock sampling should be trained and supervised by experienced applied geochemists with solid knowledge of petrology, mineralogy, metamorphism, mineralisation, weathering, *etc.* To understand better the importance of these concepts, it may be useful to consult the theory of rock sampling in Govett (1983), Esbensen *et al.* (2007, 2014), Petersen *et al.* (2005) and Esbensen (2020).

To achieve the goal of random sampling and the acquisition of a representative sample, rock chip collection is the method of choice for the Global Geochemical Reference Network project, and not bulk or channel or drill-core sampling. Nevertheless, features like veins, veinlets, fractures, weathered surfaces, and heterogeneity in the distribution of the rock grain size need to be taken into consideration during sampling and documented carefully.

The field-sample weight depends on the analytical programme and the amount to be kept in storage for future use. Normally, for routine rock-geochemical mapping surveys, a weight of 500 grams is sufficient for fine- to medium-grained rocks. If the rock is coarse-grained and inhomogeneous, then, as a rule of thumb for the sample to be representative, the number of points from where the rock chips are collected, and the total weight, should be increased by at least a factor of 2. For the more statistically oriented, Govett (1983) gives an interesting statistical account of the grain size of rocks, and the volume of sample required to meet the condition of representativeness. From the practical point of view, Table 3.1.1, used by SGS (2014), is given as a rule of thumb.

Table 3.1.1. Approximate sample weight required for rocks of a given grain size (modified from SGS, 2014, Table 2.1, p.17). It is noted that this table does not consider the number of 100-gram sub-samples needed for the analytical programme and the weight of the archived sample for future use.

Granularity	Grain size (cm)	Sample weight (kg)
Fine-grained	<0.1 – 0.1	0.1 – 0.5
Medium-grained	0.1 – 1	1
Coarse-grained	1 – 10	2 – 10
Porphyritic	0.1 – 0.3	0.5 – 1
Porphyritic	0.3 – 0.6	2 – 10

For the Global Geochemical Reference Network project, the most suitable field method is, as already mentioned, the so-called rock chip sampling technique. A composite rock sample is made by taking rock chips from 20 to 30 points from the same rock type to make an aggregate sample. A weight of 2 to 3 kg is enough to decrease the sampling variance and, therefore, if pegmatitic and porphyritic rocks are avoided, this weight is adequate even for coarse-grained rocks. In case the rock is coarse-grained and inhomogeneous, then the total weight of collected rock chips should be doubled, as has already been pointed out. Further, the sample weight needs to fulfil the requirements of the analytical programme, and sample archiving for future use. Hence, it is strongly recommended that the weight of each rock sample should be near 3 kg to ensure representativeness.

Rock samples, after preparation, must be analysed at the same laboratory for the same suite of elements. This will allow the development of an internally consistent high quality whole-rock geochemical database for multipurpose use, and suitable for continental-scale geochemical mapping. In addition, the mineralogy of all rock samples should be determined in the laboratory by XRD and optical microscopy.

3.1.2. Rock samples to be taken

Rock samples are collected from the second-order catchment basin (<100 km²), according to the Strahler (1957, 1969) stream magnitude order classification, namely:

- (a) Routine sample site of a normal grid cell:
 - 2 – 3 kg of rock
- (b) Duplicate field site of a duplicate grid cell (at least one in each country):
 - 2 – 3 kg of duplicate rock sample

Larger sample quantities can be taken and stored separately in each country.

3.1.2.1. Identifiers of rock samples

The identifier of rock samples is 'R':

(a) Routine sample site (e.g., GTN grid cell N26E14):

- Rock sample number: N26E14**R1**

Note: Number '1' represents the 1st random sample site in GTN grid cell N26E14.

(b) Duplicate field sample site (e.g., GTN grid cell N27E12):

- Routine rock sample number: N27E12**R3**
- Duplicate rock sample number: N27E12**R3D**

Note: Number '3' represents the 3rd sample site in GTN grid cell N27E12, and 'D' denotes the duplicate rock sample.

(c) Blank solid sample: The identifier for a blank solid sample is zero (0),

*i.e., GTN grid cell / R / sample no. / 0; for example, N27E12**R30**.*

3.1.3. Equipment for rock sampling

3.1.3.1. Equipment to be provided by the Project Coordinator

The following equipment must be purchased or made centrally, and provided to all sampling teams in each participating country:

- 27x45 cm white cotton bags with drawstring or strong plastic certified trace element free 25x50 cm Rilsan® bags or similar. *Important note: The cotton bags must not be impregnated with any chemical additives, which could contaminate the sample.*
- Plastic strip locks for securing the sample bags (attention: the plastic strip 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).
- 6x10 cm white cards for writing the sample number on both sides.
- 7.5x11.5 cm plastic zip-lock bags for holding the 6x10 cm white cards.
- Plastic laminated scalebar for 'photographs' (see Fig. 3.3 in Chapter 3), and
- Black permanent drawing ink markers (ONLY black coloured allowed).

3.1.3.2. Equipment to be purchased by each participating country

Each participating country must purchase the following equipment, and for all its sampling teams:

- Stainless steel chisel-end geological hammer.
- Sledgehammer of 5 kg weight.
- Sledgehammer of 2 kg weight.
- Chisel.

- Leather gloves.
- 10x magnifying lens (loupe).
- Pair of safety goggles.
- 30x60 cm strong plastic bags for packing sample bags, 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 the sample preparation laboratory.
- Strong PVC packing tape.
- 6 mm natural sisal rope.
- Heavy-duty cutter knife with replacement blades.
- Global Positioning System (GPS) for recording sample site coordinates, or a tablet with a GPS and digital topographical maps, or mobile telephone with GPS; it is strongly recommended to have a backup GPS receiver.
- Extra batteries for GPS or battery charger with rechargeable batteries.
- Topographical maps, preferred scale 1:50,000 (a must in case electronic digital positioning devices fail, *e.g.*, GPS).
- A plastic roamer or map ruler for extracting coordinates from 1:50,000 topographical maps in case GPS fails.
- An orienteering compass (a must in case GPS fails).
- Digital camera or a mobile telephone with a macro facility for field documentation (minimum 5 megapixels).
- Extra batteries for the digital camera.
- 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 or external hard drive) for backup of field data and digital photographs.
- USB cable to download photographs to a laptop computer daily.
- Threshold scintillometer to measure natural radioactivity (Total, Th, U, K); the scintillometer must be calibrated at least once a year before the field campaign at a national facility that is certified.
- Extra batteries for the threshold scintillometer.
- Field observations sheets.
- Waterproof case to hold field observation sheets.
- Writing pens.
- HB pencils, pencil sharpener and rubber (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).

3.1.4. Rock sampling procedure

3.1.4.1. Sample site selection

During the desktop study the second-order small drainage basin (<100 km²) is selected after studying the 1:50,000 scale topographical and geological maps (refer to Sections §2.4 to 2.6 in Chapter 2). The geological map provides information about the area distribution of the different rock types within the second-order drainage basin. With this information, the dominant rock type for sampling is selected. The exact site for sampling the selected rock type is determined in the field, after a careful study of exposed outcrops. It is important to avoid:

- Oxidised and mineralised outcrops (Figs. 3.1.1a, b).
- Weathered rock outcrops (Figs. 3.1.2a, b & 3.1.3a).
- Intensely fractured and jointed outcrops (Fig. 3.1.3b), and
- Pegmatitic and porphyritic rocks (Figs. 3.1.4a, b).



Figure 3.1.1. (a) Fractured and oxidised outcrop of schist (top unit), and fractured and oxidised massive marble (bottom), and (b) Fractured and mineralised marble (pyrite veinlets in grey-black colour), Lavreotiki Peninsula, S.E. Attiki, Hellas. Photographs: Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) & IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).



[http://earthwise.bgs.ac.uk/index.php/Palaeogene and Neogene deep weathering and soil development, Cainozoic of north-east Scotland](http://earthwise.bgs.ac.uk/index.php/Palaeogene_and_Neogene_deep_weathering_and_soil_development_Cainozoic_of_north-east_Scotland)

Figure 3.1.2. (a) Outcrop of weathered megacrystic Crathes Granite, Littletown quarry, west of Dunecht, Scotland (British Geological Survey, Earthwise), and (b) Corestones developed in weathered gabbroic rock, Maud, Scotland (British Geological Survey, Earthwise) (Merritt et al., 2003).

The reason for avoiding such outcrops has already been given in the introduction. The main aim must be to collect the freshest possible rock sample. If any of the above listed features occur, it means that the mineralogical and chemical composition of the rock has been altered. The pegmatitic and porphyritic rocks are avoided, because of their texture with large crystals dominate the chemical composition of the rock.



(a)



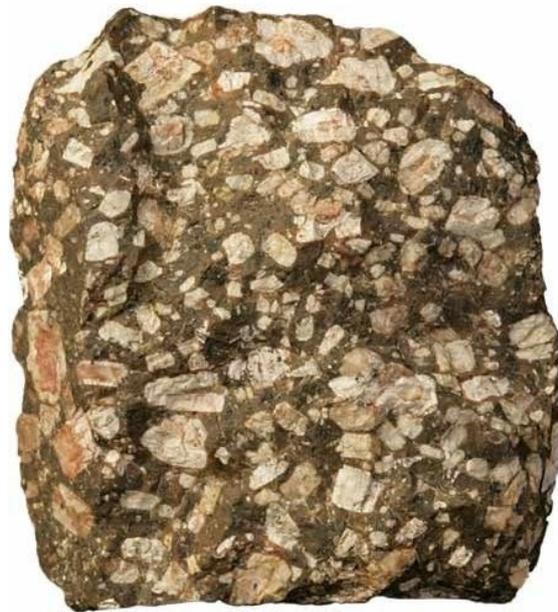
(b)

Figure 3.1.3. (a) Outcrop of weathered pillow lava, Layia-Ora Road, Larnaca District, Cyprus, and (b) Fractured and weathered schist overlying marble, Aghios Ioannis Hill, Athens, Hellenic Republic. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)

<http://www.turnstone.ca/rom100sw.htm>



(b)

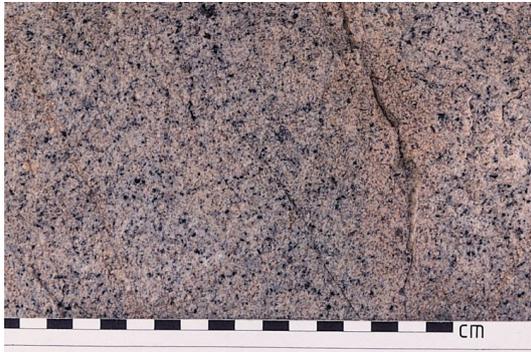
https://flexiblelearning.auckland.ac.nz/rocks_minerals/rocks/trachyte.html

Figure 3.1.4. (a) Pegmatitic granite, consisting of large pink crystals of orthoclase feldspar in a matrix of grey quartz, creamy white plagioclase, and lesser brown zinnwaldite mica – the grain size varies from >50 mm to <1 mm, Cornish granite massif, South-west England, United Kingdom (Wilson, 1980), and (b) Porphyritic trachyte (orthoclase phenocrysts set in a groundmass of orthoclase with minor plagioclase, biotite, hornblende, augite, etc.), Banks Peninsula, Dunedin Volcano, New Zealand.

3.1.4.2. Sampling procedure

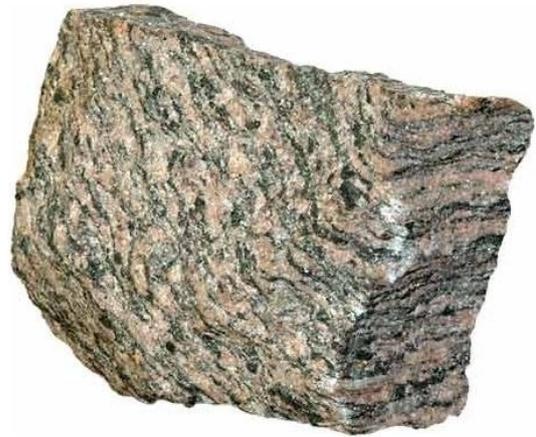
Rock chip sampling is the technique used to collect a representative rock sample from an outcrop. Sampling rocks with just the geological hammer is a futile operation. A heavy-duty 5 kg

sledgehammer is required to break up the outcrop at different points to reach a fresh rock surface. In some cases, a chisel may be needed to retrieve pieces of rock from the outcrop. A composite sample is then made by selecting rock chips from at least 20 to 30 points from the outcrop surface. The aim is always to collect fine- to medium-grained samples, and as far as possible from equigranular rocks (Fig. 3.1.5).



(a)

https://www.cedd.gov.hk/eng/about-us/organisation/org_geo/services/pub_info/memoirs/geology/vol/klb/index.html#fancyPhoto-3



(b)

https://flexiblelearning.auckland.ac.nz/rocks_minerals/rocks/gneiss.html



(c)

https://flexiblelearning.auckland.ac.nz/rocks_minerals/rocks/quartzite.html



(d)

https://flexiblelearning.auckland.ac.nz/rocks_minerals/rocks/sandstone.html

Figure 3.1.5. (a) Equigranular and fine-grained granite, Mount Butler, eastern Kowloon, Hong Kong, China. (b) Medium- to coarse-grained foliated gneiss, Westland, Fiordland, New Zealand. (c) Medium-grained quartzite, north-west Nelson, Aorere, New Zealand, and (d) Sandstone of grain size varying from 0.06 to 2 mm, North Island, New Zealand. Note: Clast size: fine-grained (0.06-0.2 mm); medium-grained (0.2-0.6 mm); coarse-grained (0.6-2 mm).

IMPORTANT SAFETY PRECAUTIONS:

- (a) Safety goggles must be worn during rock sampling. Never strike a rock with a sledgehammer (or hammer) or pry a rock with a chisel and hammer without wearing safety goggles. In some countries, it is necessary to wear a hard hat.
- (b) Wear heavy-duty leather gloves on both hands.
- (c) Before striking the rock face ensure that the sample location is safe, and there is no risk of rocks falling on you when sampling.
- (d) As the 5 kg sledgehammer is used to break up the rock outcrop, an area with good footing must be selected to prevent the sampler from falling.

The sampling procedure for collecting a representative fresh rock sample from the selected outcrop of the dominant rock type, within the second-order catchment basin, is as follows:

- (i) Switch on the GPS unit (Fig. 3.1.6a), or notebook or laptop computer with GPS, to obtain the WGS1984 decimal degree coordinates of the sample site. It is important to switch on the global positioning system upon arrival at the site, and to allow enough time for the signal to settle.
- (ii) Write the sample number with a black permanent ink marker on the cotton or plastic trace element free Rilsan[®] bag (Fig. 3.1.6b (i) & (iii)).
- (iii) Write the sample number on both sides of the small card, and place the card in the small plastic zip-lock bag and seal it (Fig. 3.1.6b (ii)).
- (iv) Select the points on the outcrop that will be sampled (Fig. 3.1.7)
- (v) Wear the safety goggles (glasses) before starting the sampling (Figs. 3.1.8a-d). This is especially important for protecting your eyes during rock sampling, because small chips may fly into your eyes.
- (vi) Break up large blocks of rock from outcrop at 20 to 30 points with a 5 kg sledgehammer or pry the fractured rock with a chisel (Figs. 3.1.8a-f).
- (vii) Break up the large blocks into manageable size rock chips with a 2 kg sledgehammer (Figs. 3.1.8e, f & Figs. 3.1.9a, b).
- (viii) Remove carefully surface weathering and oxidation from the rock chips. For this somewhat arduous job, the 5 kg sledgehammer head can be used as an anvil, and the removal of weathering and oxidation surfaces from all rock chips with the chisel-end hammer is carried out carefully (Fig. 3.1.9c). Of course, it is impossible to remove all the oxidation surfaces from the rock chips, so the attempt is to remove most of them, and the end result is a fairly clean rock chip (Fig. 3.1.9d). *Note:* Cleaning rock chips is a tedious and arduous procedure because a large volume of rock is processed (see Figs. 3.1.8e, f & 3.1.9b, e, f).
- (ix) Place all the ‘cleaned’ rock chips in a small heap (Fig. 3.1.10a).
- (x) Place the rock chips in the cotton or plastic Rilsan[®] bag (Fig. 3.1.10b).
- (xi) Place the small sample number card in the small plastic zip-lock bag on top of the rock chips (Fig. 3.1.10b), and close the cotton or Rilsan[®] bag securely with the plastic strip lock (Fig. 3.1.10c).
- (xii) Place the sample bag in a plastic bag and close it securely with a plastic strip lock (Fig. 3.1.10d). This is for the safety of the sample bag during transportation.
- (xiii) Store sample bag in plastic or carton box.
- (xiv) Mark the location of the sample site on the 1:50,000 topographical map or digital map.
- (xv) It is recommended to study the rock mineralogy and texture with a 10X hand lens (Fig. 3.1.10e). The mineralogy should be determined in the laboratory by XRD and microscopy.
- (xvi) Record sample site coordinates and general observations on the field observations sheet – Fig. 3.1.10f (refer to Appendix 1 of this Manual). *At the end of each day, the field observations should be transferred to the digital database.*
- (xvii) Record the threshold scintillometer readings. *Note: the scintillometer for measuring the natural radioactivity (Total, Th, U, K) is always held at knee height above the ground surface.*
- (xviii) Photograph at each sampling site the ‘Field Observations Sheet’ as a safety precaution in case the original sheet is somehow lost or becomes illegible.

- (xix) **Photographic documentation:** At each GTN sample site take at least four digital photographs in the following order: (a) sample site number (Fig. 3.1.11a); (b) landscape photograph of outcrop surface (Fig. 3.1.11b); (c) close-up of rock outcrop surface with natural light (Fig. 3.1.11c), and (d) use fill-in flash in case the natural light is not satisfactory (Fig. 3.1.11d). Additional photographs can be taken to show the macroscopic textural characteristics of the outcrop surface (Figs. 3.1.11e, f). Refer to Section §3D and Table 3.1 where the identification codes of the photographs are given. It is recommended that at the end of each day to add the identification codes of the photographs, and to store them on the laptop and an external hard drive for safety.

Important note: As a safety precaution, always photograph first the sample site number, and follow the same consecutive order of photograph taking.

Duplicate rock samples: Duplicate rock samples are collected randomly at least at every 20th sampling site (*i.e.*, $\approx 5\%$ duplication of the sample sites) in each country. However, countries with less than 20 GTN grid cells should collect duplicate rock samples from at least one random site. The duplicate field sample site is selected at a distance of 5 to 50 metres away from the routine sampling site, and the duplicate rock sample is collected using the same procedure as that of the routine rock sample.

3.1.4.3. Photographic documentation of rock sampling procedure

The following set of photographs shows the sampling procedure for the collection of rock samples.



Figure 3.1.6. (a) Switch on the GPS unit to record the sample site coordinates (23.733333°E, 37.955967°N). (b) Bags and other equipment for the collection of rock sample N26E14R3, Aghios Ioannis Hill, Athens, Hellenic Republic: (i) Sample number written with a black permanent ink marker on a 27x45 cm cotton bag with drawstring; (ii) Sample number written with a black permanent ink marker on both sides of a 6x10 cm white card and placed in a 7.5x11.5 cm plastic zip-lock bag; (iii) Sample number written with a black permanent ink marker on a strong certified trace element free 25x50 cm Rilsan[®] bag (used instead of the cotton bag), and (iv) Two plastic strip locks for securing bags.



(a)



(b)



(c)



(d)



(e)



(f)

Figure 3.1.7. (a-d) Outcrops of massive grey marble occurring in patches on the Aghios Ioannis Hill in Athens (Hellenic Republic) covering an area of $\approx 3700 \text{ m}^2$. (d) The IUGS bag, geological hammer, 2 and 5 kg sledgehammers indicate possible sites for collecting rock chip samples after breaking-up large blocks from the grey marble outcrops, and (e-f) Close-up of grey marble surface showing fractures and oxidations. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)



(c)



(d)



(e)



(f)

Figure 3.1.8. (a-b) Breaking-up rock with a 5 kg sledgehammer. (c) Inserting a chisel in a joint and when secured the 5 kg sledgehammer is swung until a large fragment is broken up. (d) The same action as (c) but with a 2 kg sledgehammer, and (e-f) Broken-up fragments of oxidised marble, which must be cleaned by removing oxidised parts. Note: In some countries, it is necessary to wear a hard hat, apart from safety goggles and gloves. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)



(c)



(d)



(e)



(f)

Figure 3.1.9. (a) Marble fragments with oxidation, which must be removed. (b) Removing oxidised parts with 2 kg sledgehammer – note that the 5 kg sledgehammer head is used as an anvil – it is stressed that for safety, before using the 5 kg sledgehammer as an anvil it must be set up in a stable position. (c) Removing surface weathering and oxidised parts with a chisel-end geological hammer. (d) Clean rock chips from one sample site ready for bagging, and (e-f) Showing the amount of material that was broken up from one site to extract (d) the few fragments of clean marble chips. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)



(c)



(d)



(e)



(f)

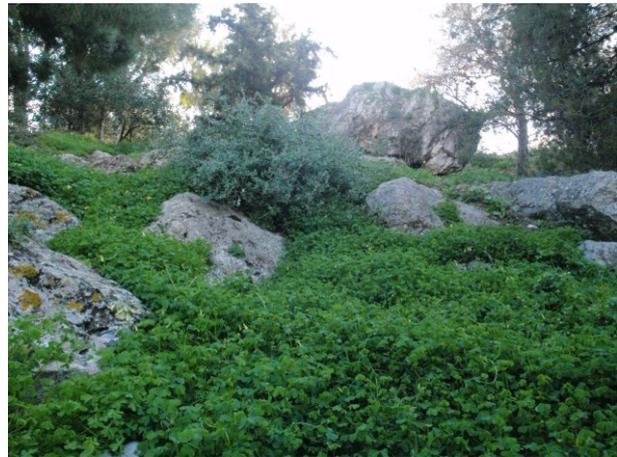
Figure 3.1.10. (a) Clean marble rock chips ready for bagging. (b) Clean rock chips packed in a 27x45 cm cotton bag and on the top right corner is the 6x10 cm white card with the sample number written on both sides and placed in a 7.5x11.5 cm plastic zip-lock bag, which is put on top of the rock chips. (c) Cotton bag with sample tied with drawstring first, and subsequently secured with plastic strip lock. (d) Cotton bag with rock chips is placed in a strong plastic bag, and secured with plastic strip lock. (e) Studying the crystal-size and texture with 10X hand lens, and (f) Recording of field observations, and upon completion a digital photograph is taken for safety purposes in case the original sheet is somehow lost or becomes illegible. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

3.1.4.4. Photographs to be taken at each rock sampling site

Take at least four photographs in the order shown in the caption of Figure 3.1.11, *i.e.*, sample number first, then the landscape photograph followed by the two close-up photographs.



(a)



(b)



(c)



(d)



(e)



(f)

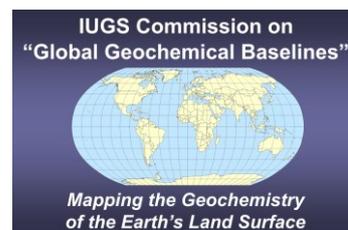
Figure 3.1.11. Photographs documenting the sample site, with their identification codes (ID): (a) Rock sample site number (R3) is situated in the south-west quadrant of GTN grid cell N26E14 of 160x160 km (ID: N26E14R3N). (b) Landscape photograph showing a few grey marble outcrops (ID: N26E14R3L). (c) Site photograph of grey marble surface with natural light (ID: N26E14R3S). (d) Site photograph of grey marble surface with fill-in flash (ID: N26E14R3F). (e) Close-up of marble surface with oxidations (ID: N26E14R3C1), and (f) Close-up of GPS unit and rock chip samples packed in a cotton bag (ID: N26E14R3C2), which is placed in a strong plastic bag – both bags are secured with a plastic strip lock. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

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Note: All hyperlinks were checked on the 12th of February 2022.

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 3.2

Residual Soil and Humus Sampling

Maria João Batista^{1,10}, Alecos Demetriades^{2,10}, Christopher C. Johnson^{3,10}, Timo Tarvainen^{4,10},
Igor Savin⁵, David B. Smith¹⁰, Edith Haslinger^{6,10}, Reijo Salminen⁴,
Virgilija Gregorauskiene^{7,10}, Zomenia Zomeni^{8,10}, Juan Pablo Lacassie Reyes^{9,10},
Felipe Astudillo^{9,10}, Pablo Sebastian Oliva Vicentelo^{9,10}

¹ Laboratório Nacional de Energia e Geologia, Amadora, Portugal

² Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

³ GeoElementary, Derby, United Kingdom

⁴ Geological Survey of Finland, Espoo, Finland

⁵ V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation

⁶ Austrian Institute of Technology GmbH, Centre for Energy, Vienna, Austria

⁷ Geological Survey of Lithuania, Vilnius, Lithuania

⁸ Geological Survey Department, Lefkosia, Cyprus

⁹ Servicio Nacional de Geología y Minería, Valdivia, Chile

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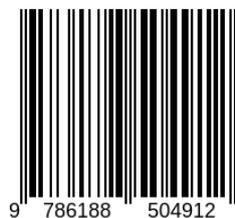
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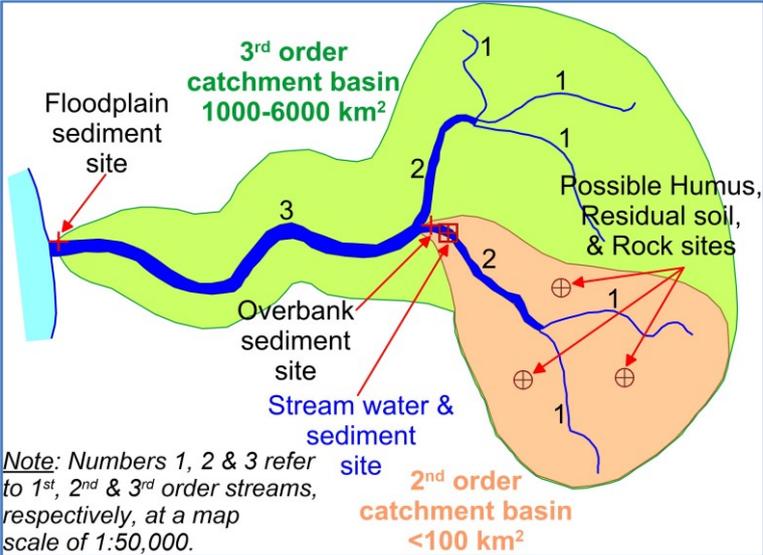
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Residual soil and humus samples are collected from second-order catchment basins



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3.2.1. Introduction

Soil is a complex natural sampling medium. It is composed of individual mineral particles (*e.g.*, quartz, feldspar, clay minerals, *etc.*) of widely varying composition, and these minerals are generally unevenly distributed throughout a given soil horizon. The nature of the soil is determined by the interaction of lithology, climate (*e.g.*, temperature, precipitation), vegetation, relief (topography), biological activity and time (Dokuchaev, 1883; Jenny, 1941; Bridges, 1970; Buckman and Brady, 1970). All soil-forming factors have great spatial variability. This leads to considerable inhomogeneity even within the area of a single sampling site. Climate is considered to be one of the most important soil-forming factors, and forms the basis for the five regional classifications described below, namely polar and subpolar, temperate, Mediterranean, desert and tropical. Figure 3.2.1 shows the effects of climate (mainly temperature and precipitation) on soil formation from the North Pole to the Equator. Further, with increasing elevation, there are climatic changes, which affect in an analogous way soil development (Fig. 3.2.2; Strahler, 1969; Bridges, 1970; Badía *et al.*, 2013, 2016). It is, therefore, quite apparent that soil differs in chemical, physical and biological characteristics in both space and time.

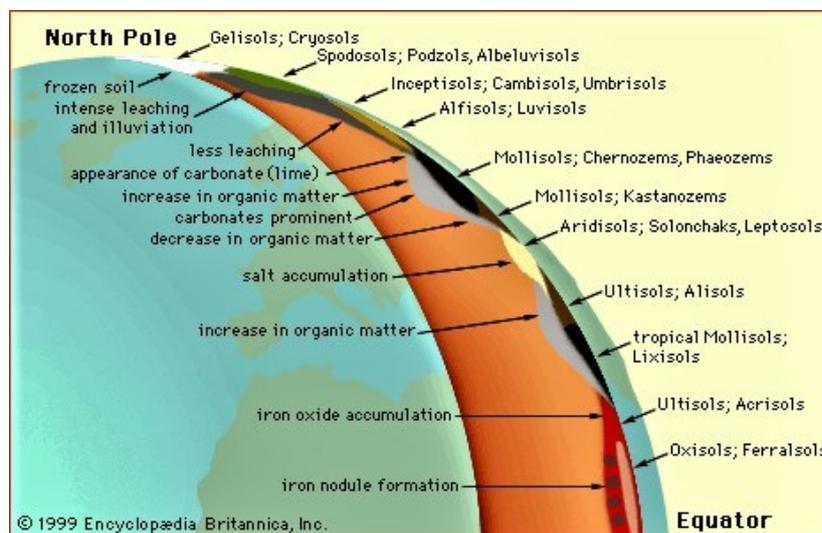


Figure 3.2.1. The effects of climate on soil worldwide (Britannica, 2012).

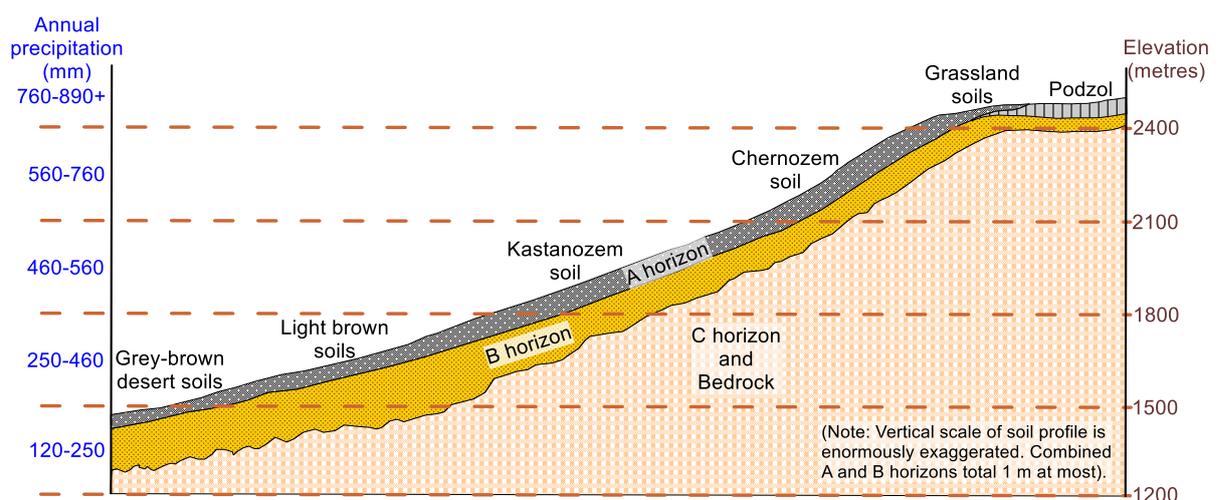


Figure 3.2.2. Schematic diagram showing the gradation of soil types from a dry steppe-climate basin (left) to a cool, humid climate (right) as one ascends the west slope of the Bighorn Mountains, Wyoming, USA (after Strahler, 1969, Fig. 19.6, p.317; redrawn with minor modifications by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) & IUGS Commission on Global Geochemical Baselines (IUGS-CGGB) with Golden Software's MapViewer™ v8).

Haslinger *et al.* (Annexe A3.2.1 of this Chapter) describe the characteristics, geographical distribution, parent material, usage, and geochemical processes of the 28 major soil units, according to the classification of the “*Harmonised World Soil Database*” (FAO/IIASA/ISRIC/ISS-CAS/JRC, 2012), *i.e.*, Regosols, Leptosols, Gleysols, Cambisols, Podzols, Arenosols, Calcisols, Histosols, Luvisols, Fluvisols, Podzoluvisols, Acrisols, Ferralsols, Kastanozems, Chernozems, Phaeozems, Solonetz, Vertisols, Lixisols, Solonchaks, Gypsisols, Greyzems, Andosols, Planosols, Nitisols, Plinthosols, Anthrosols, and Alisols. Further to the geochemical characteristics of the 28 soil units given by Haslinger *et al.* (Annexe A3.2.1 of this Chapter), a most useful classification for applied geochemists is that of Büdel (1982), which has been used as a basis for understanding the geochemistry of tropical and subtropical terrains in a definitive text by Butt and Zeegers (1992). The classification (Fig. 3.2.3) considers the extensive tropical weathering, which extended into high latitudes during the Cretaceous and Tertiary times, and the modification of large areas as a result of Pleistocene glaciation (Darnley *et al.*, 1995). It does not, however, consider mountain belts, although changes with increasing altitude generally correspond to those associated with increasing latitude.

The variations in soil, types of duricrust, the thickness of weathering zone and their relationship to mean annual temperature and rainfall are shown in Figure 3.2.4. Variations in Eh, pH, electrical conductivity and the activity of some major cationic and anionic species have been added (Darnley *et al.*, 1995). Apparently there is little chemical modification of bedrock chemistry in polar, sub-polar and cold temperate regions, in contrast to arid, tropical and equatorial terrains, which are typically affected by prolonged and deep weathering.

In some environments, *for example*, in lateritised terrains, considerable expertise is needed to interpret soil geochemical data (Blanchard, 1968; Butt and Zeegers, 1992).

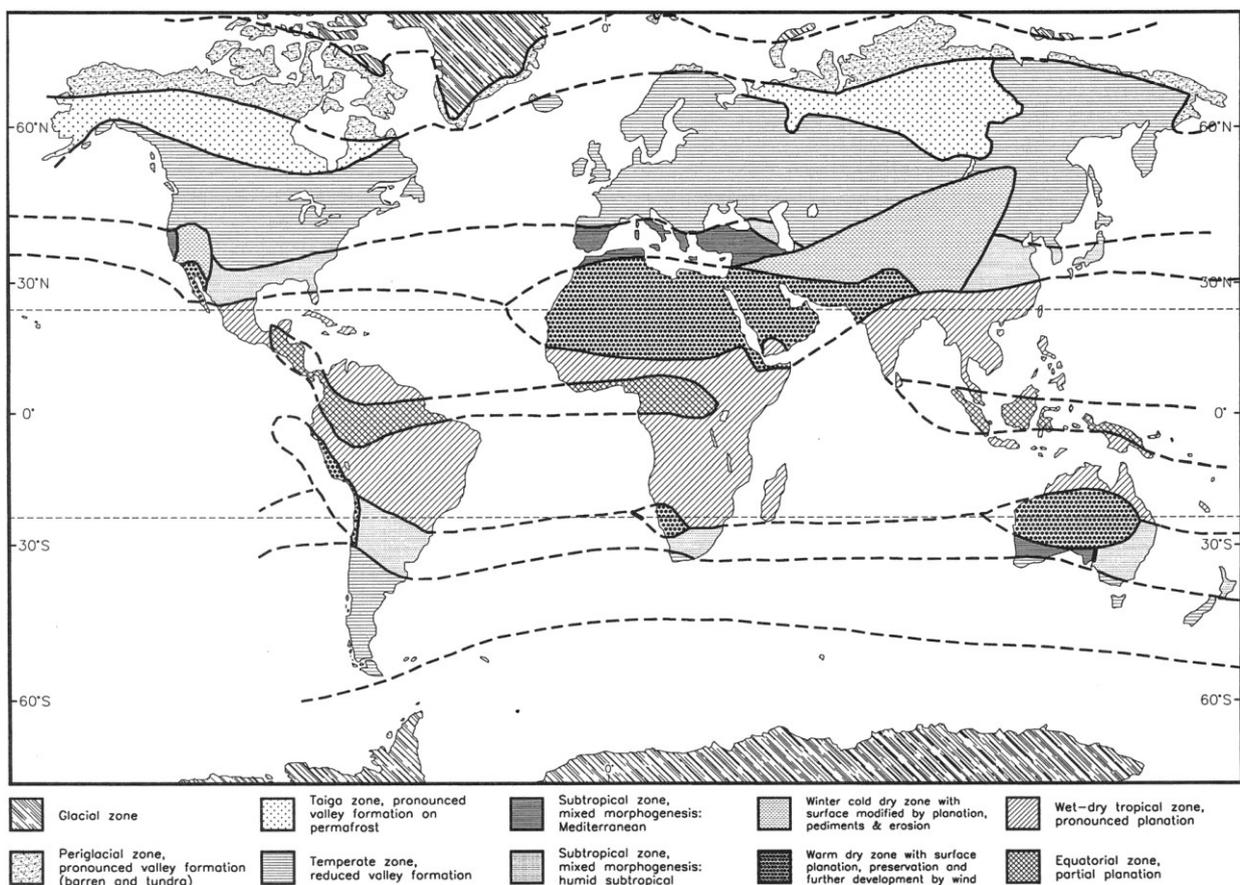


Figure 3.2.3. World morphoclimatic regions, present climatic zones, and simple geomorphology (From Giles *et al.*, 2017, Fig. 4, p.371; after Fookes, 1991, 1997). Note: The map is similar to that of Büdel (1982), which is displayed by Darnley *et al.* (1995, Fig. 5-2, p.47).

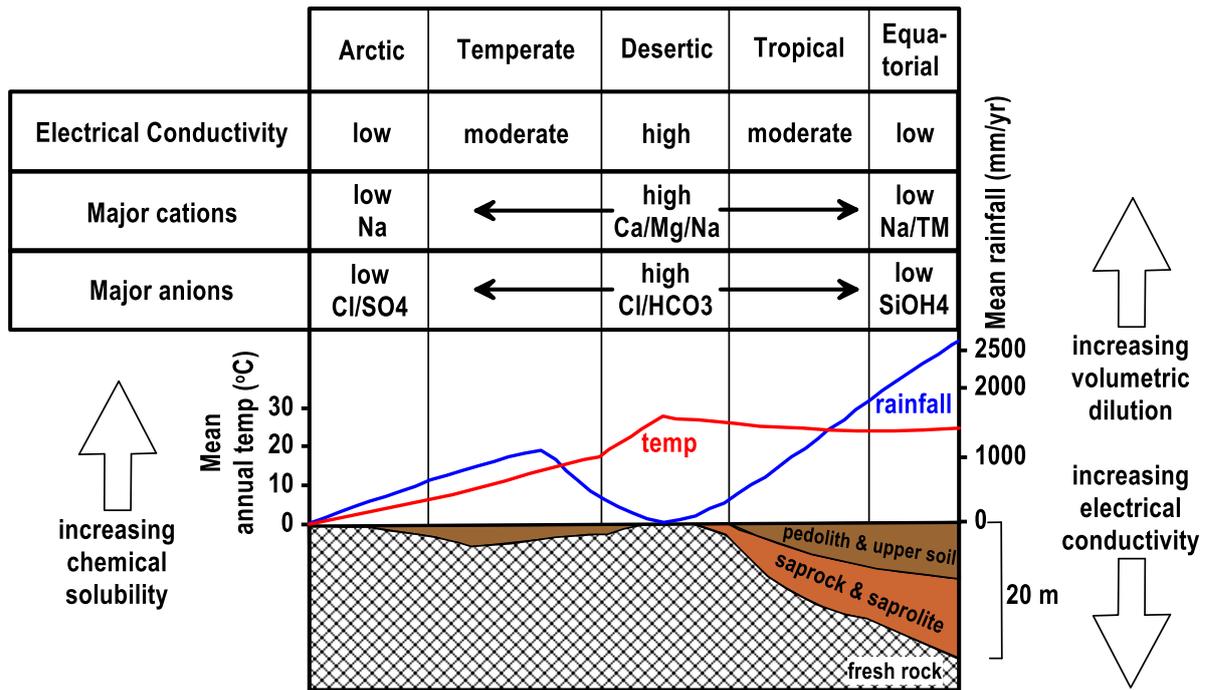


Figure 3.2.4. Generalised relationships between surface/groundwater chemistry and climate (From Darnley et al., 1995, Fig. 5-3, p. 48, based on Pédro, 1984). Notation: TM = Transition metals. Redrawn with minor modifications by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

In the Global Geochemical Reference Network project, two horizon-based samples of *residual mineral soil* shall be collected from the second-order drainage basin with an area of <100 km² (refer to Section §2.5 in Chapter 2 of this Manual), as the aim is to collect samples unaffected by human activities and to determine the natural variation worldwide. A *Topsoil* sample is collected representing the uppermost mineral soil A horizon (most often occurring at the air/earth interface or directly below the litter and/or organic material horizons), and a deeper *Bottomsoil*¹ sample is collected from the soil C horizon (generally partially weathered parent material) from the same vertical profile (see Fig. 3.2.5).

The *Topsoil* A horizon (non-humic or humic²) sample could vary in thickness from site to site and the depth range should be recorded on the field observations sheet, *i.e.*, the top boundary is between the litter and/or organic horizon and the A horizon, and the bottom boundary is between the A and either the E or B soil horizons, depending on soil type. If, however, the thickness of the residual A soil horizon is greater than 20 cm, then the top 20-cm is arbitrarily selected as the targeted sample. This is consistent with the sampling thickness of ploughed agricultural fields on the one hand, if a qualitative comparison between the two data sets needs to be made, and on the other, a greater thickness will most likely not show human influences. Further, the experience from the FOREGS Geochemical Atlas of Europe project (Salminen *et al.*, 2005) has shown that the residual A soil horizon from second-order catchment basins rarely exceeds 20-cm in thickness.

The *Bottomsoil* C horizon sample should be up to 20-cm in thickness beginning at the top of the soil C horizon, *i.e.*, from the boundary between the B and C horizons. If the *Bottomsoil* C

¹ As the top soil is referred to as '*Topsoil*' by the same token the bottom soil is referred to henceforth '*Bottomsoil*'.

² An A humic soil horizon has ≥1% organic carbon in the fine earth fraction as a weighted average to a depth of 50 cm from the mineral soil surface (FAO/IIASA/ISRIC/ISS-CAS/JRC, 2012). However, to distinguish in the field the proportion of ≥1% soil organic carbon is difficult. So, a qualitative field classification of the A residual soil horizon as either non-humic or humic can be made by using colour, namely lighter or darker, respectively (see Annexe A3.2.2 of this Chapter). Hence, the field classification is crude, and after the total organic carbon is determined in the laboratory, the classification can be corrected.

SAMPLE TYPE (Identifier)	Topsoil (T)	Bottomsoil (C)
SOIL HORIZON	#A	C
DEPTH/ THICKNESS CRITERIA	Uppermost 20 cm*	Uppermost 20 cm*

Uppermost mineral soil horizon at the air/earth interface or below the litter or organic horizon (where present)

* If soil horizon is less than 20 cm then all the horizon is sampled

Figure 3.2.5. Defining criteria of the two residual soil samples for the horizon-based sampling method. Drawn by Christopher C. Johnson, GeoElementary, Derby, United Kingdom, with Microsoft's PowerPoint.

horizon is less than 20 cm in thickness, then the entire horizon should be sampled. In either case, the depth range of the upper and lower limits of the sampled horizon should be noted on the field observations sheet.

Residual soil is formed *in-situ* by the weathering and disintegration of parent materials (e.g., rock, till, loess)³ followed by pedological processes that lead to the formation of soil horizons (Fig. 3.2.6). The collected samples should reflect the geochemical variation in the underlying soil parent materials. It is important to avoid sampling at locations that have visible or known contamination (Salminen, Tarvainen *et al.*, 1998). Comparison between the geochemical results of *Topsoil* and *Bottomsoil* samples will provide information about enrichment or depletion processes between the two soil horizons. One such process is anthropogenic contamination of the *Topsoil* horizon.

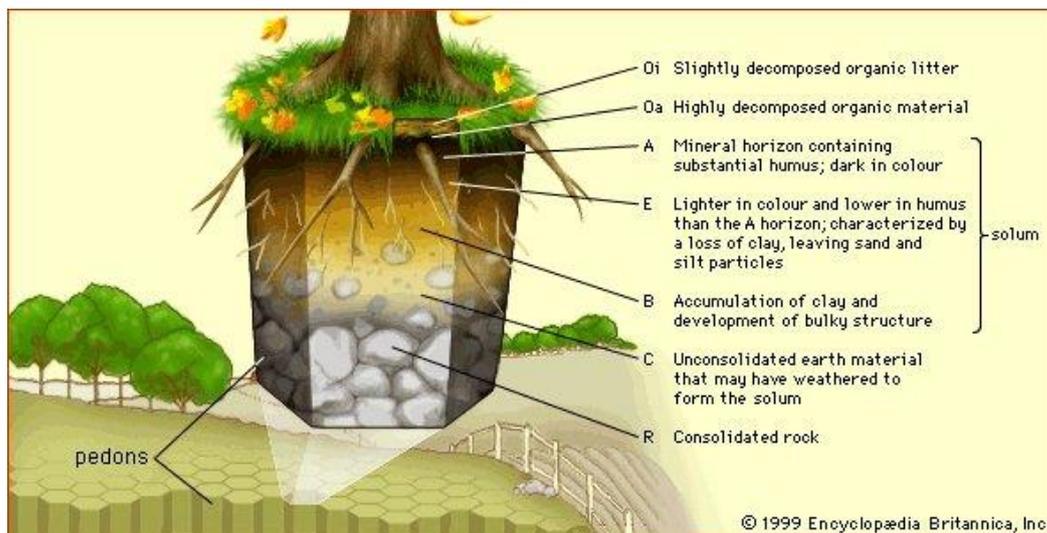


Figure 3.2.6. The soil profile shows the major layers from the O horizon (organic material) to the R horizon (consolidated rock). A pedon is the smallest unit of the land surface that can be used to study the characteristic soil profile of a landscape. The top and bottom residual soil samples are collected from the A and C soil horizons, respectively, and the humus sample from the highly decomposed organic material (Oa) horizon. Source: Britannica (2012).

³ In glacial and periglacial terrains, till and loess are considered to be the parent materials of residual soil.

Recent highly decomposed organic matter (Oa horizon), derived from an assemblage of vegetation, which is referred to as *humus* in this Manual (Fig. 3.2.6), can be used to determine the atmospheric (anthropogenic) input of chemical elements to the ecosystem (Salminen, Tarvainen *et al.*, 1998). Further, as suggested by Darnley *et al.* (1995), the collection and analysis of surface *humus*, provides a pointer to the bioavailability of elements. Although element concentrations in the *humus* samples are generally a good indication of long term atmospheric deposition, some elements (*e.g.*, Ag, Cd, Ge, Hg, Pb) have a natural tendency to enrich humus samples (Reimann *et al.*, 2007, 2015; Flem *et al.*, 2018).

The collection of a separate recently formed *humus* sample, normally occurring directly above the *soil A humic mineral horizon*, is carried out only at sites where highly decomposed organic material is developed (Fig. 3.2.6). Its thickness is normally less than 5-10 cm. The highly decomposed organic matter horizon (Oa) is developed under specific conditions, namely:

- Availability of biomass, biological activity, temperature, moisture, water saturation, topography, and
- In colder climate regimes, production exceeds the destruction of organic matter and humus accumulates. As a rule of thumb, above a mean annual temperature of 25°C, destruction exceeds production and humus is absent (Strahler, 1963, 1969).

These conditions depict that highly decomposed organic matter cannot be found at every residual soil sampling site. It is, therefore, worth mentioning that in the FOREGS Geochemical Atlas of Europe project, out of the 837 residual soil sampling sites, located in second-order catchment basins, only 367 humus samples were collected (Salminen *et al.*, 2005), *i.e.*, a proportion of about 44%, which is expected to be much lower in the global project.

3.2.1.1. Polar and subpolar regions

The polar regions are to the north and south of the 66.5° parallels (Arctic and Antarctic Circles), and the subpolar regions are between 50° and 70° latitude north and south of the equator⁴. These regions are presently glaciated or were glaciated during the Pleistocene. The major processes of physical weathering and disintegration of rocks are the action of (i) glaciers, (ii) water in various forms (liquid, ice, vapour), (iii) salt weathering, (iv) insolation (*i.e.*, exposure to the sun's rays), and (v) wind (Campbell and Claridge, 1987). Chemical weathering is relatively insignificant, and normally glacial action removes chemical weathering residua in most areas, leaving bare rock pavements or exotic morainic and other types of clastic deposits. Organic matter is not readily oxidised in the low ambient temperatures of such environments and thick accumulations of peat or bogland (muskeg) may give rise to surface conditions characterised by low Eh/pH (Darnley *et al.*, 1995).

The most common soil type in polar and subpolar regions is Podzol, which is characteristic of humid regions and strongly leached. Other soil types are Histosols (an organic rather than a mineral soil), Luvisols (iron-depleted and extremely low in organic content), Gleysols (water-saturated), and Cambisols (soil with incipient soil formation) - (refer to Annexe A3.2.1 of this Chapter to see examples of these sample types).

Another soil type occurring in polar and subpolar regions, which is not included in the Harmonized World Soil Database (FAO/IIASA/ISRIC/ISS-CAS/JRC, 2012), is Cryosol (also referred to as Gelisol, Cryozem, Cryomorphic soil and Polar Desert soil). Cryosols are characterised by frozen soil within 1 metre of the land surface (permafrost), and by waterlogging during periods of thaw (Jones *et al.*, 2009). They often show disrupted soil layers, cracks, or

⁴ It is noted that these terrain lines, as well the subsequent lines of the other regions, are without value because geographical boundaries are not keyed to the nature of the terrain. As no dividing line is completely definitive, a generally useful guide is, in the case of the Polar region, the irregular line marking the northernmost limit of the stands of trees.

patterned surface features such as frost mounds, caused by the physical actions of ice formation and melting (Britannica, 2016). Cryosols may be either mineral soil or humus-rich material.

Iron and Mn may be mobilised in the mainly podzolic soil profiles and redeposited in lower horizons or stream channels, giving rise to anomalously high values for the first-row transition elements, and also Ba and Ag (Darnley *et al.*, 1995).

3.2.1.2. Temperate regions

The north and south temperate regions extend from latitude 23.5° to 50° in both hemispheres. In general, temperate regions are characterised by increased rainfall and temperature relative to polar and subpolar regions. The characteristic soil types are Cambisols and Chernozems (refer to Annexe A3.2.1 of this Chapter). The pH/Eh and conductivity of surface water generally increase relative to polar regions (Fig. 3.2.4; Darnley *et al.*, 1995). Temperate regions are characterised by having four seasons in the year, depending on rainfall and temperature. Therefore, chemical weathering and leaching of chemical elements through the soil profile are the most crucial factors in soil development. The weathering in this case forms iron hydroxides such as amorphous hydroxides, goethite Fe(OH)₃, oxyhydroxides FeOOH, and also clay minerals derived from muscovite, such as illite by the loss of K⁺ ions. The formation of iron oxides, such as goethite, gives the soil a yellowish-brown colour. In temperate climatic regions with distinct dry summers, the formation of haematite (Fe₂O₃) leads to more red colours in soil. When the soil parent material is calcareous, chemical weathering results in dissolution of carbonates and, subsequently, the previously mentioned processes may also occur (Spaargaren and Deckers, 2005). Temperate regions correspond to 7% of the surface land area of the earth, where approximately 40% of the global population lives.

3.2.1.3. Mediterranean regions

Mediterranean climatic regions occur in both hemispheres between 30° and 45° latitude. They are found around the Mediterranean Sea, and on the western side of the other continents, *i.e.*, California, Chile, the Western Cape Province of South Africa, and West and South Australia (Fig. 3.2.3). The Mediterranean regions are characterised by warm to hot, dry summers, and cool to mild, wet winters. The most common soil types in the Mediterranean regions are, according to the Harmonised World Soil Database (FAO/IIASA/ISRIC/ISS-CAS/JRC, 2012), Cambisols, Calcisols, Leptosols, Luvisols and Regosols (see Annexe A3.2.1 of this Chapter). The best-known example is ‘*terra rossa*’ or Rhodic and Chromic Luvisol developed on carbonate rocks (Zdruli *et al.*, 2010). The climatic conditions are such for effective the dissolution and leaching of CaCO₃ and other easily soluble salts, as well as the migration of clay (Verheye and De la Rosa, 2005). During the hot and dry summer months, the soil desiccates, causing the development of red dehydrated oxidised iron compounds (*e.g.*, haematite, goethite) within the profile.

3.2.1.4. Desert regions (arid and semi-arid)

Desert regions are a difficult terrain type to define. Their common characteristic is that they are arid as they receive very little precipitation (<250 mm/annum). Meigs (1953) divided desert regions into three categories according to the amount of precipitation they receive. In this widely accepted system, extremely arid lands have at least 12 consecutive months without rainfall, arid lands have <250 mm annual rainfall, and semi-arid lands have mean annual precipitation between 250 and 500 mm; arid and extremely arid lands are deserts, and semi-arid grasslands generally are referred to as steppes and prairies. More recently, National Geographic⁵ classified the world’s deserts into five types according to the causes of their dryness, *i.e.*, (i) subtropical

⁵ <https://www.nationalgeographic.org/encyclopedia/desert/>

(Sahara, Kalahari, Tanami), (ii) coastal (Atacama), (iii) rain shadow (Death Valley), (iv) interior (Gobi), and (v) polar (parts of the Arctic and the Antarctic).

Subtropical or hot deserts are characterised by exceptionally low rainfall with high evaporation rates as a result of high temperatures and/or strong winds, and they are affected by temperature extremes (Darnley *et al.*, 1995). The most extensive and well-documented deserts are hot deserts characterised by extremely high temperatures, such as those of North Africa, Saudi Arabia and Western Australia. Evidence exists that some hot deserts were formerly subjected to extreme leaching under tropical conditions during the Cretaceous and Tertiary. In Western Australia, it has been suggested that the landscape was formed initially during the Proterozoic (Butt and Zeegers, 1992).

Desert soil is predominantly immature mineral soil, weakly developed in terms of its vertical profile, and mostly alkaline (Walker, 1992), and occurs in most cases below a stone pavement (McAuliffe *et al.*, 2018). Sands, sandy or gravelly loam, shallow stony soil, and alluvium (deposited by ephemeral rivers and streams) and scree-derived deposits predominate (Rafferty, 2011). The repeated accumulation of water in some desert soil causes distinct salt layers to form. Calcium carbonate precipitated from solution may cement sand and gravel into hard layers called 'calcrete', forming in some cases layers up to 50-m thick. Caliche is a reddish-brown to white layer found in many desert soils. Caliche commonly occurs as nodules or as coatings on mineral grains formed by the complicated interaction between water and carbon dioxide released by plant roots or by decaying organic material.

The usual topographic sequence (catena) of soil in arid regions begins with shallow rocky soil on the barren mountains and hills, then progresses downslope to coarse-textured and deeper soil on the dissected upper alluvial fans, and is followed on the lower fans and plains by finer-textured and deeper soil with more well-defined carbonate and clay horizons (Dregne, 1976).

Important constituents in desert soil are resistate detrital quartz and zircon, and secondary clay minerals. Heavy minerals such as zircon and magnetite, may become enriched in these soil types due to the removal of lower density minerals (Petrov, 1976). Calcareous soil is enriched in elements that are mobile in conditions of high pH, a feature of inland drainage basins. Soluble salts (halite, gypsum) may be present in quantities sufficient to alter the mobility of trace elements in the surficial environment (Berkel, 1982). Biological activity and, therefore, organic matter in desert soil is minimal or non-existent.

3.2.1.5. Tropical regions

Surface soil in tropical environments may have been deeply leached under a range of climatic conditions, including lengthy periods of high rainfall and high temperature, to which they have been subjected from Tertiary times or earlier, in some areas as far back as the late Proterozoic (Butt and Zeegers, 1992).

Surface conditions vary widely but there is generally intense oxidation, a lack of organic debris (which is generally stored in the biota rather than in soil), and the formation of stable insoluble secondary minerals such as clays (especially kaolinite) which increase the Al/Si ratio of the surface material (Darnley *et al.*, 1995).

In some tropical environments, laterite is common and may extend tens or hundreds of metres downwards before the fresh rock is encountered. The surface may be extremely complex, and vertical soil profiles may be truncated and/or buried by later detritus (Butt and Zeegers, 1992).

3.2.2. Residual soil and humus samples to be taken

The following horizon-based residual soil and humus samples are collected:

- (a) Routine sample site of a normal 160x160 km grid cell:
- 1 – 2 litres of *Humus* where it is present (highly decomposed organic material).
 - 2 – 3 kg of residual *Topsoil* (Top) sample representing the soil A non-humic or humic horizon, which may occur at the air/earth interface or below the litter or organic material horizon, where present. The maximum sampling range (thickness) of the *Topsoil* sample should not exceed 20 cm, *i.e.*, the upper 20 cm of the A mineral soil horizon are sampled. If the soil A horizon is less than 20-cm thick, then the *Topsoil* sample is collected from the entire horizon. The depth range of the sampled *Topsoil* A non-humic or humic horizon should be noted on the field observations sheet.
 - 2 – 3 kg of residual *Bottomsoil* (Bottom) sample. This sample should be collected from the soil C horizon, which consists, generally, of the partially weathered parent material. A 20-cm thick section should be sampled beginning at the top of the C horizon, *i.e.*, below the B-C boundary. In some cases, the C horizon may be at a depth of more than 100 cm, and in such cases, the pit should be dug until it is reached. However, if the C horizon is deeper than 200 cm, then a 20-cm thick sample is collected from a depth of 200 to 220 cm (or variants of 180 to 200 cm or 190 to 210 cm - depending on local conditions), and *always from the same horizon*. The depth range is noted on the field observations sheet. If the thickness of the soil C horizon is less than 20 cm, then the entire horizon is sampled, and the depth range is recorded.
- (b) Duplicate field sample site: At least one site out of twenty is selected for the collection of a set of duplicate field samples (*i.e.*, ≈5% duplication of the sample sites) in each country. However, countries with less than 20 GTN grid cells should collect field duplicate residual soil samples from at least one random site. The field duplicate sample site is selected at a distance of 5 to 50 metres away from the routine sampling site. **Additional** *Top* and *Bottom* residual soil samples, and an **additional** recently formed *Humus* sample (where present) are collected, according to the sampling scheme summarised in (a) above.

Enough material must be collected to yield a **minimum of 1 kg of <2 mm grain size** for each residual *Top* and *Bottom* soil sample. Larger sample quantities can be taken and stored separately in each country.

Refer to Annexe A3.2.1 of this Chapter for a description of the characteristics, geographical distribution, parent material, usage, and geochemical processes of the 28 major soil units, and Annexe A3.2.2 where the sampling scheme is shown using selected examples of diverse types of soil profiles.

3.2.2.1. Identifiers of residual soil and humus samples

The identifiers of the *Top* and *Bottom* residual soil samples are ‘T’ and ‘C’, respectively, and for *Humus* samples (where present) the identifier is ‘H’:

(a) Routine sample site (*e.g.*, GTN grid cell N26E14):

- *Topsoil* sample: N26E14**T1**
- *Bottomsoil* sample: N26E14**C1**
- *Humus* sample (where present): N26E14**H1**

Note: Number ‘1’ represents the 1st random sample site in GTN grid cell N26E14.

(b) Duplicate field sample site (e.g., GTN grid cell N27E12):

- Routine *Topsoil* sample – Routine: N27E12**T3**
- Duplicate *Topsoil* sample – Duplicate: N27E12**T3D**
- Routine *Bottomsoil* sample – Routine: N27E12**C3**
- Duplicate *Bottomsoil* sample – Duplicate: N27E12**C3D**

Note: Number '3' represents the 3rd random sample site in GTN grid cell N27E12, and 'D' denotes the duplicate Top and Bottom residual soil samples.

3.2.3. Equipment for residual soil and humus sampling

3.2.3.1. Equipment to be provided by the Project Coordinator

The following equipment must be purchased or made centrally, and provided to all sampling teams in each participating country:

- 300x600x0.04 mm strong certified trace-element free Rilsan^{®6} plastic or similar bags for packing residual soil samples (such bags are also suitable for organic compounds analysis).
- 450x750 mm white cotton bags with drawstring free of chemical impregnation for packing humus samples⁷.
- Plastic strip locks for securing the sample bags (attention: the plastic strip 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).
- 6x10 cm white cards for writing the sample number on both sides.
- 7.5x11.5 cm zip-lock plastic bags for holding the 6x10 cm white cards.
- Plastic laminated scalebar for 'photographs' (see Fig. 3.3. in Chapter 3), and
- Black permanent drawing ink markers (ONLY black coloured allowed).

Instead of the strong certified trace-element free plastic bags for packing the residual soil samples, two other types of bags can be used, and purchased by the Project Coordinator and distributed to all participating countries. These are:

- 125x250 mm wet-strength Kraft⁸ paper bags with a plastic-coated aluminium tin-tie, which can be twisted to seal the bag, or
- 254x431 mm polyester bags with nylon cord drawstring.

Whatever the decision, the same type of sample bags must be used by all countries throughout the Global Geochemical Reference Network project.

3.2.3.2. Equipment to be purchased by each participating country

Each participating country must purchase the following equipment, and for all its sampling teams:

⁶ TUB-EX: <http://www.tub-ex.com> – sales@tub-ex.com

⁷ It is known that some cotton bag manufacturers impregnate the cotton cloth with some chemicals. As the chemicals are never mentioned, and the soil samples must not be contaminated with unknown chemicals, it is important to ensure that the white cotton bags are not impregnated with any chemicals.

⁸ The Kraft paper bags need to be constructed using waterproof glue, otherwise the bags will fall apart when wet.

- Stainless-steel spade with an unpainted wooden handle is preferred. If this is not available, then an unpainted steel spade with an unpainted wooden handle is the next option. However, if these cannot be found and painted spade and varnished wooden handle are purchased, the paint/varnish must be removed by sandblasting before sampling (see Fig. 3.1 in Chapter 3); sandpapering either the spade or wooden handle will not remove completely the paint/varnish.
- Unpainted mattock cutter (if mattock cutter is painted, the paint must be removed by sandblasting prior to sampling); the wood handle must be unpainted (if varnished, it must be removed by sandblasting – not sandpapering – see Figure 3.1 in Chapter 3).
- Cylindrical sampler for sampling humus.
- Hard white plastic spatula for removing mineral soil from humus samples.
- Powder-free disposable gloves for sampling humus.
- Stainless steel knife.
- Metal-free white or colourless plastic scoop or stainless-steel scoop.
- Stainless-steel geological hammer either pointed-tip or chisel-end (preferable).
- Leather gloves.
- 10x magnifying lens (loupe).
- Hard bristle brush for cleaning plastic scoop, and geological hammer.
- Cotton-lint or white cotton rags for cleaning sampling equipment.
- Wooden folding 2-m long measure (alternate colours every 10 or 20 cm); or plastic tape with alternate colours every 10 cm.
- 30x60 cm sturdy plastic bags for packing sample bags, 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 the sample preparation laboratory.
- Strong PVC packing tape.
- 6 mm natural sisal rope.
- Heavy-duty cutter knife with replacement blades.
- Global Positioning System (GPS) for recording sample site coordinates, or a tablet with a GPS and digital topographical maps; or a mobile telephone with GPS; it is strongly recommended to have a backup GPS receiver.
- Extra batteries for GPS or battery charger with rechargeable batteries.
- Topographical maps, preferred scale 1:50,000 (a must in case electronic digital devices fail, *e.g.*, GPS).
- A plastic roamer or map ruler for extracting coordinates from 1:50,000 topographical maps in case GPS fails.
- An orienteering compass (a must in case GPS fails).
- Digital camera or a mobile telephone with a macro facility for field documentation (minimum 5 megapixels).
- Extra batteries for the digital camera.
- 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 or external hard drive) for backup of field data and digital photographs.
- USB cable to download photographs to a laptop computer daily.
- Threshold scintillometer to measure natural radioactivity (Total, Th, U, K); the scintillometer must be calibrated at least once a year before the field campaign at a national facility that is certified.
- Extra batteries for the threshold scintillometer.
- Field observations sheets.
- Waterproof case to hold field observation sheets.
- Writing pens.
- HB pencils, pencil sharpener and rubber (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 Notes for the use of an auger in soil sampling:

(1) ***Global Geochemical Reference Network project:*** The use of an auger for sampling residual soil is NOT recommended because three-dimensional information about the soil sampling site can be obtained only from a soil pit.

(2) ***Exploration Geochemistry projects:*** The use of an auger for soil sampling does have a place in applied geochemistry when a large number of samples are collected over a small area; *for example*, along traverse lines in exploration geochemistry.

3.2.4. Sampling procedure for residual soil and humus

3.2.4.1. Sample site selection

During the desktop study, the second-order drainage basin (<100 km²) is selected after studying the 1:50,000 scale topographical⁹, geological and soil maps (refer to Section §2.5 of Chapter 2 in this Manual). It is stressed that the residual soil samples should represent the dominant residual soil type of the second-order catchment basin (Strahler, 1957, 1969). Hence, if soil maps are available, they should be studied in order to identify the dominant residual soil type. If not, then the geological map should be studied, and in this case the residual soil to be taken over the dominant rock type of the second-order catchment basin.

The exact position of the residual soil sampling site is located in the field, after a careful study of the area covered by the dominant residual soil (or rock) type. The sample site must be above the alluvial plain and base-of-slope of the second-order stream, where alluvium and colluvium are respectively deposited (see Annexe A3.2.2 of this Chapter). The sample site must be situated on the dominant relief position, avoiding slopes with erosion and transport (see Chapter 2 and Annexe A3.2.1 of this Chapter). Residual soil may be developed either directly on bedrock or on till, as is the case in glaciated terrains, or on loess.

It is stressed that the aim of the Global Geochemical Reference Network project is to ***sample natural residual soil, meaning soil that is not affected by any anthropogenic activities.*** Such

⁹ If topographical maps are not available, orthophotographs or satellite photographs can be used.

natural sampling sites in the small second-order drainage basin of <100 km² are usually found in grasslands and forested areas.

The residual 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 agricultural fields as the surface soil down to a depth of 20 cm (normal ploughing depth) to over 50 cm (deep ploughing depth) has been disturbed by human activities.
- Avoid sites that are disturbed by human activities such as camping sites (*e.g.*, presence of fire-places, cans and/or bottles), graded land (*e.g.*, areas from which soil has been removed and the remaining soil cannot be classified in any soil type), levelled fields (for irrigation), mines (active or abandoned), landfills, and rehabilitated sites. It is stressed that every single contaminated site will seriously influence the generated geochemical results.
- Avoid locally atypical sites.
- Avoid, if possible, collecting soil containing large quantities of organic material or rich in Fe or Mn oxides.

Important note for selecting residual soil sampling site: As the purpose of the wide-spaced geochemical survey is the establishment of a Global Geochemical Reference Network and the 21st-century geochemical baseline of residual soil against which future changes may be recognised and quantified, even a single contaminated site will seriously influence the geochemical results. Hence, the project aims to collect the ‘*most representative natural*’ residual soil sample, and not the ‘most unusual’ residual soil sample. It is, therefore, of paramount importance to ensure that the material collected is ‘*residual*’, and not transported such as colluvium or alluvium, and is not affected by human activities.

Important note for selecting a sampling site with recent highly decomposed organic material (humus): The sampling site should be as flat-lying as possible, unless the sample is collected from a mountainous area (forest or grassland). *Local depressions with humus must be avoided.* If the sample site is in a forested area, all humus sampling locations should be selected at a sufficient distance from the nearest trees to avoid ‘throughfall’ precipitation from the trees. A minimum distance of 5 m from the nearest tree, and 3 m from the nearest bush is recommended. However, each sampling team is free to use its discretion in the selection of humus subsites in forested areas. *It is noted that these conditions apply also to the selection of the residual soil sampling site.*

Annexes A3.2.1 and A3.2.2 of this Chapter demonstrate the complexity of soil types and profiles from different morphoclimatic environments around the globe, yet in this chapter, the best effort of a single method for collecting residual soil samples from anywhere in the world is provided. With the aid of Annexe A3.2.2, clear pictorial help is given to define where in the soil

profile samples of *Top* and *Bottom* residual soil, as well as *Humus* (where present), are to be collected by following the standardised method presented in this chapter for their collection in a consistent and representative manner.

The method requires that samplers use good observational skills at sampling locations. Such skills should be acquired from a soil sampling training course. The procedures for describing the soil at location (including photographs - Fig. 3.2.7) are a vital part of providing information and a context within which users of the data generated can interpret results.

3.2.4.2. Sampling procedure for residual soil

Two different horizon-based residual soil samples are taken at each site:

- A *Topsoil* sample (abbreviated *Top*) is collected, representing the soil A non-humic or humic horizon, and which occurs either at the air/earth interface, or directly below the surface litter and/or highly decomposed organic (Oa) material horizon (humus), where present. As noted above, the maximum sampling thickness range of the *Topsoil* sample should not exceed 20 cm, *i.e.*, the upper 20 cm of the soil A non-humic or humic horizon are sampled. If the soil A non-humic or humic horizon is less than 20 cm thick, then the *Topsoil* sample is collected from the entire thickness of the horizon. The depth range of the sampled soil A non-humic or humic horizon should be noted on the field observations sheet. Although the measure is placed at the air/earth interface of the profile, the 0 cm depth essentially starts from the upper mineral soil surface, *i.e.*, the thickness of the litter or organic material (Oa) horizon, where present, is not considered, as these parts are removed before sampling the soil A non-humic or humic and C horizons. Hence, the A non-humic or humic mineral soil surface at the air/earth interface of the profile is considered to be the top boundary of the first mineral soil horizon that can support plant/root growth. This equates to for:
 - Bare mineral soil: the air/earth interface, and
 - Vegetated mineral soil: the upper boundary of the first horizon that supports root growth, *excluding both* freshly fallen plant litter, and litter that has compacted and begun to decompose but remains somewhat recognisable, and includes slightly and moderately decomposed organic material – see Fig. 3.2.7); and
- A *Bottomsoil* sample (abbreviated *Bottom*) is collected from the soil C horizon (generally partially weathered parent material). The soil C horizon sample should be approximately 20 cm in thickness beginning at the top of the C horizon, *i.e.*, the B-C boundary. If the soil C horizon is less than 20-cm thick, then the entire horizon should be sampled, and the depth range recorded on the field observations sheet.

At each residual soil sample site:

- (i) Switch on the GPS (Fig. 3.2.8a), or notebook or laptop computer with GPS (Fig. 3.2.8b), to obtain the WGS1984 decimal degree coordinates of the sample site. It is important to switch on the GPS upon arrival at the site, and to allow enough time for the signal to settle.
- (ii) Write the sample numbers of *Top* and *Bottom* residual soil samples with a black permanent ink marker on a plastic trace element free plastic Rilsan[®] bag (or Kraft paper or cotton bag; Figs. 3.2.9a-b).
- (iii) Write the sample numbers of *Top* and *Bottom* residual soil samples on both sides of a small card, and place each card in a small plastic zip-lock bag and seal it (Figs. 3.2.9c-d).
- (iv) Clean spade and mattock cutter by sticking it several times into the soil at each new sample site.

- (v) Remove surface litter and grass to begin with a knife or spade, and a mattock cutter if necessary.
- (vi) Dig a pit down to the C horizon with a stainless-steel or an unpainted steel spade and mattock cutter, thus uncovering a clean vertical surface for sampling (Fig. 3.2.10). If it is at all possible, the pit should be rectangular in plan-view with the vertical face for sampling and description to be facing, preferably, the sun or the direction of maximum light; when marking out the pit, allowance should be made for the movement of the sun, which will occur during digging, so that there are no shadows in the corners of the pit during the taking of photographs (Hodgson, 1976).
- (vii) Mark the soil horizons with the aid of a stainless-steel knife (Figs. 3.2.11a).
- (viii) Place an alternate coloured-section 2-m measure on the vertical face of the pit and secure it (Fig. 3.2.11b).
- (ix) Photographic documentation of sample site: At this stage, ensure that the alternate coloured-section wooden 2-m measure is on the face of the pit, and then take at least six digital photographs (see Section §3.2.4.4 & Fig. 3.2.7). Additional photographs can be taken to show the textural characteristics of both the *Top* and *Bottom* residual soil horizons.
IMPORTANT CAUTION: As a safety precaution, always photograph first the sample number of the *Top* residual soil sample (Fig. 3.2.7a). Thus, the succeeding photographs are classified to belong to this particular sampling site.
- (x) 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.
- (xi) Record sample site coordinates and general observations on the field observations sheet (refer to Appendix 1 of this Manual), leaving the grain size to be completed after the collection of the *Top* and *Bottom* soil samples.
- (xii) *First, collect the Bottom C horizon residual soil sample (Figs. 3.2.11c-f) using a geological hammer to excavate the soil from the pit face, and a white plastic scoop to collect each soil aliquot, which is placed in a strong certified trace-element free plastic Rilsan® bag (or Kraft paper bag; Figs. 3.2.11d-f) until the required amount is collected. This procedure avoids cleaning the surface of the Bottom soil horizon from fallen Topsoil sample material, if the latter is taken first. Handpick and remove any large rock fragments.*
- (xiii) *Upon collecting the Bottom soil (C 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 (Fig. 3.2.11e).*
- (xiv) *Twist the top of the sample bag, and seal it securely with a plastic strip lock (Fig. 3.2.11f).*
- (xv) *For safety during transportation of the sample, place the sample bag in a strong ordinary plastic bag, and seal it securely with a plastic strip lock (Fig. 3.2.13b).*
- (xvi) *Clean thoroughly the sampling equipment with a hard bristle brush and cotton lint.*
- (xvii) Second, collect the *Top* residual soil sample from the A horizon using the same procedure as that for the *Bottom* sample (refer to steps (xii) to (xvi); Figs. 3.2.12a-f & Figs. 3.2.13a-b). Handpick and remove any large rock fragments.
- (xviii) Store the two samples in different strong carton or plastic boxes.
- (xix) Switch on the portable threshold scintillometer, hold it at knee height and record the count readings of total radiation, K, U, and Th on the field observations sheet (Figs. 3.2.14a-b).
- (xx) Record the grain size of *Top* and *Bottom* residual soil samples, and digital photograph numbers on the field observations sheet (Fig. 3.2.14b; refer to Appendix 1 of this Manual).
- (xxi) Take a photograph of the field observations sheet as a safety precaution in case the original sheet is somehow lost or becomes illegible.

Duplicate field samples: Duplicate *Top* and *Bottom* residual soil samples are collected randomly at least at every 20th sampling site (*i.e.*, $\approx 5\%$ duplication of the sample sites) in each country. However, countries with less than 20 GTN grid cells should collect duplicate *Top* and *Bottom* residual soil samples from at least one random site. The duplicate sample site is selected at a distance of 5 to 50 metres away from the routine sampling site following the same procedure as for collecting the routine *Top* and *Bottom* residual soil samples.

Important Note 1: After collecting the *Top* and *Bottom* residual soil samples, using the procedure described above, the dug-up soil is returned to the pit, the two samples are placed on the surface together with the sample number 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 (Fig. 3.2.7g).

Important Note 2: The soil C horizon is especially important, and must be reached at all sampling sites because it is the reference horizon, *i.e.*, the C horizon is composed of unconsolidated parent material, which may be either relatively unweathered or deeply weathered. Samples collected at sites where the C horizon is unweathered or only slightly weathered represent very closely the chemical composition of the parent material.

The upper 20-cm thick section of the C horizon is sampled, and the depth range is noted on the field observations sheet. *In case the C horizon has a thickness of less than 20 cm, then the entire horizon is sampled, and the thickness range is recorded on the field observations sheet.*

It is anticipated that the C horizon will be reached in most cases at a depth of less than 100 cm, or in the worst-case scenario is less than 200 cm. If it is deeper, then the pit should be dug until the C horizon is reached. *In extreme cases, where the C horizon is deeper than 200 cm, the Bottom sample is collected from a depth range of 200 to 220 cm, and **always from the same horizon**, which means that this depth range, depending on local conditions, maybe slightly changed to either 180 to 200 cm or 190 to 210 cm or similar thickness variants below a depth of 180 cm (e.g., 185-205 cm).*

Important Note 3: The *Top* and *Bottom* residual soil samples are always collected from a SINGLE¹⁰ site, and a SINGLE soil profile.

3.2.4.3. Sampling procedure for humus

If there is a recognisable well-developed highly decomposed organic material (*humus*) above the A humic residual mineral soil horizon, collect this sample first by using either a cylindrical steel sampler or a spade (Salminen, Tarvainen *et al.*, 1998), and before digging the pit deeper to expose the other horizons. Each humus sample should be a composite sample from at least five (5) locations within a 50x50 m area around the residual soil sampling site, and the uppermost three (3) cm of humus should be sampled. The reason for collecting a composite humus sample is that from a single site it is not possible to collect the required 1 to 2 litres. Hence, the first humus sub-sample is collected from the site of the pit that will be dug for the collection of the *Top* and *Bottom* residual soil samples. The additional four sub-sites (at least) are located around this location. Refer to “*Important note for selecting sampling site with recent highly decomposed organic material (humus)*” (Section §3.2.4.1) before starting the sampling of humus. Collect the humus samples using the following sampling procedure:

¹⁰ **Note:** It is not necessary to take composite soil samples when a pit has been dug, as enough sample can be collected from the target horizon, provided the horizon is not too thin. In cases where the horizons are thin the pit is extended sideways in order to collect the required sample weight from the same *Top* and *Bottom* horizons.

- (i) Write the humus sample number with a black permanent ink marker on a white cotton bag with a drawstring free of chemical impregnation or a certified trace-element free plastic Rilsan[®] bag (Fig. 3.2.15a).
- (ii) Write the humus sample number on both sides of a small card, place the card in a small plastic zip-lock bag and seal it (Fig. 3.2.15b).
- (iii) Wear on both hands powder-free disposable gloves (Figs. 3.2.16a-d).
- (iv) *Remove carefully from each location the living surface vegetation, fresh litter, big roots and rock fragments.*
- (v) *Drive the cylindrical steel sampler into the humus and down to a depth of 3 cm, twist it to cut the highly decomposed organic material, and then lift it up. If a spade is used for the collection of the humus sample, cut with the spade square blocks down to the boundary with the A humic residual soil horizon, and sample the upper 3-cm of the highly decomposed organic material.*
- (vi) *Check if mineral soil is attached to the bottom of the retrieved humus aliquot; if mineral soil is attached, remove it very carefully using a hard plastic spatula (Fig. 3.2.16b).*
- (vii) *Place each humus aliquot in the white cotton bag (or certified trace-element free Rilsan[®] bag), and press it down hard.*
- (viii) Repeat steps (iv) to (vii) at other locations within the 50x50 m area until 2 litres of compacted humus are collected.
- (ix) Upon collecting the humus sample, the numbered small card in the plastic zip-lock bag (Fig. 3.2.15b) is placed on top of the sample.
- (x) Twist the top of the cotton bag, and tie it securely with a drawstring (or secure the certified trace-element free Rilsan[®] bag with a plastic strip lock).
- (xi) Record observations on the field observations sheet (Fig. 3.2.14b; refer to Appendix 1 of this Manual).
- (xii) Upon collecting each humus sample, clean thoroughly the sampling equipment.
- (xiii) After collecting the *Humus* sample, the pit is dug further down to reach the C horizon for the collection of the *Bottom* C horizon sample first, and the *Top* A humic mineral soil sample second by following the procedure described in Section §3.2.4.2.

Important cautionary note: Do not collect raw humus because it is extremely difficult to define an exact boundary between litter and raw humus.

3.2.4.4. Photographs to be taken at each sample site

At each residual soil sampling site at least 6 digital photographs (>5 megapixels) are taken (Figs. 3.2.7a-g):

- First photograph: Top residual soil sample site number (Fig. 3.2.7a).
- Second photograph: General landscape photograph of the sampling site (Fig. 3.2.7b).
- Third photograph: Soil surface photograph taken from a height of about 1 m from the ground surface (Fig. 3.2.7c); either the Top residual soil sample site number or plastic laminated scalebar should be placed on the ground surface.
- 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 (Figs. 3.2.7d-e).
- 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 (Fig. 3.2.7f), and
- Sixth photograph: This is an important photograph as proof that dug-up soil has been returned to the pit, and the landscape 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 (Fig. 3.2.7g).



(a)



(b)



(c)



(d)



(e)



(f)



(g)

Figure 3.2.7. Photographs (a) Residual soil sample site number. (b) General landscape. (c) Surface of sample site taken from a height of 1 m. (d) Pit showing residual soil profile. (e) Close-up of the residual soil profile with natural light. (f) Close-up with fill-in flash showing textural characteristics of soil horizons, and (g) Last photograph of bagged Top and Bottom residual soil samples with sample number and GPS on top of fill-in pit, as evidence that dug-up soil has been returned to the pit, and the land to its original state. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

3.2.4.5. Photographic documentation of residual soil sampling procedure

The following photographs show the residual soil sampling procedure.



Figure 3.2.8. Photographs showing (a) GPS instrument and (b) Laptop with GPS for recording sample site coordinates – Step (i) of sampling procedure (see Section §3.2.4.2). The reason for switching on the GPS upon reaching the sample site is that in a few remote and forested areas it takes some time to locate the satellites. If the GPS is struggling to find the three satellites to triangulate the sample site coordinates without success, as in this case, move it a few metres to an open space or the nearest forest track road (c). Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

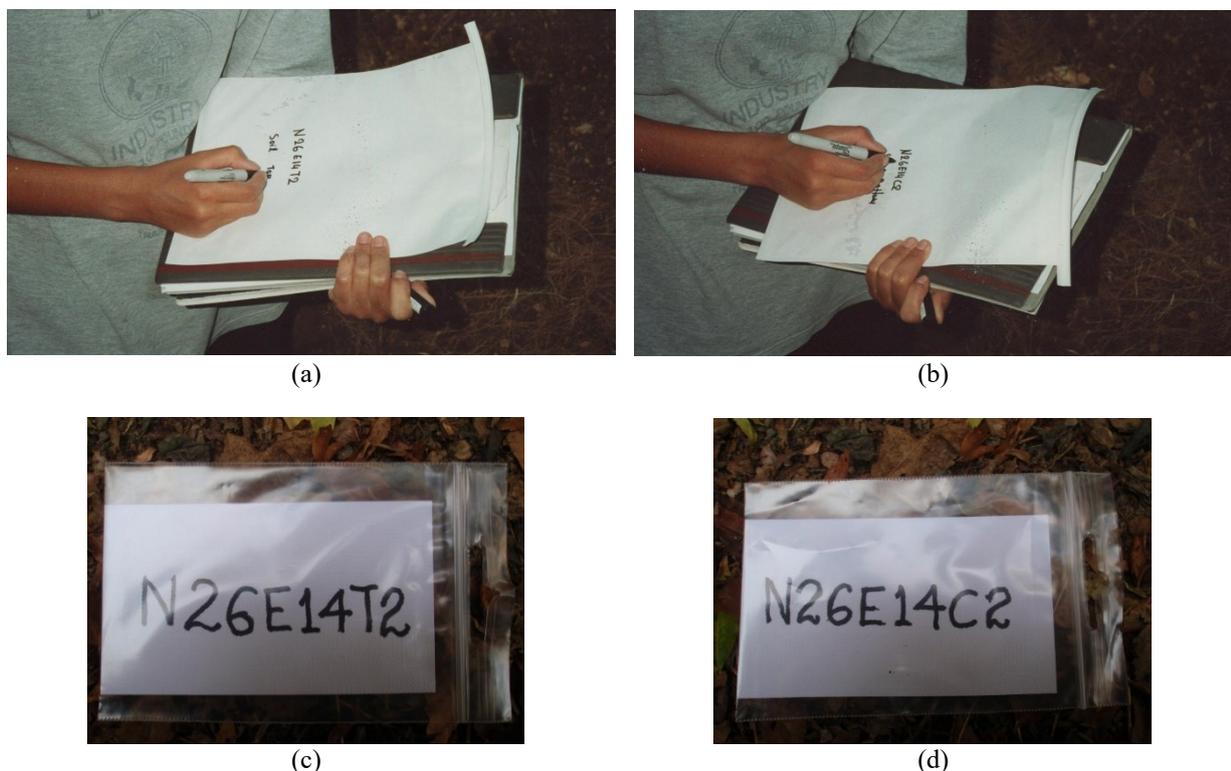


Figure 3.2.9. Photographs showing Steps (ii) and (iii) of the sampling procedure (see Section §3.2.4.2): (a & b) Write sample numbers of Top and Bottom residual soil samples with a black permanent ink marker on a white Kraft paper bag (this case) or plastic trace element free Rilsan® bag, and (c & d) write sample numbers of Top and Bottom residual soil samples on both sides of a small card, and place each card in a small plastic zip-lock bag and seal it. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)

Figure 3.2.10. Photographs showing the procedure of digging a pit with (a) Mattock cutter, and (b) Spade (Step (vi) of sampling procedure – see Section §3.2.4.2). Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



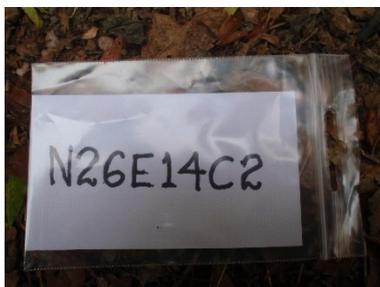
(b)



(c)



(d)



(e)



(f)

Figure 3.2.11. Photographs showing (a) Marking of soil horizons with the stainless-steel knife (Step (vii) of sampling procedure – see Section §3.2.4.2). (b) Placing and securing of 2-m measure on vertical pit phase (Step (viii)). (c) Sampling of Bottom residual soil sample using a geological hammer for excavating soil, which is then collected in a white plastic scoop (Step (xii)). (d) Bagging each Bottom soil aliquot in white Kraft bag (Step (xiii)). (e) Small, numbered card in a plastic zip-lock bag is placed on top of Bottom soil sample in white Kraft bag (Step (xiii)), and (f) Sealing white Kraft bag by twisting the aluminium tin tie (Step (xiv)). Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



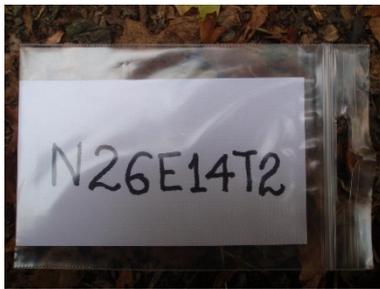
(b)



(c)



(d)



(e)



(f)

Figure 3.2.12. Photographs showing (a) Removal of grass and litter with the aid of a spade. (b) Sampling of Topsoil sample using a geological hammer for excavating soil, which is then collected in a white plastic scoop (Step (xii) of sampling procedure – see Section §3.2.4.2). (c) Breaking-up soil lumps with the hammer. (d) Bagging each Topsoil aliquot in white Kraft bag (Step (xii)). (e) Small, numbered card in the plastic zip-lock bag is placed on top of Topsoil sample in white Kraft bag (Step (xiii)), and (f) Sealing white Kraft bag by twisting the aluminium tin tie (Step (xiv)). Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)

Figure 3.2.13. Photographs showing placement of (a) Topsoil and (b) Bottomsoil sample bags in a sturdy plastic bag for storage and transportation (Step (xv) of sampling procedure – see Section §3.2.4.2). Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)

Figure 3.2.14. (a) Taking scintillometer readings at knee height (Step (xix) of sampling procedure – see Section §3.2.4.2), and (b) Recording field observations on the field observations sheet (Steps (xi, xix & xx)). Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

3.2.4.6. Photographic documentation of humus sampling procedure

The following photographs show the humus sampling procedure.



Figure 3.2.15. Photographs showing numbered (a) Certified trace-element free plastic Rilsan® bag with a plastic strip lock for packing the humus sample (Step (i) of humus sampling procedure – see Section §3.2.4.3), and (b) Small card in a plastic zip-lock bag (Step (ii) of the sampling procedure for Humus, see Section §3.2.4.3). Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.2.16. (a) Humus sampling in Finland using cylindrical sampler. (b) Removal of all mineral soil with a plastic scoop. (c) Pull apart Humus (on left) and roots (on right), and (d) Final Humus sample for bagging in either certified trace element free Rilsan® bag or white cotton bag free of chemical impregnation; when full the small-numbered card in a plastic zip-lock bag is placed on top, and the plastic bag is secured with the plastic strip lock or the cotton bag is securely tied with the drawstring. Photographs: Timo Tarvainen, Geological Survey of Finland (Salminen, Tarvainen et al., 1998, Figs. 8a to 8d, p.23-24).

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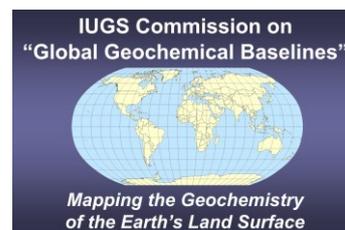
Note: All hyperlinks were checked on the 13th of February 2022.

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Annexe A3.2.1

**Residual Soil and Humus Sampling:
The Soils of the World**

Edith Haslinger¹, Harald Loishandl-Weisz², Robin Friedrich¹, Thomas Rosmann²

¹ AIT Austrian Institute of Technology GmbH, Centre for Energy, Giefinggasse 6, 1210 Vienna, Austria

² Federal Environment Agency Austria, Department of Groundwater, Spittelauer Lände 5, 1090 Vienna, Austria

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A3.2.1.1. The Harmonised World Soil Database

The Harmonised World Soil Database (HWSD) is the result of an enormous effort by the International Institute for Applied Systems Analysis (IIASA) in collaboration with the Food and Agriculture Organization of the United Nations (FAO), the World Soil Information (ISRIC – International Soil Reference and Information Centre), the Institute of Soil Science of the Chinese Academy of Sciences (ISSCAS), and the European Soil Data Centre (ESDAC) of the Joint Research Centre (JRC) of the European Commission.

The HWSD is in Microsoft Access format and can be downloaded together with a viewer and comprehensive documentation from <http://webarchive.iiasa.ac.at/Research/LUC/External-World-soil-database/HTML/> (FAO/IIASA/ISRIC/ISS-CAS/JRC, 2012).

Four source databases were used to compile version 1.2 of the 2012 HWSD:

- The European Soil Database (ESDB).
- The 1:1 million soil map of China.
- Various regional Soil and Terrain (SOTER) databases as well as Harmonised SOTER-derived databases (SOTWIS-Databases), and
- The Soil Map of the World.

The HWSD is composed of a GIS raster image file linked to an attribute database in Microsoft Access format. While these two components are separate data files, they can be linked through a commercial GIS system. A viewer provided with the database generates this link automatically and gives direct access to the two data sources.

The HWSD is a 30 arc-second raster database (resolution of about 1 km) resulting in 21,600 rows and 43,200 columns of which 221 million grid cells cover the globe's land territory. Over 16,000 different soil mapping units (SMUs) were identified in the HWSD, which combines existing regional and national updates of soil information worldwide, with the information contained within the 1:5,000,000 scale FAO-UNESCO Soil Map of the World (FAO/UNESCO, 1971-1981).

The SMUs are linked to harmonised attribute data. The standardised structure allows a linkage of the attribute data with GIS to display or query the composition in terms of soil units, and the characterisation of selected soil parameters (organic Carbon, pH, water storage capacity, soil depth, cation exchange capacity of soil and clay fraction, total exchangeable nutrients, lime and gypsum contents, sodium exchange percentage, salinity, textural class and granulometry).

To retrieve the most abundant soil types from the comprehensive HWSD Microsoft Access Data Base, it was necessary to complete the harmonised codes and symbols for the different soil types and subtypes of the single classifications (FAO-74, FAO-85, FAO-90). In the table HWSD_SMU, a harmonised code is only available for the soil type with the largest share in each soil mapping unit (SMU). Therefore, the soil types with a lower share in each mapping unit had to be assigned by referencing these soil types to the soil type with the largest share per SMU manually, in order to obtain the same code for all soil types in each SMU, and not only for the one with the largest share. For some soil types or subtypes, which are not dominant in any SMU, there was no code available. Therefore, they were summarised under the category 'Not assigned' (Soil not assigned in SMUs).

From the GIS-raster data, the respective areas in km² for each SMU were retrieved. The area of each SMU was assigned to the soil types, according to the shares of the respective soil types in this SMU (Table A3.2.1.1). One obstacle in this assignment was the fact that during the harmonisation of the classifications, subtypes present in older classifications were generalised in the harmonised classification. Therefore, in some SMUs one soil type code occurred several times with different shares. To take this into account and for clear and distinct calculation steps, the subareas of each SMU were summed up separately per harmonised soil type code. The result

is a worldwide sum of area per soil type that allows for a description of the most abundant soil types.

For the generation of the KML-files per SMU, HWSD data (raster and Microsoft Access file) were downloaded from the HWSD website, where the key information for linking the data sets was the MU_GLOBAL code for each Soil Mapping Unit. This code was used both as a cell value in the raster data set and also as the ID in the Microsoft Access database. The raster file was transformed into a vector data set, thus combining all contiguous raster cells with the same MU_GLOBAL code into one polygon per Soil Mapping Unit (SMU). In most cases, these were multipart polygons, consisting of multiple not connected polygons, which often extended over very large areas; in other cases, the polygons were only a few raster cells in size. Cells with the value 0, representing non-land surface, were ignored.

The resulting table with area per harmonised soil type was joined to the geodata set via the MU_GLOBAL code, where some specific soil types were not considered (soil types: Glacier; Rock Outcrop; Sand Dunes; Water Bodies; No data; Salt flats; Urban, mining, *etc.*; Island).

For each of the remaining 28 soil types, all of the associated polygons were extracted into separate geodata sets, and there is an additional file for soil not assigned in SMUs. The data are available as an ESRI shapefile and also in KML format, and include the attribute information of the MU_GLOBAL code, the name and code of the soil type and its share of the total area of the polygon, as well as an indication of the source that was used for the classification of the data (see Supplementary Material at the end of this Annex). The KML files were styled in a way that the transparency of the polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon. For data processing, Safe Software's FME¹ was used.

In Table A3.2.1.2 (Section §A3.2.1.2) the characteristic features of each soil type are described, namely, the origin of name, concise description of main characteristics, geographical distribution, parent material, usage and prevailing geochemical processes. A map of the geographical distribution of each soil type is given on the opposite page.

In Section §A3.2.1.3 the hyperlinks to web pages with soil descriptions are given.

¹ <https://www.safe.com/>; last access: 13.02.2022.

Table A3.2.1.1. The identifiers and area in km² of the Soil Mapping Units (SMU). The SMUs marked in grey colour are not described in Table A3.2.1.2.

Soil Mapping Unit (SMU)	Identifier	Sum of area (km ²)	Figure number
Regosols	RG	45,669,926	A3.2.1.1
Glaciers	GG	34,896,366	-
Leptosols	LP	30,596,578	A3.2.1.2
Gleysols	GL	26,472,277	A3.2.1.3
Cambisols	CM	23,897,770	A3.2.1.4
Podzols	PZ	21,078,050	A3.2.1.5
Arenosols	AR	14,325,966	A3.2.1.6
Calcisols	CL	12,618,755	A3.2.1.7
Histosols	HS	12,231,620	A3.2.1.8
Luvisols	LV	11,610,542	A3.2.1.9
Fluvisols	FL	9,399,214	A3.2.1.10
Podzoluvisols	PD	8,272,991	A3.2.1.11
Acrisols	AC	7,437,353	A3.2.1.12
Ferralsols	FR	6,773,512	A3.2.1.13
Kastanozems	KS	6,767,433	A3.2.1.14
Chernozems	CH	5,125,216	A3.2.1.15
Rock Outcrops	RK	5,112,773	-
Phaeozems	PH	4,855,142	A3.2.1.16
Sand Dunes	DS	4,725,730	-
Solonetz	SN	4,042,532	A3.2.1.17
Water Bodies	WR	3,624,653	-
Vertisols	VR	3,326,842	A3.2.1.18
Lixisols	LX	2,990,753	A3.2.1.19
Solonchaks	SC	2,596,954	A3.2.1.20
Gypsisols	GY	2,052,558	A3.2.1.21
Greyzems	GR	1,903,896	A3.2.1.22
No data	NI	1,873,847	-
Andosols	AN	1,773,493	A3.2.1.23
Planosols	PL	1,758,899	A3.2.1.24
Nitisols	NT	1,689,435	A3.2.1.25
Plinthosols	PT	1,210,678	A3.2.1.26
Anthrosols	AT	796,687	A3.2.1.27
Alisols	AL	643,311	A3.2.1.28
Not assigned	N/A	1,305,761	A3.2.1.29
Salt Flats	ST	210,735	-
Urban, mining, etc.	UR	66,856	-
Island	IS	278	-

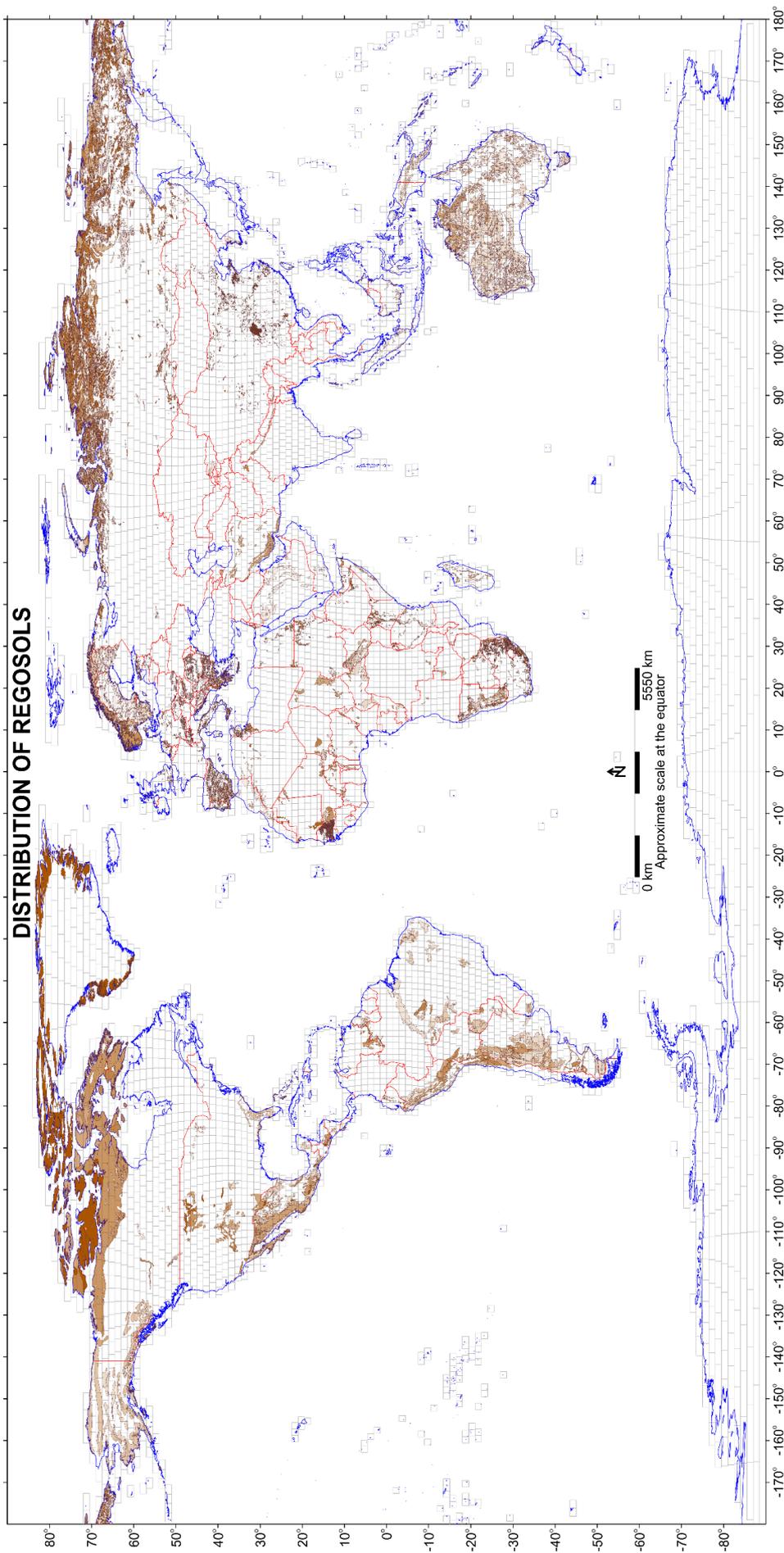


Figure A3.2.1.1. Map showing the global distribution of Regosols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades Hellenic Institute of Geology and Mineral Exploration (IGME) & IUGS Commission on Global Geochemical Baselines (UGS-CGGB) with Golden Software's Surfer v.20 using the kml file (HWSD_CLASS_RG-Regosols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

A3.2.1.2. The 28 major World soil types

Table A3.2.1.2. The World's soil types by area, their geographical distribution, parent material, usage and the most important geochemical processes.

<p>Regosols</p>	<p>From the Hellenic word <i>rhégos</i> (ρήγος) = blanket.</p>
 <p>Source: Jones <i>et al.</i> (2005, p.32).</p>	<p>Regosols are AC-profiles with a minimal profile development as a consequence of (1) retardation of soil formation in a dry or hot desert climate, (2) truncation or exposure of the soil material, or (3) steady rejuvenation of the soil material. The matrix shows little or low coherence, and the soil colours are normally determined by the composition of the mineral soil fraction.</p> <p>In the World Reference Base for Soil Resources (WRB), Regosols are a taxonomic rest group of soil types with no other diagnostic horizons than an <i>ochric</i> horizon. The ochric horizon is a surface horizon lacking fine stratification and which is either light coloured, or thin, or has a low organic carbon content, or is massive and (very) hard when dry.</p> <p>Since Regosols are a taxonomic rest group with a great variation, a general characterisation of Regosols is not possible. However, the central concept of a Regosol is a deep, well-drained, medium-textured, non-differentiated mineral soil that has minimal expression of diagnostic horizons (other than ochric), properties and materials.</p>
<p>Geographical distribution:</p>	<p>Regosols occur in all climate zones without permafrost and at all elevations (Fig. A3.2.1.1). They are particularly common in arid areas, the dry tropics and mountain regions.</p>
<p>Parent material:</p>	<p>Unconsolidated, finely grained weathered material.</p>
<p>Usage:</p>	<p>Regosols in desert or mountainous areas cannot be used for agricultural purposes. In steppes, with limited precipitation, irrigation is necessary for crop production. However, the water holding capacity in Regosols is low, and the low coherence of the matrix makes them prone to erosion.</p>
<p>Geochemical processes:</p>	<p>The geochemical processes in Regosols are very limited since they are only weakly developed soil types.</p> <p>Soil formation is limited to the development of a thin ochric surface horizon over (almost) unaltered parent material. In areas with considerable evaporation, the accumulation of lime and/or gypsum may occur.</p>

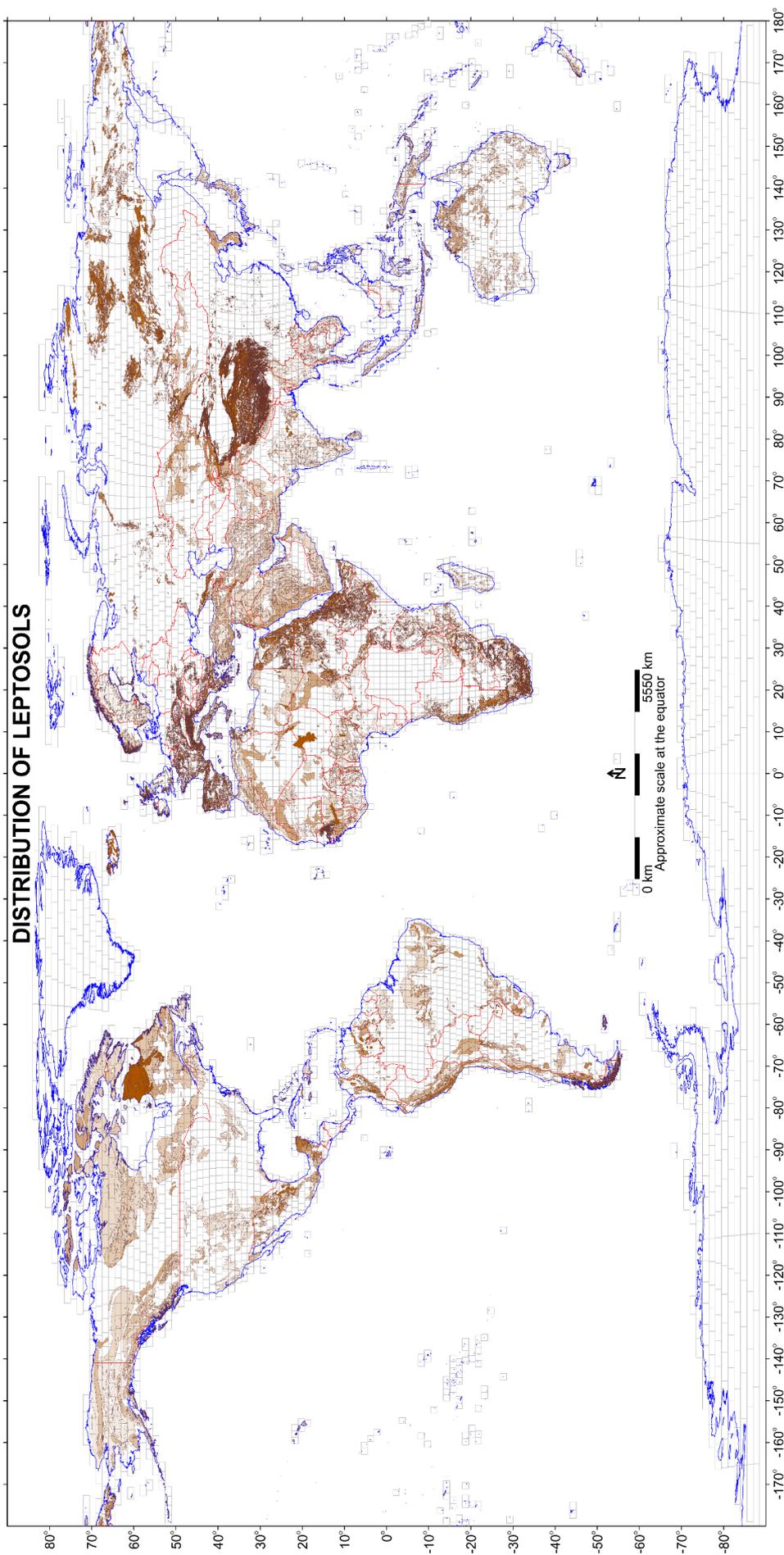


Figure A3.2.1.2. Map showing the global distribution of Leptosols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_LP-Leptosols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Leptosols</p>	<p>From the Hellenic word <i>leptós</i> (λεπτός) = thin.</p> <p>Leptosols are shallow soil types, which develop over solid or only slightly weathered solid rock (calcareous or non-calcareous). The humus-rich topsoil horizon is directly over the bedrock with no or only a weak weathering horizon in between. Leptosols indicate initial pedogenesis or are located with inhibited pedogenesis due to erosion or high altitude.</p>
	
<p>Photograph: Edith Haslinger (Austrian Institute of Technology GmbH, AIT)</p>	
<p>Geographical distribution:</p>	<p>Leptosols are found from the tropics to the cold polar, and from sea level to the highest mountains (Fig. A3.2.1.2). In mountainous areas, often on hills that are constantly subjected to erosion. Especially in Asia and South America, in the Saharan and Arabian deserts, the Ungava peninsula of northern Canada and the Alaskan Mountains.</p>
<p>Parent material:</p>	<p>Calcareous or non-calcareous solid rock.</p>
<p>Usage:</p>	<p>Leptosols are not suitable for agricultural use due to shallowness and high rock content. Used as grazing land or forest, whereas the development of terraces helps to inhibit erosion.</p>
<p>Geochemical processes:</p>	<p>Physical and chemical weathering leads to loss of base cations and subsequent disintegration of rocks.</p>

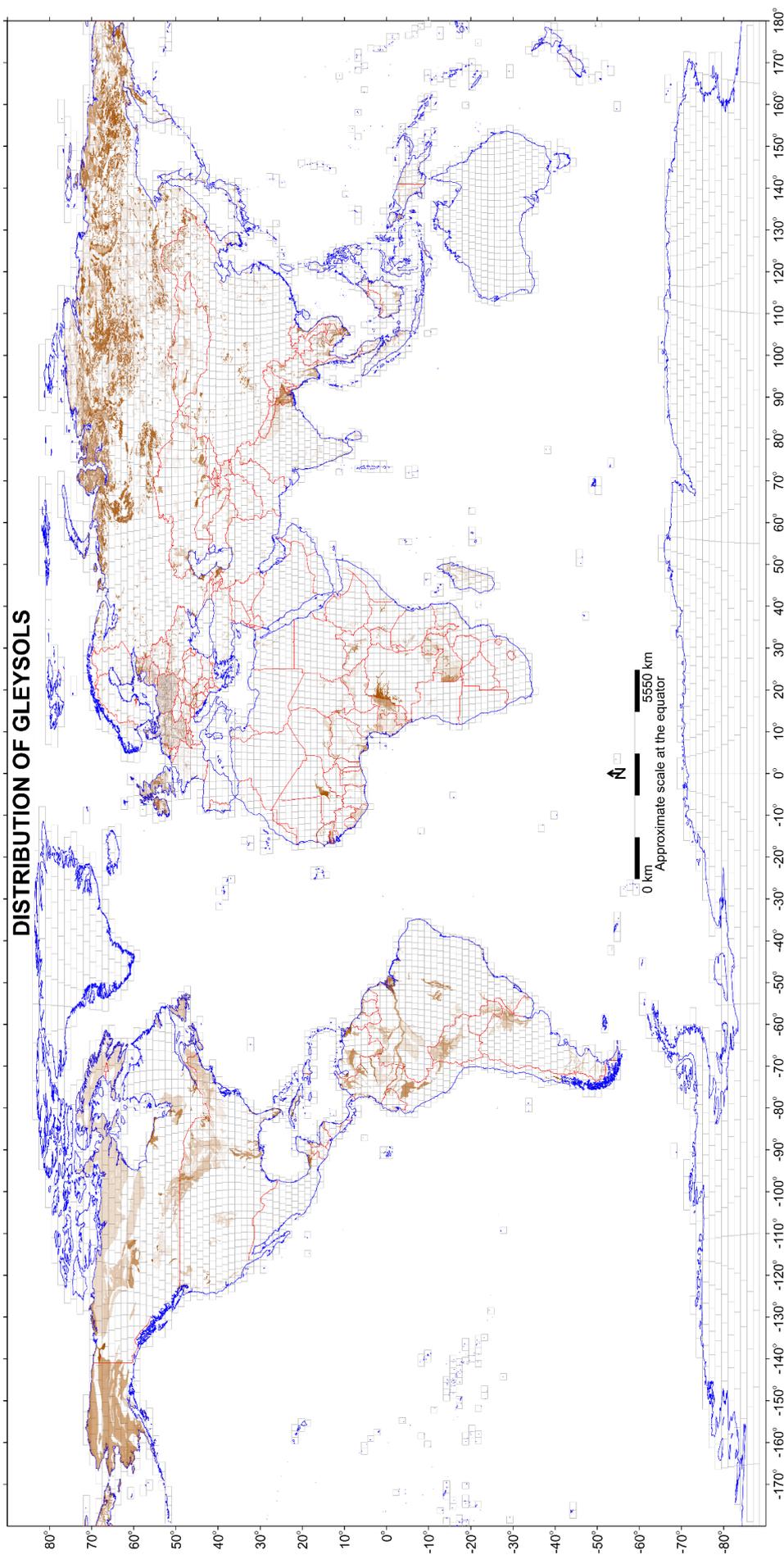


Figure A3.2.1.3. Map showing the global distribution of Gleysols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_GL-Gleysols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Gleysols</p>	<p>From the Russian word <i>gley</i> (глей) = muddy soil mass.</p>
 <p>Source: Peter Schad²</p>	<p>In contrast to most of the other soil types, the Gleysols are affected by groundwater. The groundwater comes near the surface and the lower part of the soil is more or less constantly saturated with water. This part, therefore, shows a grey or even bluish colour, since there is no oxygen to oxidise the iron-bearing minerals, which would lead to a reddish-brown soil colour. The horizon above the saturated horizon is saturated with water only from time to time (according to the fluctuation of the groundwater table). Hence, this horizon shows a scattered pattern of reddish-brown and grey parts, reflecting the varying conditions of saturation with water.</p>
<p>Geographical distribution:</p>	<p>Gleysols occur in depressions, valleys, riverine wetlands, lake and coastal swamps. The largest extent of Gleysols is in sub-arctic areas, in northern Russia, Siberia, Canada and Alaska and in humid temperature and subtropical lowlands (Fig. A3.2.1.3).</p>
<p>Parent material:</p>	<p>Fine- to medium-grained sediments. Unconsolidated materials, mainly fluvial, marine and lacustrine sediments with felsic mineralogy.</p>
<p>Usage:</p>	<p>Wetness is the main limitation of Gleysols. Due to the almost constant saturation with groundwater, Gleysols are scarcely used for agricultural purposes. Intensive drainage would be needed to make these soil types suitable for crop production. Forest use with trees accustomed to high water content (e.g., alder) is possible. Areas with Gleysols are often protected areas with regard to groundwater preservation.</p>
<p>Geochemical processes:</p>	<p>In the oxidation zone, there is the formation of Fe-oxides. In the groundwater-saturated zone with little oxygen, Fe- and Mn-compounds (Fe^{2+}, Mn^{2+}) are mobilised and transported laterally or ascend to the oxidation zone and are oxidised. Ascending carbonate-rich groundwater can lead to precipitation of carbonates in the soil profile or on the surface.</p>

² <https://www3.ls.tum.de/en/boku/wrb-working-group/pictures/gleysol/>; last access: 13.02.2022.

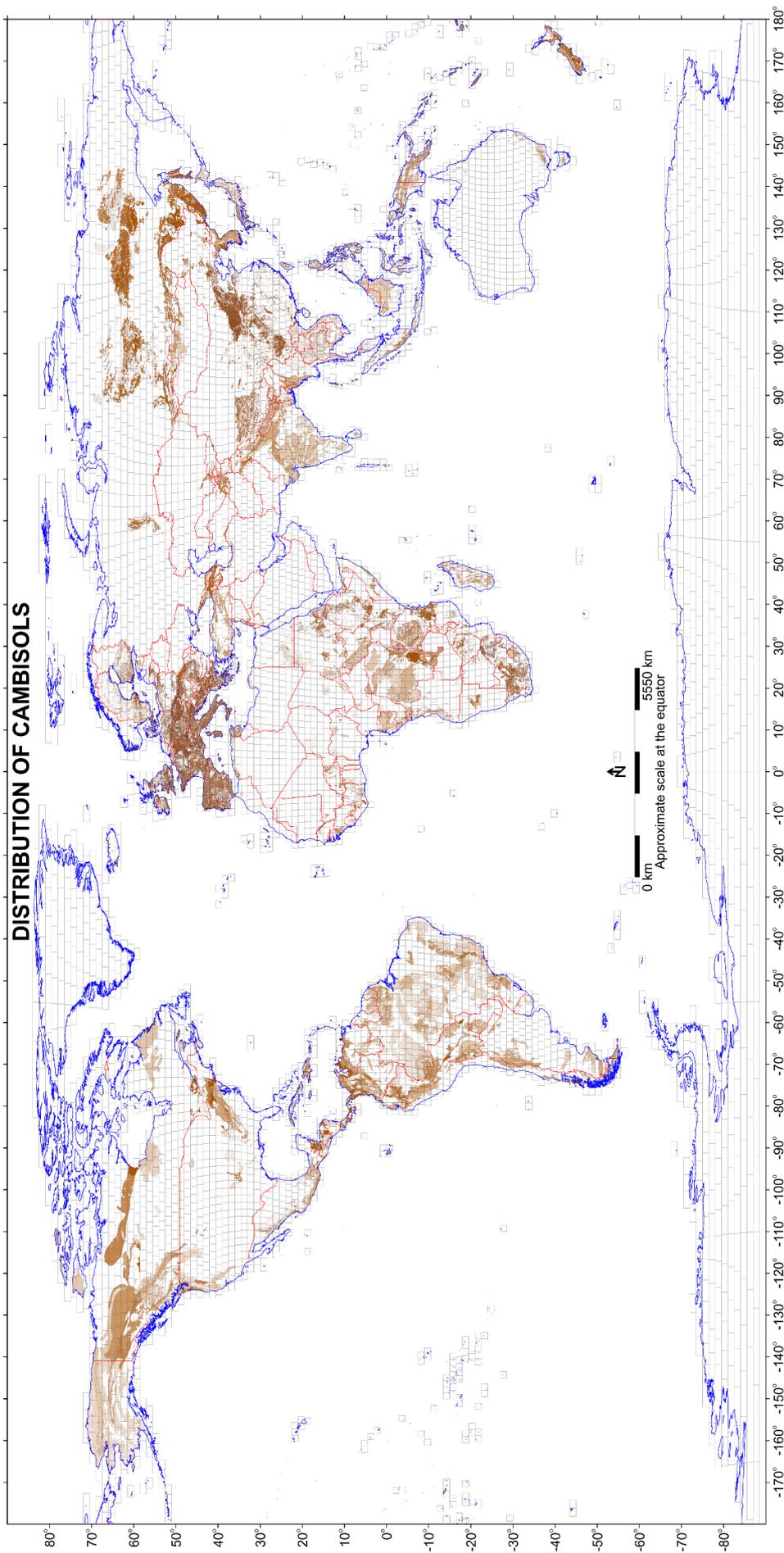


Figure A3.2.1.4. Map showing the global distribution of Cambisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area; the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_CM-Cambisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Cambisols</p>	<p>From Italian word <i>cambiare</i> = to change.</p>
 <p>Photograph: Edith Haslinger (AIT)</p>	<p>The name of the Cambisols points to the changes taking place mainly in the soil horizon below the topsoil horizon. Another name of the Cambisols used in several national classifications – brown soil – indicates the overall appearance of the soil profile. The brown colour comes from iron-bearing minerals of parent rocks (e.g., olivine, pyroxene, amphibole), which are transformed to iron oxides such as <i>goethite</i> (brown) and – in tropical climates – <i>haematite</i> (red) during weathering. During weathering of the parent rocks, they are also physically broken down to smaller particle sizes – from sand to silt and finally to clay. Clay minerals which form during weathering give the Cambisols an almost loamy texture.</p> <p>Cambisols are relatively young, moderately developed and weathered soil types.</p>
<p>Geographical distribution:</p>	<p>Cambisols develop on a wide variety of rocks and in different climatic zones – from continental boreal to temperate humid as well as (sub)tropical climates (Fig. A3.2.1.4). Erosion and deposition cycles explain the occurrence of Cambisols in mountain regions.</p>
<p>Parent material:</p>	<p>Calcareous and non-calcareous rocks.</p>
<p>Usage:</p>	<p>Highly suitable for agricultural purposes, especially on calcareous bedrock. On silicate bedrock, Cambisols are best used for grazing land or forest. This is also the case for shallow or rocky soil types.</p>
<p>Geochemical processes:</p>	<p>Chemical weathering of Fe-bearing silicates → base cations often leached from the soil profile, silicic acid forms clay minerals together with Al; Fe-oxides (Fe³⁺) are formed, and are responsible for the brownish colour; formation of iron-humus-complexes.</p>

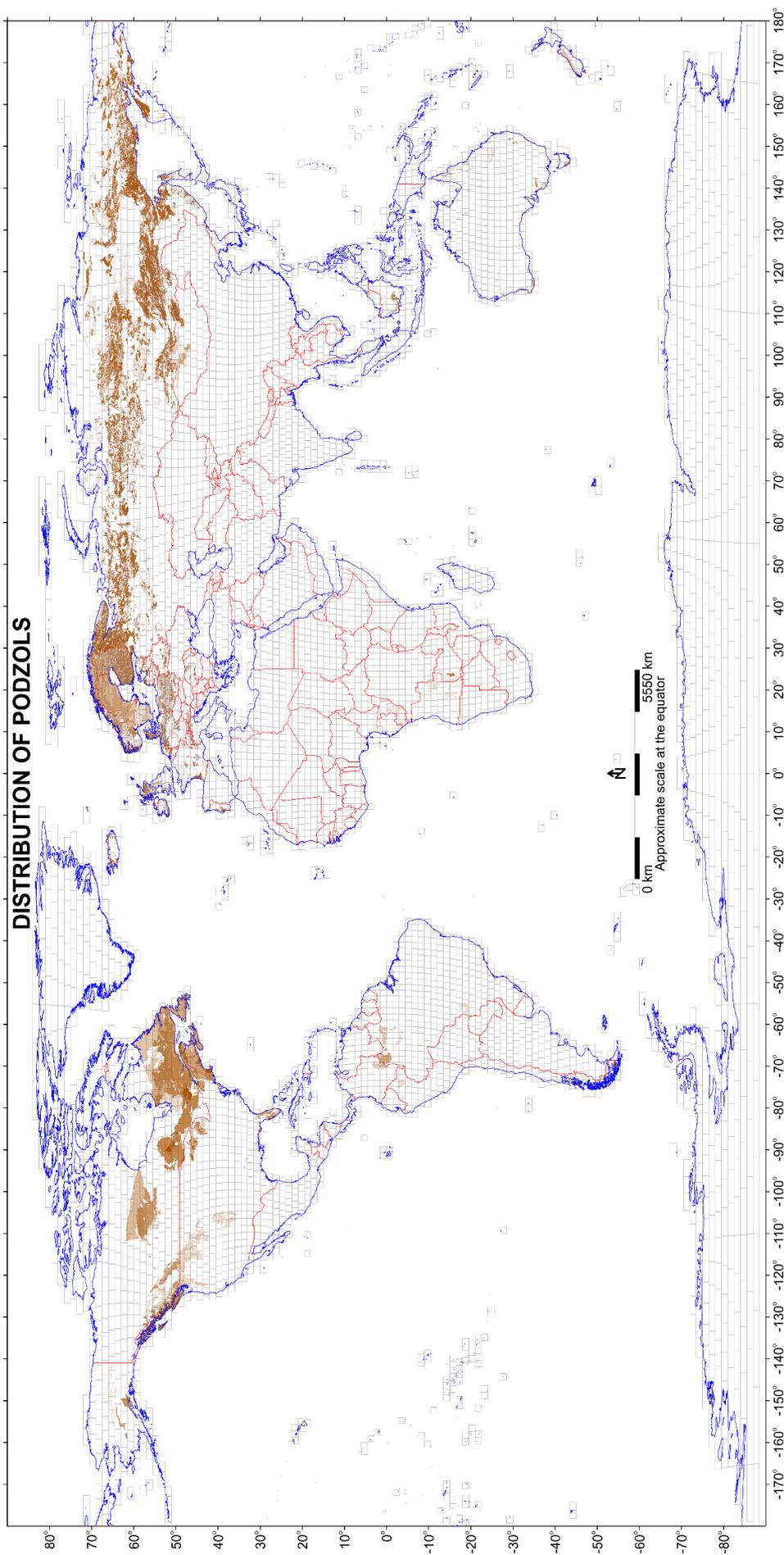


Figure A3.2.1.5. Map showing the global distribution of Podzols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_PZ-Podzols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Podzols</p>	<p>From the Russian words <i>pod</i> (под) = under and <i>zola</i> = ash.</p> <p>Similar to Albeluvisols, they are characterised by a pale to white horizon below the organic topsoil. However, from the eluviation horizon, mainly organic matter, iron and aluminium are leached and accumulated in horizons below (in well-developed podzols, there is one distinct dark horizon with illuviated organic matter and one orange-brown horizon with illuviated iron and aluminium). Podzols have very (or extremely) low pH values and develop under coniferous forests. The cold climate hinders the decomposition of organic matter, leading to an accumulation and partially very thick layers of vegetation litter.</p>
	
<p>Photograph: Edith Haslinger (AIT)</p>	
<p>Geographical distribution:</p>	<p>Mainly in the temperate and boreal regions of the Northern Hemisphere (Fig. A3.2.1.5). They are extensive in Scandinavia, NW Russia, Canada and NE part of the United States of America.</p>
<p>Parent material:</p>	<p>Quartz-rich, lime-free rocks such as granite, gneiss and quartzite and their weathering detritus (sandy sediment).</p>
<p>Usage:</p>	<p>Hardly suitable for agricultural use due to low nutrient content, low water retention capacity and low to very low pH values.</p> <p>Application of lime and manure might make podzols suitable for potato cultivation.</p>
<p>Geochemical processes:</p>	<p>Leaching of base cations (to groundwater); eluviation of Fe, Al, Mn, organic matter and potentially toxic elements downwards and illuviation in the lower part of the soil profile; toxic levels of Al are possibly due to low pH values.</p>

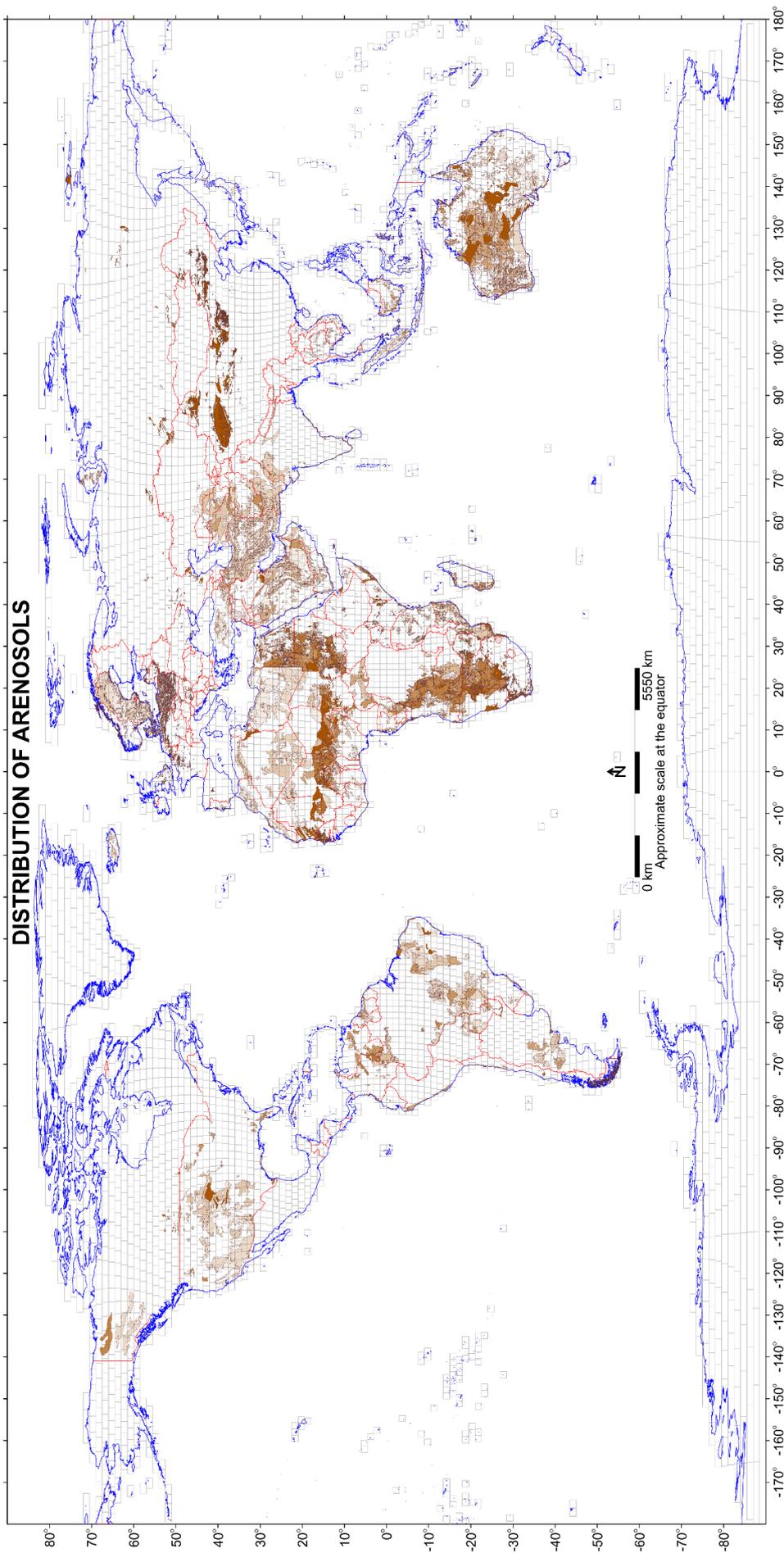


Figure A3.2.1.6. Map showing the global distribution of Arenosols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_AR-Arenosols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Arenosols</p>	<p>From the Latin word <i>arena</i> = sand.</p>
 <p>Source: Peter Schad³</p>	<p>Arenosols are sandy types of soil with slight to moderate profile development, and are distributed over a wide range of climatic zones. They are one of the most extensive soil types in the world. Arenosols are widespread in aeolian landscapes, such as the central African plateau, but occur also in marine, littoral and lacustrine sands and coarse-grained weathering mantles of siliceous rocks (Fig. A3.2.1.6).</p>
<p>Geographical distribution:</p>	<p>Arenosols occur over large areas in Africa, central and western Australia, the Middle East and central China (Fig. A3.2.1.6). Smaller areas are found along coastlines all over the world. If shifting sands and active sand dunes were included in the classification, the share of Arenosols would be even higher.</p>
<p>Parent material:</p>	<p>Unconsolidated sand with more or less coarse texture. Arenosols develop on residual sands, <i>in-situ</i> after weathering of old, usually quartz-rich soil material or rock. They also develop in recently deposited sands in deserts and beach lands.</p>
<p>Usage:</p>	<p>Arenosols occur in vastly different environments. Thus, the possibilities to use them for agriculture vary accordingly. However, Arenosols are sandy soil types with nearly a coarse texture. Therefore, their water and nutrient storage capacity are low in general, limiting the possibilities. Especially in arid areas, the use of Arenosols is restricted to extensive grazing lands. The cultivation of crops requires irrigation and fertilisation.</p>
<p>Geochemical processes:</p>	<p>In humid and tropical regions, Arenosols mostly are deeply leached and decalcified soil types with a low capacity to store bases and contain no or little decomposed organic matter. In dry regions, Arenosols can be rich in base cations. However, moderate leaching and decalcification may still occur.</p>

³ <https://www3.ls.tum.de/en/boku/wrb-working-group/pictures/arenosol/>; last access: 13.02.2022

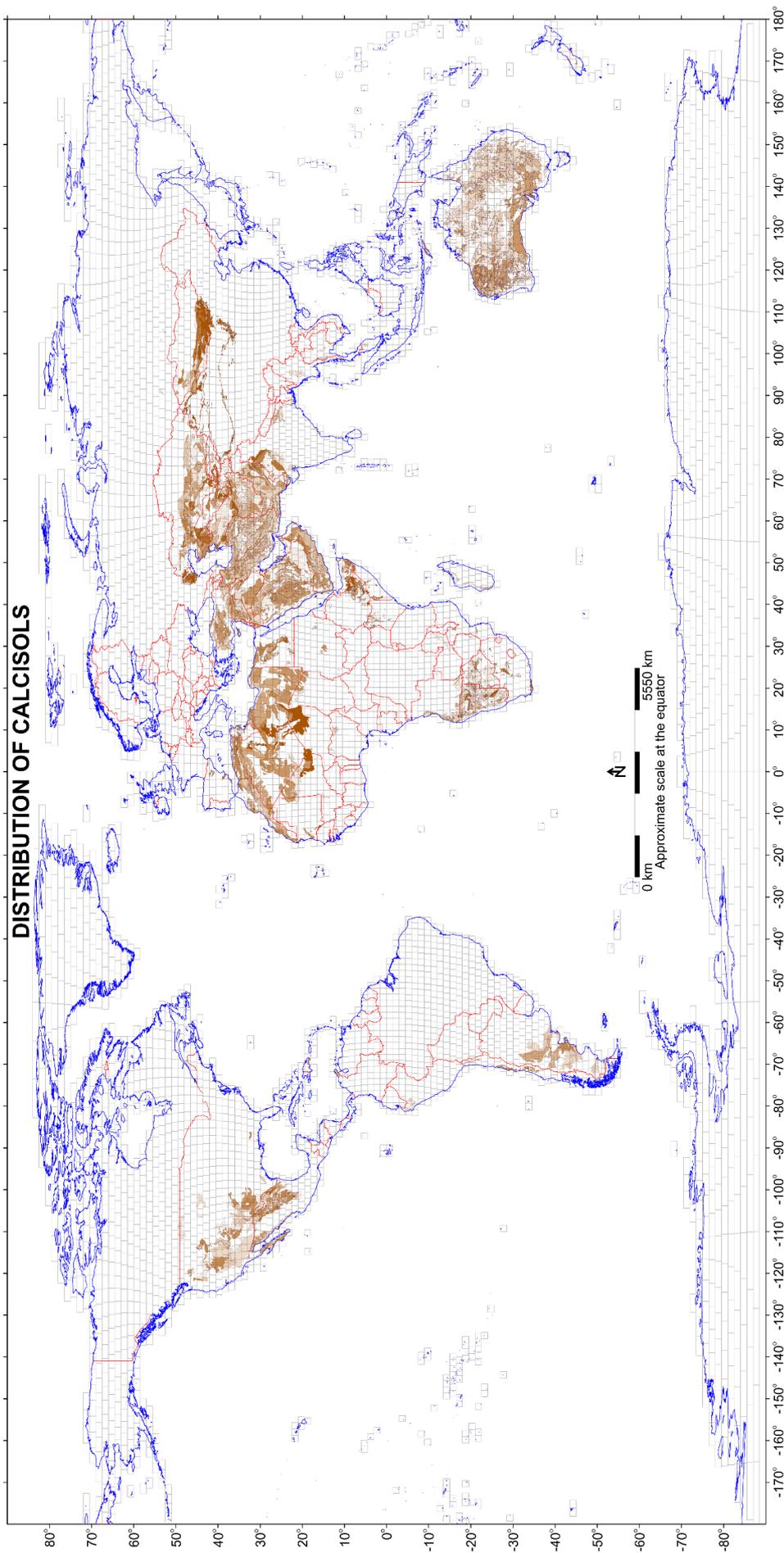


Figure A3.2.1.7. Map showing the global distribution of Calcisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_CL- Calcisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Calcisols</p>  <p>Photograph: Edith Haslinger (AIT)</p>	<p>From the Latin words <i>calx</i> = limestone or <i>calcarius</i> = calcareous.</p> <p>As the name indicates, the Calcisols are characterised by their high content of secondary carbonates (CaCO_3), which comes from the parent material of these soil types - calcareous sediments. The carbonates are leached from the upper part of the soil and precipitate in lower parts as so-called pseudo mycelium – since it resembles the hyphens of fungi – and/or as a hard, massive layer ('calcrete').</p>
<p>Geographical distribution:</p>	<p>In dry, arid and semiarid (sub)tropics of both hemispheres (Fig. A3.2.1.7).</p>
<p>Parent material:</p>	<p>Calcareous sediments.</p>
<p>Usage:</p>	<p>Due to the dry climate, most Calcisols must be irrigated. In this case, they are rather productive for vegetables and forage crops. Plants must be adapted to the high lime content, otherwise, there is a risk of chlorosis.</p>
<p>Geochemical processes:</p>	<p>Low availability of nutrients (<i>e.g.</i>, N); deficiency in Fe and Mn; inhibition of K-uptake and proneness to chlorosis in plants due to high Ca-contents. Precipitation of carbonate leads to hard dry carbonatic horizons, which hinder root development.</p>

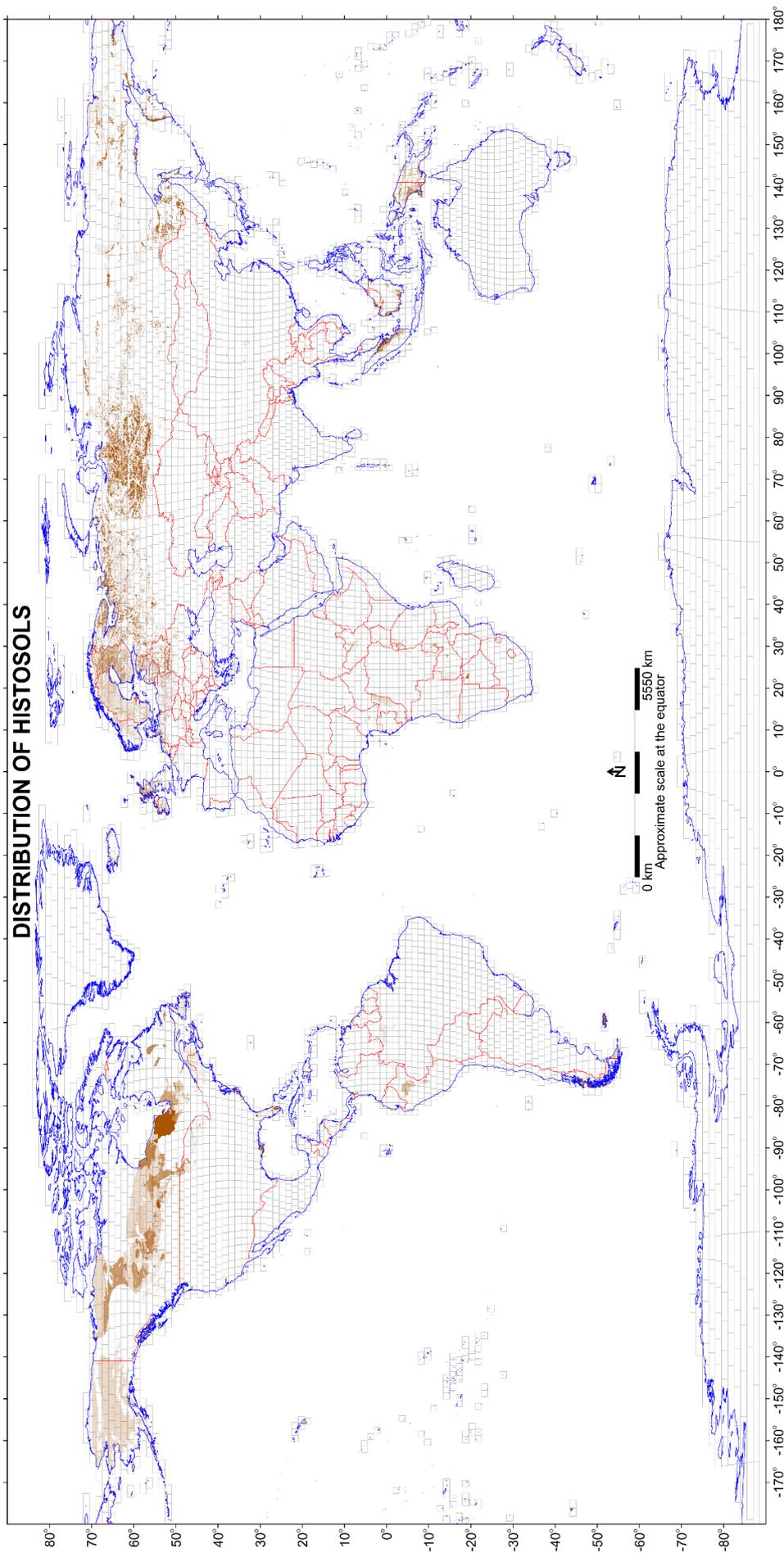


Figure A3.2.1.8. Map showing the global distribution of Histosols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_HS-Histosols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Histosols</p>	<p>From the Hellenic word <i>histós</i> (ἵστός) = tissue.</p>
 <p>Source: Peter Schad⁴</p>	<p>Histosols are made up nearly entirely of partially decomposed organic material, hence their colour is nearly completely dark brown to black. Commonly, the material of Histosols is known as <i>peat</i> or <i>turf</i>. Histosols develop in areas where more organic material is produced than decomposed. This is the case in recent or former fens, lagoons or mangroves, in which the organic matter accumulated. Since Histosols can mainly be found in a presently cold climate, the decomposition of the organic material is inhibited. As there is no bedrock, which could deliver nutrients, the soil is very acidic (low pH values) and the oxygen content is very low.</p>
<p>Geographical distribution:</p>	<p>Mainly in boreal, subarctic and low arctic areas of the northern hemisphere (Fig. A3.2.1.8). The remaining occurs in temperate lowlands and mountainous areas with much rainfall and low evapotranspiration, <i>e.g.</i>, in bogs, moors and mires. Especially in the United States of America (Alaska), Canada, Western Europe, northern Fennoscandia and central Russian Federation.</p>
<p>Parent material:</p>	<p>Organic matter.</p>
<p>Usage:</p>	<p>Peat is agriculturally used mainly in horticulture to improve the structure and water retention of soil and to lower the pH values for plants, which require more acidic conditions. However, since bogs and moors are unique ecosystems, which are irretrievably lost when used, many horticulturists now refrain from using peat.</p> <p>The most common use of peat is for energy generation as biomass fuel, mainly in Finland and Ireland.</p>
<p>Geochemical processes:</p>	<p>Availability of nutrients low due to lacking replenishment by weathering rocks; very high Cation Exchange Capacity (CEC) due to very high amount of organic matter; partially very low pH, especially in upland moors. In low-level moors, the pH values can be higher due to ascending hydrogen carbonate [Ca(HCO₃)₂]-rich groundwater; anaerobic, wet and cool conditions lead to inhibited decomposition of organic matter.</p>

⁴ <https://www3.ls.tum.de/en/boku/wrb-working-group/pictures/histosol/>; last access: 13.02.2022

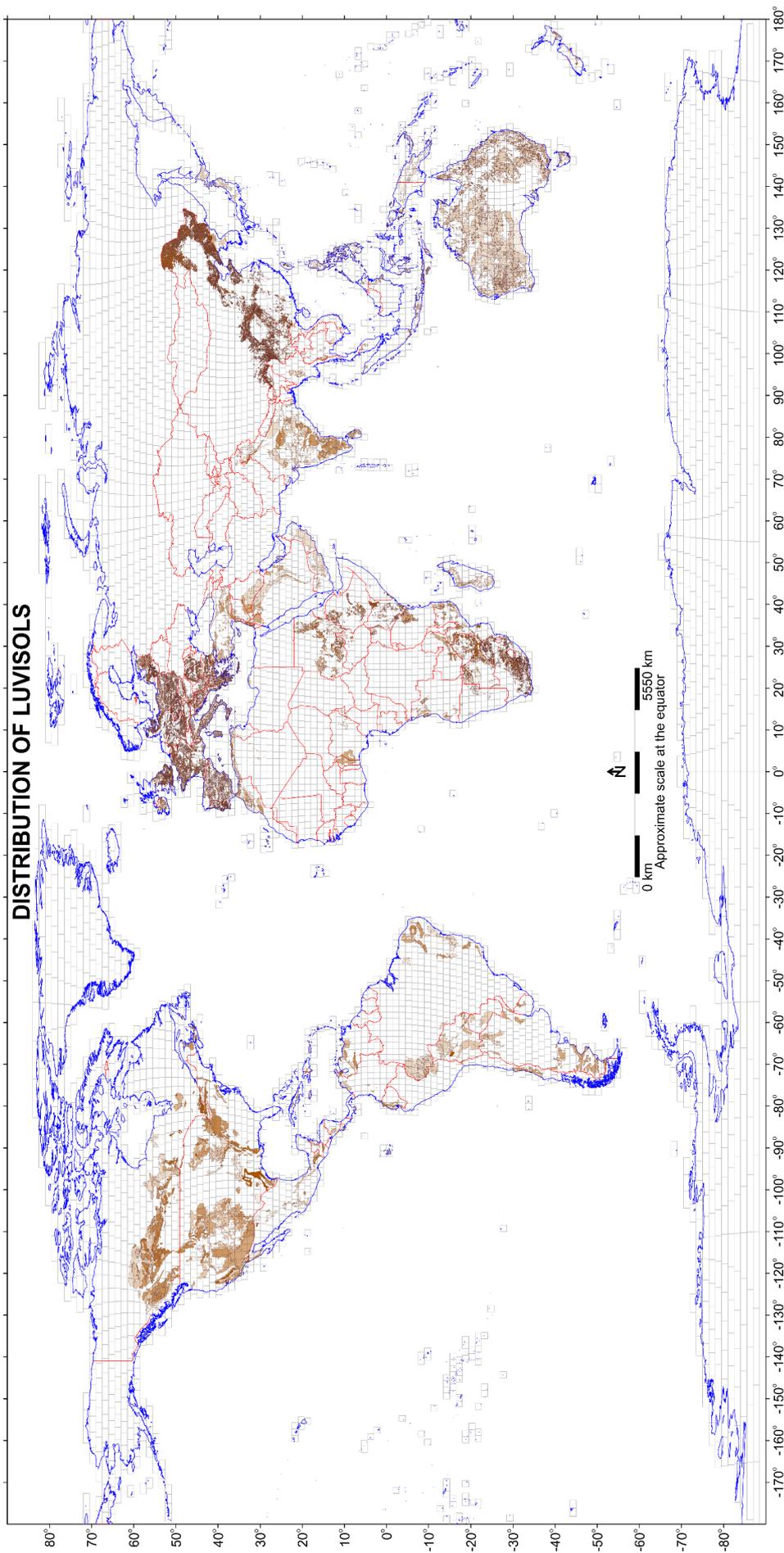


Figure A3.2.1.9. Map showing the global distribution of Luvisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IMGE/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_LV-Luvisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Luvisols</p>	<p>From Latin word <i>luere</i> = to wash.</p>
	<p>The process of the eluviation of clay minerals from the topsoil to the subsoil is equal to the paedogenetic processes in the Albeluvisols, whereas the tonguing of the eluviated layer into the horizon below is missing in the Luvisols.</p>
<p>Photograph: Edith Haslinger (AIT)</p>	
<p>Geographical distribution:</p>	<p>Luvisols can be found in the temperate humid zones such as Canada, the United States of America and central Europe, often in former glacial or periglacial zones (Fig. A3.2.1.9). But also, in the Mediterranean region and (sub)tropical regions.</p>
<p>Parent material:</p>	<p>Unconsolidated sediments including glacial till, such as loess, aeolian sediments, and sandy-silty gravel.</p>
<p>Usage:</p>	<p>Luvisols are highly suitable for agricultural purposes due to their high nutrient content, and favourable water and oxygen conditions. Due to the fine soil texture, Luvisols are prone to compaction and water retention. In hilly areas, preventive measures against erosion have to be taken (<i>e.g.</i>, terraces).</p>
<p>Geochemical processes:</p>	<p>Decalcification of upper soil parts; translocation of Fe, Mn, Al and Si downwards; leaching of base cations.</p>

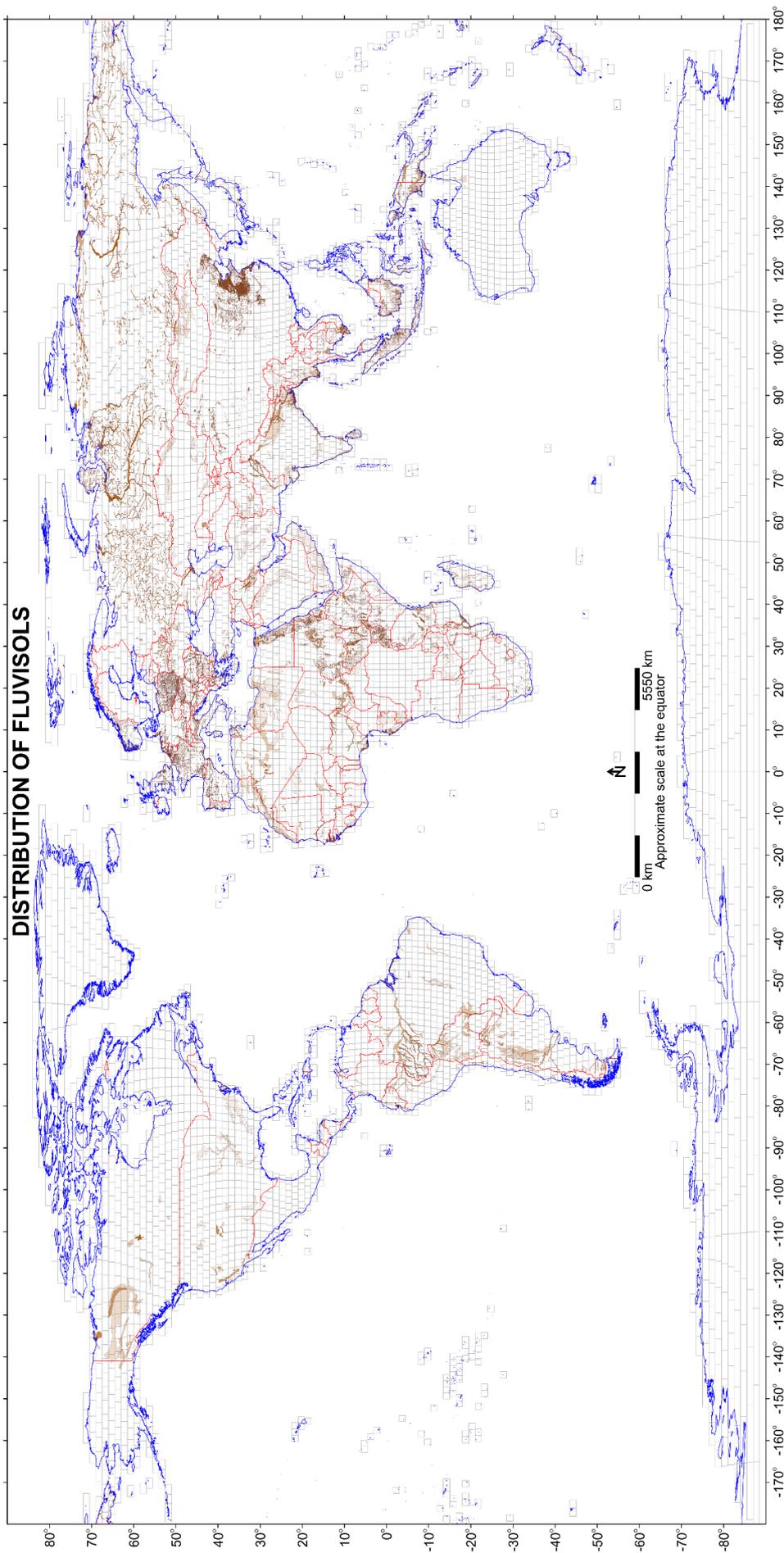


Figure A3.2.1.10. Map showing the global distribution of Fluvisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_FL-Fluvisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Fluvisols</p>	<p>From the Latin word <i>fluvius</i> = river.</p>
 <p>Photograph: Edith Haslinger (AIT)</p>	<p>Fluvisols are soil types of areas that are regularly inundated. These areas can be in river basins or marine or lacustrine environments. Thus, the sediments deposited during inundation can be fluvial, marine or lacustrine. The sediments reflect the respective source area. The horizons of Fluvisols are not a result of pedogenesis but consist of the layers of deposited sediments.</p> <p>The sediments reflect the geological provenance or source area. When a river flows a long distance and through various geological zones, for instance, in the cases of the Danube, Mississippi, Amazon, Ganges, Yellow and Nile Rivers, the sediments are very different in their mineralogical composition in the areas further downstream.</p> <p>In areas with regular inundation (close to the water), there is not enough time for pedogenetic processes, which would allow for the formation of clay minerals and/or iron oxides that would give the soil a brownish colour. Therefore, these Fluvisols have a greyish appearance. In areas farther from the water, which are inundated only occasionally or during extensive floods, the Fluvisols are subsequently affected by pedogenesis and have a brownish colour and a loamy texture.</p>
<p>Geographical distribution:</p>	<p>Along rivers and lakes, riverbanks and marine and lacustrine coasts in all climate zones (Fig. A3.2.1.10).</p>
<p>Parent material:</p>	<p>Sediments.</p>
<p>Usage:</p>	<p>Depends on the regularity of inundation, the chemistry of groundwater and the mineralogical composition of sediments. Most Fluvisols are not suitable for large agricultural machines, since their bearing capacity is limited. In case of big flood events, Fluvisols can be contaminated with material or fluids from, e.g., industrial sites.</p>
<p>Geochemical processes:</p>	<p>Chemical properties are dependent on the type and provenance of deposited sediments; nutrient availability generally good, but the threat of high contaminant contents, when, e.g., industrial areas are inundated during extensive floods.</p>

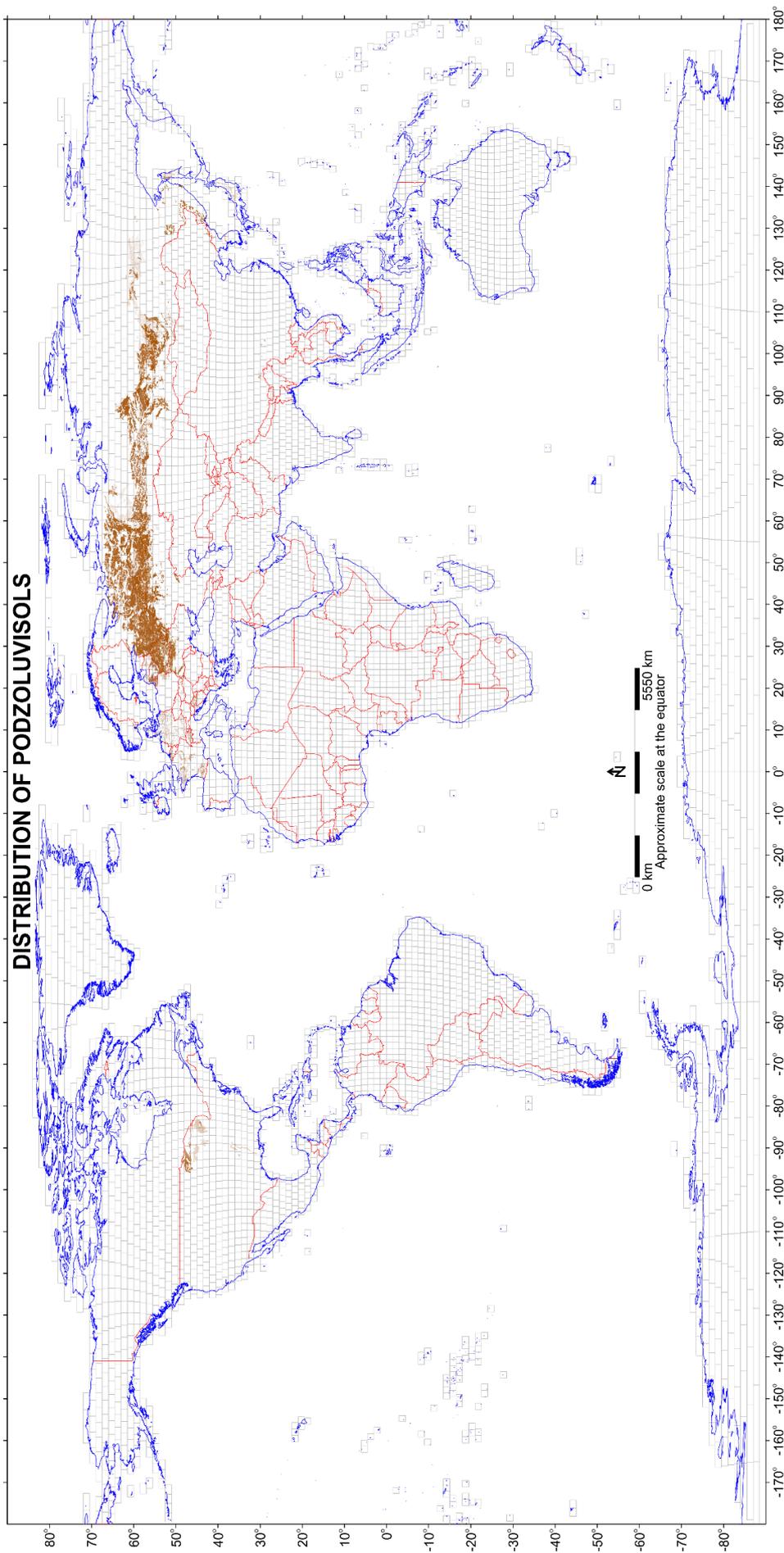


Figure A3.2.1.11. Map showing the global distribution of Podzoluvisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_PD-Podzoluvisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Podzoluvisols</p>	<p>From the Latin words <i>albus</i> = white, and <i>eludere</i> = to wash out / leach.</p>
 <p>Photograph: Edith Haslinger (AIT)</p>	<p>Albeluvisols (common international name = Podzoluvisol (FAO)) are soil types that are characterised by a pale brown to a white layer below the organic topsoil rich in organic matter. From the pale/white layer, clay minerals are mainly washed out and accumulated in the horizon below. These processes are referred to as eluviation (washing out) and illuviation (accumulation). The longer or the more intense the eluviation processes are, the more the colour of the horizon will turn white. The pale/white horizon forms tongues reaching into the horizon below, which is known as the characteristic albeluvisol tonguing.</p> <p>In the boreal zone, the subsoil can freeze and will retain water in the topsoil during snowmelt.</p>
<p>Geographical distribution:</p>	<p>Continental boreal to temperate humid climate zones with cold winters and short and cool summers (Fig. A3.2.1.11). Albeluvisols are concentrated in two regions: in cold continental parts of NE Europe, NW Asia and SW Canada, and loess and coversand areas in temperate regions such as France, Belgium, The Netherlands and Germany.</p>
<p>Parent material:</p>	<p>Mostly unconsolidated glacial till, materials of lacustrine or fluvial origin, lime-free, fine-grained sediments (sand, aeolian sands, such as loess, delta sediments, <i>etc.</i>).</p>
<p>Usage:</p>	<p>Forms mediocre farmland due to low pH, low content of nutrients, the tendency to water retention as well as erosion in hilly terrain.</p> <p>Cultivation of spring wheat, barley, sugar beet, forage plants and potatoes after application of manure lime.</p> <p>Best used as grazing land and forest.</p>
<p>Geochemical processes:</p>	<p>Translocation of base cations (together with clay) downwards due to eluviation processes; Fe and Mn are laterally transported above the clay-rich and dense illuviation zone and form Fe-/Mn-oxide and hydroxide concretions; clay minerals are often enriched in Al.</p>

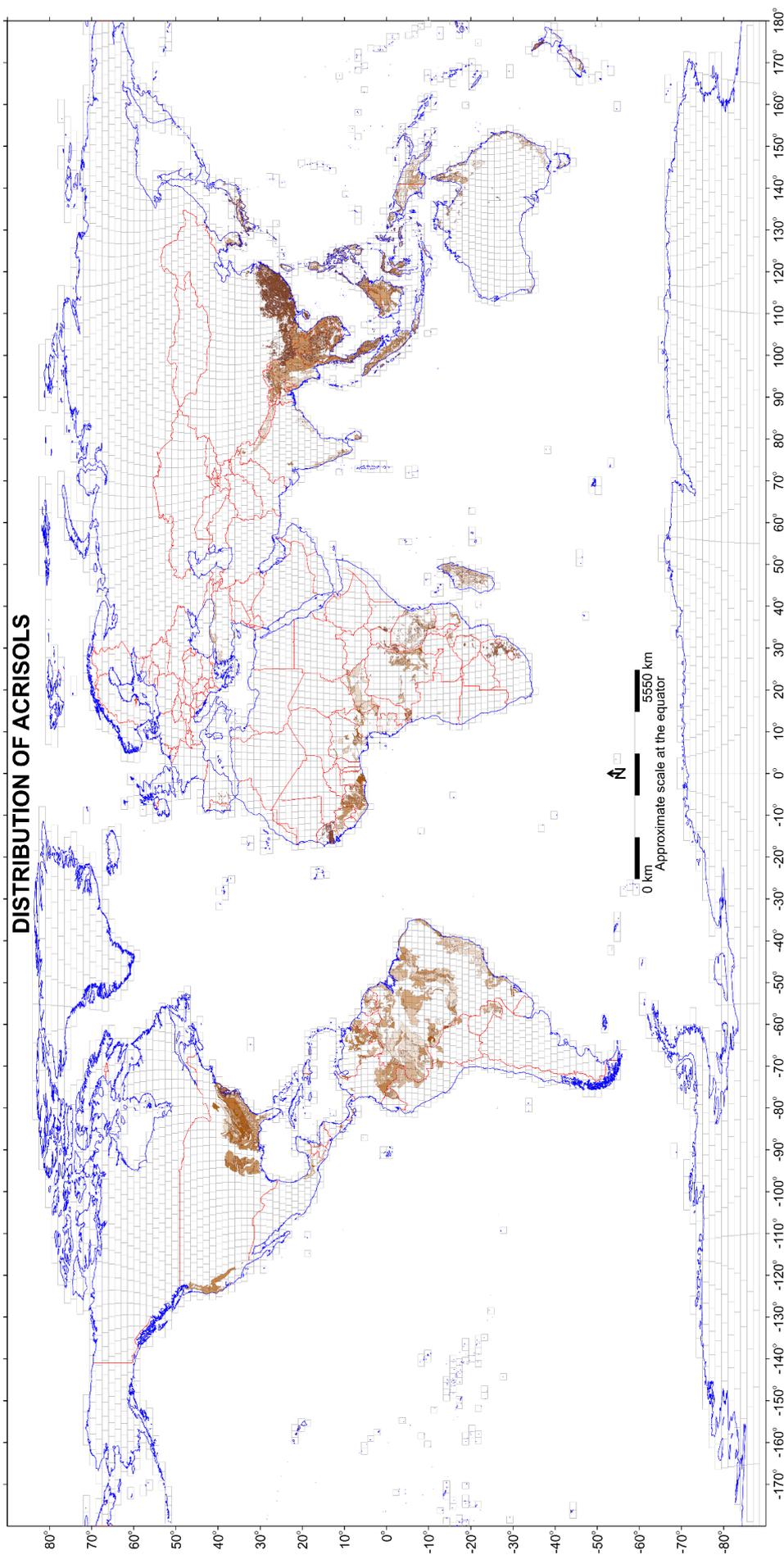


Figure A3.2.1.12. Map showing the global distribution of Acrisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_AC-Acrisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Acrisols</p>	<p>From the Latin word <i>acris</i> = very acid.</p> <p>Acrisols are strongly weathered acid soil types that are characterised by accumulation of low activity clays in an argic subsurface horizon and by a low base saturation level.</p>
 <p>Source: Peter Schad⁵</p>	
<p>Geographical distribution:</p>	<p>They are found in old land surfaces with hilly or undulating topography. In regions with wet tropical/monsoonal, subtropical or warm temperate climates (Fig. A3.2.1.12). – Light forests.</p>
<p>Parent material:</p>	<p>Weathering debris of felsic rocks, especially on strongly weathered clays.</p>
<p>Usage:</p>	<p>A general paucity of plant nutrients, aluminium toxicity, strong phosphorus sorption, slaking/crusting and high susceptibility to erosion impose severe restrictions on arable land uses. Large areas are used for subsistence farming. Acrisols are not very productive soil types and are only suitable for acidity-tolerant crops, such as pineapple, cashew, oil palm and rubber.</p>
<p>Geochemical processes:</p>	<p>The level of plant nutrients in Acrisols is low. Aluminium toxicity and P-sorption are strong limiting factors. Acrisols are characterised by <i>ferralitisation</i>, i.e., the accumulation of sesquioxides as a result of advanced hydrolysis of weatherable primary minerals, and the redistribution of iron compounds (<i>cheluviation</i> and <i>chilluviation</i>).</p>

⁵ <https://www3.ls.tum.de/en/boku/wrb-working-group/pictures/acrisol/>; last access: 13.02.2022.

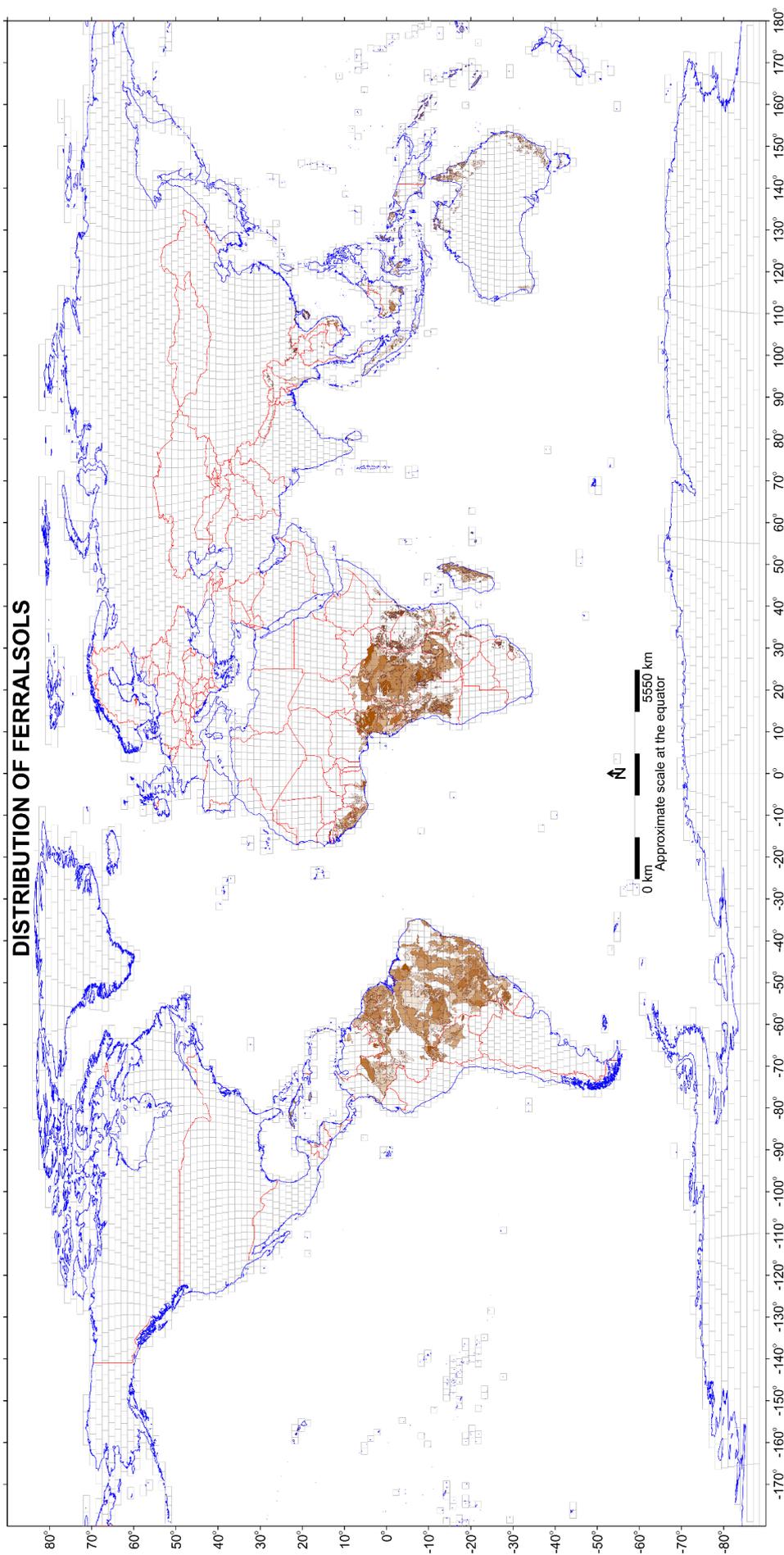
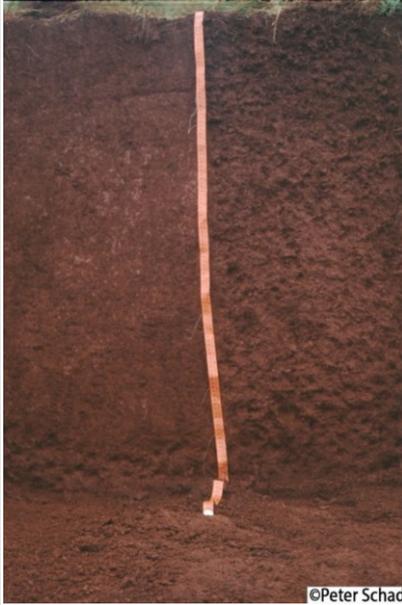


Figure A3.2.1.13. Map showing the global distribution of Ferralsols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area; the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_FR-Ferralsols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Ferralsols</p>	<p>From the Latin word <i>ferrum</i> = iron and aluminium.</p>
 <p>Source: Peter Schad⁶</p>	<p>Ferralsols are deeply weathered, red or yellow soil types of the humid tropics with a high content of sesquioxides, containing strongly weathered materials on old, stable geomorphic surfaces; in weathering material from mafic rocks.</p>
<p>Geographical distribution:</p>	<p>In the humid tropics on the continental shields of South America and Africa (Fig. A3.2.1.13). Ferralsols are restricted to regions with easily weathered mafic rock and a hot and humid climate.</p>
<p>Parent material:</p>	<p>Strongly weathered material on old, stable geomorphic surfaces. Mostly on weathering material from mafic than from felsic rocks.</p>
<p>Usage:</p>	<p>Their low natural fertility and tendency to 'fix' phosphates are serious limitations. Ferralsols are mainly used for shifting cultivation. Liming and full fertilisation are necessary for sedentary agriculture.</p>
<p>Geochemical processes:</p>	<p>The main chemical process in Ferralsols is <i>ferralitisation</i>, i.e., the accumulation of sesquioxides as a result of advanced hydrolysis of weatherable primary minerals. The weatherable primary minerals in these soil types are dissolved and removed, whereas the less soluble compounds such as iron and aluminium oxides and hydroxides, as well as coarse quartz grains, remain behind.</p>

⁶ <https://www3.ls.tum.de/en/boku/wrb-working-group/pictures/ferralsol/>; last access: 13.02.2022.

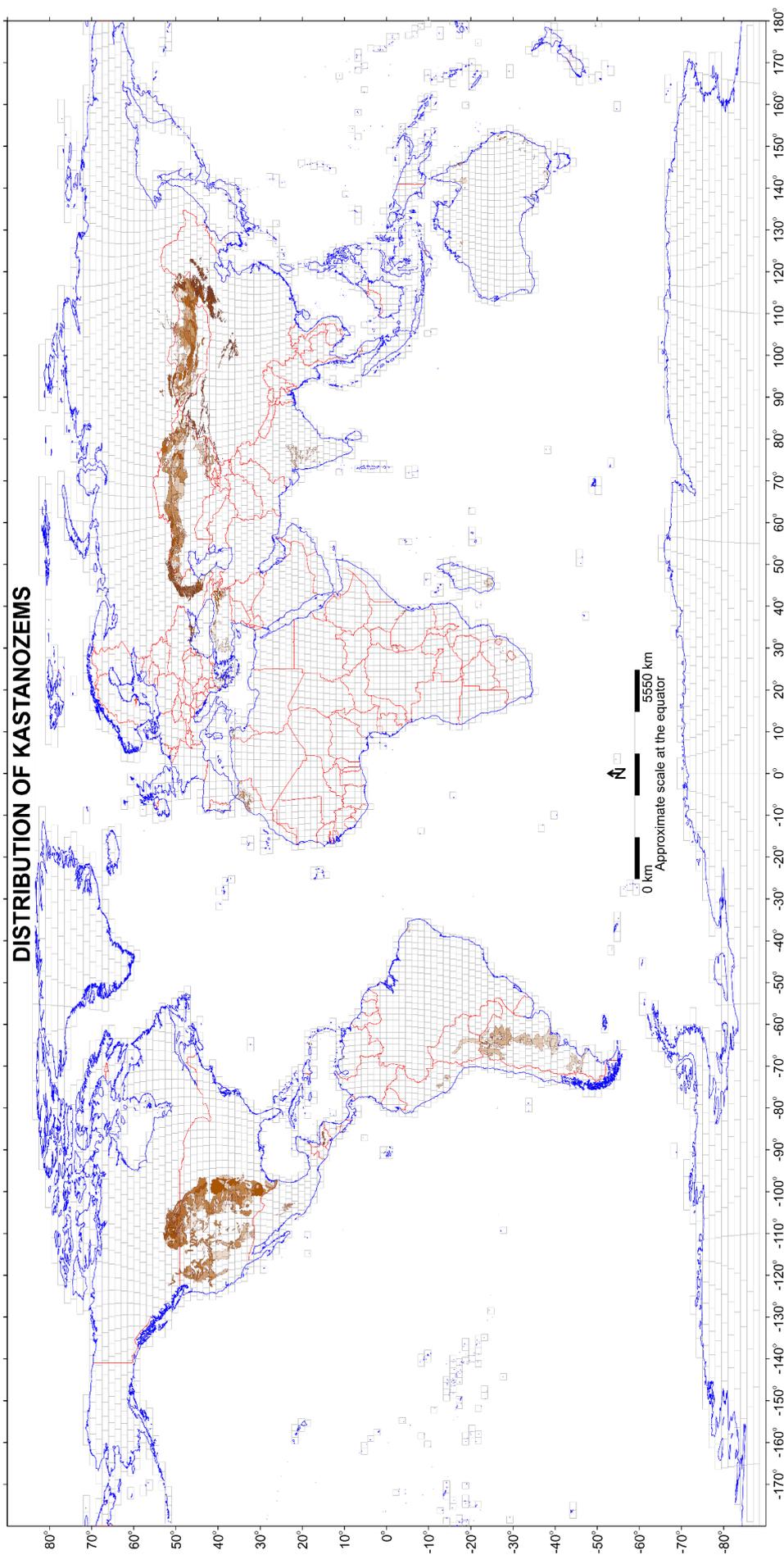


Figure A3.2.1.14. Map showing the global distribution of Kastanozems. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_KS-Kastanozems.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Kastanozems</p>	<p>From the Hellenic word <i>kástano</i> (κάστανο) = chestnut or Russian каштан = chestnut; and from the Russian word <i>zemlja</i> (земля) = earth, land. In Russian, ‘Kashtanozem’ is a soil with chestnut colour.</p>
 <p>©Peter Schad</p> <p>Source: Peter Schad⁷</p>	<p>The soil group of Kastanozems holds the ‘zonal’ soil types of the short grass steppe belt, consisting of (dark) brown soil, which is rich in organic matter. They have the same horizons such as the Chernozems, but the humus-rich surface horizon is less deep and less black and shows a more prominent accumulation of secondary carbonates.</p>
<p>Geographical distribution:</p>	<p>Major areas are in the dry and warm regions with a focus on the Eurasian short-grass-steppe belt, and the western USA (Fig. A3.2.1.14).</p>
<p>Parent material:</p>	<p>Unconsolidated sediments. Most Kastanozems are developed on loess.</p>
<p>Usage:</p>	<p>Kastanozems are potentially rich soil types. Periodic lack of soil moisture can make irrigation necessary for high yields. Secondary salinisation might pose a problem. The production of small grains and (irrigated) food and vegetable crops is the principal arable land use. Many Kastanozems are used for extensive grazing. Drought, wind and water erosion are serious limitations.</p>
<p>Geochemical processes:</p>	<p>The accumulation of secondary carbonates and gypsum, as well as salinisation, is common.</p>

⁷ <https://www3.ls.tum.de/en/boku/wrb-working-group/pictures/kastanozem/>; last access: 13.02.2022.

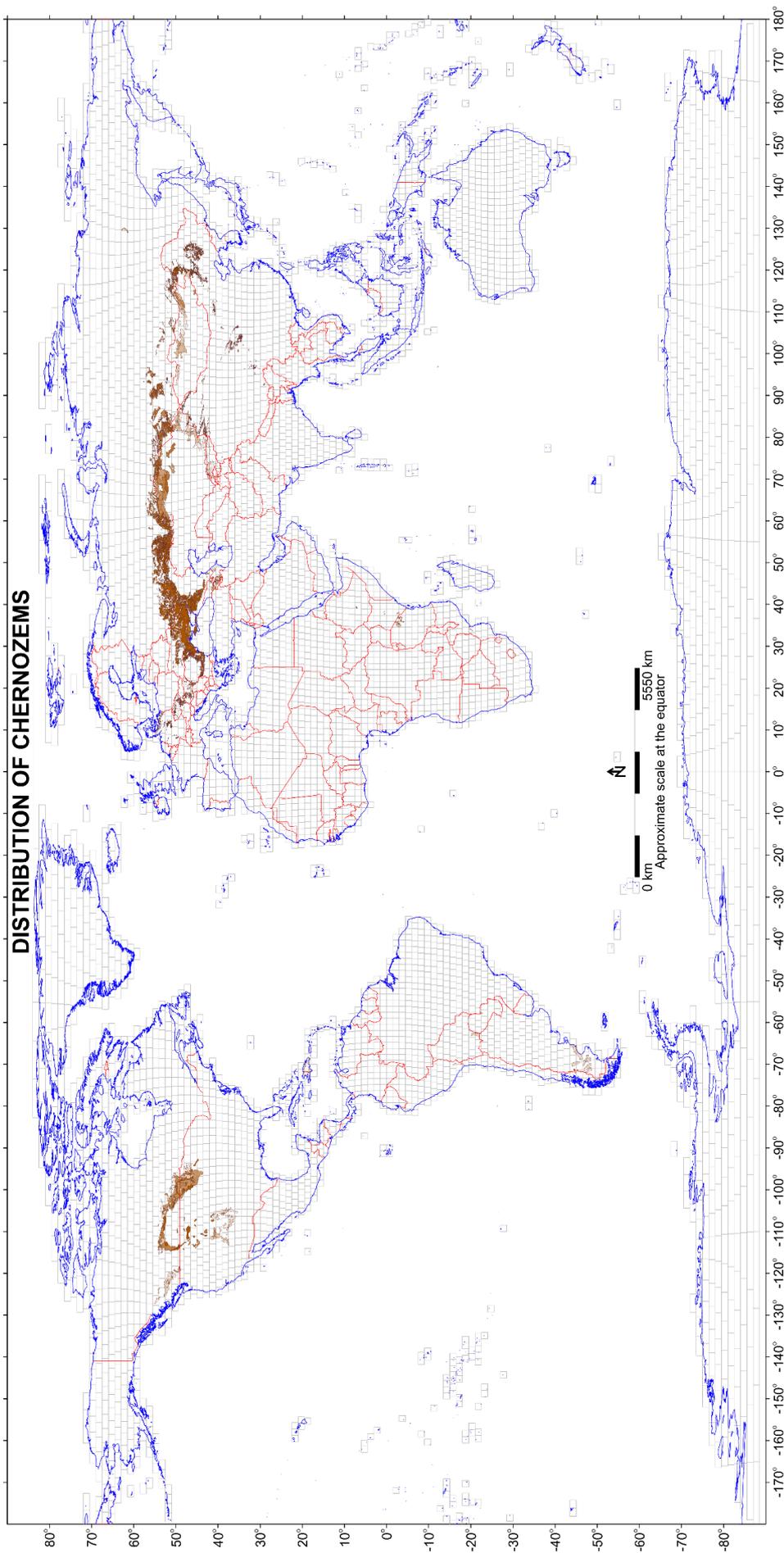


Figure A3.2.1.15. Map showing the global distribution of Chernozems. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_CH- Chernozems.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Chernozems</p>	<p>From the Russian words <i>tshornyj</i> (чёрная) = black and <i>zemlja</i> (земля) = earth, land.</p>
 <p>Photograph: Edith Haslinger (AIT)</p>	<p>Chernozems are soil types of the humid continental zone with cold winters and short, hot summers. In the dry summer months and during winter, mineralisation is inhibited. Therefore, organic matter is accumulated, leading to the characteristic thick dark topsoil layer of the Chernozems. The biological activity is very high - burrowing animals and insects mix the organic matter with the mineral soil. The burrows that are formed by their activities – the so-called <i>krotovinas</i> (from the Russian word ‘<i>krot</i>’ (крот) = mole) – are filled with dark soil material.</p>
<p>Geographical distribution:</p>	<p>Main occurrence in the middle latitude steppes of Eurasia and North America (Fig. A3.2.1.15).</p>
<p>Parent material:</p>	<p>Mainly loess and similar sediments.</p>
<p>Usage:</p>	<p>Chernozems are one of the most fertile soil types and, therefore, have a very high agricultural productivity.</p> <p>The dryness in the summer months and the extreme temperatures can be limiting factors. Furthermore, Chernozems are prone to erosion in times of heavy rainfall.</p>
<p>Geochemical processes:</p>	<p>Decalcification of upper parts of the soil profile → precipitation of secondary carbonates and Ca-concretions in lower parts; in summer months ascending $\text{Ca}(\text{HCO}_3)_2$-rich soil solution → precipitation of secondary carbonates.</p>

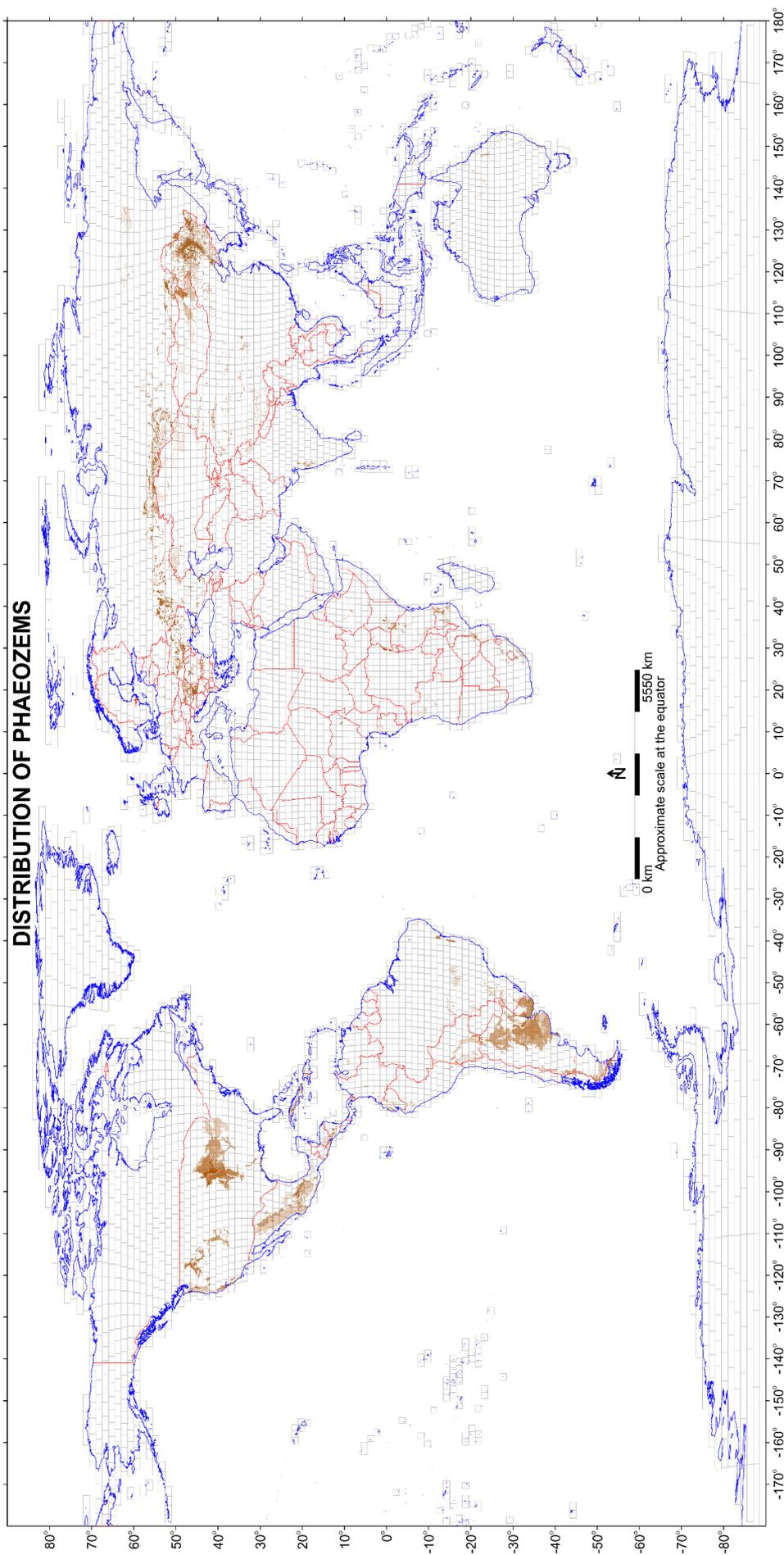


Figure A3.2.1.16. Map showing the global distribution of Phaeozems. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_PH- Phaeozems.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Phaeozems</p>	<p>From the Hellenic word <i>phaeós</i> (φαίος) = dusky and the Russian word <i>zemlja</i> (земля) = earth, land.</p>
 <p>Source: Peter Schad⁸</p>	<p>Phaeozems are porous, well-aerated dark soil types with moderate to strong, very stable, crumb to blocky structures. They are rich in organic matter and occur in steppe, forest-steppe or forest-prairie areas that border on the humid side of the Chernozem belt in the temperate climatic zone, and on the humid border of the Kastanozem belt in the subtropics.</p>
<p>Geographical distribution:</p>	<p>Flat to undulating land in warm to cool (<i>e.g.</i>, tropical highland) regions and humid enough that there is some percolation of the soil in most years but also with periods in which the soil dries out. The natural vegetation is tall grass steppe and/or forest. The largest area distribution of Phaeozems is found in the United States of America, Argentina, Uruguay and China (Fig. A3.2.1.16).</p>
<p>Parent material:</p>	<p>Aeolian (loess), glacial till, organic matter and other unconsolidated material.</p>
<p>Usage:</p>	<p>Phaeozems are fertile soil types and make excellent farmland. In the United States of America and Argentina, Phaeozems are in use for the production of soybean and wheat.</p>
<p>Geochemical processes:</p>	<p>Biomass and faunal activity are high; earthworms and burrowing mammals homogenise the soil. The C/N-ratio of the organic matter is 10-12; pH values are between 5 and 7 and increase towards the C horizon.</p>

⁸ <https://www3.ls.tum.de/en/boku/wrb-working-group/pictures/phaeozem/>; last access: 13.02.2022.

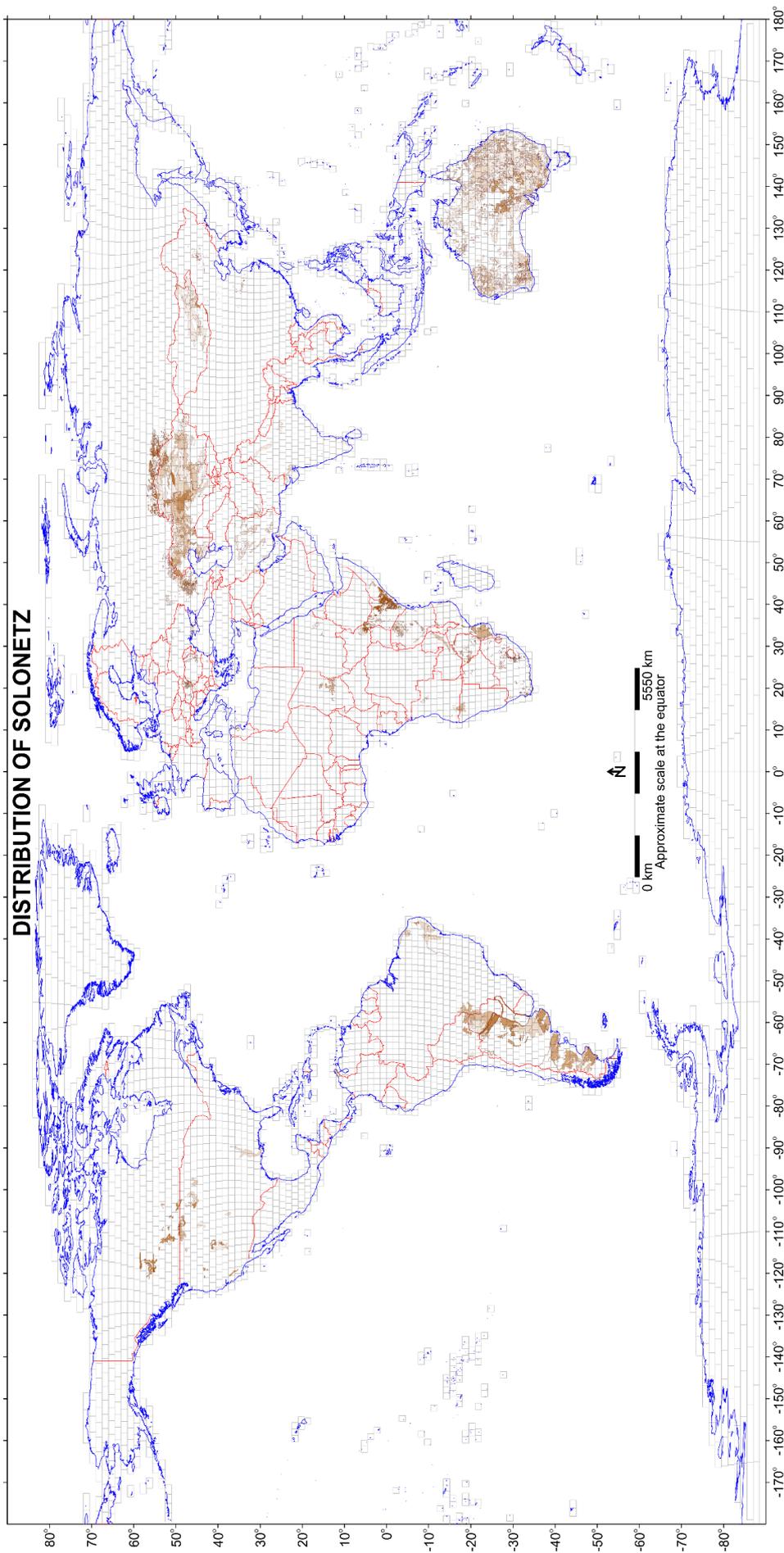


Figure A3.2.1.17. Map showing the global distribution of Solonetz. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_SN-Solonetz.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Solonetz</p>	<p>From the Russian words <i>sol</i> (соль) = salt and <i>etz</i> (etz) = strongly expressed - soil with salts.</p>
 <p>Source: Peter Schad⁹</p>	<p>Solonetz are soil types with a dense, strongly structured, clay illuviation horizon that has a high content of exchangeable sodium and/or magnesium ions. Further, a typical Solonetz feature is a thin, loose litter horizon resting on black humified material about 2-3 cm thick.</p>
<p>Geographical distribution:</p>	<p>Solonetz occurs predominantly in areas with a steppe climate (hot, dry summers). Major concentrations of Solonetz are in flat or gently sloping grasslands with loess/loam or clay in semi-arid, temperate and subtropical regions (Fig. A3.2.1.17).</p>
<p>Parent material:</p>	<p>Unconsolidated materials, mostly fine-textured sediments.</p>
<p>Usage:</p>	<p>Most Solonetz type soil in temperate regions has a humus-rich surface horizon and can (still) be used for arable farming or grazing.</p>
<p>Geochemical processes:</p>	<p>It is widely thought that sodium bicarbonate, common ‘soda’, (NaHCO_3), can form in two ways, either by evaporation of water that contains excess bicarbonate ions over ($\text{Ca}^{2+} + \text{Mg}^{2+}$) or biologically, by reduction of sodium sulphate.</p> <p>The presence of ‘free soda’ in the soil is associated with a field-pH > 8.5. Under such conditions, organic matter tends to dissolve and move through the soil body with moving soil moisture.</p> <p>The strong sodium saturation of Solonetz is harmful to plants in several ways. Too much sodium in the soil is directly toxic to Na^+-sensitive plants and disturbs the uptake of essential plant nutrients.</p>

⁹ <https://www3.ls.tum.de/en/boku/wrb-working-group/pictures/solonetz/>; last access: 13.02.2022.

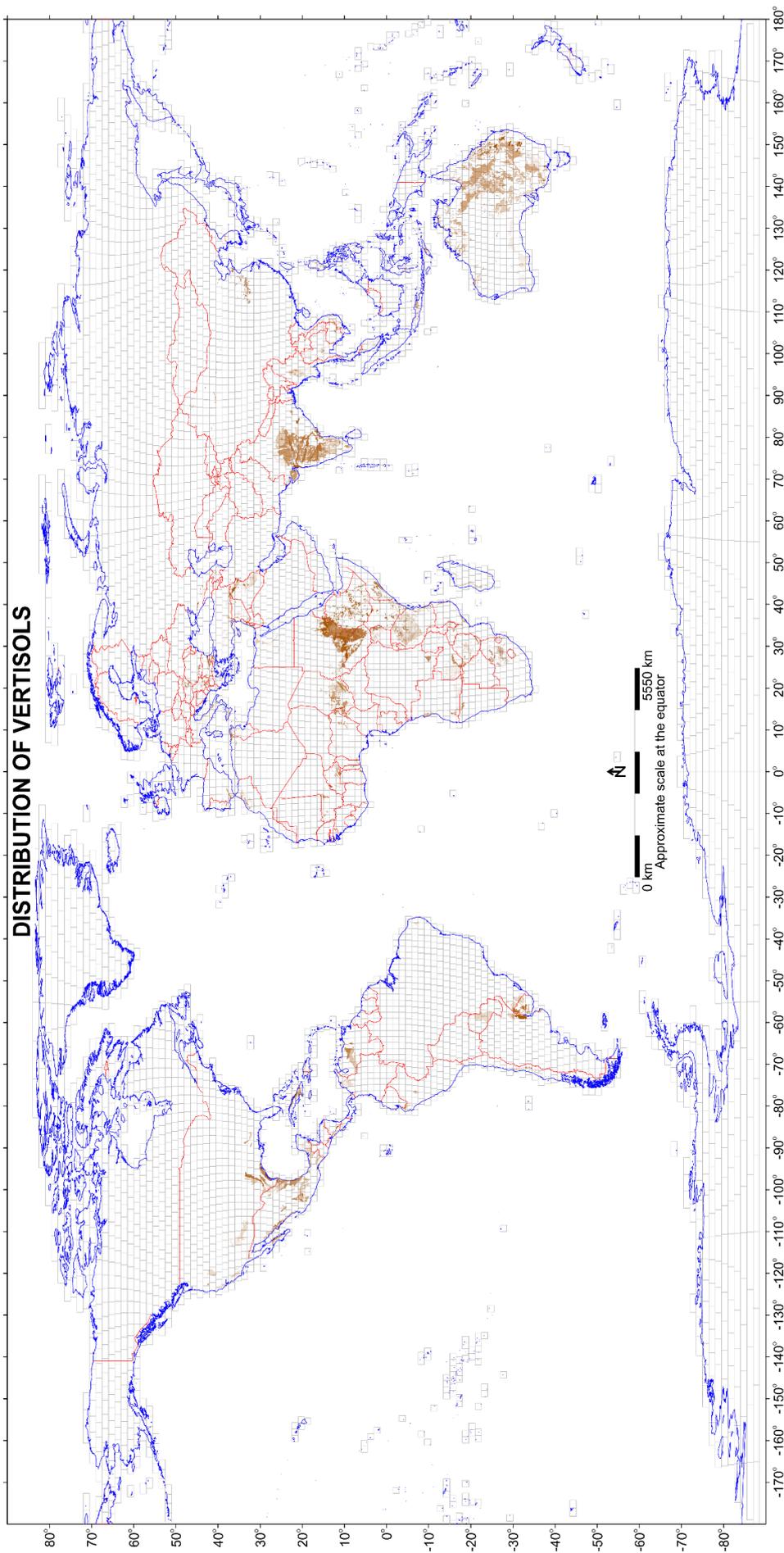


Figure A3.2.1.18. Map showing the global distribution of Vertisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_VR_Vertisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

Vertisols



Source: Peter Schad¹⁰

From the Latin word *vertere* = to turn.

Vertisols are churning heavy clay soil types with a high proportion of swelling clays. These soil types form deep wide cracks from the surface downward when they dry out. In the dry season, they become very hard and in the wet season sticky. Most Vertisols develop a surface mulch, but some develop a hard surface crust.

Geographical distribution:

Mainly in tropical, semi-arid to (sub)humid and Mediterranean climates with an alternation of distinct wet and dry seasons (Fig. A3.2.1.18). The climax vegetation is savanna, natural grassland and/or woodland. Vertisols occur in bottomlands or also on contiguous lower foot slopes or, as residual soil, even on (gently) sloping hillsides.

Parent material:

Sediments that contain a high proportion of smectite clay, or products of rock weathering that have the characteristics of smectite clay; Organic matter.

Usage:

Vertisols are productive soil types but, tillage is difficult, except for a short period during the transition between the wet and dry seasons.

Geochemical processes:

The environmental conditions that lead to the formation of a vertic soil structure are also conducive to the formation of suitable parent materials.

- Rainfall is sufficient to enable weathering but not so high that leaching of bases occurs.
- Dry periods allow crystallisation of clay minerals that form upon rock or sediment weathering.
- Impeded drainage hinders leaching and curbs loss of weathering products.
- High temperatures, finally, promote weathering processes. Under such conditions, smectite clays can be formed in the presence of silica and basic cations — especially Ca^{2+} and Mg^{2+} — if the soil-pH is above neutral.

¹⁰ <https://www3.lis.tum.de/en/boku/wrb-working-group/pictures/vertisol/>; last access: 13.02.2022.

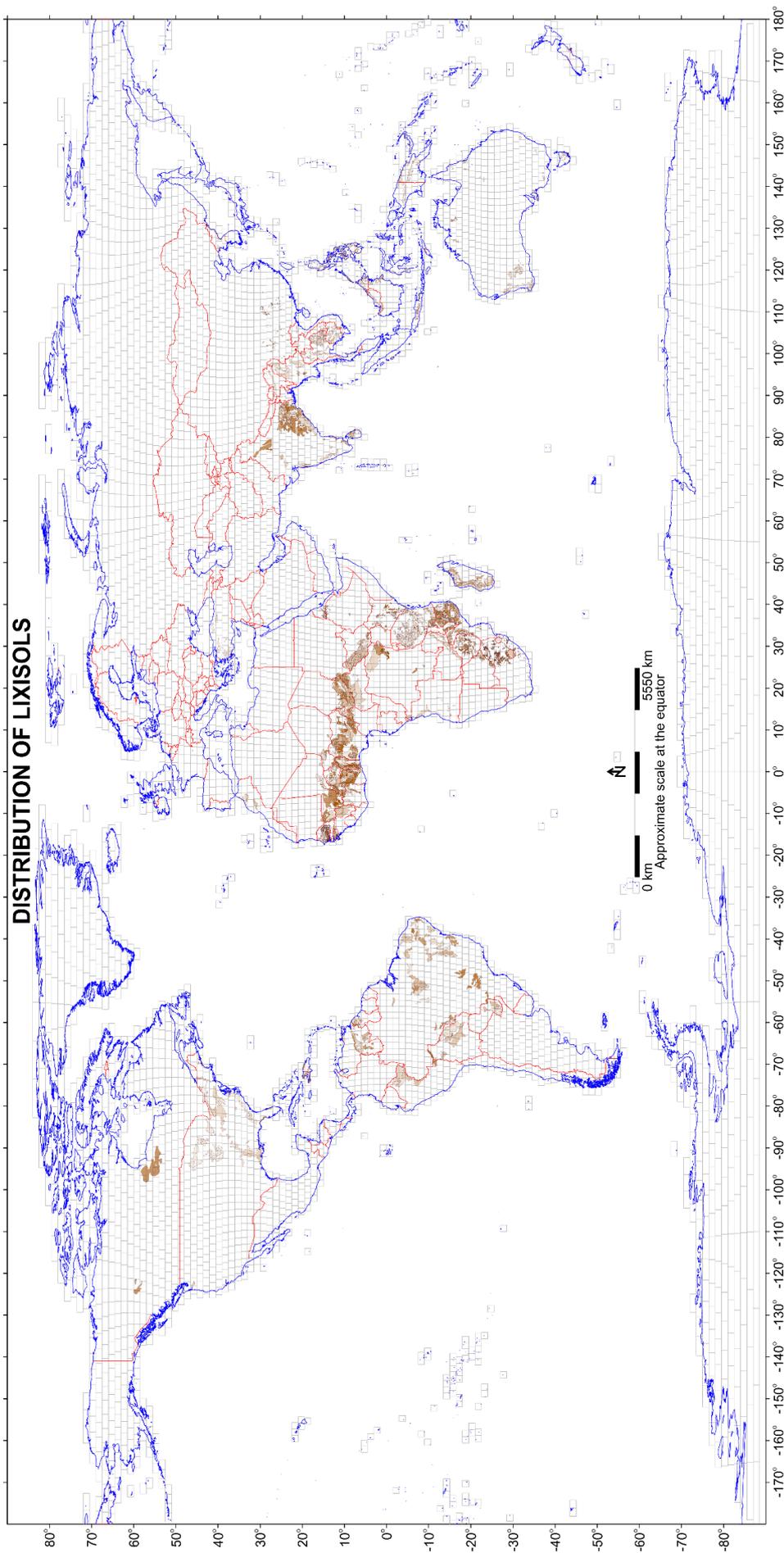


Figure A3.2.1.19. Map showing the global distribution of Lixisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_LX-Lixisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Lixisols</p>	<p>From the Latin word <i>lixivia</i> = washed-out substances.</p>
 <p>Source: Peter Schad¹¹</p>	<p>Lixisols are strongly weathered soil types in which clay is washed down from the surface soil to an accumulation horizon that has low activity clays and a moderate to high base saturation level.</p>
<p>Geographical distribution:</p>	<p>In regions with a tropical, subtropical or warm temperate climate with a pronounced dry season, notably on old erosional or depositional surfaces. Most Lixisols occur in Sub-Saharan and East Africa, about one quarter in South and Central America and the remainder on the Indian subcontinent (Fig. A3.2.1.19).</p>
<p>Parent material:</p>	<p>Unconsolidated, strongly weathered and strongly leached, finely textured materials.</p>
<p>Usage:</p>	<p>Areas with Lixisols that are still under natural savannah or open woodland vegetation are widely used for low volume grazing. Perennial crops or forestry are suitable land uses; arable farming requires recurrent inputs of fertilisers and/or lime.</p>
<p>Geochemical processes:</p>	<p>Lixisols are strongly weathered soil types with low levels of available nutrients and low nutrient reserves. However, the chemical properties of Lixisols are generally better than those of Ferralsols and Acrisols because of their higher soil-pH and the absence of serious Al-toxicity.</p>

¹¹ <https://www3.lis.tum.de/en/boku/wrb-working-group/pictures/lixisol/>; last access: 13.02.2022.

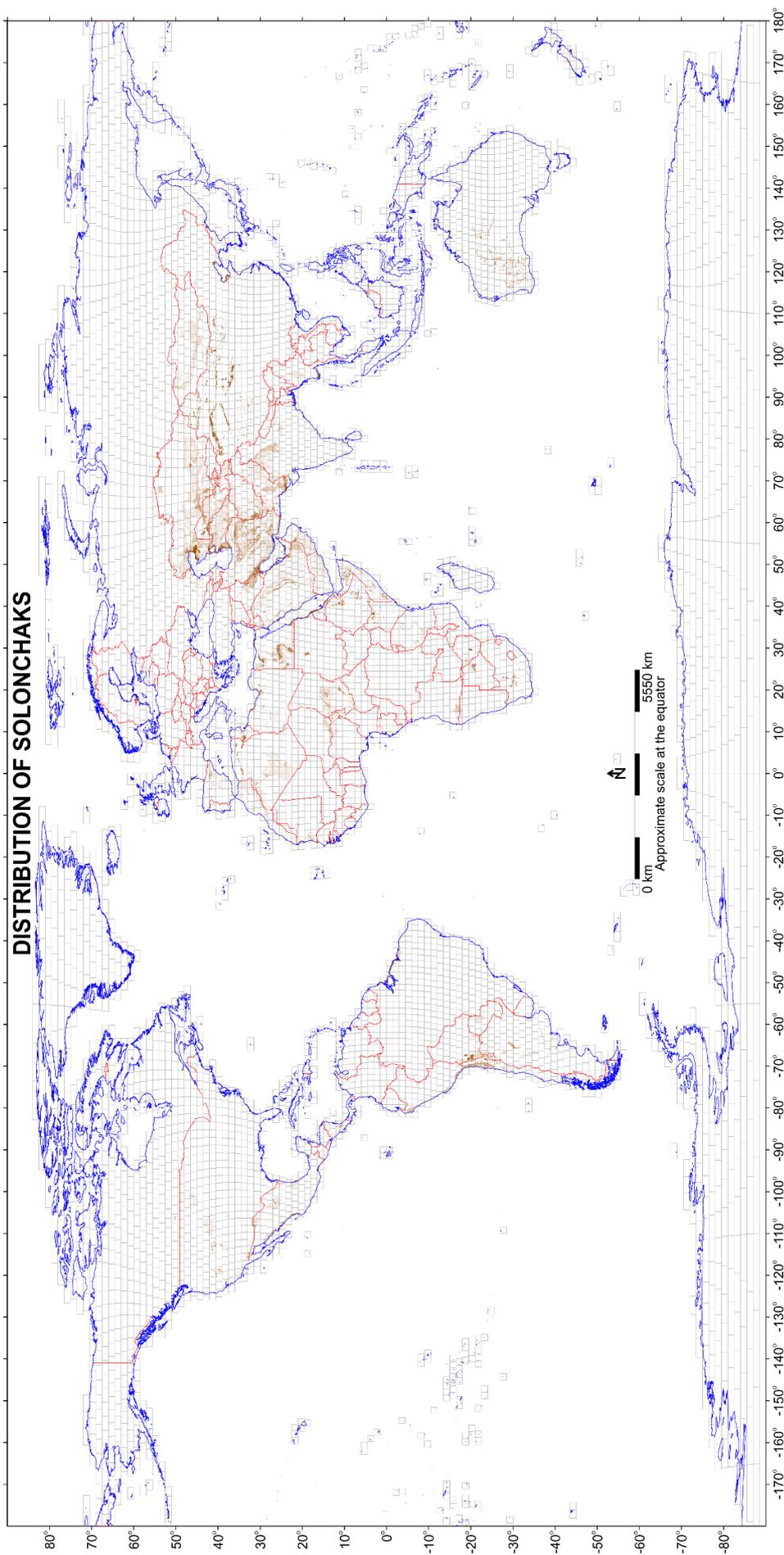


Figure A3.2.1.20. Map showing the global distribution of Solonchaks. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_SC-Solonchaks.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Solonchaks</p>	<p>From the Russian words <i>sol</i> (соль) = salt and <i>chak</i> (чяк) = salty area, salt marsh.</p>
 <p>Source: Peter Schad¹²</p>	<p>Solonchaks include soil types that have a high concentration of 'soluble salts' at some time in the year. Most Solonchaks occur in inland areas where evapotranspiration is considerably greater than precipitation, at least during part of the year. Salts dissolved in soil moisture remain behind after evaporation/transpiration of water and accumulate at the surface of the soil ('external Solonchaks') or at some depth ('internal Solonchaks').</p>
<p>Geographical distribution:</p>	<p>Solonchaks are largely confined to the arid and semi-arid climatic zones, notably in parts of northern Africa, the Middle East, the former Union of Soviet Socialist Republics and central Asia, and in coastal regions in all climatic zones (Fig. A3.2.1.20). They occur in seasonally or permanently waterlogged areas with vegetation of grasses and/or halophytic herbs, and in inadequately managed irrigation areas.</p>
<p>Parent material:</p>	<p>Any unconsolidated soil material.</p>
<p>Usage:</p>	<p>Solonchaks have limited potential for the cultivation of salt-tolerant crops. Most are used for extensive grazing or are not used for agriculture at all.</p>
<p>Geochemical processes:</p>	<p>When the salt content is lowered by winter rain or irrigation water, soil structure tends to degrade, particularly if the salts contain sodium and/or magnesium compounds. A strong peptisation of clays at the onset of (winter) rain may make the surface soil virtually impermeable to water.</p> <p>In severely salt-affected lands, the vegetation is sparse and limited to halophytic shrubs, herbs and grasses that tolerate severe physiological drought (and can cope with periods of excessive wetness in areas with seasonally flooded Solonchaks).</p>

¹² <https://www3.lis.tum.de/en/boku/wrb-working-group/pictures/solonchak/>; last access: 13.02.2022.

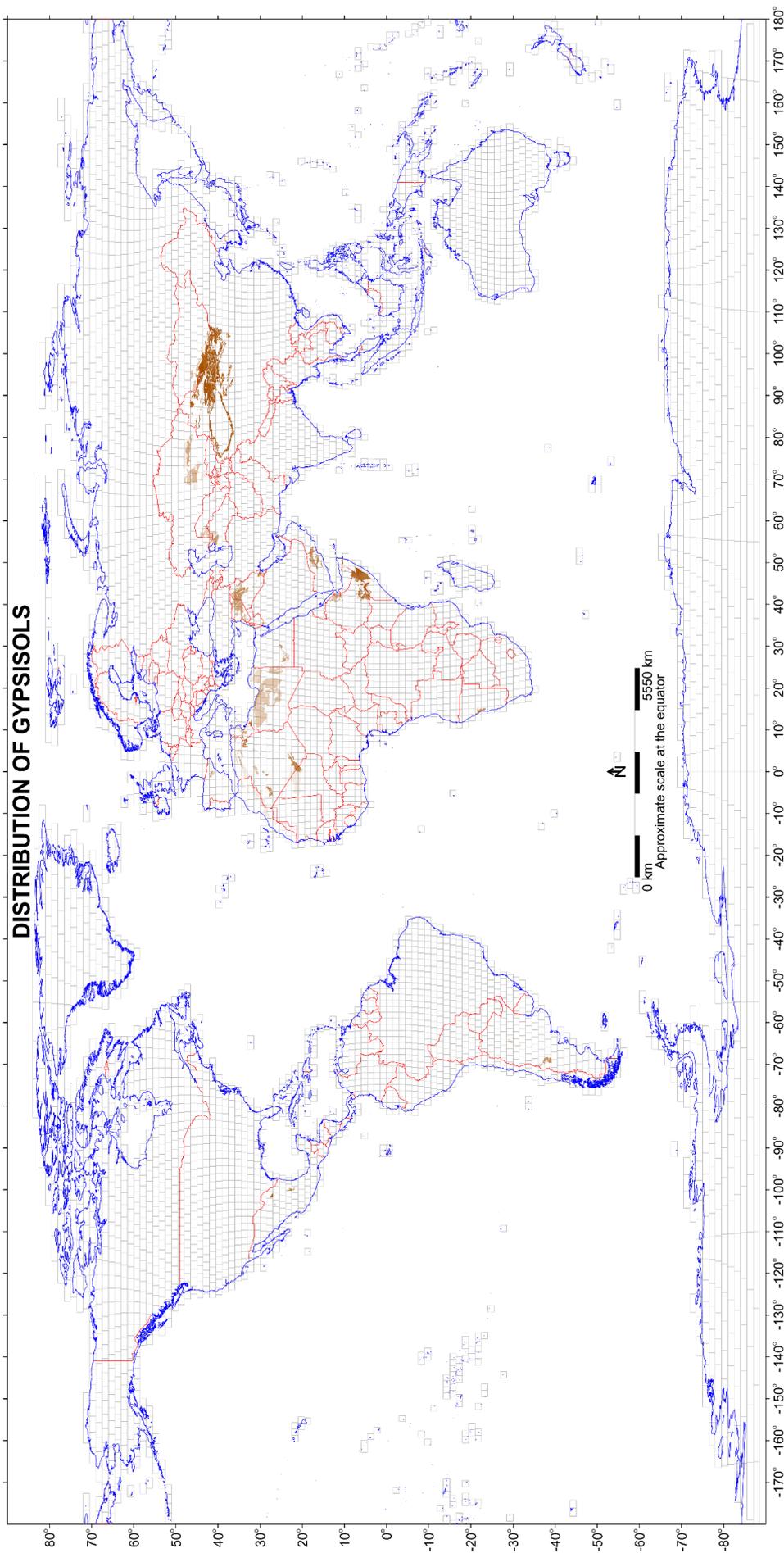


Figure A3.2.1.21. Map showing the global distribution of Gypsisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area; the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_GY-Gypsisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Gypsisols</p>	<p>From the Hellenic word <i>gýpsos</i> (γύψος) = gypsum.</p>
 <p>©Peter Schad</p> <p>Source: Peter Schad¹³</p>	<p>Gypsisols are soil types with a substantial secondary accumulation of calcium sulphate. Most Gypsisols are formed when gypsum, dissolved from gypsiferous parent materials, is moved through the soil by the soil moisture, and is precipitated in an accumulation horizon. Where soil moisture moves predominantly upward, a gypsic or petrogypsic horizon occurs at a shallower depth than a horizon with lime accumulation.</p>
<p>Geographical distribution:</p>	<p>Predominantly level to hilly land depression areas in regions with an arid climate. The natural vegetation is sparse and dominated by xerophytic shrubs and trees and/or ephemeral grasses. Major occurrences are in and around Mesopotamia, in desert areas in the Middle East and adjacent central Asian republics and the Lybian and Namib deserts (Fig. A3.2.1.21).</p>
<p>Parent material:</p>	<p>Mostly unconsolidated alluvial, colluvial or aeolian deposits of base-rich weathering material.</p>
<p>Usage:</p>	<p>For low volume grazing; irrigation canals must be lined; deep Gypsisols located close to water resources can be planted with a wide range of crops.</p>
<p>Geochemical processes:</p>	<p>Gypsum is leached from surface soil in relatively wet winter seasons. In arid regions with hot, dry summers, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) dehydrates to lose, and powdery hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), which reverts to gypsum during the moist winter. The so-formed (highly irregular) gypsum crystals may cluster together to compact layers or surface crusts that can become tens of centimetres thick.</p> <p>Small quantities of gypsum are not harmful to plants but gypsum contents of more than 25 per cent, as common in the gypsiferous subsoil, upset the nutrient balance, and lower the availability of essential plant nutrients such as phosphorus, potassium and magnesium.</p>

¹³ <https://www3.lis.tum.de/en/boku/wrb-working-group/pictures/gypsisol/>; last access: 13.02.2022.

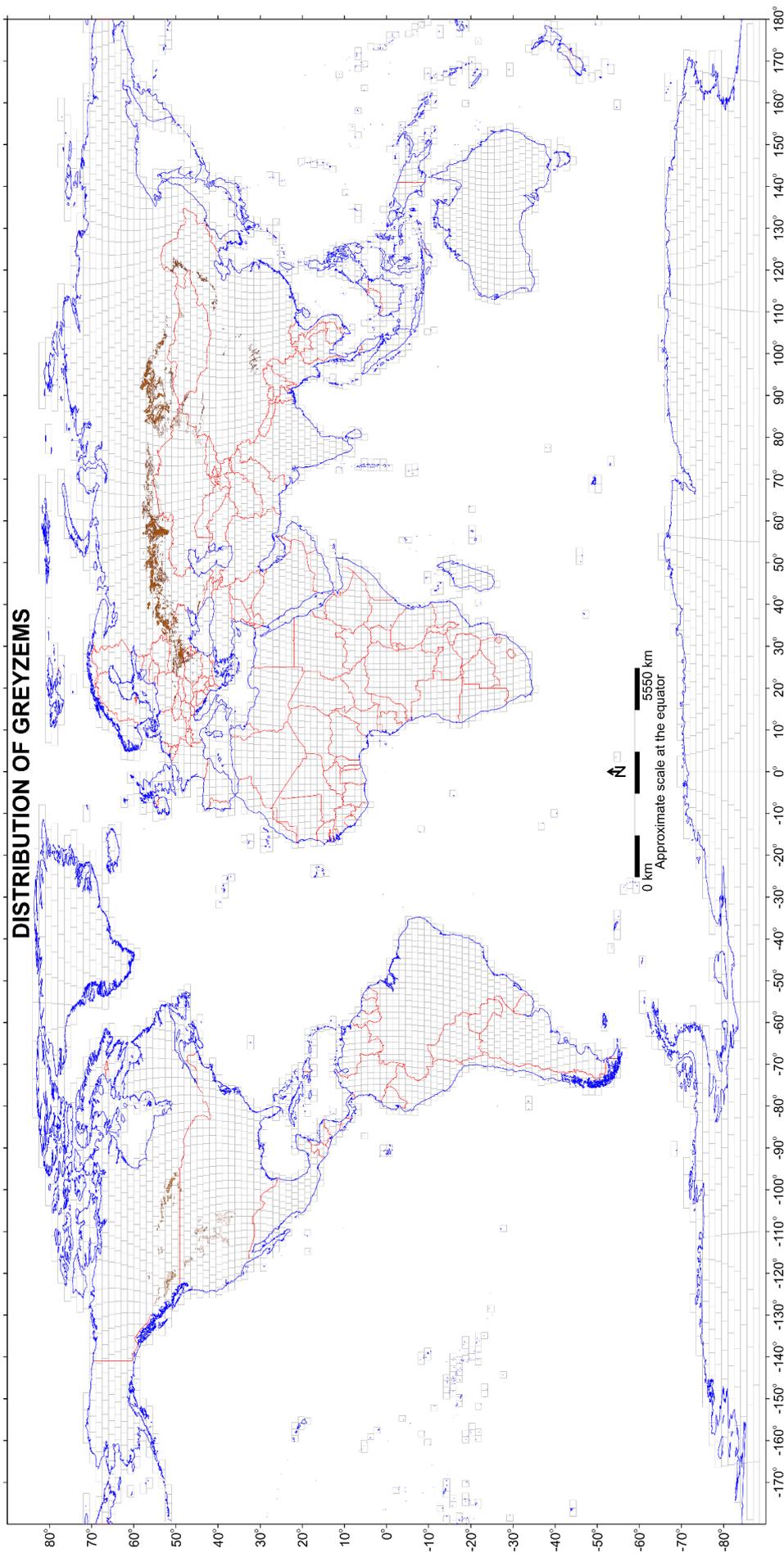


Figure A3.2.1.22. Map showing the global distribution of Greyzems. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area; the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_GR-Greyzems.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Greyzems</p>	<p>From English word <i>grey</i> and the Russian word <i>zemlja</i> (земля) = earth, land.</p>
	<p>Greyzems are thick and dark soil types with a grey tinge due to the presence of bleached (uncoated) quartz sand and silt in horizons rich in organic matter. The most striking characteristic of Greyzems is the presence of uncoated sand and silt particles in a mollic A horizon. The bleached grains can be seen with a hand lens or even with the naked eye. They may appear in approximately horizontal bands associated with a weakly platy structure, but they occur also in spots ('pepper and salt' appearance).</p>
<p>Source: ISRIC¹⁴</p>	
<p>Geographical distribution:</p>	<p>Flat to gently undulating plains in mild temperate to cold, sub-humid climates (Fig. A3.2.1.22). In montane areas, Greyzems occur at altitudes corresponding with the change of steppe to forest (vertical zonality).</p>
<p>Parent material:</p>	<p>Decalcified unconsolidated materials including aeolian, fluvial and lacustrine deposits, solifluction material and glacial till.</p>
<p>Usage:</p>	<p>Forestry and the growing of fodder crops minimise soil disturbance and structural deterioration. If arable crops are grown, tillage operations should be performed under favourable moisture conditions.</p>
<p>Geochemical processes:</p>	<p>The organic carbon content of the surface soil lies between 3 and 5 per cent, with a C/N-ratio around 10. They have favourably high CEC values (25 to 35 cmol(+)/kg dry soil), and a base saturation close to 100 per cent. The natural fertility status of Greyzems is good, and they respond favourably to moderate applications of nitrogen and phosphorus fertilisers.</p>

¹⁴ <https://www.isric.org/>; last access: 13.02.2022.

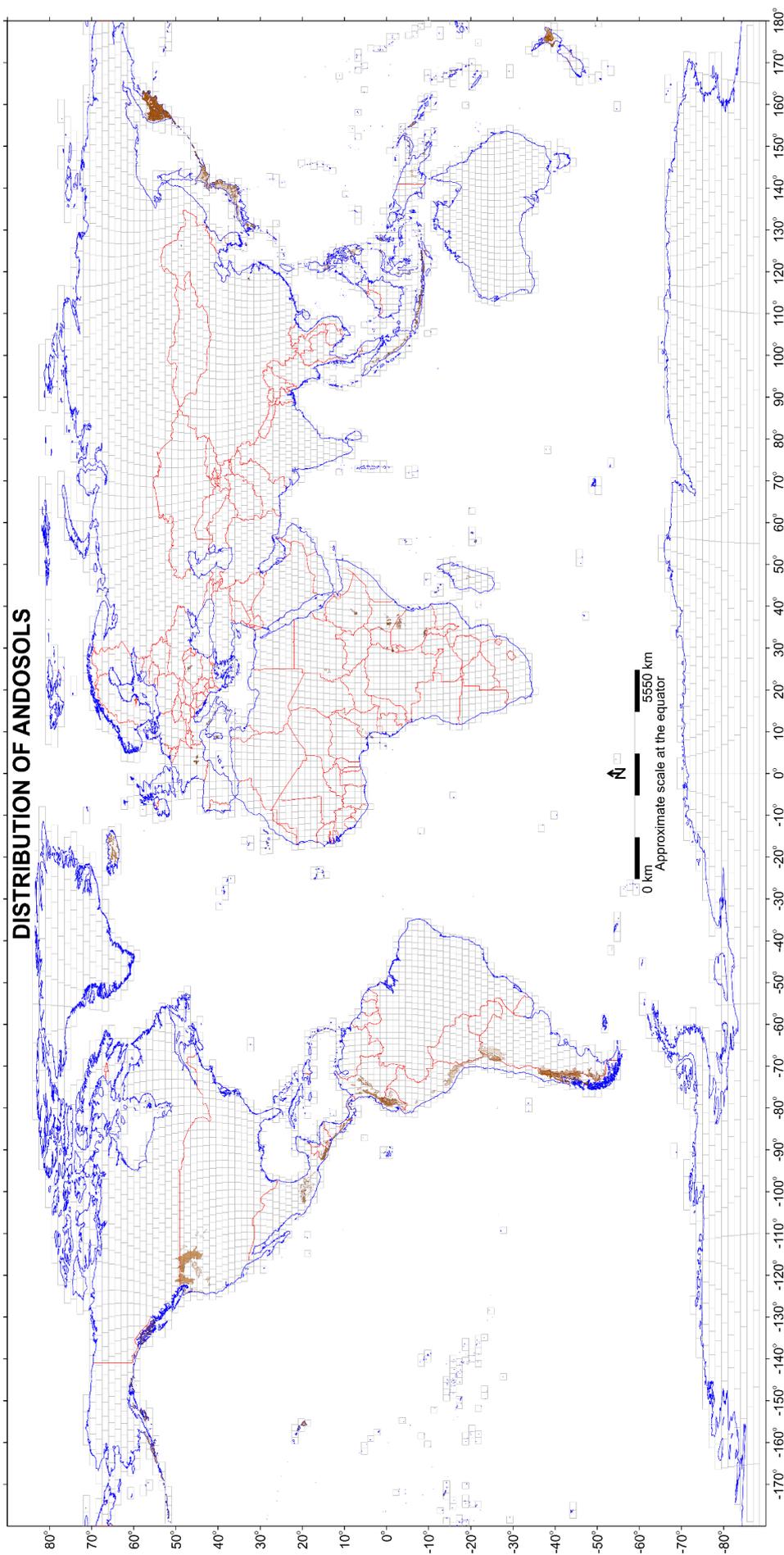


Figure A3.2.1.23. Map showing the global distribution of Andosols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_AN-Andosols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

Andosols



Source: Peter Schad¹⁵

From the Japanese words *an* = black and *do* = soil.

Andosols are black and azonal soil types of volcanic landscapes occurring in all climates and at all altitudes. The good aggregate stability of Andosols, and their high permeability to water, make these soil types (relatively) resistant to water erosion. Furthermore, Andosols are characterised by the presence of either an ‘andic’ horizon or a ‘vitric’ horizon. Andic horizons are rich in allophanes (and similar minerals) or aluminium-humus complexes whereas the vitric horizon contains an abundance of ‘volcanic glass’.

Geographical distribution:	Undulating to mountainous, volcanic regions all over the earth and humid, arctic to tropical regions with a wide range of vegetation types (Fig. A3.2.1.23).
Parent material:	Mainly volcanic ash.
Usage:	Fertile soil types for agricultural production; are easy to cultivate, and have good root-ability and water storage properties.
Geochemical processes:	Andosol formation depends essentially on rapid chemical weathering of porous, permeable, fine-grained mineral material in the presence of organic matter. The strong chemical reactivity of Andosols has long been attributed to X-ray amorphous compounds. It is more appropriate, however, to ascribe this Andosol characteristic to the presence of 'active aluminium' which may occur in various forms.

¹⁵ <https://www3.lis.tum.de/en/boku/wrb-working-group/pictures/andosol/>; last access: 13.02.2022.

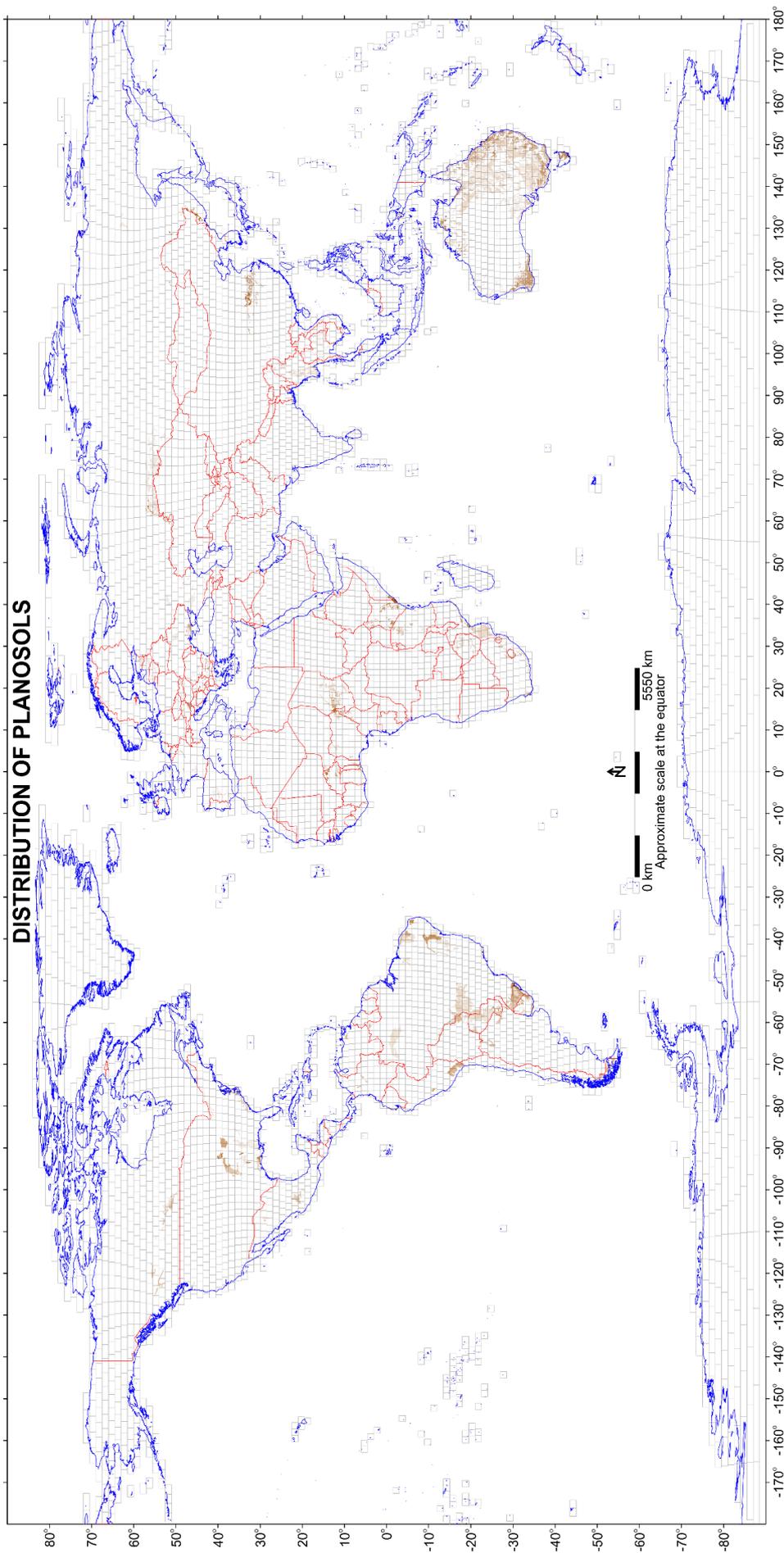


Figure A3.2.1.24. Map showing the global distribution of Planosols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_PL-Planosols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Planosols</p>	<p>From the Latin word <i>planus</i> = flat.</p> <p>Planosols are soil types with a degraded, eluvial surface horizon abruptly over dense subsoil and occur predominantly in seasonally waterlogged flat lands but can also be found in the lower stretches of slopes, in a strip intermediate between uplands and lowlands (plain or basin) areas. Further, they occur on terraces or somewhat higher up, together with Acrisols or other soil types with an argic subsurface horizon.</p>
 <p>Source: Peter Schad¹⁶</p>	
<p>Geographical distribution:</p>	<p>The world's major Planosol areas occur in subtropical and temperate, semi-arid and sub-humid regions with distinct alternation of wet and dry seasons and regions with light forest or grass vegetation (Fig. A3.2.1.24).</p>
<p>Parent material:</p>	<p>Mostly clayey alluvial and colluvial deposits.</p>
<p>Usage:</p>	<p>In regions with a warm summer season, they are mostly under wetland rice. Elsewhere, Planosols are sown to dryland (<i>e.g.</i>, fodder) crops or used for extensive grazing.</p>
<p>Geochemical processes:</p>	<p>The most prominent feature of Planosols is the marked increase in clay content on passing from the degraded eluvial horizon to the deeper soil. The abrupt change in clay content and, in some Planosols, the clay can only develop and persist if there is little homogenisation of the soil. The poor structure stability of the topsoil, the compactness of the subsoil and the abrupt transition from topsoil to subsoil all impair the rooting of crops.</p> <p>Mature Planosols are chemically strongly degraded. The surface soil becomes acidic and loses (much of) its clay, and ion exchange properties deteriorate as a consequence.</p>

¹⁶ <https://www3.lis.tum.de/en/boku/wrb-working-group/pictures/planosol/>; last access: 13.02.2022.

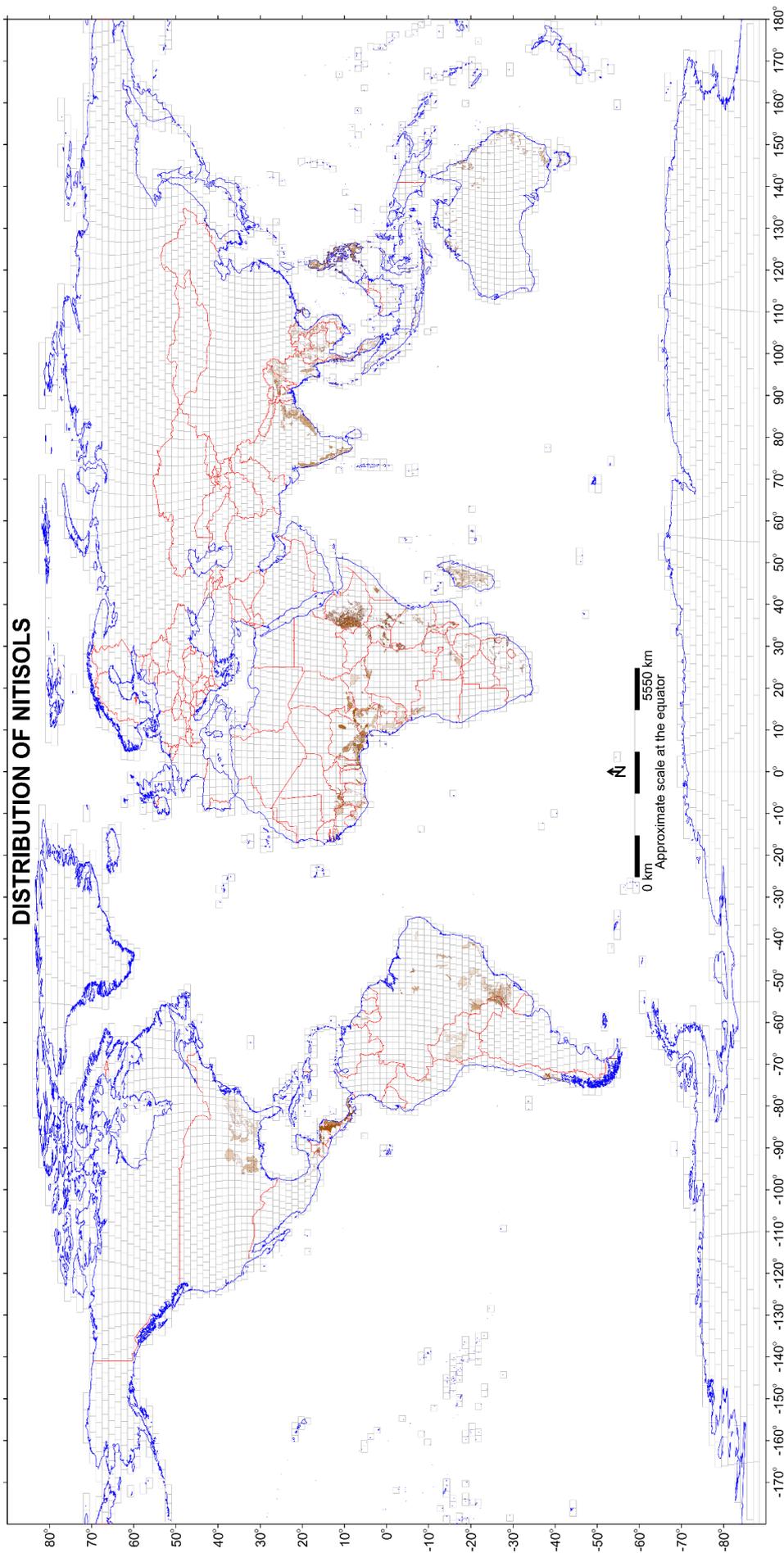


Figure A3.2.1.25. Map showing the global distribution of Nitisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_NT-Nitisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Nitisols</p>	<p>From the Latin word <i>nitidus</i> = shiny.</p> <p>Nitisols accommodate deep, well-drained, red, tropical soil types with a clayey ‘nitic’ subsurface horizon that has typical ‘nutty’, polyhedric, blocky structure elements with shiny ped faces.</p> <p>Nitisols are among the most productive soil types of the humid tropics. The deep and porous solum and the stable soil structure of Nitisols permit deep rooting and make these soil types quite resistant to erosion. The good workability of Nitisols, their good internal drainage and fair water-holding properties are complemented by chemical (fertility) properties that compare favourably to those of most other tropical soil types.</p>
 <p>Source: Peter Schad¹⁷</p>	
<p>Geographical distribution:</p>	<p>Found in level to hilly land under tropical rain forest or savanna vegetation; in volcanic landscapes, uplifted and dissected landscapes and landscapes on limestone (Fig. A3.2.1.25).</p>
<p>Parent material:</p>	<p>Consists of several per cent of organic matter, under forest or tree crops; rich in iron and little water-dispersible clay.</p>
<p>Usage:</p>	<p>Fertile, deep and stable soil types in which plantation crops are grown, and widely used for food crop production.</p>
<p>Geochemical processes:</p>	<p>The cation exchange capacity of Nitisols is high if compared to that of other tropical soil types. Although the clay assemblage is dominated by low-activity clays, the clay content is high. Soil organic matter makes a considerable contribution to the overall CEC, especially in mollic or umbric soil units. Base saturation varies from less than 10 to more than 90 per cent and the soil-pH(H₂O) is typically between 5.0 and 6.5.</p>

¹⁷ <https://www3.lis.tum.de/en/boku/wrb-working-group/pictures/nitisol/>; last access: 13.02.2022.

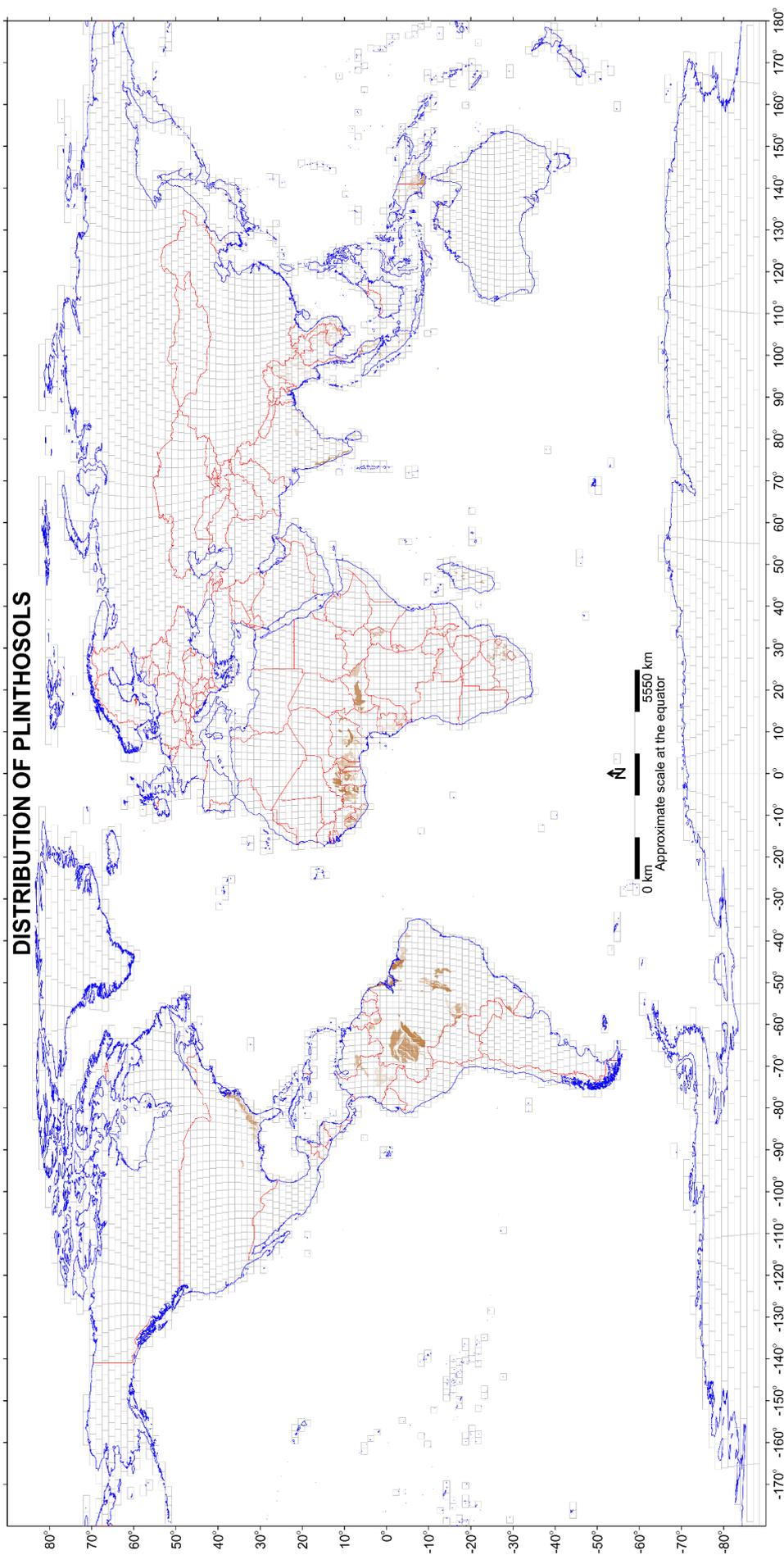


Figure A3.2.1.26. Map showing the global distribution of Plinthosols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_PT-Plinthosols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Plinthosols</p>	<p>From the Hellenic word <i>plinthos</i> (πλίνθος) = brick.</p> <p>Plinthosols are wet soil types that contain ‘plinthite’, an iron-rich, humus-poor mixture of kaolinitic clay with quartz, and other constituents that changes irreversibly to a hardpan, or to irregular aggregates on exposure to repeated wetting and drying. Areas, where the formation of plinthite is still active, have a hot and humid climate with a high total annual rainfall and a short dry season.</p>
 <p>©Peter Schad</p> <p>Source: Peter Schad¹⁸</p>	
<p>Geographical distribution:</p>	<p>Plinthosols occur in tropical regions. Soil types with residual ‘soft’ plinthite occur in less well-drained positions in the landscape, and are most common in the wet tropics, notably in the western Amazon basin, the central Congo basin and parts of Southeast Asia (Fig. A3.2.1.26). Extensive areas of hardened plinthite occur in the Sudano-Sahelian zone.</p>
<p>Parent material:</p>	<p>Weathering material from mafic rock.</p>
<p>Usage:</p>	<p>Plinthite is a valuable material for making bricks; ironstone gravel can be used in foundations and as surfacing material on roads and airfields.</p> <p>Poor natural soil fertility, water logging in bottomlands and drought on shallow and/or skeletal Plinthosols are serious limitations. Therefore, Plinthosols can at best be used for low volume grazing. Arable cropping is hindered by poor rooting conditions, associated with frequent water logging, and/or excessive stoniness and low chemical soil fertility.</p>
<p>Geochemical processes:</p>	<p>All Plinthosols have high contents of iron and/or aluminium, but most Plinthosols have poor cation exchange properties and low base saturation.</p> <p>Plinthite forms in perennially moist (sub)soil horizons. The formation of plinthite involves two processes:</p> <ol style="list-style-type: none"> 1. Through the accumulation of sesquioxides, and 2. Through segregation of iron (mottles) by alternating reduction and oxidation.

¹⁸ <https://www3.ls.tum.de/en/boku/wrb-working-group/pictures/plinthosol/>; last access: 13.02.2022.

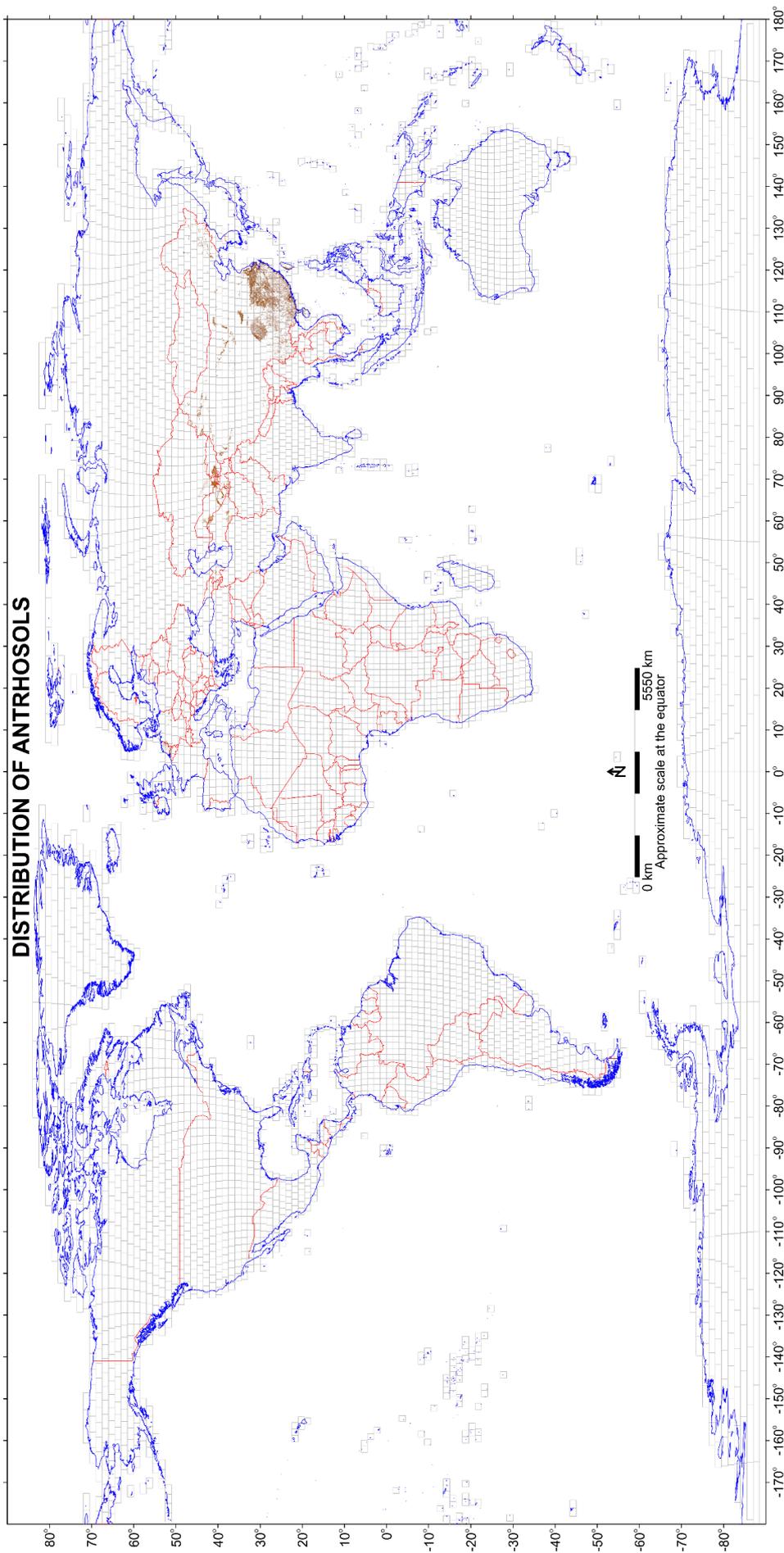


Figure A3.2.1.27. Map showing the global distribution of Anthrosols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_AT-Anthrosols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<h2>Anthrosols</h2>	<p>From the Hellenic word <i>ánthropos</i> (άνθρωπος) = human.</p>
 <p>Source: Peter Schad¹⁹</p>	<p>Anthrosols comprise soil types that were buried or profoundly modified through human activities such as the addition of organic materials or household wastes, irrigation or cultivation. They occur where soil conditions were initially unattractive for food crop cultivation.</p>
<p>Geographical distribution:</p>	<ul style="list-style-type: none"> • <u>Plaggic Anthrosols</u> occur in areas with periglacial cover sands. • <u>Terric Anthrosols</u> are commonly found alongside wetland soil, and are largely restricted to north-western Europe. • <u>Hydragric Anthrosols</u> occur in upland areas and riverine and volcanic systems in Southeast and East Asia (Fig. A3.2.1.27). • <u>Irragric Anthrosols</u> are found in irrigation areas in dry regions. • <u>Hortic Anthrosols</u> are found all over the world where humans have fertilised the soil with household wastes and manure.
<p>Parent material:</p>	<p>Any soil material.</p>
<p>Usage:</p>	<p>Anthrosols are used for agriculture, but also for tree nurseries and pastures.</p>
<p>Geochemical processes:</p>	<p>Plaggic horizons are more acid (pH KCl between 4 and 4.5) and contain more organic carbon (1 - 5 %) than Terric horizons.</p> <p>The C/N ratio is generally between 10 and 20, with higher values in black soil types. Reported CEC values are between 5 and 15 cmol(+)/kg soil and the ‘total’ phosphorus content is high.</p> <p>Irragric horizons have a high base saturation. They may contain free lime and can even be alkaline in reaction. Some irrigric horizons are saline after the accumulation of salts that were dissolved in the irrigation water.</p> <p>Anthraquic horizons have a (near) neutral soil reaction when submerged. Under reducing conditions, Fe²⁺ and Mn²⁺ may be present in toxic quantities. Most hortic horizons have a high CEC, acquired after long-continued application of organic residues, and are well supplied with nutrients.</p>

¹⁹ <https://www3.lis.tum.de/en/boku/wrb-working-group/pictures/anthrosol/>; last access: 13.02.2022.

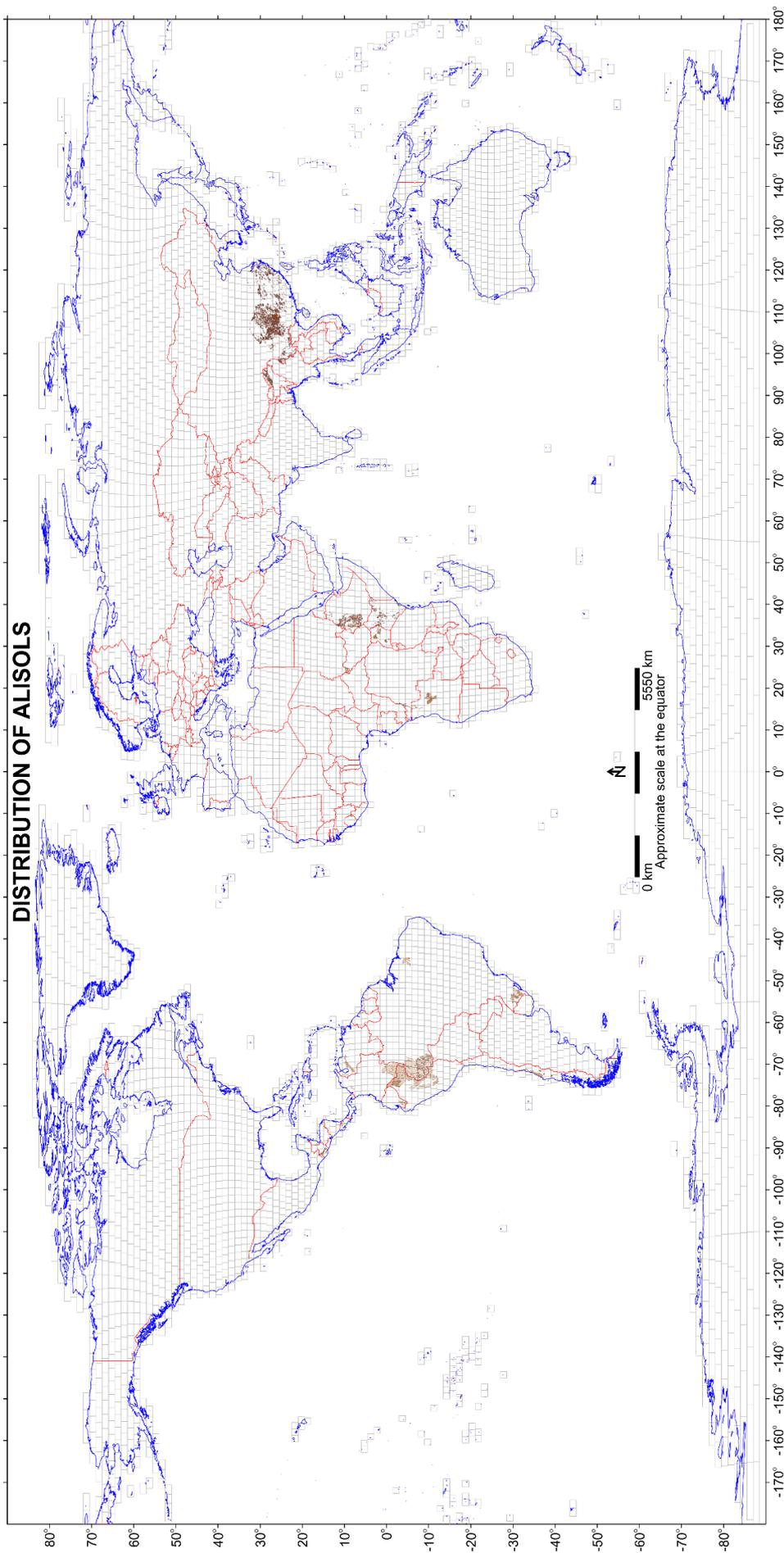


Figure A3.2.1.28. Map showing the global distribution of Alisols. The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS_AL-Alisols.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

<p>Alisols</p>	<p>From the Latin word <i>aluminium</i> = alum.</p> <p>Alisols are strongly acid soil types with subsurface accumulation of high activity clays in the subsoil. They occur in humid (sub)-tropical and warm temperate regions (Fig. A3.2.1.28), on parent materials that contain a substantial amount of unstable Al-bearing minerals.</p>
 <p>Source: Peter Schad²⁰</p>	
<p>Geographical distribution:</p>	<p>Most common in old land surfaces with hilly topography. In the humid tropics, Alisols can be found on slopes where smectitic saprolites outcrop. They may also occur on slopes that are exposed to frequent rain-bearing winds.</p> <p>Major occurrences of Alisols are found in Latin America, West Indies, West and East Africa, Madagascar, Southeast Asia and northern Australia (Fig. A3.2.1.28).</p>
<p>Parent material:</p>	<p>Weathering products of mafic rocks.</p>
<p>Usage:</p>	<p>Alisols are traditionally used in shifting cultivation, and for low volume production of undemanding crops. In the past decades, they have increasingly been planted with Al-tolerant estate crops such as tea and rubber, and also oil palm.</p>
<p>Geochemical processes:</p>	<p>Ongoing weathering of high-activity Al-bearing clay leads to severe chemical infertility: Al and possibly Mn are present in toxic quantities, whereas levels of other plant nutrients are low and unbalanced.</p> <p>However, the fact that Alisols have favourable cation exchange properties, makes some Alisols productive under intensive management with adequate liming and application of manure and fertilisers.</p> <p>The organic matter content of cultivated Alisols is usually modest, in contrast with Alisols under natural forests.</p>

²⁰ <https://www3.lis.tum.de/en/boku/wrb-working-group/pictures/alisol/>; last access: 13.02.2022.

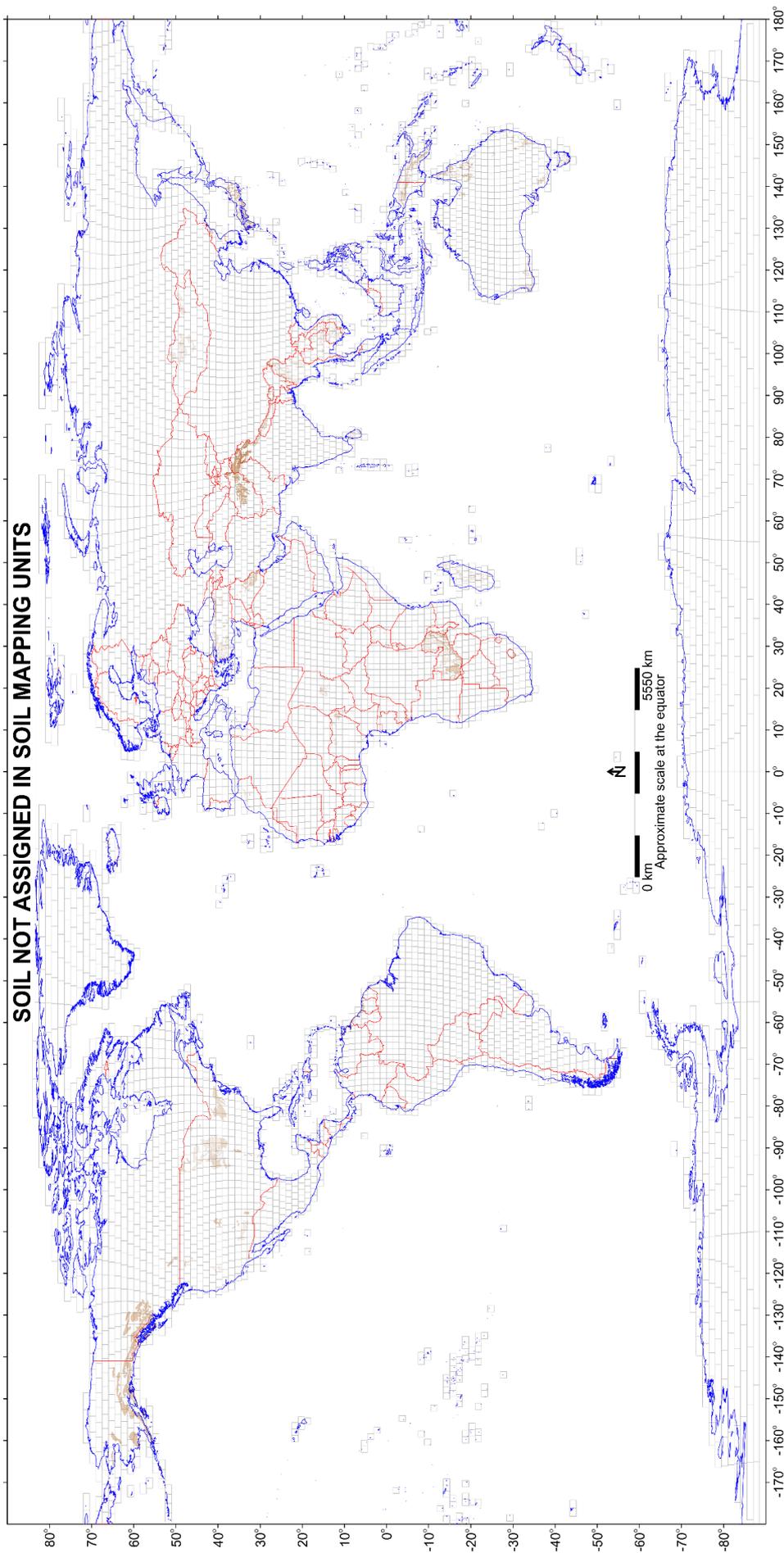


Figure A3.2.1.29. Map showing the global distribution of areas with soil not assigned in soil mapping units (SMUs). The intensity of the brown colour shades within each polygon corresponds to the share of the soil type with respect to the total area: the lower the share, the higher is the transparency of the polygon (lighter brown shades). The Global Terrestrial Network grid cells of 160x160 km are displayed in grey colour parallelograms. The map scale distortion is caused by the orthographic projection in degrees. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Surfer v24 using the kml file (HWSD_CLASS Not assigned.kml), which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>).

A3.2.1.3. Hyperlinks to websites with soil descriptions

Acrisols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set6/ac/acrisol.pdf
<http://www.fao.org/docrep/003/Y1899E/y1899e08a.htm>

Alisols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set6/al/alisol.pdf
<http://www.fao.org/docrep/003/Y1899E/y1899e08a.htm>

Andosols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set3/an/andosol.pdf
<http://www.fao.org/docrep/003/y1899e/y1899e06.htm>

Anthrosols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set2/at/anthroso.pdf
<http://www.fao.org/docrep/003/Y1899E/y1899e05.htm>

Arenosols

<https://www.isric.org/explore/world-soil-distribution/arenosols>

Calcisols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set7/cl/calcisol.pdf
<http://www.fao.org/docrep/003/Y1899E/y1899e09.htm>

Cambisols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set5/cm/cambisol.pdf
<http://www.fao.org/docrep/003/y1899e/y1899e08.htm>

Chernozems

https://www.isric.org/sites/default/files/major_soils_of_the_world/set8/ch/chernoze.pdf
<http://www.fao.org/docrep/003/Y1899E/y1899e11.htm>

Ferralsols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set6/fr/ferralsol.pdf
<http://www.fao.org/docrep/003/Y1899E/y1899e08a.htm>

Fluvisols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set4/fl/fluvisol.pdf
<http://www.fao.org/docrep/003/Y1899E/y1899e07.htm>

Gleysols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set4/gl/gleysol.pdf

<http://www.fao.org/docrep/003/Y1899E/y1899e07.htm>

Greyzems

<http://edepot.wur.nl/408828>

Gypsisols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set7/gy/gypsisol.pdf

<http://www.fao.org/docrep/003/Y1899E/y1899e09.htm>

Histosols

<http://www.fao.org/docrep/003/y1899e/y1899e04.htm>

Kastanozems

https://www.isric.org/sites/default/files/major_soils_of_the_world/set8/ks/kastanoz.pdf

<http://www.fao.org/docrep/003/Y1899E/y1899e11.htm>

Leptosols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set4/lp/leptosol.pdf

<http://www.fao.org/docrep/003/Y1899E/y1899e07.htm>

Lixisols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set6/lx/lixisol.pdf

<http://www.fao.org/docrep/003/Y1899E/y1899e08a.htm>

Luvisols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set9/lv/luvisol.pdf

<http://www.fao.org/docrep/003/y1899e/y1899e12.htm>

Nitisols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set6/nt/nitisol.pdf

<http://www.fao.org/docrep/003/Y1899E/y1899e08a.htm>

Phaeozems

https://www.isric.org/sites/default/files/major_soils_of_the_world/set8/ph/phaeozem.pdf

<http://www.fao.org/docrep/003/Y1899E/y1899e11.htm>

Planosols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set9/pl/planosol.pdf

<http://www.fao.org/docrep/003/Y1899E/y1899e12.htm>

Plinthosols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set6/pt/plinthos.pdf
<http://www.fao.org/docrep/003/Y1899E/y1899e08a.htm>

Podzols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set9/pz/podzol.pdf
<http://www.fao.org/docrep/003/y1899e/y1899e12.htm>

Podzoluvisols (Albeluvisols)

https://www.isric.org/sites/default/files/major_soils_of_the_world/set9/ab/albeluvi.pdf
<http://www.fao.org/docrep/003/y1899e/y1899e12.htm>

Regosols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set4/rg/regosol.pdf

Solonchaks

https://www.isric.org/sites/default/files/major_soils_of_the_world/set7/sc/soloncha.pdf
<http://www.fao.org/docrep/003/Y1899E/y1899e09.htm>

Solonetz

https://www.isric.org/sites/default/files/major_soils_of_the_world/set7/sn/solonetz.pdf
<http://www.fao.org/docrep/003/Y1899E/y1899e09.htm>

Vertisols

https://www.isric.org/sites/default/files/major_soils_of_the_world/set3/vr/vertisol.pdf

Supplementary material

The following files can be downloaded from the [Publications](#) web page of the IUGS Commission on Global Geochemical Baselines:

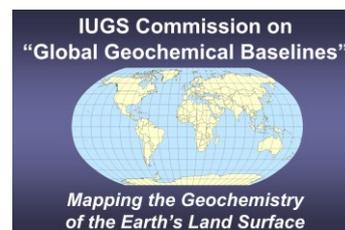
- IUGS-CGGB_HWSD_World_soil_type_symbols.xlsx. The file contains the names and abbreviated symbols of the major soil units.
- IUGS-CGGB_HWSD_KML_transparent_files.zip. The file contains the kml files of the major soil units.
- IUGS-CGGB_HWSD_shapefiles.zip. The file contains the shapefiles of the major soil units.

References

Note: All hyperlinks were checked on the 13th of February 2022.

FAO/UNESCO, 1971-1981. The FAO-UNESCO Soil Map of the World. Legend and 9 volumes. UNESCO, Paris; <https://www.fao.org/soils-portal/data-hub/soil-maps-and-databases/faunesco-soil-map-of-the-world/en/>.

- FAO/IIASA/ISRIC/ISS-CAS/JRC, 2012. Harmonized World Soil Database (version 1.2). FAO, Rome, Italy and IIASA, Laxenburg, Austria;
https://www.isric.org/sites/default/files/isric_report_2012_01.pdf.
- Jones, A., Montanarella, L. & Jones, R., 2005. Soil Atlas of Europe. European Soil Bureau Network, European Commission, Office for Official Publications of the European Communities, Luxembourg, L-2995,128 pp.;
https://esdac.jrc.ec.europa.eu/Projects/Soil_Atlas/Download/Atlas.pdf.



**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Annexe A3.2.2

**Residual Soil and Humus Sampling:
Soil Profiles**

Alecos Demetriades^{1,7}, Igor Savin², Timo Tarvainen^{3,7}, Edith Haslinger^{4,7},
Virgilija Gregorauskiene^{5,7}, Juan Pablo Lacassie Reyes^{6,7}, Felipe Astudillo⁶,
Pablo Oliva Vicentelo⁶

¹ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

² V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation

³ Geological Survey of Finland, Espoo, Finland

⁴ Austrian Institute of Technology GmbH, Centre for Energy, Vienna, Austria

⁵ Geological Survey of Lithuania, Vilnius, Lithuania

⁶ Servicio Nacional de Geología y Minería, Valdivia, Chile

⁷ IUGS Commission on Global Geochemical Baselines

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A3.2.2.1. Introduction

The sampling instructions in Chapter 3.2 state that samples of residual soil and humus are collected from a suitable site within the second-order catchment basin with an area of <math><100\text{ km}^2</math> (Fig. 2.8 in Chapter 2 of this Manual). In the Global Geochemical Reference Network project, two horizon-based samples of residual soil shall be collected:

- A *Topsoil* sample representing the uppermost mineral soil horizon occurring either at the air/earth interface or directly below the litter or organic (O) horizons (see Fig. 3.2.6 in Chapter 3.2 of this Manual), and this is designated as either the *A humic* or *A non-humic mineral soil horizon* (FAO, 2006), and
- A deeper *Bottomsoil* sample from the *C horizon* (Fig. 3.2.6 in Chapter 3.2).

It may be possible at some sampling sites to collect a recent highly decomposed organic material sample, which is referred to as *Humus* in this Manual, and when present occurs above the soil A humic mineral horizon.

Figure A3.2.2.1 shows a pictorial section of a second-order catchment basin valley with potential sites for collecting residual soil, and sites that should be avoided as, *for example*, colluvium from slopes and alluvial material from the valley bottoms.

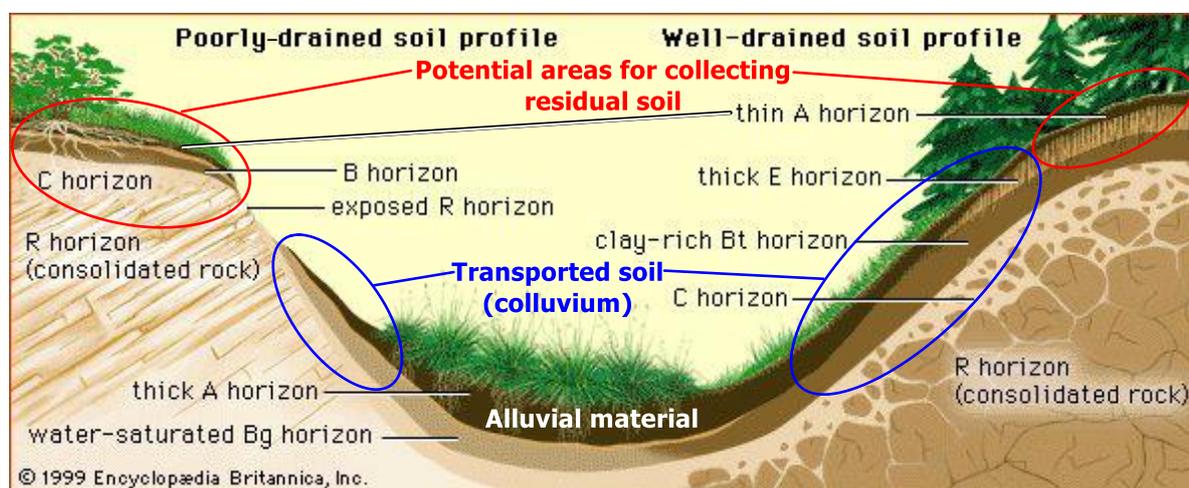


Figure A3.2.2.1. Soil profiles on hillslopes of a second-order seasonal catchment basin. The thickness and composition of soil horizons vary with position on a hillslope and with water drainage. For example, on the upper slopes of poorly-drained profiles, underlying rock may be exposed by surface erosion, and nutrient-rich soil (A humic horizon) may accumulate at the summit and shoulder. On the other hand, in well-drained profiles under forest cover, the leached soil horizon (E horizon) may be relatively thick and surface erosion minimal. The diagram shows potential sampling sites of residual soil on the hill summit and shoulder. Transported soil (colluvium) on hill slopes and alluvial material deposited on the valley bottom are not suitable for sampling. Source: Britannica (2012) – additional annotation was added for the purposes of this manual.

A3.2.2.2. Annotated soil profiles

The following photographs of annotated soil profiles show different residual soil types from where *Topsoil*, *Bottomsoil* and *Humus* samples can be taken, as well cases from where soil samples must not be collected.

Some of the soil profiles indicate that the thickness range of the A humic and non-humic mineral soil horizons is less than 20 cm.

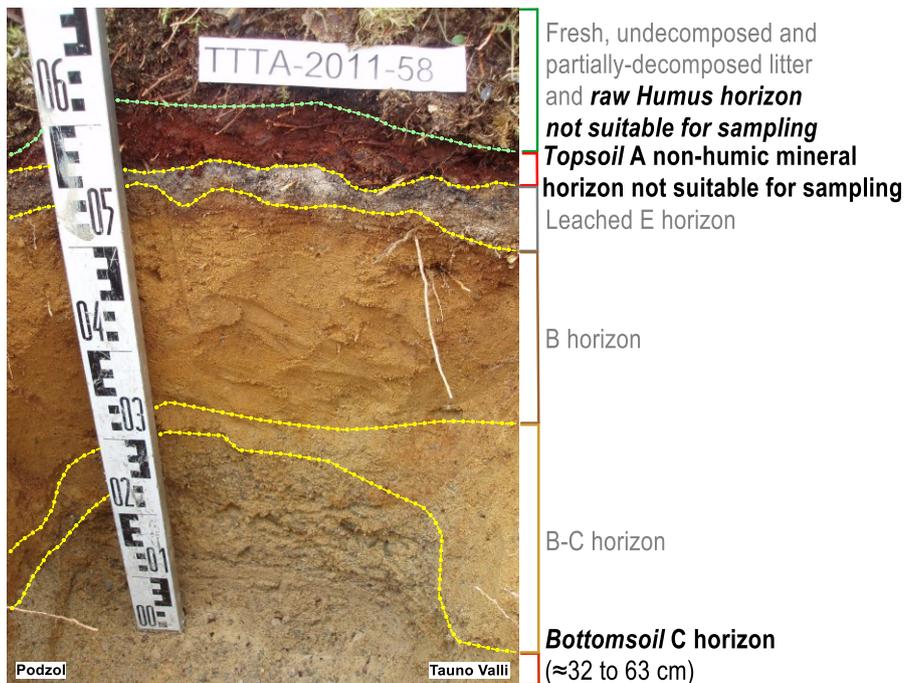


Figure A3.2.2.2. Podzol, Pirkanmaa-Häme province, Southern Finland. Residual soil developed on a sand deposit. The Humus horizon is very thin (0 to ≈2 cm) and cannot be observed as is hidden by the undecomposed and partially decomposed litter. The Topsoil A non-humic mineral horizon below the organic Humus horizon is thin (≈2 to ≈5 cm) and has a dark reddish colour, indicating that is rich in Fe oxides, and according to the instructions soil rich in Fe or Mn oxides should be avoided if possible. If this soil profile was suitable for sampling, the pit should be dug further down in order to collect a 20-cm thick Bottomsoil C horizon sample. Photograph: Tauno Valli, Geological Survey of Finland (GTK).

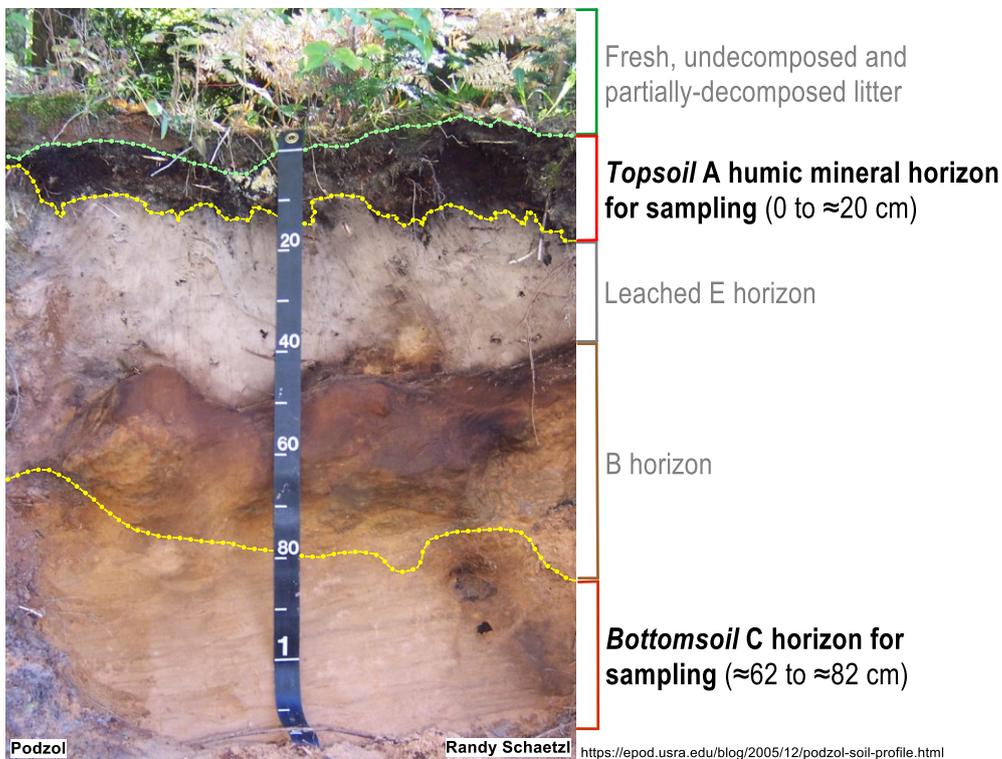


Figure A3.2.2.3. Podzol, Newbury, Michigan, United States of America (USA). The Topsoil sample is taken from the A humic mineral horizon, and the Bottomsoil from the C horizon as indicated on the profile. Note the whitish E horizon, which is known to be leached from major and trace elements (eluvial horizon). Source: <https://epod.usra.edu/blog/2005/12/podzol-soil-profile.html>.

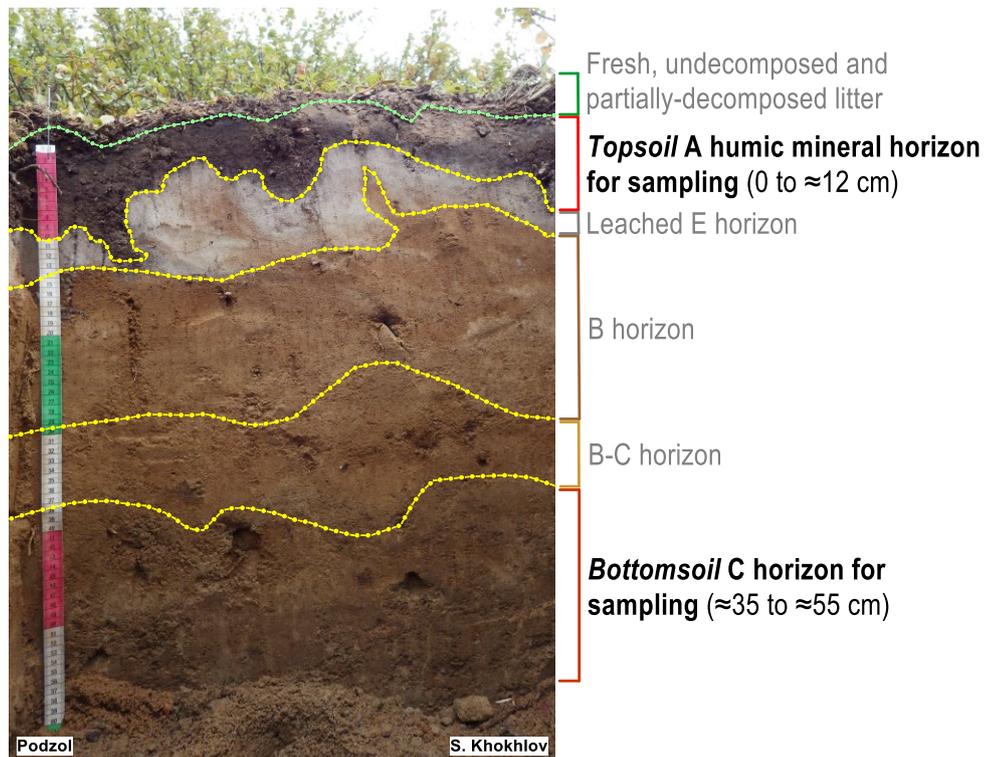


Figure A3.2.2.4. Podzol, Bolshezemelskaya Tundra, Siberia (north of Arctic Circle), Russian Federation. The Topsoil is collected from the A humic mineral horizon, and the Bottomsoil from the C horizon as indicated on the profile. Note the variable thickness of the eluvial E horizon. Photograph: S. Khokhlov, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation.

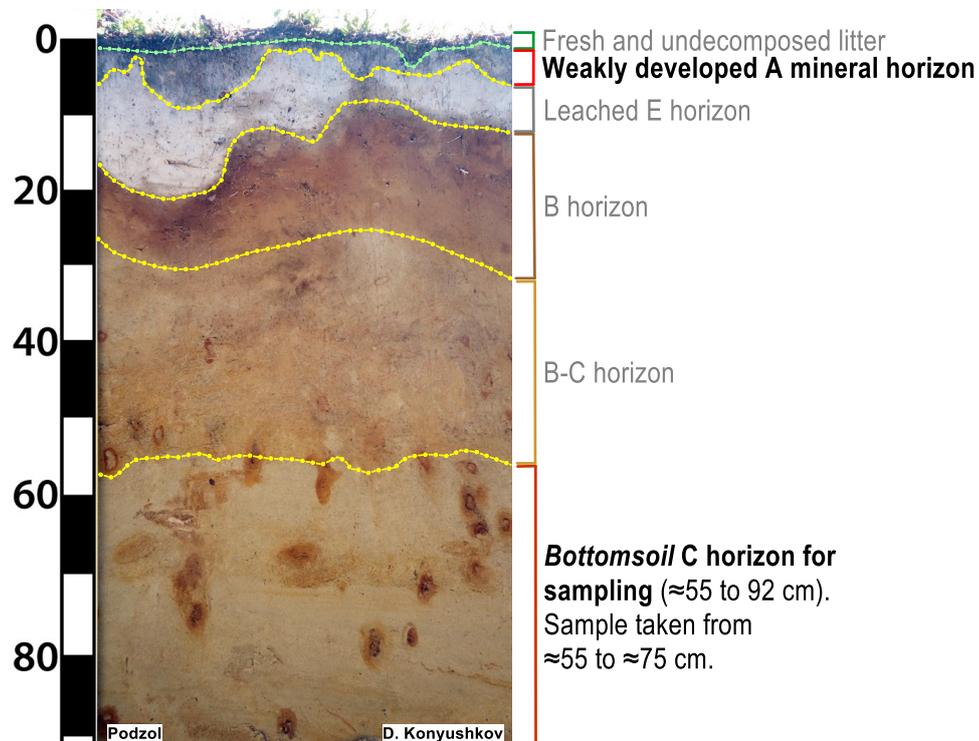


Figure A3.2.2.5. Podzol, Bolshezemelskaya Tundra, Siberia (north of Arctic Circle), Russian Federation. The Topsoil sample cannot be collected from the weakly developed A mineral horizon, while the Bottomsoil can be collected from the C horizon as shown on the profile. However, this soil profile is NOT suitable for sampling. Hence, another pit should be dug at another site. Photograph: D. Konyushkov, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation.

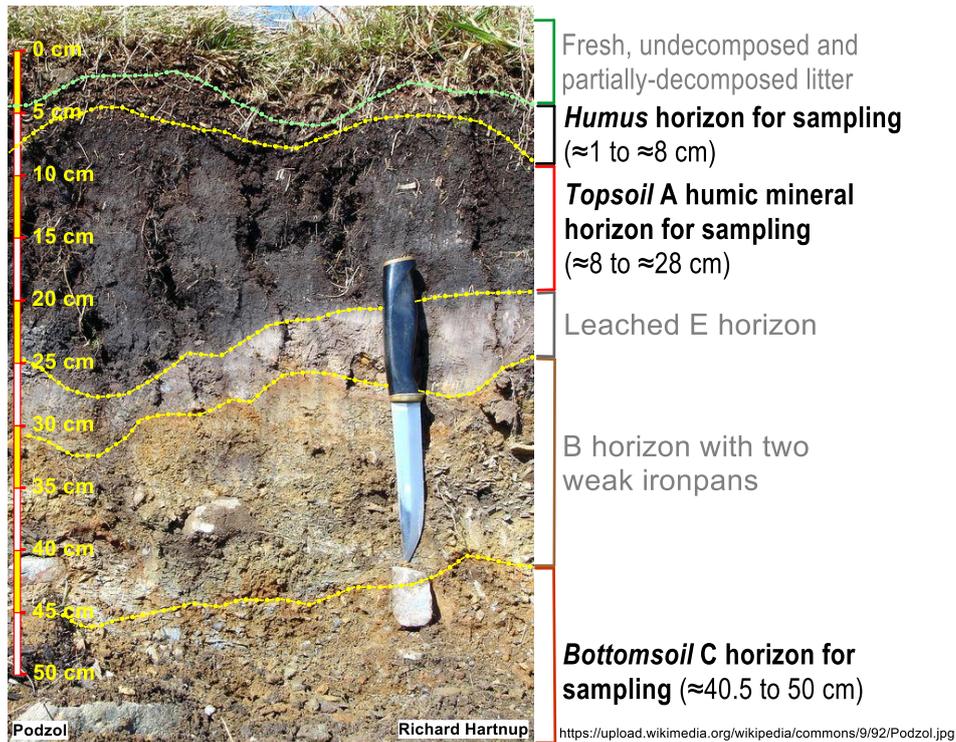


Figure A3.2.2.6. Podzol, upland North Wales, United Kingdom. The Humus horizon occurs below the fresh, undecomposed and partially decomposed litter, which is removed before taking a 3-cm thick Humus sample. The Topsoil sample is collected from the A humic mineral horizon, which is approximately 20-cm thick, and the Bottomsoil sample from the C horizon; the pit should be dug further down to 61 cm depth for collecting a 20-cm thick C horizon sample. Source: <https://upload.wikimedia.org/wikipedia/commons/9/92/Podzol.jpg>.

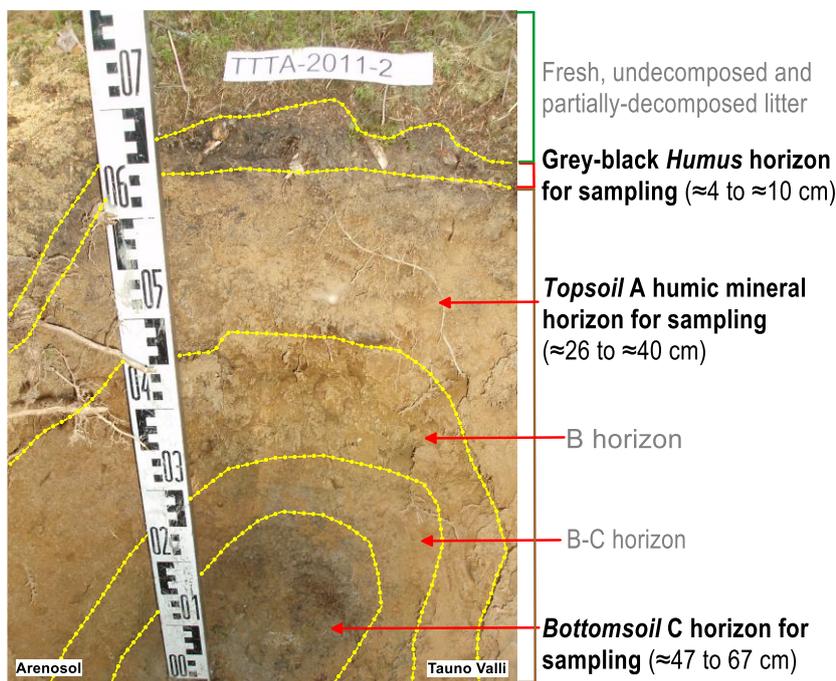


Figure A3.2.2.7. Arenosol, Pirkanmaa-Häme province, Southern Finland. Residual soil developed on glacial sandy till. The grey-black Humus horizon is thin and poor, varying in thickness from 3 to 5 cm; it is noted that as the humus horizon is very thin and poor, it may be difficult to take a good humus sample, as ten subsamples may be needed around the soil profile pit. The Topsoil sample is collected from the A humic mineral horizon, which is ≈ 14 cm thick (note the greyish colour caused by a small percentage of organic matter). The Bottomsoil sample is collected from the C horizon below a depth of 47 cm. The pit should be dug further down in order to collect a 20-cm thick C horizon sample. Photograph: Tauno Valli, GTK.

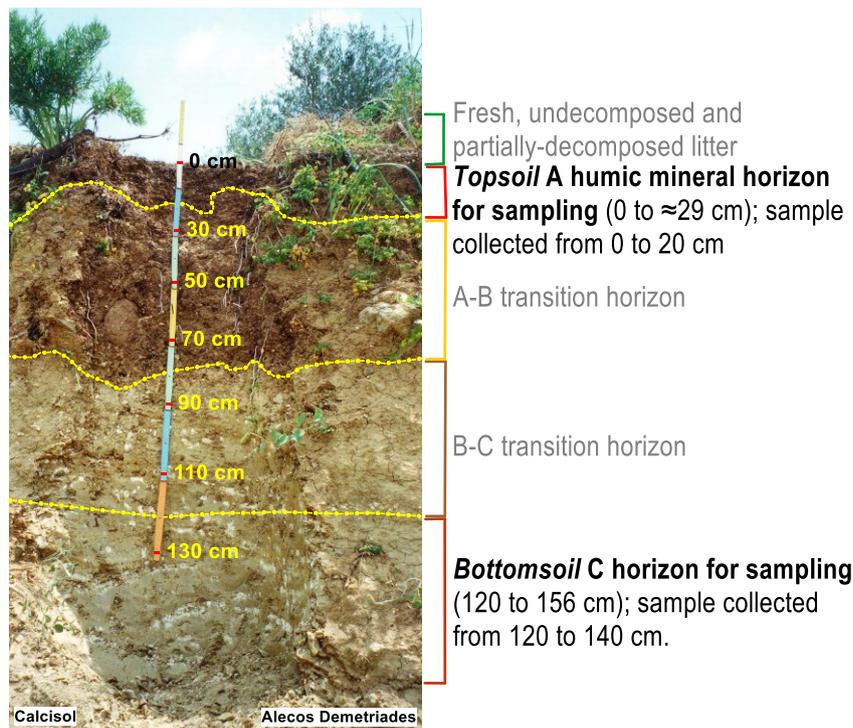


Figure A3.2.2.8. Calcisol, HELLAS, FOREGS Geochemical Atlas of Europe, Sample site N24E15T4 (25.28°E; 35.04°N). Residual soil developed on carbonate parent material. Topsoil is collected from the A humic mineral horizon, and the Bottomsoil sample from the C horizon is indicated on the profile. Photograph: Alecios Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) and IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).

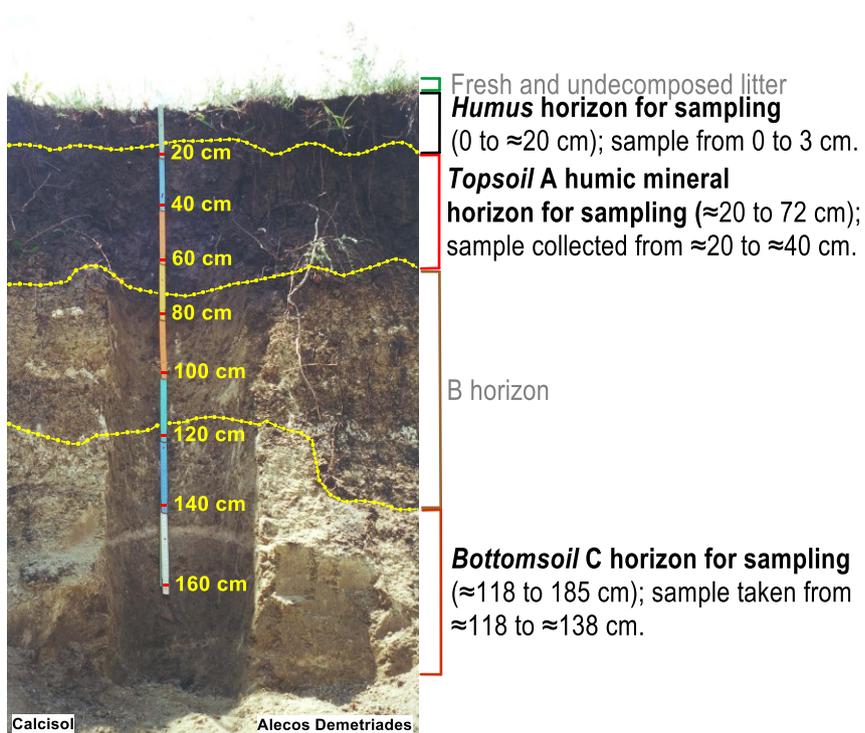


Figure A3.2.2.9. Calcisol, HELLAS. Residual soil developed on carbonate parent material, FOREGS Geochemical Atlas of Europe, Sample site N27E12T1 (21.61°E; 39.96°N). The Humus sample is collected from the highly decomposed organic material horizon, and the Topsoil from the A humic mineral horizon directly below it from a depth of ≈20 to ≈40 cm. The Bottomsoil sample is collected from the C horizon from a depth of ≈118 to ≈138 cm. Photograph: Alecios Demetriades (IGME/IUGS-CGGB).

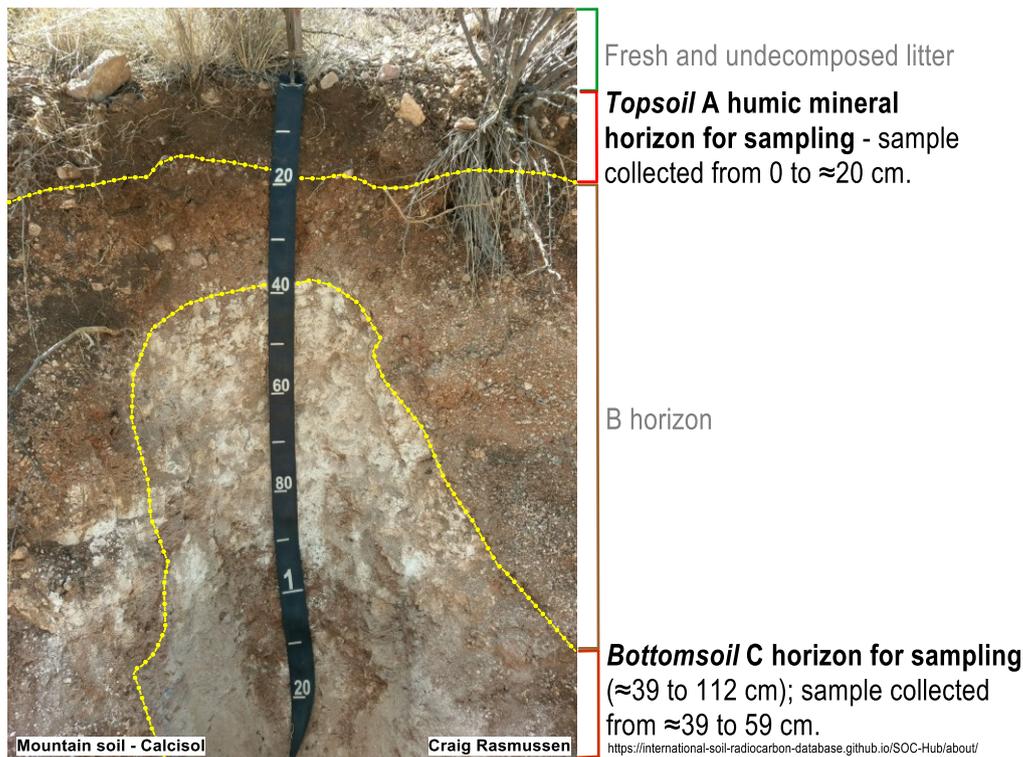


Figure A3.2.2.10. Mountain soil, Calcisol, Tombstone, Arizona, USA. The Topsoil is collected from the A humic mineral horizon, and the Bottomsoil from the C horizon as shown in the photograph. Source: <https://international-soil-radiocarbon-database.github.io/SOC-Hub/about/>.

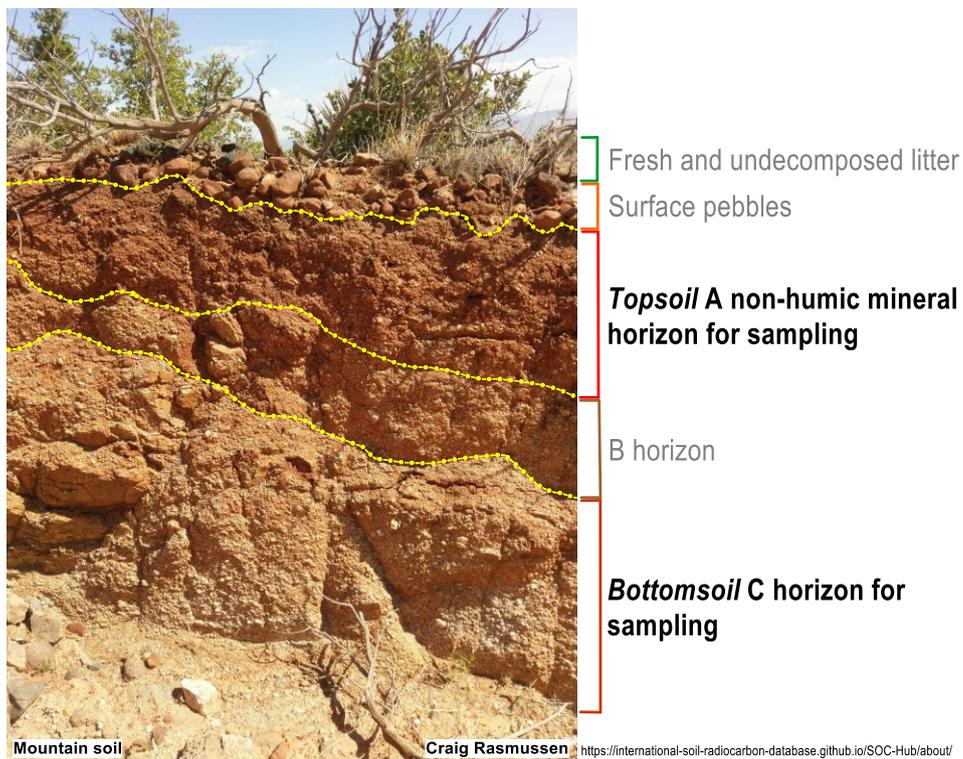


Figure A3.2.2.11. Mountainous soil profile developed on biotite-rich granodiorite, Santa Catalina Mountain, Arizona, USA. It shows a weathering profile, and the Topsoil A non-humic and Bottomsoil C horizons for sampling. Although in the sampling procedure it is stated to avoid, if at all possible, collecting soil rich in Fe or Mn oxides, this is a case that this cannot be avoided. Source: <https://international-soil-radiocarbon-database.github.io/SOC-Hub/about/>.

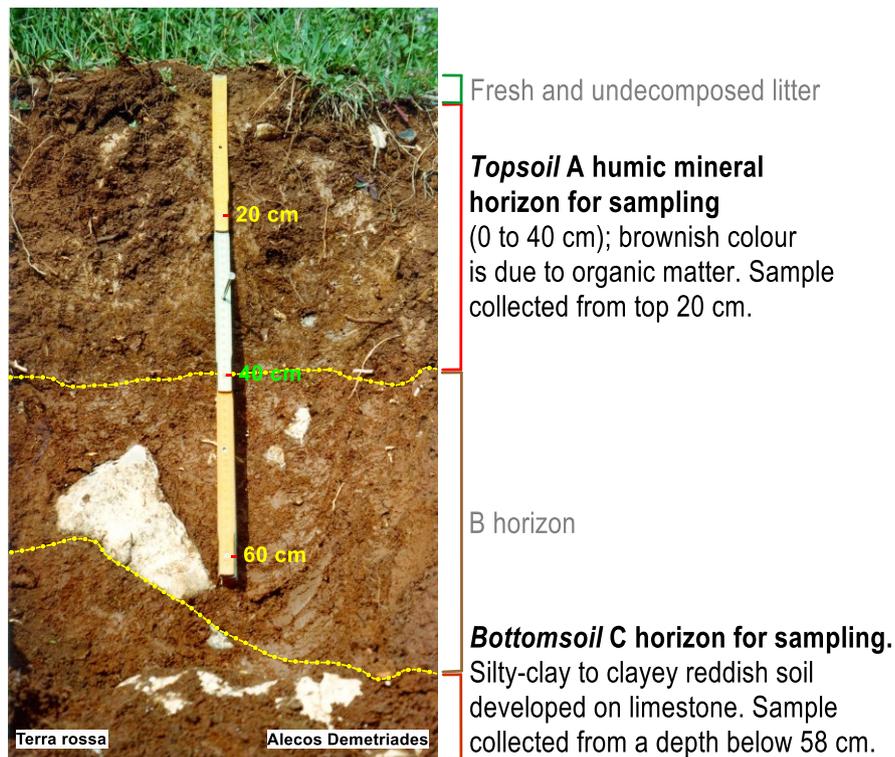


Figure A3.2.2.12. Terra rossa, Hellas, FOREGS Geochemical Atlas of Europe, Sample site N27E12T2 (20.76°E; 40.06°N). Residual soil developed on karst terrain. The Topsoil sample is collected from the A humic mineral horizon, which contains a small percentage of organic matter, and the Bottomsoil sample is taken from the C horizon. The pit should be dug further down to about 70 cm depth in order to collect a 20-cm thick C horizon sample. Photograph: Alecoss Demetriades (IGME/IUGS-CGGB).



Figure A3.2.2.13. Luvisol is developed on loess, Belgium. The Humus sample is collected from the surface horizon after clearing the fresh and undecomposed litter. The Topsoil sample is collected from the A humic mineral horizon (note the greyish colour which is due to a small percentage of organic matter). The Bottomsoil sample is collected from the C loess horizon as indicated on the profile. Source: <https://soilsciencesocietyofbelgium.files.wordpress.com/2015/01/luvisol3.jpeg>.

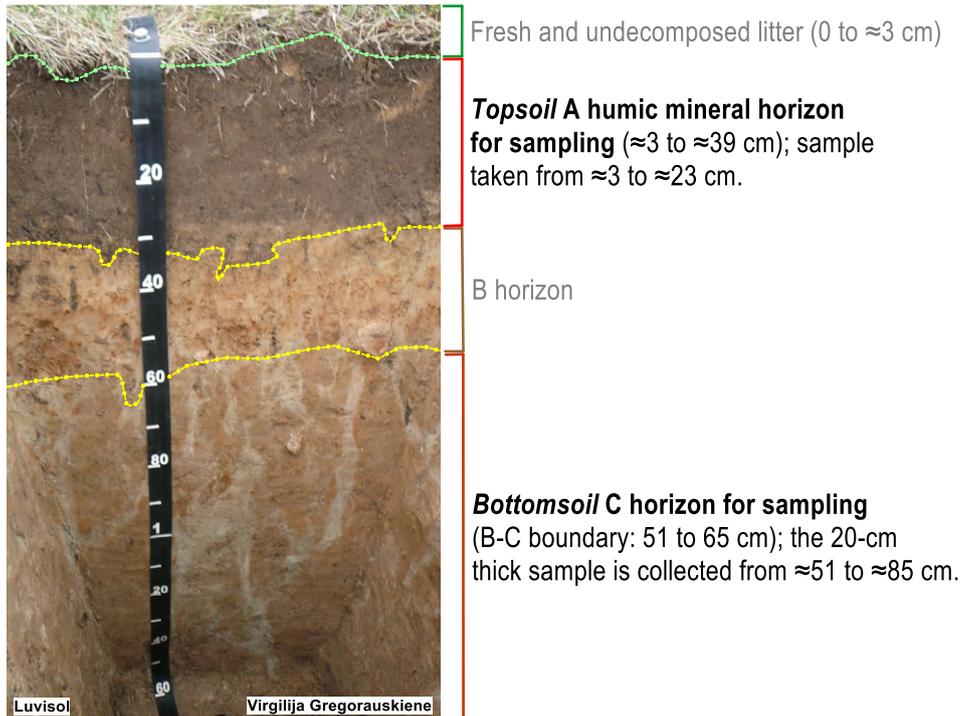


Figure A3.2.2.14. Luvisol is developed on loess, Lithuania. The Topsoil sample is collected from the A humic mineral horizon and the Bottomsoil sample from the C loess horizon as shown on the profile. Source: Virgilija Gregorauskiene, Geological Survey of Lithuania, Vilnius, Lithuania.

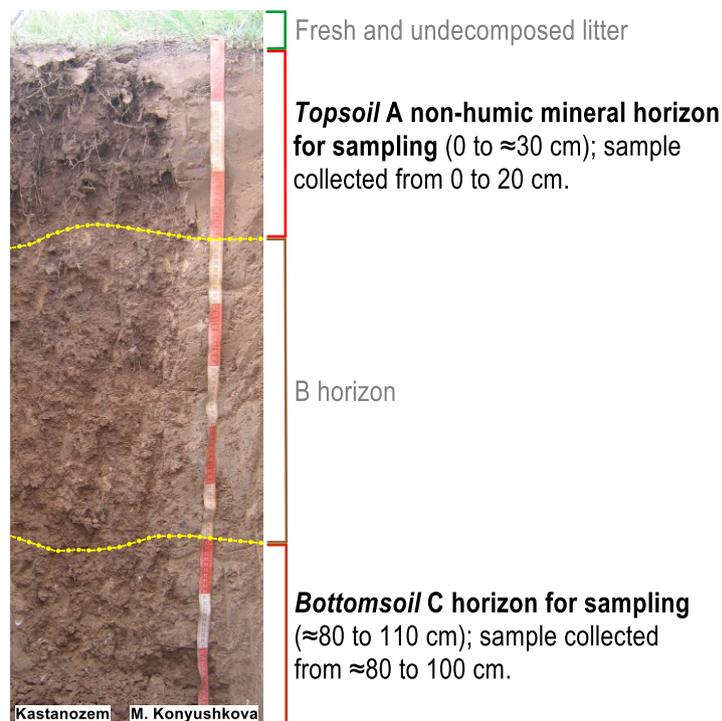


Figure A3.2.2.15. Kastanozem, Kalmykia region, north-west Caspian Sea, Russian Federation. The Topsoil sample is collected from the A non-humic mineral horizon (note the greyish colour which is due to a small percentage of organic matter). The Bottomsoil sample is collected from the C horizon as indicated on the profile. Photograph: M. Konyushkova, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation.

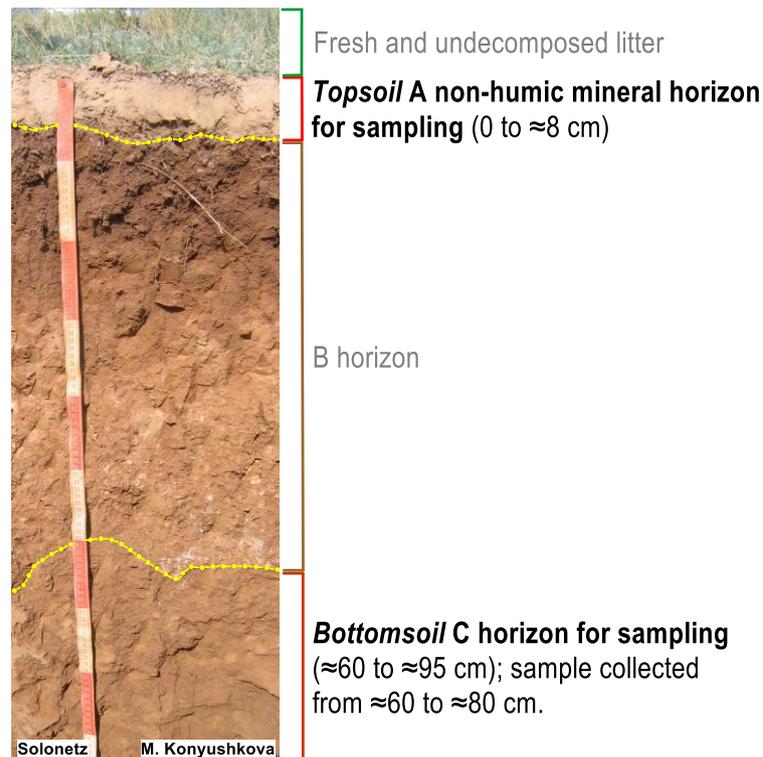


Figure A3.2.2.16. Solonetz, Kalmykia region, NW Caspian Sea, Russian Federation. The Topsoil sample is collected from the A non-humic mineral soil horizon, and the Bottomsoil from the C horizon as shown on the profile. Photograph: M. Konyushkova, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation.

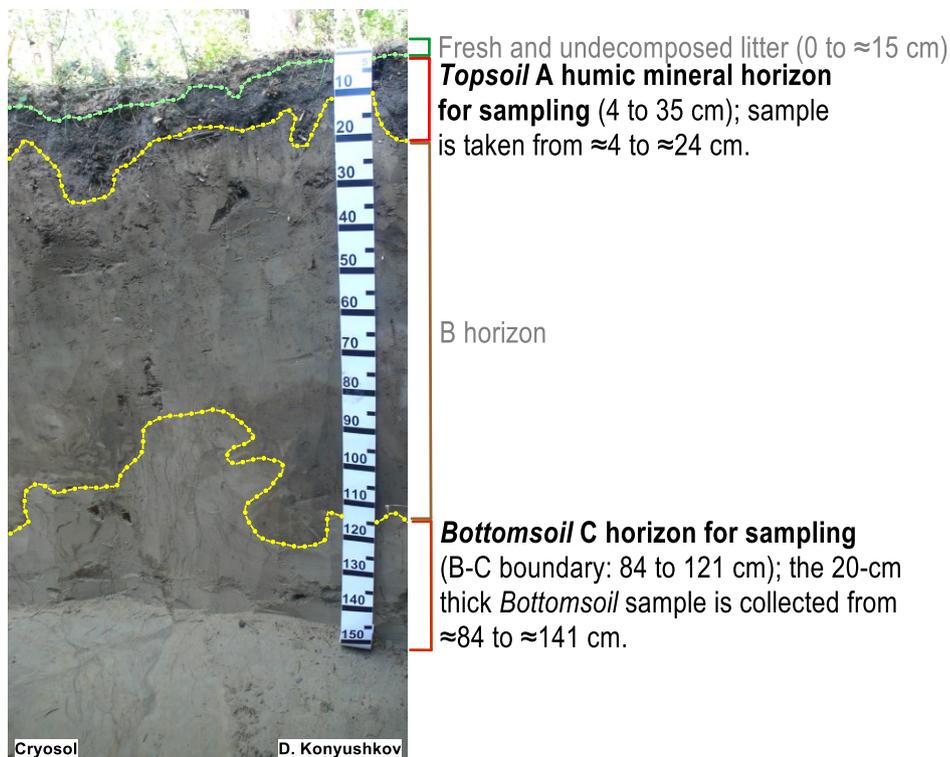
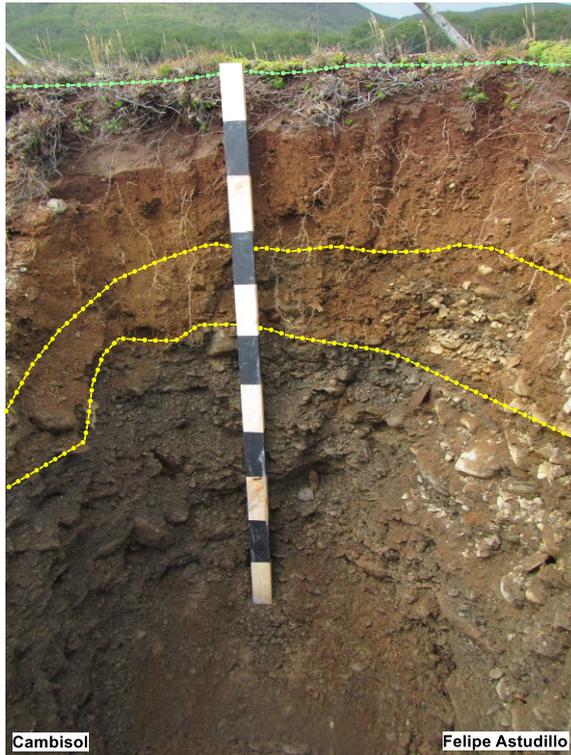


Figure A3.2.2.17. Cryosol, Central Yakutia, Russia. This soil profile is from a sub-polar region. The Topsoil sample is collected from the A non-humic mineral horizon, and the Bottomsoil from the C horizon as indicated on the profile. Photograph: D. Konyushkov, V.V. Dokuchaev Soil Science Institute, People's Friendship University of Russia, Moscow, Russian Federation.



Fresh and undecomposed litter

Topsoil A humic mineral horizon for sampling (0 to ≈32 cm); sample collected from 0 to ≈20 cm.

Reddish brown silt-clay with sub-rounded polymictic clasts; high content of organic matter

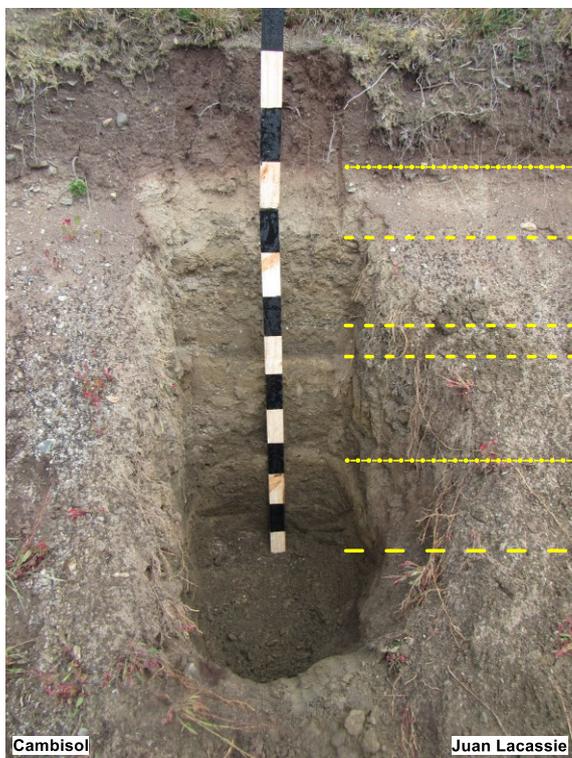
B horizon (≈32 to ≈48 cm) is made-up from sub-rounded polymictic clasts and brown silt-clay

Bottomsoil C horizon for sampling (≈48 to 110 cm); sample collected from ≈48 to ≈68 cm consisting of subrounded polymictic clasts, and grey silty-sand.

Cambisol

Felipe Astudillo

Figure A3.2.2.18. Cambisol, Tierra del Fuego, Chile (Field site JP-764; 68.740081°W; 54.289828°S). This soil profile is from a sub-polar region. The Topsoil sample is collected from the A humic mineral soil horizon, and the Bottomsoil sample is taken from the C horizon as shown on the profile. Photograph: Felipe Astudillo, Servicio Nacional de Geología y Minería (SNGM), Valdivia, Chile.



Fresh and undecomposed litter

Topsoil A horizon (0 to 20 cm). Dark grey to grey-black colour consisting of medium- to coarse-grained sand and organic material

B horizon (20 to 95 cm) consisting of four sub-horizons. Upper sub-horizon is made up of medium- to coarse- grained sand. Middle sub-horizon made up from medium- to fine-grained sand and clay. Lower sub-horizon made up from clay and medium- to fine-grained sand

Bottomsoil C horizon (95 to 125 cm); sample collected from 95 to 115 cm, consisting of clay and medium- to fine-grained sand (glacial till).

Cambisol

Juan Lacassie

Figure A3.2.2.19. Cambisol, Tierra del Fuego, Chile (Field site JP-760; 68.810301°W; 53.955174°S). This soil profile is from a sub-polar region. The Topsoil sample is collected from the A humic mineral soil horizon, and the Bottomsoil sample is taken from the C horizon as indicated on the profile. Photograph: Juan Lacassie, SNGM, Valdivia, Chile.

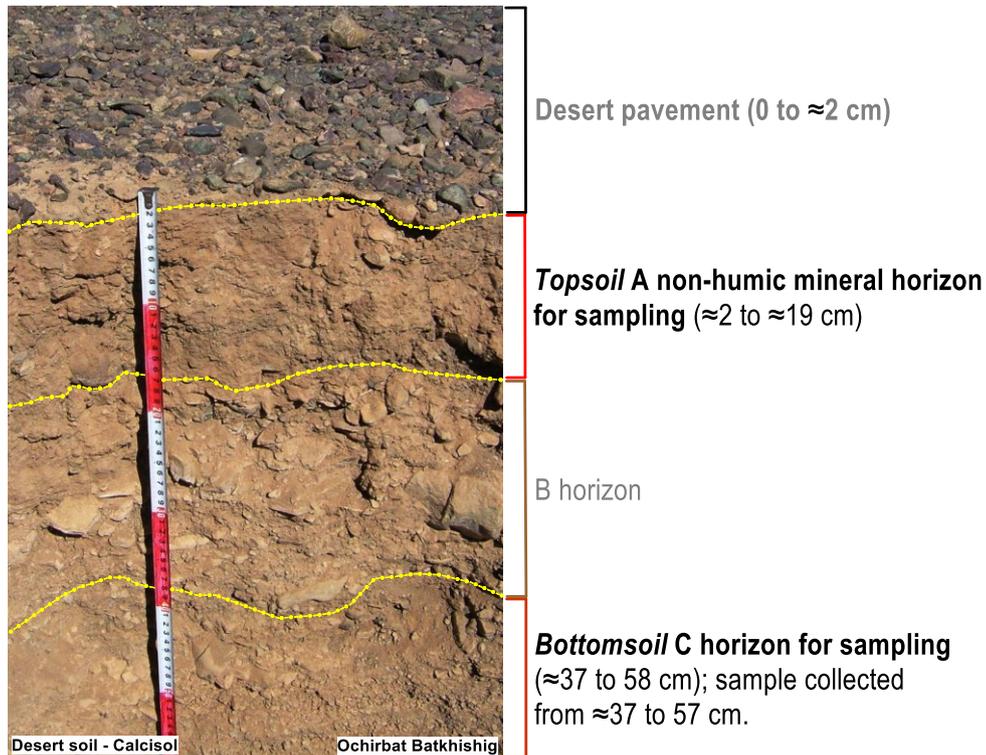


Figure A3.2.2.20. Desert soil, Gobi Desert, Mongolia (101.2267°E; 42.89222°N). The Topsoil sample is collected from the A non-humic mineral soil horizon (note the greyish colour which is due to a small percentage of organic matter). The Bottomsoil sample is taken from the C loess horizon as shown on the profile. Photograph: Ochirbat Batkhisig, Mongolian Academy of Sciences, Ulaanbaatar, Mongolia.

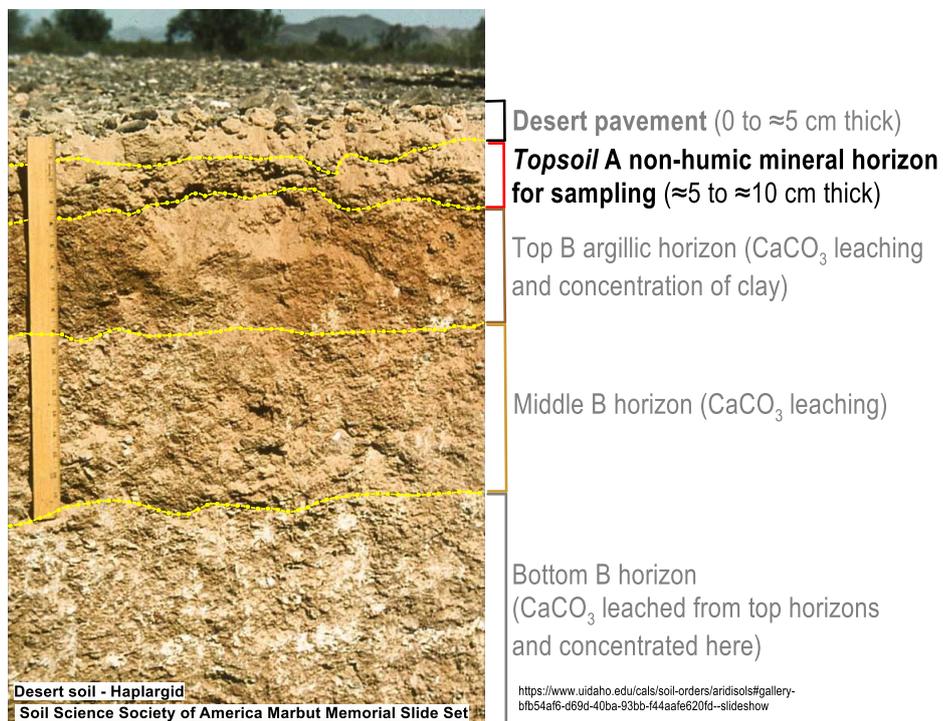


Figure A3.2.2.21. Desert soil, Sonoran desert, Arizona, USA. This soil has formed on older alluvial fans and is mantled by the desert pavement. The desert pavement is approximately 5 cm thick and overlies a highly vesicular layer, which is classified in this case as the A non-humic mineral soil horizon. Calcium carbonate has been leached to a depth of approximately 36 cm, allowing some clays to accumulate in the darker brown, argillic B horizon. Some soluble salts are also present in the lower part of the profile. The ruler used as a scale is 48 cm long. This is not an ideal soil profile for sampling. Nevertheless, it has been added for educational purposes. Source: <https://www.uidaho.edu/cals/soil-orders/aridisols#gallery-bfb54af6-d69d-40ba-93bb-f44afe620fd--slideshow>.



Transported overburden,
which is not suitable for
sampling

https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/office/ssr7/profile?cid=nrcs142p2_048011
https://www.nrcs.usda.gov/Internet/FSE_MEDIA/nrcs142p2_047698.jpg

Figure A3.2.2.22. Skeletal immature soil on a hill slope, USA. This is a shallow skeletal overburden material formed from weathered limestone bedrock. It occurs on hill slopes ranging from 5 to 60 per cent, gentle to a very steep slope, respectively. Observing the boulders and subangular limestone pebbles this appears to be colluvium (see Fig. A3.2.2.1), which is transported material, and definitely not residual and, therefore, MUST NOT be sampled. Source: https://www.nrcs.usda.gov/Internet/FSE_MEDIA/nrcs142p2_047698.jpg.



Transported overburden
(colluvium) on a slope
with an angle of 20°,
which is not suitable
for sampling

<http://greenmountainwildflowers.blogspot.com/2014/09/the-end-of-confusing-summer.html>

Figure A3.2.2.23. Mountainous immature soil on a slope of 20°, Green Mountain, Vermont, USA. This is transported material (colluvium) over cemented scree. Transported overburden (colluvium) MUST NOT be sampled, because it is not residual (see Fig. A3.2.2.1). Source: <http://greenmountainwildflowers.blogspot.com/2014/09/the-end-of-confusing-summer.html>.

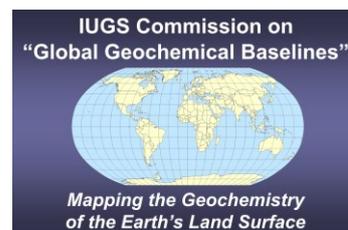
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Note: All hyperlinks (above and below) were checked on the 14th of February 2022.

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 3.3

Stream Water Sampling

Timo Tarvainen^{1,4}, Tarja Hatakka¹, Mikael Eklund¹, Reijo Salminen¹,
Christopher C. Johnson^{2,4}, Alecos Demetriades^{3,4}

¹ Geological Survey of Finland, Espoo, Finland

² GeoElementary, Derby, United Kingdom,

³ Institute of Geology and Mineral Exploration (retired), Athens, Hellenic Republic

⁴ IUGS Commission on Global Geochemical Baselines

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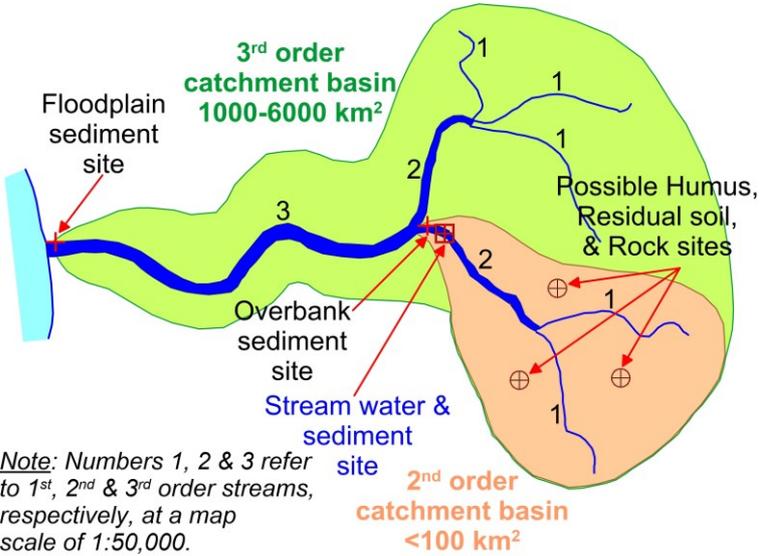
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Stream water samples are collected from second-order catchment basins



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3.3.1. Introduction

Water is a precious natural resource, and dependence on clean water for human consumption, agriculture and animal husbandry requires that the reliability of data collected from water sampling campaigns is carefully monitored. According to objective 18.36 of Agenda 21 of the United Nations Programme of Action, as stated in the 1992 Earth Summit in Rio de Janeiro (UN, 1992): “*The complex interconnectedness of freshwater systems demands that freshwater management be holistic (taking a catchment management approach) and based on a balanced consideration of the needs of people and the environment. The Mar del Plata Action Plan has already recognised the intrinsic linkage between water resource development projects and their significant physical, chemical, biological, health and socio-economic repercussions. ...*”.

In this manual, a catchment basin approach is used, as stipulated in objective 18.36 of Agenda 21, by the collection of stream water samples from second-order streams with a catchment basin of <100 km² in area. The reason for selecting second-order streams is that the aim of this continental-scale survey, apart from the establishment of the Global Geochemical Reference Network, is to determine the geochemical baseline of the drainage system, and to define the geochemical background levels in stream water. Completely pristine stream water is difficult to find because of atmospheric transport of contaminants, and their subsequent deposition at locations distant from their source. Hence, streams that are normally least disturbed by human activities are selected for sampling (refer to Stream Sediment Sampling Chapter 3.4 for more details).

According to Simpson *et al.* (1993, p.63): “*... bedrock geochemistry and mineralisation are the most important variables which influence the surface water geochemistry. The primary control by geological parameters is variously modified by secondary influences which include geomorphological factors (especially altitude) atmospheric (climatic and coastal effects), and anthropogenic (agriculture, urban and industrial developments).*” This statement has been challenged by the FOREGS Geochemical Atlas of Europe project (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006). In this continental-scale stream water sampling project, with an average density of 1 sample/4800 km², “*Most patterns appear to be controlled less directly by geology, but more by climate-related parameters such as rainfall, temperature, acidity and organic matter, in combination with topography and distance from the ocean, i.e., the source of precipitation*” (De Vivo *et al.*, 2006, p.33). The difference in the conclusions reached by Simpson *et al.* (1993) versus De Vivo *et al.* (2006) may be due to the average density of sampling, *i.e.*, 1 sample/km² and 1 sample/4800 km², respectively.

In the compilation of these stream water sampling instructions, the main source is the FOREGS Geochemical Mapping Field Manual (Salminen, Tarvainen *et al.*, 1998). However, other sampling manuals have been consulted (*e.g.*, Bartram and Ballance, 1996; Chapman, 1996; US EPA, 1996, 2013; Gregorauskiene *et al.*, 2000; Myumbilwa *et al.*, 2007; Musselman, 2012; Danielson, 2014).

3.3.2. Stream water sampling

Flowing stream water is collected from a small, second-order, drainage basin (<100 km²; see Figs. 2.5 & 2.8 in Chapter 2) at the same site as active stream sediment (see Chapter 3.4 and Fig. 3.4.1). In semi-dry and dry terrains, such as southern Europe, North and South Africa, Namibia, parts of North, Central and South America, Australia, and other countries with dry late spring, summer and early autumn seasons, streams may not have flowing water if sampling is carried out during these periods, yet ponds with stagnant water may be found. No samples should be collected from such ponds, since the geochemistry of stagnant water is normally different from that of flowing stream water.

In true humid tropical and temperate climates, streams will rarely run dry and there is always an abundance of water. However, the wettest time of the year should be avoided in order

not to sample during periods of high rainfall and flood events when the stream water is diluted with substantial surface water run-off. Ideally, stream water samples should not be collected within forty-eight hours of a rainfall event in the selected second-order catchment basin. If this is not possible, the time of the rainfall event should be recorded on the field observations sheet.

If the sampling campaign is to be carried out over several years, it is important to collect the stream water samples during the same climatic season. Other parameters to be considered are the transient character of stream water chemical composition, and that element concentrations are susceptible to various sources of temporal variation. Thus, the generated data are ‘*snapshots*’ of the chemical state of stream water at the time of sampling (Lark *et al.*, 2016). These authors recommend setting up monitoring sites on selected streams, where daily stream water samples are collected over variable time intervals. The statistical analyses of water geochemical data from these monitoring sites can supplement the results from the analysis of routine stream water samples, collected in a once-off sampling campaign to predict temporal effects on water geochemistry.

Stream water, as stream sediment, is always sampled upstream from bridges, artificial channels (culverts, flumes), and settlements (refer to Stream Sediment Sampling Chapter 3.4 and Sections §3.4.1 and §3.4.4 for information about selecting a suitable sampling site on a second-order stream).

3.3.2.1. Stream water samples to be collected

The following stream water samples are collected from a second-order stream:

- (a) Routine sample site of a normal GTN grid cell:
- 1 x 500 ml bottle for unfiltered stream water for major IC ion analysis.
 - 1 x 100 ml bottle for filtered stream water for ICP-MS and ICP-AES analysis.
 - 1 x 100 ml bottle for mercury analysis, and
 - 1 x 60 ml bottle for Dissolved Organic Carbon (DOC) analysis.
- (b) Duplicate field site of a duplicate GTN grid cell (at least one in each country):
- The same stream water samples, and field measurements, are taken at the duplicate field site (see below).
- Sampling quantities:** See bottle sizes above. However, before starting the stream water sampling campaign, the Project Manager should check with the laboratory the required volume for analysis.

Duplicate stream water sample: Duplicate stream water samples are collected randomly at least at every 20th sampling site (*i.e.*, ≈5% duplication of the sample sites) in each country. However, countries with less than 6 GTN grid cells should collect field duplicate stream water samples from at least one random site. The field duplicate stream water sample is collected from the same site less than five (<5) minutes after taking all field measurements (pH, electrical conductivity (EC), alkalinity).

3.3.2.2. Identifiers of stream water samples

The identifier of stream water samples is ‘W’:

(a) Routine sample site (e.g., GTN grid cell N26E14):

- Stream water sample: N26E14W**1**

Note: Number '1' represents the 1st sample site in GTN grid cell N26E14.

(b) Duplicate field site (e.g., GTN grid cell N27E12):

- Stream water sample: N27E12W**3**
- Stream water sample – Duplicate: N27E12W**3D**

Note: Number '3' represents the 3rd sample site in GTN grid cell N27E12, and 'D' denotes the duplicate stream water sample.

(c) Blank water sample: The identifier for a filtered blank water sample is zero (**0**), i.e., GTN grid cell / W / sample no. / **0**; for example, N27E12W**30**.

3.3.3. Equipment for stream water sampling

3.3.3.1. Equipment to be provided by the Project Coordinator

- 500 ml new certified trace element free Nalgene[®] bottles or comparable (for non-filtered water samples for major IC ion analysis).
- 100 ml new certified trace element free Nalgene[®] bottles or comparable (for ICP-MS analysis) for mercury analysis. It is proposed, however, to use instead new 100 ml borosilicate glass bottles for mercury analysis by ICP-MS, as these are recommended by US EPA (1996).
- 60 ml new certified trace element free Nalgene[®] bottles or comparable (for filtered, unacidified samples for Dissolved Organic Carbon (DOC) analysis).
- Disposable white-colour powder-free vinyl gloves (e.g., Medi-Point or Kingfisher vinyl gloves or comparable).
- Disposable 50 ml syringes (e.g., Becton & Dickinson Plastipak[™], or HSW[®] Norm-Ject[®] or comparable).
- Disposable syringe filters 0.45 µm (e.g., Schleicher & Schuell pyrogen-free, or Corning[®] or Whatman[®] or comparable), and
- Droplet bottles made of Teflon FEP (fluorinated ethylene propylene).
- Black permanent drawing ink markers (ONLY black coloured allowed).

Whatever the decision, the same type of materials must be used by all countries throughout the Global Geochemical Reference Network project. The same applies to national stream water geochemical projects.

Important note: The volume of stream water samples needed for analysis should be confirmed with the laboratory before purchasing the bottles. This is an issue that must be examined by the Laboratory Committee.

3.3.3.2. Equipment to be purchased by each participant country

Each participating country must purchase the following equipment, and for all its sampling teams:

- pH-meter (*e.g.*, WTW pH3310 or HACH® HQ11D or comparable)¹.
- EC-meter (*e.g.*, WTW Cond3310 or HACH® HQ14D or comparable).
- Buffer solutions for calibration of pH- and EC-meters, as specified by instrument manufacturers, *i.e.*, pH buffer solution at pH 4, pH 7 and pH 10.
- Class 1 water² at 18.2 MΩ/cm (<5 µg/l TOC), and a washing bottle.
- Class 1 water or sterile water for injection (purchased from pharmacy or drugstore) to be used as a field blank sample (Sterile water for injection is clear, colourless, odourless, sterile, hypotonic, nonpyrogenic, and contains no bacteriostatic or antimicrobial agents).
- Concentrated nitric acid (HNO₃) 65%, density 1.40 kg/l (Merck Suprapur® 100441 or equivalent).
- Teflon dark bottle for storing potassium dichromate solution for the preservation of stream water sample taken for Hg analysis.
- Potassium dichromate solution for Hg preservation. Prepare in the laboratory: 0.2 grams of K₂Cr₂O₇ (Pro analysis, PA, quality) / 100 ml nitric acid HNO₃ (Merck Suprapur® quality).
- Plastic disposable pipettes of 1 ml capacity for acidifying stream water samples with concentrated nitric acid.
- Plastic disposable pipettes of 3 ml capacity for adding acidified potassium dichromate solution to stream water sample bottles for Hg preservation.
- 2 polyethylene decanters of 1 litre capacity for sample water to measure pH and EC.
- Plastic 100 ml measuring cylinder (for alkalinity measurements, methods A and B).
- 250 ml plastic conical flask (for alkalinity measurements, methods A and B).
- Plastic zip-lock bags (10 x 20 cm) for packing used water filters.
- Transparent waterproof adhesive tape for protecting the bottle labels, which are written with the black permanent drawing ink markers.
- Bailer device for water sample collection from deep and fast-flowing streams.
- Lint-free disposable wipes, such as those made by Kimtech (Kimwipe paper) or by Bounty (kitchen paper rolls), both do not leave fuzz or comparable lint-free paper.
- Car refrigerator or battery-powered cool box or cool boxes with ice packs.
- Strong carton or plastic boxes for packing samples for despatch to the laboratory.
- Insulating material boards to line the carton boxes to retain a low temperature until samples reach the laboratory.
- Paper rubbish bags.
- Global Positioning System (GPS) for recording sample site coordinates, or a tablet with a GPS and digital topographical maps, or a mobile telephone with GPS; it is strongly recommended to have a backup GPS receiver.
- Extra batteries for GPS or battery charger with rechargeable batteries.
- Topographical maps, preferred scale 1:50,000 (a must in case electronic digital positioning devices fail, *e.g.*, GPS failure).
- A plastic roamer or map ruler for extracting coordinates from 1:50,000 topographical maps in case GPS fails.
- An orienteering compass (a must in case GPS fails).

¹ It is recommended to search the market and find other products, such as the Oakton PCTSTestr™ 50, which can measure pH/Conductivity/Total Dissolved Solids/Salinity.

² Mercury can be accumulated in distilled water.

- Digital camera or a mobile telephone with a macro facility for field documentation (minimum 5 megapixels).
- Extra batteries for the digital camera.
- 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 or external hard drive) for backup of field data and digital photographs.
- USB cable to download photographs to a laptop computer daily.
- Threshold scintillometer to measure natural radioactivity (Total, Th, U, K); the scintillometer must be calibrated at least once a year before the field campaign at a national facility that is certified.
- Extra batteries for the 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.
- Rope or wading pole as river conditions are not the safest, 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).

If alkalinity is measured using method A (see below), the following equipment is required:

- HACH® Model 16900-01 digital titrator or equivalent with solution delivery straws.
- HACH® digital titration cartridges sulphuric acid 1.6 N.
- HACH® digital titration cartridges sulphuric acid 0.16 N, and
- Bromocresol green acid-base indicator solution to be prepared in the laboratory before starting the field sampling campaign: Accurately weigh 0.1 g of bromocresol green into a brown container flask. Add 14.3 ml of 0.01 M NaOH + 235.7 ml distilled and deionised water and swirl to dissolve (Lide, 1991). **Note:** HACH® provides ready-prepared sachets of bromocresol green, which can be added directly to the stream water sample for titration.

If alkalinity is measured using method B (see below), the following materials are required:

- 1.6 N H₂SO₄: Dilute 44.4 ml of concentrated H₂SO₄ (mass-% = 96; density = 1840 g/l) to 1000 ml with deionised water.
- 0.16 N H₂SO₄: Dilute 10 ml of 1.6 N H₂SO₄ to 100 ml with deionised water.
- Bromocresol green indicator solution: Accurately weigh 0.1 g of bromocresol green into a brown container flask. Add 14.3 ml of 0.01 M NaOH + 235.7 ml distilled and deionised water and swirl to dissolve (Lide, 1991).
- Volumetric flasks of 100 and 1000 ml capacity.
- Burette or equivalent equipment, 10 ml capacity, graduated in divisions of 0.02 ml, and
- Disposable Pasteur-pipettes.

Field observation sheets are included in this manual (see Appendix 1).

3.3.4. Stream water sampling procedure

It would be best if water sampling is carried out by persons who have practical experience in this procedure. Individuals, who are inexperienced in stream water sampling, should be trained for one to two weeks, and closely supervised for at least 10 days after the training programme to ensure that they follow the field sampling procedure, and safety precautions.

Calibration: The pH and electrical conductivity meters must be calibrated, according to the manufacturer's instructions, at the start of each day.

Location of stream water sample: As the stream sediment sample is composited from 5 to 10 subsamples in the field (see Chapter 3.4), the stream water sample should be taken from the first, lowermost stream sediment sampling point.

CAUTIONS:

- ✓ All hand jewellery must be removed.
- ✓ Samplers must not use insect repellent before sampling even when wearing gloves.
- ✓ All tools and containers must be free of contaminants.
- ✓ Note that the samplers are not allowed to smoke, or have the vehicle running when stream water samples are taken.
- ✓ Avoid sampling during rainy periods and flood events.
- ✓ The stream water sample must be taken before the stream sediment sample, for obvious reasons, *i.e.*, during the collection of the stream sediment, fine-grained material is agitated and transported in suspension.

Stream water samples at each sampling site should be taken according to the following procedure:

1. Switch on the GPS unit, or notebook or laptop computer with GPS, to obtain the WGS1984 decimal degree coordinates of the sample site. It is important to switch on the global positioning system upon arrival at the site, and to allow enough time for the signal to settle.
2. Write the sample number on the 60 ml, 100 ml and 500 ml bottles (Fig. 3.3.1); distinguish the stream water samples for determination of mercury (Hg – Fig. 3.3.1b) and dissolved organic carbon (DOC) by writing 'Hg' on 100 ml and 'DOC' on 60 ml sample bottles, respectively. The marked labels should be protected with transparent waterproof adhesive tape.
3. Write sample number on field observations sheet, and coordinates of sample site as recorded by GPS unit.
4. Mark sample site position on the 1:50,000 topographical map. **Note:** Even if you have a notebook with a GPS and digital topographical map, where the position is recorded and saved digitally, it is strongly recommended, as a safety precaution, to mark the sample site position on the paper topographical map.
5. **Important:** Before collecting stream water samples, wear disposable powder-free gloves on both hands (Fig. 3.3.2), and keep them on until all stream water samples are collected and stored safely in a portable refrigerator. One pair of powder-free disposable gloves should be used at each sampling site.

Important caution: Do not touch anything except the stream water sample bottles upon wearing the powder-free disposable gloves. Avoid glove and sample bottle contact with the ground or with human skin or clothing, and avoid breathing directly in the bottle or cap during sample collection.

6. **Unfiltered stream water sample for major IC analysis:** Take a 500 ml sample bottle and rinse it twice with stream water (Figs. 3.3.3a-b), *i.e.*, fill up the bottle with 50 to 100 ml of stream water, close the bottle with a cap and shake it vigorously; remove the cap and decant stream water. Repeat this procedure a second time.
- submerge 500 ml sample bottle completely, with bottle mouth facing upstream. Fill up the bottle up to its brim (*i.e.*, completely full) with stream water so that no air bubbles are left in the bottle (Fig. 3.3.3c). Close the bottle by screwing the cap tightly below stream water level (Fig. 3.3.3d).

Cautions:

- If the stream is too shallow to immerse the bottle fully, submerge it at a low angle with the bottle mouth facing upstream, and with care not to touch the bottom sediment. If the stream is too shallow even for this procedure, then use the disposable syringe to fill up the bottle with stream water.
- If the stream is too deep and fast flowing the water sample can be collected with a bailer device (Fig. 3.3.4).
- This procedure can potentially agitate bottom sediment by stepping on a bank composed of loose material or loose rocks. So, extra care is necessary not to agitate bottom sediments during stream water sampling. It is, therefore, safer to use a bailer device for all occasions (Fig. 3.3.4), as the stream water samples can be collected by standing on the stream bank.

7. **Unfiltered stream water sample for Hg analysis:** Take a marked 100 ml Hg sample bottle and rinse it with stream water twice, *i.e.*, fill up the bottle with 10 to 20 ml of stream water, close the bottle with cap and shake it vigorously; remove cap and decant stream water. Repeat the procedure a second time.
- Fill up the 100 ml Hg sample bottle with stream water to almost its neck and close it by screwing the cap tightly. **Note:** Remember to leave room for the addition of 5 ml acidified potassium dichromate (see Section §3.3.6).
8. **Filtered stream water for ICP-MS and ICP-AES analysis:** Filter one 100 ml stream water sample (Fig. 3.3.5) by using the following procedure:
- Rinse a disposable syringe two times with stream water, and each time dispose of the water either downstream from the sampling point or on land (Figs. 3.3.5a-b).
 - Fill up disposable syringe with stream water (Fig. 3.3.5c).
 - Place 0.45 μm filter on the disposable syringe (Fig. 3.3.5d).
 - Discard the first 10 ml of filtered stream water from each new filter unit used (Fig. 3.3.5e).
 - Take a 100 ml marked sample bottle for the acidified sample and rinse the bottle twice with filtered sample water, *i.e.*, fill up the bottle with 10 to 20 ml of filtered stream water (Fig. 3.3.5f), close the bottle with the cap and shake it vigorously (Fig. 3.3.5g); remove the cap and decant filtered stream water (Fig. 3.3.5h); repeat the procedure a second time.

- Fill up 100 ml bottle up to its neck with filtered stream water (Fig. 3.3.5i; change the filter if needed), and close it tightly with screw cap (Fig. 3.3.5j). Care should be taken for the filtered stream water sample to go straight into the bottle without contact with your hands. **Note:** Remember to leave room for the addition of 1 ml of concentrated ultra-pure nitric acid (see Section §3.3.5).
 - It is recommended to preserve the used filter unit in a labelled zip-lock bag for later analysis of the filter for suspended sediment chemistry. The suffix for used filter units is 'F', for example, N43E09W4F.
9. **Filtered stream water for DOC analysis:** Take 60 ml marked sample bottle for DOC determination and rinse it twice with filtered stream water, *i.e.*, fill up the bottle with 10 to 20 ml of filtered stream water, close the bottle with cap and shake it vigorously; remove cap and decant filtered stream water. Repeat the procedure a second time.
- Fill up the 60 ml DOC bottle up to its brim with filtered stream water (change the filter if needed) and close the bottle tightly with screw cap.
 - Place the filter unit in the same labelled zip-lock bag that the filters of filtered stream water for ICP-MS and ICP-AES analysis are kept.
10. Directly after sampling, the filled stream water sample bottles are placed into a cool box or car refrigerator (Fig. 3.3.6a).
11. In the evening, store all stream water samples in the field camp or hotel refrigerator at a temperature of <math><4^{\circ}\text{C}</math> (Fig. 3.3.6b).
12. **Measurement of pH and Electrical conductivity:** Mark with a permanent drawing ink marker two 1 litre polyethylene decanters, one for pH (write pH) and another for electrical conductivity (write EC). Rinse the two decanters twice with stream water, and then fill them up with stream water. Place the electrodes in water and measure the pH and electrical conductivity with calibrated meters.
- Record the pH (with 1 decimal figure) and EC value (mS/m) on the field observations sheet.
 - Rinse the electrodes and decanters with distilled and deionised water and keep the electrodes in their measuring decanters until all daily sampling sites are visited.
 - At the end of the day, place the meters in their cases.
 - As already cautioned, the pH and Conductivity meters are calibrated every day before the first measurements are taken.
13. **Total alkalinity measurements:** Alkalinity means the ability of water to neutralise acid. It is defined as the quantity of ions, such as CO_3^{2-} , HCO_3^- , OH^- , HSiO_3^- , H_2BO_3^- , HPO_4^{2-} and H_2PO_4^- , in water that will neutralise hydrogen ions. However, in most waters, HCO_3^- is the dominant ion between pH 4.5 and 8.3. The alkalinity is often expressed as milligrams per litre of CaCO_3 . This means that the determined total amount of all ions neutralising acid is transformed to an equivalent concentration of CaCO_3 by calculation. Many digital titrators and standard acid cartridges are already calibrated to read in mg/l CaCO_3 .
- The determination of alkalinity is made by titrating a known amount of stream water with acid (*e.g.*, H_2SO_4 or HCl) to pH 4.5. At this point, all the ions which neutralise acid are used and the colour of the indicator (*e.g.*, phenolphthalein or bromocresol green) will change.
- There are two methods to determine the alkalinity. Follow either method (A) or method (B) in the field.

Method A: Using HACH® digital titrator and standard acid cartridges:

- Select a sulphuric acid cartridge of 1.6 N or 0.16 N, according to the expected alkalinity of stream water samples. This can be judged from the pH and conductivity of the stream water. Specifically, use the 0.16 N cartridge if the conductivity is below 5 mS/m (50 µS/cm), and the 1.6 N cartridge if the conductivity is above this level.
- Fit the cartridge to the hand-held digital titrator and push the titrator piston down until it meets the top of the cartridge.
- Remove the cap from the cartridge and fit a feeder straw into the end of the cartridge.
- Wind up the large wheel of the titrator until all air is removed from the cartridge and the straw, and a drop of acid leaves the end of the straw.
- Wipe the end of the straw to remove excess acid with a lint-free paper towel.
- Reset the titrator scale to zero by winding the small wheel to the left of the scale forwards.
- Rinse the measuring cylinder and conical flask with distilled and deionised water, and directly afterwards rinse them with a small amount of stream water.
- Using the measuring cylinder, measure 100 ml of stream water, and decant it into the conical flask.
- Add a few (two) drops of bromocresol green indicator using a small pipette (or add the content of bromocresol green sachet).
- Add the sulphuric acid using the large wheel on the titrator until the solution changes from blue to green-yellow, and note the reading on the titrator scale when this occurs.
- When the 0.16 N cartridge is used the readings should be multiplied by 0.1.
- The reading is the total alkalinity expressed as mg/l CaCO₃.
- Record the measured alkalinity on the field observations sheet.
- The digital titrator should be reset to zero, and the conical flask and measuring cylinder rinsed with deionised water before leaving the sampling site.
- **Important Note:** Titrations should be carried out as quickly as possible to reduce degassing effects.

Method B: Using normal burette and non-standard acid:

- Transfer 100 ml of stream water to a 250 ml conical flask with a measuring cylinder.
- Add two drops of bromocresol green indicator with a disposable Pasteur-pipette (or add the content of bromocresol green sachet).
- Select a sulphuric acid cartridge either 1.6 N or 0.16 N, according to the expected alkalinity of the stream water sample.
- Mix and titrate immediately.
- Add the H₂SO₄ dropwise from a burette, while continuously stirring the stream water sample.
- The end-point is reached when the colour has changed to yellow.
- Write down the volume of sulphuric acid used on the field observations sheet.
- **Note:** If sample water is very coloured and turbid the end-point is difficult to observe, and in such a case use a pH meter to determine the end-point. Titrate solution as above to pH 4.5.
- After titration, wash the pH meter electrode with distilled and deionised water and calibrate the pH meter.
- If 0.16 N H₂SO₄ is used for titration, the alkalinity of the sample, expressed as milligrams of CaCO₃ per litre, is given by equation (1):

$$\text{Alkalinity (mg/l CaCO}_3\text{)} = 80 * V_{0.16N} \quad (1)$$

where $V_{0.16N}$ = the volume of 0.16 N H_2SO_4 (ml) used in the titration.

- If 1.6 N H_2SO_4 is used for titration, the alkalinity of the sample, expressed as milligrams of CaCO_3 per litre, is given by equation (2):

$$\text{Alkalinity (mg/l CaCO}_3\text{)} = 800 * V_{1.6N} \quad (2)$$

where $V_{1.6N}$ = the volume of 1.6 N H_2SO_4 (ml) used in the titration.

14. Field water blank sample: At every 20th stream water sample (and at least once in every country) the field water blank sample is filtered:

- Filter distilled and deionised water in a 60 ml bottle in the same manner as the normal stream water sample (Sterile water for injection is recommended instead of distilled and deionised water).
- This sample is treated (acidified and handled) like the normal stream water samples.
- The suffix for a filtered field blank water sample is zero (0) and the full identifier is GTN grid cell / W / sample number / 0; *for example*, N43E09W40.

3.3.4.1. Photographs to be taken at each sampling site

At each stream sediment/water sample site at least three digital photographs should be taken (refer to Chapter 3.4, Section §3.4.4.4 and Figs. 3.4.20a-c).

3.3.5. Treatment of stream water samples

- In laboratory or comparable conditions, soon after sampling (at least on the same day) add to a 100 ml filtered stream water sample bottle 1.0 ml of ultrapure concentrated HNO_3 acid with a disposable single-use 1 ml plastic pipette or droplet bottle.
 - Close the bottle tightly and shake it to thoroughly mix the acid with the stream water sample.
 - Mark the top of the bottle cap with a black cross as a clear sign that the sample has been acidified.

Important cautions:

- Use disposable clean powder-free vinyl gloves and wear safety glasses, because the acid is very corrosive.
- Do not let the droplet bottle or the tip of the pipette touch the sample of stream water in the bottle.

- **Do not add acid to the 60 ml DOC stream water sample bottle!**
- Add nitric acid and potassium dichromate to stream water samples in Hg sample bottles. A volume of 5 ml $\text{HNO}_3\text{-K}_2\text{Cr}_2\text{O}_7$ to each 100 ml stream water bottle is added with disposable single-use 3 ml pipettes.
- Close the bottle tightly and shake it thoroughly.

Caution:

- Remember that this solution is extremely aggressive and extra care must be exercised. Safety glasses and clean powder-free vinyl gloves are essential.

3.3.6. Storage and despatch of stream water samples to the laboratory

- As noted above, place the stream water sample bottles in the field camp or hotel refrigerator at a temperature of $<4^{\circ}\text{C}$ (Fig. 3.3.6b).
- All stream water samples should be stored in the dark.
- Packed the stream water samples in strong carton boxes lined with insulating material boards (blue) to retain a low temperature until samples reach the laboratory (Fig. 3.3.7).
- Send stream water samples to the laboratory soon after sampling.

3.3.7. Anticipated problems at remote locations

Treatment of stream water samples with acidification and storage in a refrigerator can be problematic in remote locations. Planning of logistics should try and ensure acidification of water samples and storage in cooled containers to be done as soon as possible after collection. In the worst case, it may be possible to obtain ice cubes at petrol stations or even carry a large bottle of CO_2 and make ice on the spot.

3.3.8. Photographic documentation of stream water sampling procedure



(a)

Figure 3.3.1. Labelling bottles for stream water sampling by writing the sample number on each bottle with a black permanent ink marker, e.g.,

(a) Bottle for ICP-MS and ICP-AES analysis, and

(b) bottle for Hg analysis; similarly, the DOC is marked.



(b)

As the labels with permanent ink may be damaged during transport, it is recommended to be covered by transparent waterproof adhesive tape.

Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)

Figure 3.3.2. Wearing disposable powder-free gloves on both hands before the start of stream water sampling. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(b)



(a)



(b)



(c)



(d)

Figure 3.3.3. Sampling unfiltered stream water sample for major IC ion analysis:

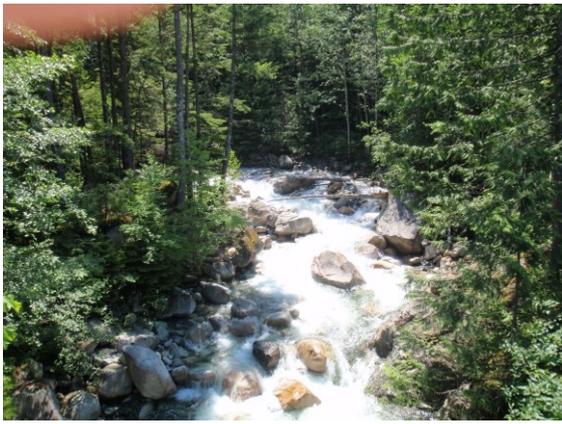
(a) Rinse 500 ml bottle with 50 to 100 ml of stream water, cap it and shake it, and

(b) Decant the stream water downstream of the sampling point; repeat the rinsing procedure a second time.

(c) Submerge a 500 ml sample bottle completely, with its mouth facing upstream, and fill it up to its brim (i.e., completely full) with stream water in such a way that no air bubbles are left in the bottle, and

(d) Close the bottle by screwing the cap tightly below stream water level.

Almost the same procedure is followed by rinsing and filling up with unfiltered stream water the 100 ml bottle for Hg analysis, except that in this case the bottle is filled up to its neck leaving space for the addition of 5 ml $\text{HNO}_3\text{-K}_2\text{Cr}_2\text{O}_7$ stabilising solution. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)



(c)



(d)

Figure 3.3.4. (a) Fast flowing stream, Britannia Creek, British Columbia, Canada. (b-d) Stream water sampling with a bailer by Ray Lett. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)



(c)



(d)

Figure 3.3.5. Continued on next page.



(e)



(f)



(g)



(h)



(i)



(j)

*Figure 3.3.5. Filtering stream water for ICP-MS and ICP-AES analysis (100 ml bottle). Rinse the disposable syringe two times with stream water: (a) Fill up the disposable syringe with stream water, and (b) Eject stream water downstream; repeat the rinsing procedure a second time. (c) Fill up the disposable syringe with stream water and (d) Add 0.45 μm filter. (e) Discard downstream the first 10 ml of filtered stream water from each new filter used; rinse the bottle two times with filtered water by (f) Adding 10 to 20 ml of filtered water in the bottle. (g) Close the bottle with cap and shake it rigorously, and (h) Decanting the filtered water downstream. (i) Fill-up the bottle with filtered stream water, taking care for the filtered stream water to go straight into the bottle without any contact with your hands, and (j) Close the bottle tightly with the screw cap. **Note:** The bottle is filled up to its neck and room is allowed for the addition of 1.0 ml ultrapure nitric acid. Almost the same procedure is used for the collection of the filtered stream water for DOC analysis, but this time the 60 ml bottle is filled up to its brim. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).*



(a)



(b)

Figure 3.3.6. In the field, the stream water samples are stored in (a) A car refrigerator, and in the evening are stored in (b) A refrigerator at a temperature $<4^{\circ}\text{C}$. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.3.7. Samples of stream water are packed in a strong carton box with insulating material boards (blue) in order to retain a low temperature during the transportation of the samples to the laboratory. Note: Addition of dry ice or ice cubes may be necessary, especially under hot environmental conditions. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).

3.3.9. Photographs to be taken at each stream/water sediment sampling site

Refer to Section §3.4.4.4. in Chapter 3.4 ‘Stream Sediment Sampling’ and Figure 3.4.20.

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Note: All hyperlinks were checked on the 19th of February 2022.

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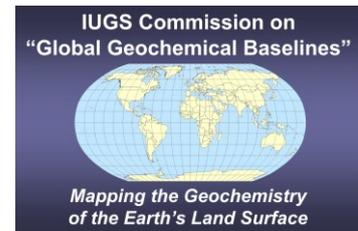
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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 3.4

Stream Sediment Sampling

Fiona Fordyce^{1,9}, Alecos Demetriades^{2,9}, Christopher C. Johnson^{3,9}, Timo Tarvainen^{4,9},
Reijo Salminen⁴, Mikael Eklund⁴, Juan Locutura^{5,9}, Alejandro Bel-Ian^{5,9}, Iván Martín^{5,9},
Ignace Salpeteur⁶, Laura Cecilia Tristán Capetillo^{7,9}, Luis Vargas Rodriguez^{8,9},
César De La Cruz Poma^{8,9}

¹ British Geological Survey Scotland, Edinburgh, United Kingdom

² Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

³ GeoElementary, Derby, United Kingdom

⁴ Geological Survey of Finland, Espoo, Finland

⁵ Instituto Geológico y Minero de España, Madrid, Spain

⁶ Bureau de Recherches Géologiques et Minières, Orléans, France

⁷ Servicio Geológico Mexicano, San Luis Potosi, México

⁸ Instituto Geológico Minero y Metallúrgico, Lima, Perú

⁹ IUGS Commission on Global Geochemical Baselines

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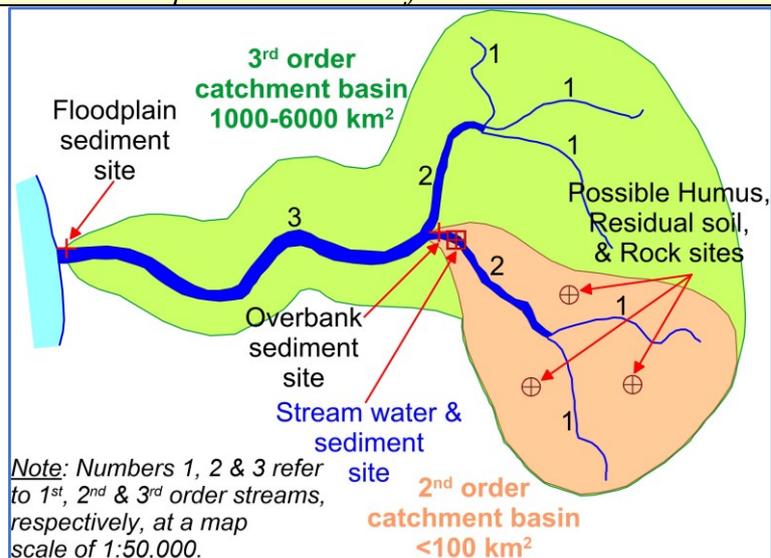
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Stream sediment samples are collected from second-order catchment basins



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3.4.1. Introduction

Active stream sediment is the most widely used sampling medium for regional geochemical surveys worldwide for the delineation of potentially mineralised areas, but also for defining geochemical baseline conditions (*e.g.*, Hawkes and Bloom, 1955; Hawkes, 1957; Hawkes and Webb, 1962; Levinson, 1974, 1980; Plant and Moore, 1979; Rose *et al.*, 1979; Plant *et al.*, 1989; Hale and Plant, 1994; Fletcher, 1997; Key and Pitfield, 2009; Lapworth *et al.*, 2012; Kirwood *et al.*, 2016). Further, it can locate anthropogenically contaminated areas (*e.g.*, Howarth and Thornton, 1983; Appleton and Ridgway, 1993; SedNet, 2004; Mufenda and Ellmies, 2009; Sekabira *et al.*, 2010; Ahmedat *et al.*, 2018; Lin *et al.*, 2019).

The technique involves the sampling of fine- to medium-grained bed load material (sandy-silty-clayey), which is transported by running stream or river water and deposited in an active stream channel. The stream or river may be ephemeral, that is, with water flowing intermittently. The underlying premise is that a stream sediment sample is a composite product of weathering and erosion of geological materials, derived from active erosion points at the time of sampling, occurring upstream from the sample site. Stream sediment is characterised by a variable mineralogical composition, grain size and colour. This variability is a function of geology (some rocks are more easily weathered and, thus, eroded), terrain (erosion rate is higher in mountainous and hilly areas), and climate of the upstream catchment basin from the sample site. Therefore, the chemical and mineral composition of a stream sediment sample commonly reflects, the chemistry and mineralogy of the source catchment basin area, *i.e.*, bedrock lithology, overburden cover (soil, till, aeolian loess), and human influences, such as urban, industrial and agricultural activities. Thus, stream sediment surveys can delineate anomalous areas for mineral exploration, and can be used to assess the environmental status of a catchment basin. Further, the active stream sediment composition is more stable than that of stream water.

Stream sediment samples are normally collected from minor tributaries (first- and second-order streams), according to the Strahler (1964, 1969) stream magnitude classification, which are subject to less complex dilution than the major, third- or higher-order, stream (Fig. 3.4.1). However, in regional geochemical surveys, fill-in sampling from third- or higher-order streams is sometimes carried out to cover segments between confluence points with second-order streams. Sample density varies according to survey objectives. *For example*, national regional stream sediment surveys vary in average sampling density from:

- (a) 1 to 2 samples/km² (Smith *et al.*, 1976; Fauth *et al.*, 1985; Bodis *et al.*, 1999; Salpeteur *et al.*, 1999; Cheng *et al.*, 2014).
- (b) 1 sample/2.5 km² (IGS, 1978; BGS, 1987, 1992, 1996, 1999, 2000; Wilhem and Zeegers, 1984; Barbier, 1996; Johnson *et al.*, 2005; Young and Donald, 2013; Everett *et al.*, 2019).
- (c) 1 sample/3 km² (Webb *et al.*, 1978; Gallagher *et al.*, 2016).
- (d) 1 sample/10 to 15 km² (Leduc and Itard, 2003), and
- (e) 1 sample/40 km² (Locutura *et al.*, 2012).

The average sampling density of continental-scale stream sediment surveys range from:

- (a) 1 sample/120 km² for the location of metallogenic provinces (Garrett and Nichol, 1967; Armour-Brown and Nichol, 1970).
- (b) 1 sample/500 km² (Ridgway *et al.*, 1991), and
- (c) 1 sample/5030 km² in the FOREGS Geochemical Mapping of Europe (Salminen *et al.*, 2005a, b; De Vos, Tarvainen *et al.*, 2006).

The nominal sampling density for the Global Geochemical Reference Network project is 1 sample site/5120 km², *i.e.*, 5 random sampling sites within the 160x160 km GTN grid cell.

In the Global Geochemical Reference Network project, the active stream sediment sample is collected from the second-order catchment basin of <math><100\text{ km}^2</math> at a suitable site above its confluence point with the third-order (larger) stream (Fig. 3.4.1; see also Figs. 2.5 & 2.8 in Chapter 2 of this Manual). The lowermost sampling point should be selected sufficiently upstream of the confluence with the third-order stream to avoid sampling sediment that may result from the mixing of material from two adjacent streams during a flood event.

Important caution: Sampling sites should be located at least 100 m upstream from:

- ***Roads (dirt or asphalted)***
- ***Railway lines***
- ***Bridges***
- ***Industrial sites***
- ***Landfills (waste dumps), and***
- ***Settlements***

to avoid any potential anthropogenic contamination.

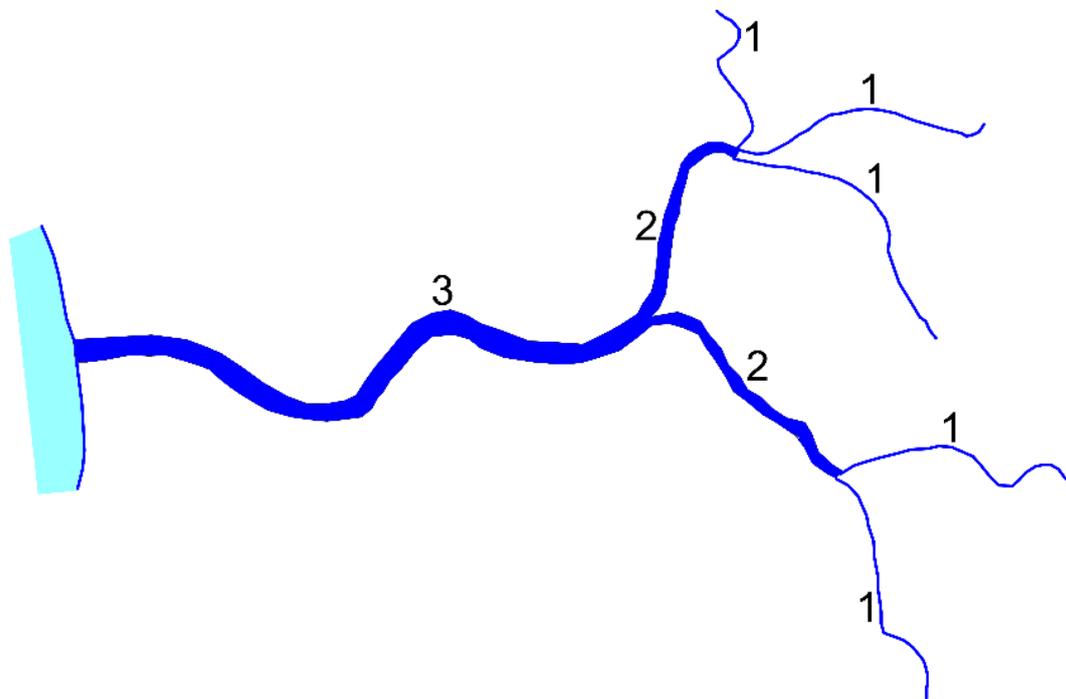


Figure 3.4.1. Strahler stream-order classification is used to define stream size based on a hierarchy of tributary magnitude. At the junction of two 1st order streams, a 2nd order stream is produced, and extends downstream to the point where it joins another second-order stream, whereupon a third-order stream results, and so forth (Strahler, 1969). Plotted by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) & IUGS Commission on Global Geochemical Baselines (IUGS-CGGB). Drawn with Golden Software's MapViewer v8.

In rugged terrain, where collapsed bank material into the stream channel is probable, sediment from as near the centre of the stream as possible is collected to avoid sampling bank-slip material.

For continental-scale geochemical surveys, the stream sediment sample is normally a composite from 5 to 10 sampling points over a stretch of 250 to 500 metres (Salminen, Tarvainen *et al.*, 1998; Salminen *et al.*, 2005a, b). While in regional geochemical surveys the stream sediment sample is usually a composite from 5 to 10 sampling points over a stretch of 50 to 100 metres, depending on sampling density and stream geometry.

Studies into the distribution of trace elements in relation to the grain size fraction of stream sediments generally show that several elements including Mo, Cu, Zn, Mn and Fe are concentrated in the finest sediment fractions (*e.g.*, Horowitz and Elrick, 1987; Ranasinghe *et al.*, 2002; Ali, 2011). Therefore, most stream sediment surveys have been based on the collection of <0.180 mm (<80 mesh) material (Garrett, 2019).

The standard sieve size for the Global Geochemical Reference Network project is <0.150 mm as this is fine enough to include only the very fine sand, silt, clay and colloidal fractions, but is coarse enough to yield enough fine-grained material in most situations. This is a compromised solution, because it is known that in semi-arid environments a slightly coarser fraction (0.250 mm) gives a better contrast between background and anomalies (BGS, 1999; Johnson *et al.*, 2001, 2005). However, many investigations in arid regions have achieved satisfactory results using the fine fractions of stream sediment (*e.g.*, Mazzucchelli, 1994 and references therein).

In arid environments, Salpeteur *et al.* (1999) have demonstrated for regional gold exploration surveys that the finest fraction of stream sediment (<0.063 mm) is more homogeneous and gives the best contrast. However, an analytical method with a low detection limit (0.001 mg Au/kg) is strongly recommended. Similarly, a low sampling density survey (1 sample/10 km²) in tropical and arid terrains is efficient for gold exploration using the same finest grain-size fraction (Leduc and Itard, 2003).

For platinum group element exploration in tropical terrains, the platinum signal is clearly enhanced in the >0.063 to <0.125 mm stream sediment fraction, whereas palladium is enhanced in the <0.063 mm grain size (Salpeteur and Jezequel, 1992).

Studies in the United Kingdom have shown the recovery of stream sediments by dry sieving methods is not quantitative owing to the agglomeration of fine-grained material to form larger particles which are then screened out in varying amounts (Plant and Moore, 1979). Therefore, a system of wet sieving stream sediments wherever possible is recommended. However, in the FOREGS Geochemical Mapping of Europe project (Salminen, Tarvainen *et al.*, 1998; Salminen *et al.*, 2005) dry sieving of completely dried stream sediment was carried out successfully, without any such problems reported.

In the Global Geochemical Reference Network project, which will cover different morphoclimatic terrains there are three variants of composite stream sediment sampling, *i.e.*,

- (i) Wet sieving in the field.
- (ii) Dry sieving in the field, where the stream sediment is completely dry, and
- (iii) Collection of the stream sediment sample without sieving in the field at places where the stream sediment is moist and cannot be sieved in the field. In this case, a large volume of sample is collected (3 to 5 kg) to ensure that, after sieving in the laboratory, there is enough fine-grained material for analysis and storage.

3.4.2. Stream sediment samples to be taken

Active stream sediment samples, representing the bottom load of the small second-order drainage basin (<100 km²) are collected above its confluence point with the main, third-order, river (see Fig. 3.4.1 & Figs. 2.5 & 2.8 in Chapter 2). The following stream sediment samples are taken:

- (a) Routine sample site of a normal GTN grid cell:
 - 2 – 3 kg stream sediment sample
- (b) Duplicate field site of a duplicate GTN grid cell (at least one in each country):
 - 2 – 3 kg stream sediment sample

Enough material must be collected to yield a **minimum of 1 kg of <0.150 mm grain size** stream sediment. Larger sample quantities can be taken and stored separately in each country.

3.4.2.1. Identifier of stream sediment samples

The identifier of the active stream sediment sample is 'S':

(a) Routine sample site (e.g., GTN grid cell N26E14):

- Stream sediment sample: N26E14**S1**

Note: Number '1' represents the 1st sample site in GTN grid cell N26E14.

(b) Duplicate field sample site (e.g., GTN grid cell N27E12):

- Routine stream sediment sample: N27E12**S3**
- Duplicate stream sediment sample: N27E12**S3D**

Note: Number '3' represents the 3rd sample site in GTN grid cell N27E12, and 'D' denotes the field duplicate stream sediment sample.

3.4.3. Equipment for stream sediment sampling

3.4.3.1. Equipment to be provided by the Project Coordinator

The following equipment must be purchased or made centrally, and provided to all sampling teams in each participating country:

- 300x600x0.04 mm strong certified trace-element free Rilsan[®] plastic bags for packing stream sediment samples (such bags are also suitable for organic compounds analysis).
- Plastic strip locks for securing the plastic sample bags (attention: the locks cannot be opened once closed; this is a safety precaution for checking that the samples were not tampered with from the time of sampling until they reach the sample preparation laboratory).
- 6x10 cm white cards for writing the sample number on both sides.
- 7.5x11.5 cm zip-lock plastic bags for holding the 6x10 cm white cards, and
- Black permanent drawing ink markers (ONLY black coloured allowed).

Instead of the strong certified trace-element free plastic bags for packing the stream sediment samples, two other types of bags can be used, and purchased by the coordinator and distributed to all participating countries. These are either:

- 125x250 mm wet-strength Kraft¹ paper bags with a plastic-coated aluminium tin-tie, which can be twisted to seal the bag (this size of Kraft bag allows ease of drying the samples), or

¹ The Kraft paper bags need to be constructed using waterproof glue, otherwise the bags will fall apart when wet.

- 450x750 mm white cotton² bags with nylon cord drawstring.

Whatever the decision, the same type of sample bags must be used throughout the Global Geochemical Reference Network project.

3.4.3.2. Equipment to be purchased by each participant

Each participating country must purchase the following equipment, and for all its sampling teams:

- Sieve set with preferably wooden³ or ABS polymer plastic frame sieve sets with nylon 2.0 mm and 0.150 mm mesh screens (**Note:** It is important to carry in the field extra nylon mesh screens of both sizes to replace damaged screens).
- 5 mm nylon mesh screen mounted on a trace-element free plastic frame for dry sieving of stream sediment samples (**Note:** It is important to carry in the field extra nylon mesh screen for replacement of damaged screen).
- Metal-free circular pan or white plastic bucket.
- Metal-free white or colourless polyethylene or polypropylene scoop.
- Metal-free polyethylene funnel.
- Heavy duty elbow-length rubber gloves.
- Metal-free plastic buckets or containers with lids.
- Wooden stirring rod.
- Stainless steel geological hammer either pointed-tip or chisel-end for dry and semi-dry areas (*e.g.*, Mediterranean, arid and semi-arid climate countries).
- Hard bristle brush for cleaning plastic scoop, and geological hammer.
- Cotton-lint or white cotton rags for cleaning sampling equipment.
- 350x650 mm strong plastic bags for packing sample bags (or Kraft bags or cotton bags), as a safety precaution.
- Plastic strip locks for securing the outside plastic sample bags.
- Plastic or hard carton boxes for packing sample bags in the field, and subsequent transportation to the sample preparation laboratory.
- Strong PVC packing tape.
- 6 mm natural sisal rope.
- Heavy-duty cutter knife with replacement blades.
- Global Positioning System (GPS) for recording sample site coordinates, or a tablet with a GPS and digital topographical maps, or a mobile telephone with GPS; it is strongly recommended to have a backup GPS receiver.
- Extra batteries for GPS or battery charger with rechargeable batteries.
- Topographical maps, preferred scale 1:50,000 (a must in case electronic digital devices fail, *e.g.*, GPS).
- A plastic roamer or map ruler for extracting coordinates from 1:50,000 topographical maps in case GPS fails.
- An orienteering compass (a must in case GPS fails).
- 10x magnifying lens (loupe).

² It is known that some cotton bag manufacturers impregnate the cotton cloth with some chemicals. As the chemicals are never mentioned, and the soil samples must not be contaminated with unknown chemicals, it is important to ensure that the white cotton bags are not impregnated with any chemicals.

³ Wooden and ABS polymer plastic sieve frames can be made to order by the Makers company (<https://www.makers.uk.com/>).

- Digital camera or a mobile telephone with a macro facility for field documentation (minimum 5 megapixels).
- Extra batteries for the digital camera.
- 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 or external hard drive) for backup of field data and digital photographs.
- USB cable to download photographs to a laptop computer daily.
- Threshold scintillometer to measure natural radioactivity (Total, Th, U, K); the scintillometer must be calibrated at least once a year before the field campaign at a national facility that is certified.
- Extra batteries for the threshold scintillometer.
- Field observations sheets.
- Waterproof case to hold field observation sheets.
- Writing pens.
- HB pencils, pencil sharpener and rubber (back-up in case the pens fail to write in the field).
- First-aid kit.
- Rope or wading pole as river conditions are not the safest, 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).

3.4.4. Stream sediment sampling procedure

3.4.4.1. Sample site selection

During the pre-survey preparation, the second-order small drainage basin (<100 km²) is selected from the 1:50,000 scale topographical and geological maps (refer to Section §2.5 in Chapter 2 of this Manual). However, the exact position of the sampling site is determined in the field, after a careful study of a suitable 250 to 500 m stream stretch, where there are no obvious signs of contamination, and a suitable fine-grained stream sediment sample can be collected from 5 to 10 different locations according to the following criteria:

- The selected lowermost stream sediment sampling site on the second-order stream must be well above its confluence point with the third-order river or trunk river. The reason for this is to avoid sampling sediment that may result from the mixing of material from two adjacent streams during a flood event. It is noted that the lowermost location is the site from where the stream water sample is collected.
- Sampling sites should be located at least 100 m upstream from asphalted roads (particularly major roads), dirt roads, railway lines, bridges, settlements, landfills and industrial sites to avoid any potential anthropogenic contamination.
- Avoid locally atypical sites.
- The field composite stream sediment sample should not be made from aliquots taken from stream beds of a different nature (ISO 5667-12: 1995), *i.e.*, “*The individual portions may be derived from the same stratum or at the same sediment thickness*”.

- It is important to ensure that the stream sediment is transported active sediment, and not collapsed material from the nearby banks. The latter can happen in steeply incised stream valleys, but it does occur in other situations too, especially in narrow mountain valleys.
- **Difficult cases:** In semi-dry and dry terrains, due to prolonged periods of drought, the second-order streams may not have had running water and, hence, no new active stream sediment. In such cases, the stream bed may be covered by falling bank material, wind-blown sediment and vegetation. The recommendation is to find an alternative second-order stream valley for sampling. However, if similar conditions are found in the alternative valleys, then the only practical solution is to dig pits at the centre of the stream valley until the last deposited active stream sediment is reached. These difficult cases, require an experienced applied geochemist who will be able to recognise the active stream sediment deposited by the last flash flood. In cases where the dry stream bed is not covered by falling material and vegetation, the best stream sediment sample should be taken from the upper stratified clayey crust, which is often enriched in heavy mineral patches corresponding to the sediment deposited by the last flash flood event. This clayey layer may be partially covered by aeolian sand (Sabir and Salpeteur, 1992), which must be removed before collecting the stream sediment sample.

3.4.4.2. Sampling procedure

It is important to avoid metal contamination at every stage of sampling by taking the following precautions:

- No hand jewellery or medical dressings should be worn during sampling. If medical dressings are worn, heavy-duty rubber gloves must be worn at all times to avoid contamination of the samples.
- Metal-free polyethylene scoops, funnels and buckets/containers must be used.
- Metal-free nylon sieve-mesh housed in inert wooden, or metal-free plastic frames must be used.

Note: If it is not possible to use non-metal equipment (sieve frames, scoops), unpainted steel or stainless steel equipment should be used, and in such cases, they must be reported. Aluminium and brass equipment must be avoided.

At each stream sediment sample site:

- Switch on the GPS, or notebook or laptop computer with GPS, to obtain the WGS1984 decimal degree coordinates of the sample site. It is important to switch on the global positioning system upon arrival at the site, and to allow enough time for the signal to settle (**Note:** This is the same site as that of the stream water sampling site in the cases of streams with running water).
- Write the number of the stream sediment sample with a black permanent ink marker on the Kraft (Fig. 3.4.2a) or strong certified trace-element free Rilsan[®] plastic bag (Fig. 3.4.2b) or a cotton bag.
- Write the number of the stream sediment sample on both sides of the small card, and place the card in the small zip-lock bag and seal it (Fig. 3.4.2c).

- Mark the exact location of the first and last sampling points on the paper or digital 1:50,000 topographical map by means of a small line perpendicular to the stream flow using an ink pen or portable field computer.
- Record the general observations on the field observations sheet (Fig. 3.4.3; refer to Appendix 1 for Field Observations Sheet). Any additional observations are recorded at the end of sampling.

3.4.4.2.1. Collection of stream sediment from streams with running water

Rubber gloves are recommended for protection throughout wet- and dry-sieving of stream sediment samples.

Remember that the stream water sample is collected first (see Section §3.3.4 in Chapter 3.3), and directly afterwards the equipment for collecting stream sediment by wet-sieving is prepared:

- Wash all stream sediment sampling equipment (buckets, sieves, collection pans, funnel, gloves and spade) with stream water (Fig. 3.4.4).
- Set up the circular collection pan or collection bucket in a stable position (Fig. 3.4.5). Since transported material is collected from 5 to 10 points over a distance of 250 to 500 m, it is recommended that the sieving site is located at the half-way point.
- Place the sieve with the 0.150 mm aperture nylon cloth in a stable position resting on the collection pan or bucket.
- Place the sieve with the 2 mm aperture nylon cloth over the 0.150 mm sieve.
- The sieve frames must fit closely over the collection pan or bucket to avoid loss of material over the edge of the pan/bucket.
- At each sampling location, remove and scrape off surface stones and the top 10 centimetres of oxidised sediment, if such sediment occurs, to reveal unoxidised sediment below.
- Load equal amounts of coarse active unoxidised sediment from 5 to 10 points on the stream into plastic buckets taking care to drain off excess water (Fig. 3.4.6).
- Avoid collecting stream sediment samples enriched in black sand.
- Enough coarse-grained material should be collected to yield a minimum of 1 kg of <0.150 mm material (dry weight).

The amount of coarse-grained material required will vary substantially depending on the underlying geology and terrain. Applied geochemists should use their knowledge and judgement to assess how much coarse-grained material will be required. Ideally, the percentage of coarse- and fine-grained fractions will have been investigated by a pre-survey orientation.

In rugged terrain, where the collapse of bank material into the channel is common, sediment from as near the centre of the stream as possible should be collected to avoid sampling bank-slip material.

In areas of low relief, active stream sediment in the centre of channels may be enriched in quartz and depleted in clays and other fine-grained particles. In these instances, material deposited along stream margins during flood events may be finer-grained and more suitable for geochemical sampling.

The wet-sieving sampling procedure is described below:

- Mix the buckets of the coarse sediment thoroughly with a wooden or plastic stirring rod (Fig. 3.4.7).
- Load sediment into the top sieve with the scoop or spade (Fig. 3.4.8). If more than one bucket of coarse-grained sediment has been collected, equal amounts of sediment should be loaded into the sieve from each bucket in turn.

- Rub the material through the top sieve wearing rubber gloves for protection (Fig. 3.4.9).
- Take care to remove large stones from the sediment by hand.
- Once the bottom sieve contains a reasonable quantity of <2 mm sediment, remove the top sieve and discard the >2 mm material (Fig. 3.4.10).
- The <2 mm sediment in the bottom sieve is washed and rubbed through the sieve with the aid of water and shaken down (Fig. 3.4.11).
- It is particularly important at this stage that coarse-grained material, which would bias the sample, does not enter the collection pan/bucket. This may be avoided by carefully washing the outside of the bottom sieve prior to shaking.
- To enhance the trace element signature, it is important that all the <0.150 mm material is collected. Therefore, a minimum amount of water should be used to wash the sediment through the bottom sieve and all washing water should be retained in the collection pan/bucket until the sample is allowed to settle.
- The stream sediment sample in the sieve should be repeatedly washed and shaken down until all the fine-grained material has passed through the sieve.
- The whole sieving process should be repeated until the pan/bucket contains sufficient fine-grained wet sediment to yield at least 1 kg of dry weight material.
- The <0.150 mm sediment is collected in a circular collection pan (Fig. 3.4.12).
- The <0.150 mm sediment is transferred to a collection bucket (Fig. 3.4.13). Ideally, the bucket should have a lid as it should be covered during the settling of the sediment.
- Once enough wet sediment has been collected, secure the lid on the bucket. The sediment should be allowed to stand for at least 45 minutes or until all the suspended material has settled and clear water sits on top of the sediment (Fig. 3.4.14). *Whilst waiting for the <0.150 mm sediment to settle, the overbank sediment, residual soil and rock samples can be collected, thus, giving the necessary time for fine-grained sediment to settle in the bucket.*
- Once the suspended material has settled, excess water on the surface of the sediment should be carefully decanted (Fig. 3.4.15). Care should be taken to remove only water and not the fine-grained sediment at this stage.
- The remaining sediment should be thoroughly homogenised and mixed using the wooden or plastic stirring rod or plastic scoop before being transferred into sample bags (Fig. 3.4.16a).
- Once the sample has been homogenised, carefully transfer the <0.150 mm stream sediment sample into the strong certified trace-element free plastic bag or cotton bag or in this case Kraft bag (Fig. 3.4.16b).
- Before sealing the strong certified trace-element free plastic or Kraft bag, place the numbered small card in the zip-lock bag (Fig. 3.4.2c) on top of the stream sediment sample.
- Twist the top of the strong certified trace-element free plastic bag, and seal it securely with a plastic strip lock; in this case, the Kraft bag is sealed (Fig. 3.4.17a).
- The strong certified trace-element free plastic bag (or Kraft or cotton bag) is placed in a polyethylene bag and is secured with a plastic strip lock (Fig. 3.4.17b). This is a safety precaution to protect the sample bag and to prevent loss or cross-contamination of samples during transportation.
- The number of bags for each sample site should be recorded on the field observations sheet and a sample checklist sheet. **Note:** If more than one bag is used for storing the collected sample, for each one a small card in a zip-lock bag should be placed on top of each stream sediment in the sample bag.

- The samples should be secured upright in a plastic crate or hard carton box and transported carefully to the next location or the survey field base.
- Measure the natural radioactivity at the first sampling location with a threshold scintillometer, which is held at knee height (Fig. 3.4.18); record the measurements of Total, Th, U and K on the field observations sheet.
- **IMPORTANT:** All sampling equipment must be thoroughly washed and cleaned before moving to the next site to avoid cross-contamination (Fig. 3.4.19). Of course, all sampling equipment is thoroughly washed at the next stream water sampling site too.
- **Photographic documentation of sample site conditions:** Take at least three digital photographs:
 - (i) The sample number (Fig. 3.4.20a).
 - (ii) Landscape photograph upstream from the sample site (Fig. 3.4.20b), and
 - (iii) Site photograph with natural light showing, if possible, the nature of the stream bed (Fig. 3.4.20c).

Additional photographs can be taken to show the *in-situ* textural characteristics of the stream sediment sample provided, of course, the site conditions are favourable.

Labelling photographs: The landscape photograph bears the sample site number with the suffix 'L', and the site photograph is assigned the sample site number with the suffix 'W', e.g., N27E12W1L and N27E12W1S, respectively, as in this case the stream water sample identification code is given (refer to Fig. 3.2 in Chapter 3).

IMPORTANT: As a safety precaution, always photograph first the stream water/sediment sample number, and last the bagged sample with the sample number.

- Record the digital photograph numbers on the field observations sheet.

Duplicate field samples: Field duplicate stream sediment samples are collected randomly at least at every 20th sampling site (*i.e.*, ≈5% duplication of the sample sites) in each country. However, countries with less than 20 GTN grid cells should collect field duplicate stream sediment samples from at least one random site. The starting point of the field duplicate sample should be at a distance of 5 to 50 metres away from the routine sampling site following the same procedure as for collecting the routine stream sediment samples.

3.4.4.2.2. Collection of stream sediment from dry streams

This is a special condition where water is not available to sieve the stream sediment on-site to the required grain size of <0.150 mm. There are two cases, *i.e.*,

- a) Dry stream with moist stream sediment, which cannot be sieved on-site, and
- b) Completely dry stream sediment bed, where the sediment can be sieved on-site.

In both cases, the procedure for the selection of sampling sites, recording their location on the field paper or digital 1:50,000 topographical map, completion of field observation sheets, wearing of rubber gloves, packing of stream sediment samples, *etc.* are the same as for the wet-sieving sampling method (refer to Section §3.4.4.2.1).

Sampling of moist stream sediment: When the stream sediment is moist (Fig. 3.4.21), a bulk composite sample from 5 to 10 points over a distance of 250 to 500 metres is collected. The total dry weight of the composite stream sediment sample (free of stones and other coarse-grained material) should be about 5 kg to ensure that the required amount of 1000 grams of analytical <0.150 mm material will be obtained after sieving at the sample preparation laboratory.

Collect material of finer grain size (or, if possible, scrape off the top thin layer of stream sediment, provided is unoxidised, otherwise collect unoxidised stream sediment below the

surface layer on the sand bar) from the centre of the stream. Care should be taken to sample stream sediment with as little as possible organic matter, and to avoid the reduced material (mostly dark grey colour and bad-smelling), which occurs at greater depths. Also, in the case of narrow channels take extra care not to collect material that has fallen from the banks.

Removal of stones and other coarse-grained material is achieved by sieving through a 5 mm nylon screen, and collecting the material in a plastic bowl. Collect equal amounts of material from the 5-10 subsites. The use of the 2 mm nylon sieve is not recommended for dry sieving, because it is too small for clay agglomerates and slightly moist samples.

Sampling of stream sediment from streams that had no running water for many years: This is an extremely special case of sampling seasonal second-order streams in Mediterranean countries, arid and semi-arid terrains. Some seasonal streams have had no water flow for many years, and the stream bed may be covered by fallen bank material in which grass or other plants may have grown. Sampling of such streams must be carried out with utmost care. Since active stream sediment must be sampled, the fallen bank material, covering the 'old' active stream sediment, must be removed by digging before taking the sample at each subsite. The pits should be dug up near the centre of the channel. As in most cases, the dug-up stream sediment is moist, the procedure of collection of moist samples is followed. If the stream sediment is completely dry, the procedure for the collection of dry samples is followed.

Sampling completely dry stream sediment: Since the stream sediment is completely dry (Figs. 3.4.22 & 3.4.23) it can be dry-sieved on-site to the required <0.150 mm grain size, using exactly the same procedure as in wet-sieving (see Section §3.4.4.2.1; Fig. 3.4.24). The only care that must be taken is to break up any clay agglomerates during sampling.

3.4.4.3. Photographic documentation of stream sediment sampling procedure

The following set of photographs shows the sampling procedure for stream sediment.



Figure 3.4.2. Write stream sediment sample number with a black permanent ink marker on either (a) Wet strength Kraft paper bag (12.5x25 cm) with a plastic-coated aluminium tin tie for sealing bag, or (b) Strong certified trace-element free plastic bag (300x600 mm) that is secured with a plastic strip lock, and (c) Write sample number on both sides of a small card (6x10 cm), and place card in a small plastic zip-lock bag (7.5x11.5 cm) and seal it. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.4.3. Recording the observations on the stream sediment field observations sheet. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)



(c)



(d)

Figure 3.4.4. Washing of stream sediment sampling equipment with stream water (a) Bucket. (b) Sieve. (c) Pan, and (d) Scoop. Of course, all the other equipment is washed. **IMPORTANT:** Although no gloves are worn in these photographs, it is strongly recommended to wear gloves. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.4.5. Setting up the circular collection pan, the 0.150 and 2 mm sieve on a stable position; the collection pan is below the bottom sieve⁴. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.4.6. Collecting aliquots of active stream sediment from different points and placing them in a bucket⁴. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

⁴ IMPORTANT: Although no gloves are worn in the photographs by the sampler, it is strongly recommended to wear gloves as a safety precaution.



Figure 3.4.7. Mix the stream sediment by stirring with a wooden rod⁵. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.4.8. Loading sediment into the top 2 mm sieve⁵. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.4.9. Rubbing sediment through the top 2 mm sieve⁵. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).

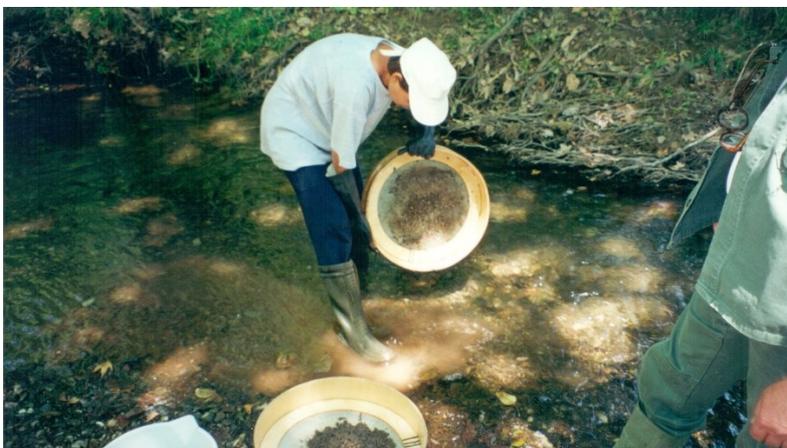


Figure 3.4.10. Discarding coarse-grained stream sediment (>2 mm) from the top sieve, and afterwards washing it with stream water. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).

⁵ IMPORTANT: Although no gloves are worn in the photographs by one of the samplers, it is strongly recommended that both samplers wear gloves as a safety precaution.



Figure 3.4.11. Rubbing <2 mm stream sediment through the 0.150 mm sieve using a minimum amount of water⁶. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.4.12. Collection of <0.150 mm stream sediment in circular pan. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.4.13. Fine-grained <0.150 mm stream sediment is transferred to the collection bucket⁶. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).

⁶ IMPORTANT: Although no gloves are worn in the photographs by one of the samplers, it is strongly recommended that both samplers wear gloves as a safety precaution.



*Figure 3.4.14. Fine-grained sediment has settled at the bottom of the bucket. It is recommended that during the settling of sediment the bucket is covered by a cover.
Photograph: Alecos Demetriades (IGME/IUGS-CGGB).*



*Figure 3.4.15. Decanting very slowly excess water⁷. In this case, more time should have been allowed for the sediment to settle. Hence, the reason for suggesting to collect first the stream water and then the stream sediment sample. Whilst the stream sediment is settling in the bucket to collect the rock, residual soil and overbank sediment samples.
Photograph: Alecos Demetriades (IGME/IUGS-CGGB).*



(a)



(b)

Figure 3.4.16. After thorough homogenisation (a) Successive scoops of the <math><0.150\text{ mm}</math> stream sediment are taken, and are (b) Placed in the Kraft bag⁷. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

⁷ IMPORTANT: Although no gloves are worn in the photographs, it is strongly recommended that both samplers wear gloves as a safety precaution.



(a)



(b)

Figure 3.4.17. (a) Closing of Kraft bag containing the <0.150 mm stream sediment (it is noted that before closing the bag the little zip-lock bag with the sample number is placed on top of the sample), and (b) Placing the Kraft bag in a polyethylene bag for protection during transportation and closing it. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.4.18. Taking radiometric measurements with a scintillometer at knee height. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.4.19. Washing thoroughly with water all the stream sediment sampling equipment. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

3.4.4.4. Photographs to be taken at each stream water/sediment sampling site

For the photographic documentation of the stream water/sediment sampling site, the first photograph uses the identification code of the stream water (W) sample (Fig. 3.4.20a), because this is collected first.

Take at least three digital photographs in the following order: (i) sample number (Fig. 3.4.20a); (ii) landscape photograph upstream from the sample site (Fig. 3.4.20b), and (iii) site photograph with natural light showing, if possible, the nature of the stream bed (Fig. 3.4.20c). Additional photographs can be taken to show other features of the stream valley.



(a)



(b)



(c)

Figure 3.4.20. Photographic documentation of stream sediment sampling site: (a) Sample number (remember the identification code of the stream water sample is used). (b) Landscape photograph N27E12W1L (21.62°E, 39.96°N), and (c) Close-up of bedload material (N27E12W1S), FOREGS Geochemical Atlas of Europe, Hellas. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

3.4.4.5. Photographs of stream sediment in dry streams

3.4.4.5.1. Photograph of moist stream sediment



Figure 3.4.21. Moist stream sediment, N25E13W2S (22.43°E, 37.09°N), FOREGS Geochemical Atlas of Europe, Hellas. As it is not possible to sieve in-situ the stream sediment, enough moist stream sediment should be collected to yield at least 1000 grams of <0.150 mm dry stream sediment. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).

3.4.4.5.2. Photographs of stream sediment in arid and semi-arid terrains



Figure 3.4.22. Dry stream beds with completely dry stream sediment in a mountainous terrain, Atacama desert, El Salvador map sheet, Chile. Photographs: Francisca Espinoza, Servicio Nacional de Geología y Minería, Chile.



Figure 3.4.23. Dry stream beds with completely dry stream sediment in a semi-arid terrain, Gocheganas Nature Reserve (17.214°E, 22.812°S), Namibia. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

3.4.4.5.3. Photograph of dry stream sediment sampling



Figure 3.4.24. Dry sieving of completely dry stream sediment, N26E14S4, Lavreotiki peninsula, Hellas (24.00°E, 37.68°N), FOREGS Geochemical Atlas of Europe. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).

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Note: All hyperlinks were checked on the 19th of February 2022.

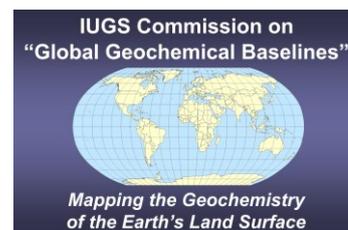
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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

**Chapter 3.5
Overbank and Floodplain Sediment Sampling**

Alecos Demetriades^{1,8}, Rolf Tore Ottesen², Jim Bogen³, Ignace Salpeteur⁴, Iván Martín^{5,8},
Juan Locutura^{5,8}, Alejandro Bel-Ian^{5,8}, Xueqiu Wang^{6,8}, Juan Pablo Lacassie Reyes^{7,8},
Felipe Astudillo^{7,8}, Pablo Sebastian Oliva Vicentelo^{7,8}

¹ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

² Geological Survey of Norway, Trondheim, Norway

³ Norwegian Water Resources and Energy Directorate, Oslo, Norway

⁴ Bureau de Recherches Géologiques et Minières, Orléans, France

⁵ Instituto Geológico y Minero de España, Madrid, Spain

⁶ UNESCO International Centre on Global-Scale Geochemistry, Langfang, Hebei, P.R. China

⁷ Servicio Nacional de Geología y Minería, Valdivia, Chile

⁸ IUGS Commission on Global Geochemical Baselines

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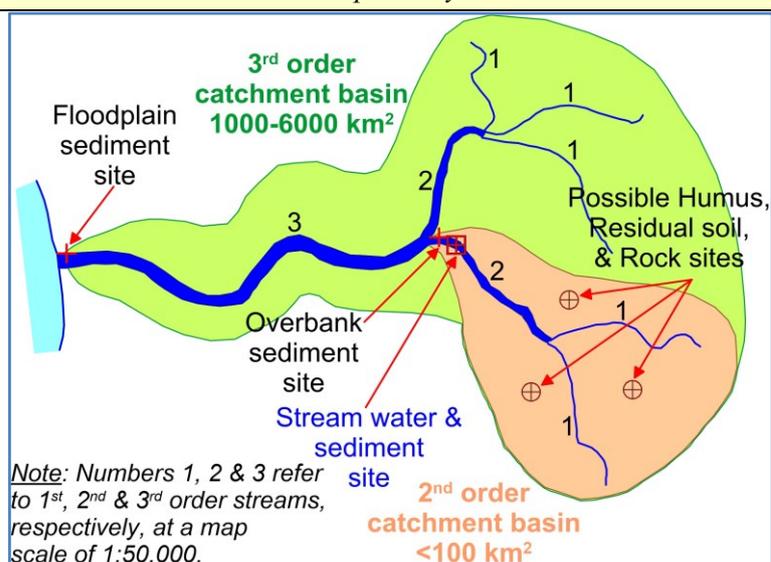
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Overbank and Floodplain sediment samples are collected from second- and third-order catchment basins, respectively



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3.5.1. Introduction

Both overbank and floodplain sediments are fine-grained alluvial sediments (fine sand, silt, silty-clay, clayey-silt, clay) deposited during flood events. The distinction made by Darnley *et al.* (1995) between overbank and floodplain sediments is completely arbitrary. However, in the context of the Global Geochemical Reference Network project, this distinction serves in the differentiation of the samples collected from small and large floodplains, namely:

- *Overbank sediment* is the fine-grained sediment (alluvium) deposited on the floodplain of small streams (second-order catchment basins of <100 km² in area), which are tributaries to a larger river (Figs. 2.5 & 2.8 in Chapter 2, and Fig. 3.4.1 in Chapter 3.4), and
- *Floodplain sediment* is the fine-grained sediment (alluvium) deposited on the floodplain of large rivers (third- or higher-order catchment basins of 1000 to 6000 km² in area), which usually have their outlet to the sea or a lake (Figs. 2.5 & 2.8 in Chapter 2 and Fig. 3.4.1 in Chapter 3.4).

Overbank and floodplain sediments are also called ‘*vertical accretion deposits*’ by geomorphologists, physical geographers and physical geologists (Morisawa, 1968; Neuendorf *et al.*, 2011).

Another term that is considered synonymous with overbank/floodplain sediments is ‘*natural levee sediments*’ (Holmes, 1965; Morisawa, 1968; Strahler, 1969; Press and Siever, 2002), which characterise many meandering rivers. Natural levees are elongate ridges on either side of the river channel (Figs. 3.5.1 & 3.5.2), formed by successive flood events, as floodwater loses much of its velocity and transport capacity and is forced to deposit first the coarsest part of its load (gravel and coarse-grained sand) at the margin of the channel, as it spills over its bank, and secondly the settling of fine-grained suspended material (fine-grained sand and clay) from tranquil water at distal parts of the floodplain, but also near and over its banks as the water recedes.

Soil scientists or pedologists called them ‘*alluvial soil*’, because of their texture and use in agriculture. However, they should not be classified as ‘soil’ as in most climatic zones, soil formation processes may need hundreds of years to develop significant vertical patterns akin to normal undisturbed soil. For overbank and floodplain sediments, the available time interval is normally more restricted, as with every flooding incident new layers of sediment are deposited on top of the older ones. Hence, in the case of this manual, ‘*alluvial soil*’ is a term that should not be used as synonymous with overbank and floodplain sediments.

Since Ottesen *et al.* (1989) advocated that overbank sediments could be a potentially more representative sample type than active stream sediments of the upstream drainage basin geochemistry, considerable research was carried out from 1989 to 1992 by the Regional Geochemistry Working Group of the Western European Geological Surveys¹ to verify their usefulness in continental- and regional-scale geochemical surveys (*e.g.*, Bølviken *et al.*, 1990, 1993, 1996, 2004; Demetriades *et al.*, 1990, 1993, 1994, 2018; Bogen *et al.*, 1992; Swennen *et al.*, 1994, 1998, 2000; Ridgway *et al.*, 1995; De Vos *et al.*, 1996; Hindel *et al.*, 1996; Demetriades and Volden, 1997; Pulkkinen and Rissanen, 1997; Van der Sluys *et al.*, 1997; Volden *et al.*, 1997; Swennen and Van Der Sluys, 1998; Salpeteur *et al.*, 1999, 2000, 2001; Ottesen *et al.*, 2000, 2010; Bogen and Ottesen, 2008; Demetriades, 2008, 2014; Salpeteur and Maldan, 2011).

Working Group members also supervised research work in Norway (Langedal, 1996, 1997a, 1997b, 1997c; Langedal and Ottesen, 1998), and Spain (Adánez, 2012; Adánez *et al.*, 2009, 2018; Adánez Sanjuán *et al.*, 2014a, b, 2016, 2018).

¹ Succeeded to begin with by the Geochemistry Task Group, then the Geochemistry Task Force and Geochemistry Working Group of the Forum of European Geological Surveys (FOREGS), and presently the Geochemistry Expert Group of EuroGeoSurveys.

Moreover, the use of overbank sediments in geochemical mapping was addressed in several publications during the last three decades (*e.g.*, McConnell *et al.*, 1993; Edén and Björklund, 1994, 1996; Macklin *et al.*, 1994; Shen and Yan, 1995; Cheng *et al.*, 1997; Matschullat *et al.*, 1997; Xie *et al.*, 1997; Xie and Cheng, 1997, 2001; Peh and Miko, 2001; Xie and Yao, 2010; Belyaev *et al.*, 2011).

The reason that overbank and floodplain sediments are considered to be more representative than active stream sediments of the upstream drainage basin geochemistry is that during flood events, the heavy rainfall resulting in a large quantity of water falling in the drainage basin increases the erosion capacity of a stream or river, thus activating many sediment sources in the drainage area. Overbank and floodplain sediments, deposited from successive flood events, provide material from various sediment sources that have been active at different times. Thus, representing a larger part of the drainage basin, and the material in suspension, deposited in layers, may reflect the composition of these and earlier developed sources.

It is again stressed that the mode of formation of both overbank and floodplain sediments is the same, and as the sampling procedure is the same, it is described in this Chapter, following the description of their mode of formation and other characteristics.

3.5.1.1. Formation and nature of overbank and floodplain sediments

Overbank and floodplain sediments occur along streams or rivers with variable water discharge. In flooded streams or rivers, the temporarily enhanced discharge may exceed the amount of water that can be contained within the normal channel (Fig. 3.5.1). The material in suspension is transported onto levees and floodplains, where it is laid down and accumulated, especially during the latest phases of flooding by the slowly receding water under tranquil conditions (low energy environment; Fig. 3.5.1b). Figure 3.5.2 shows the hydraulic sorting of overbank sediments in a large river like the Mississippi in the United States of America.

Since floods are recurring events in the geomorphological history of a drainage basin, a succession of almost horizontal layers is built up (Fig. 3.5.3). Overbank and floodplain deposits, therefore, consist of successive nearly horizontal layers of younger sediments overlying older ones. A vertical section through such a deposit may reflect the history of sedimentation through time to pre-industrial natural (pristine) conditions (Figs. 3.5.3 & 3.5.4). In several countries of central-north Europe, the lower section of floodplain sediment may be coarser and contains a large amount of loessic material (0.002-0.050 mm) inherited from the last deglaciation (Würm). Dating of these lower layers has shown a time span of 8000-6500 BC, corresponding to the boundary between the upper Pleistocene and lower Holocene (Hindel *et al.*, 1996).

Due to channel shifting and flow variation upstream, in addition to the fine-grained (silty-clay, clayey-silt) overbank and floodplain sediment layers, there may occur in the vertical section gravelly and sandy layers, representing the bed load of the channel of high- to medium-energy environments, respectively (Fig. 3.5.3b).

In most cases, deposits of overbank and floodplain sediments contain mainly natural material throughout. However, in some situations, anthropogenic material may have contaminated the most recent layers. Human-induced contamination of overbank and floodplain sediments may be of two types:

- (1) Mine waste and other anthropogenic material may enter the stream or river from local sources and then fluvially transported downstream (Fig. 3.5.4), and
- (2) Airborne contaminants originating from distant sources may reach the catchments.

Situation (1) is often recognisable since the sources may be easily identified, but the situation (2) can be more difficult to detect (Langedal and Ottesen, 1998). Although floodplain sediments occurring in estuaries may have a marine influence, a study of a core down to 13 m depth in alluvial sediments from the estuary of the Odiel River near Huelva (Spain) provided a good example of the use of overbank sediment to record the history of mining activity in the upstream

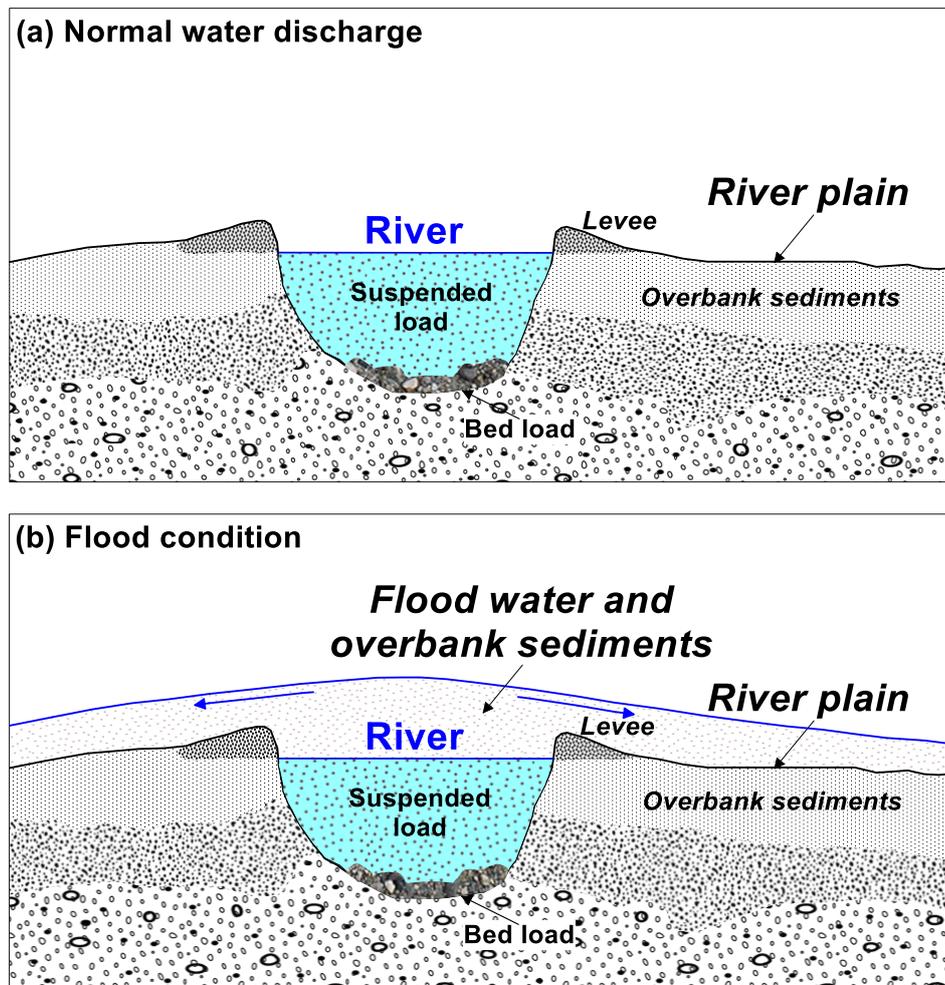


Figure 3.5.1. Schematic diagrams showing river water discharges during (a) Ordinary conditions with a normal amount of water, and (b) Major flooding with suspended overbank sediment (Source: modified from Ottesen *et al.* (1989, Figs. 6 and 7 on p.262 and 263, respectively) by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) & IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).

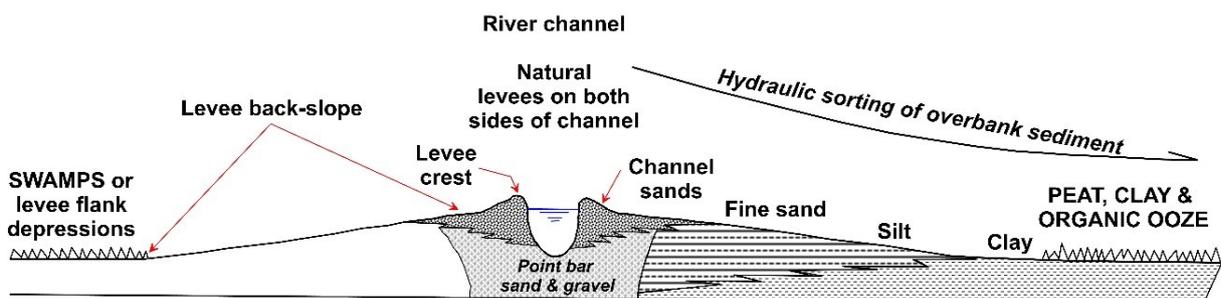


Figure 3.5.2. Schematic cross-section illustrating hydraulic sorting of overbank sediments with increasing distance from Mississippi River in the vicinity of Carrollton, New Orleans, Louisiana, United States of America. Levee back-slope zone lies between elevated levees and poorly drained swamps (Source: redrawn from Rogers (2008, Fig. 3, p.604) by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8.

basin (Rio Tinto district) going back to the Roman period (Leblanc *et al.*, 2000). Similar studies on the Rio Tinto River estuarine floodplain sediments (Borrego *et al.*, 2004), and terrace deposits (Cáceres *et al.*, 2013), verify the power of overbank sediments to depict the palaeo-geochemistry of the upstream catchment basin. In France also, sampling of overbank sediment in the Gartempe River, 20 km downstream from the abandoned uranium mine of Bessines, mapped an enhanced uranium background level, *i.e.*, the top layer is four times more enriched (12 mg/kg U) than the lower layer at 80 cm depth (3 mg/kg U) (Salpeteur and Maldan, 2011).

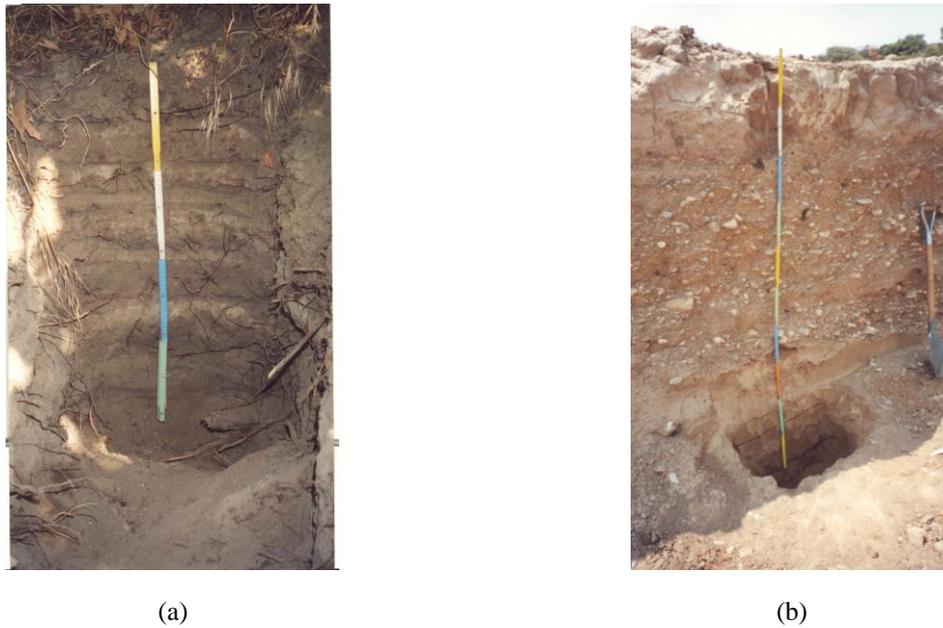


Figure 3.5.3. Floodplain sediment sections: (a) Comparatively recent unconsolidated floodplain sediment sequence, Euboea Island, Hellenic Republic (Hellas), N26E14F2 (23.468°E, 38.831°N), FOREGS Geochemical Atlas of Europe (Salminen et al., 2005). (b) Older indurated overbank/floodplain sediment sequence; note the channel shift from a low-energy environment at the bottom with four fine-grained overbank/floodplain sediment layers (clayey-silt), then a high-energy environment with variable size bottom load pebbles and sand (central part), and at the top again back to a low-energy environment with two fine-grained overbank/floodplain sediment layers, Lavreotiki peninsula, Hellas – N26E14F6; 24.055°E, 37.755°N (Source: Demetriades, 2014, Photo 5, p.13).

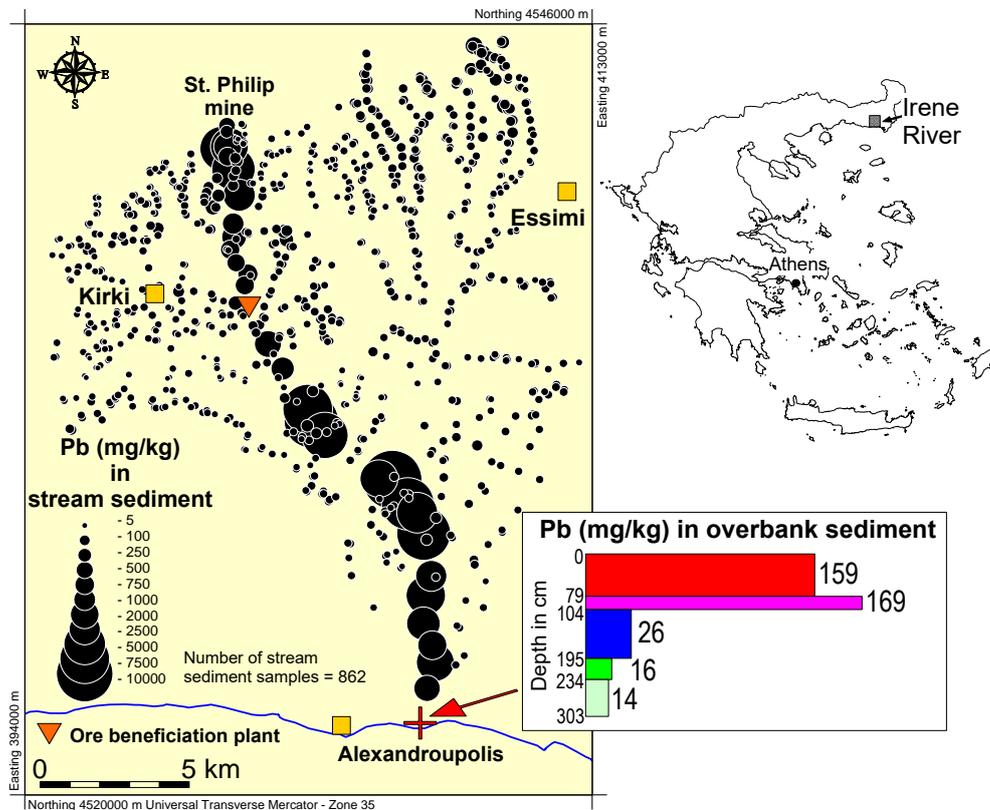


Figure 3.5.4. Distribution of Pb in the <0.180 mm reconnaissance stream sediment fraction, and the <0.063 mm fraction of overbank/floodplain sediment layers, Irene River, Thrace, N.E. Hellas (25.902°E, 40.848°N). Note (i) the contamination train in the stream sediment from the St. Philip mine and ore beneficiation plant, and (ii) the two surface layers of overbank sediment that show contamination, and the lower layers tending towards background conditions (Source: Demetriades, 2014, Fig. 8, p.14; WEGS Pilot project).

Overbank and floodplain sediments at depth may still be natural and represent pristine conditions. However, in some occurrences of overbank/floodplain sediments, the stratigraphy may be complex as older sediments are being reworked during floods, and redeposited downstream. Hence, younger overbank/floodplain sediments are then intermixed with material derived from older overbank/floodplain sediment layers. In such cases, it may be difficult to identify sediments that represent pre-industrial conditions, and a more thorough study of sediment sequences may be necessary. Another issue concerns acidic environments where mobile elements can be easily leached to lower sediments. *For example*, Adánez *et al.* (2014a) in their study of overbank sediments in the Tinto and Odiel basins (Huelva, Spain), observed that Cu and Zn are leached to lower levels and, therefore, their highest concentrations are located in the lowest part of the studied profile. While other elements, such as Pb, Au, Ag and Sb, were not affected and still register elevated concentrations in the upper parts of the profile that are due to the increasing mining activity in the Iberian Pyrite Belt. Despite these expected issues, the representativeness of overbank/floodplain sediments for describing the upstream drainage basin geochemistry is not reduced because the reworked sediments still represent material from the upstream drainage basin, and comparatively immobile elements in acidic environments map their original vertical distribution.

In wide and flat plain areas of sedimentary basins in central Europe, like the Paris basin, *for example*, erosion speed is slow, and the average deposition speed of overbank/floodplain sediments has been estimated at 1 mm/year (Salpeteur *et al.*, 1999). Their composition is mostly clayey. In contrast, in young mountainous landscapes, like the foreland of the Pyrenees Mountains, the erosion speed is far higher: 40 cm/year and the grain size of overbank sediments is coarser with pebbly layers interbedded with sandy layers, a feature commonly observed in southern Mediterranean countries.

According to Ottesen *et al.* (2010), overbank/floodplain sediment sample locations may be classified into three categories according to river channel type:

- (1) *Meandering and/or straight stream segments*: In meandering or straight stream segments, the natural levee or slack water parts of the river floodplain may provide sites for both a recent and a pre-industrial overbank or floodplain sediment sample (Fig. 3.5.5).
- (2) *Braided rivers*: In braided rivers, the overbank or floodplain sediment layers are generally thin and spread out over large areas (Fig. 3.5.6). The ages of braids may vary, however, across the channel. In such cases, sufficient knowledge of the sedimentation history is required to be able to distinguish between pristine and contaminated overbank or floodplain sediments. A striking example of this process has been very well illustrated by the downstream dispersion of mining wastes in the South Tyne River (Northumbria, United Kingdom) from 1860 to 1952 by Macklin and Lewin (1989). Reworking of the ancient terraces by a recent braided stream produced an erratic distribution of potentially hazardous elements (*e.g.*, As, Pb, Cd, Zn, *etc.*) in the alluvial sedimentary complex redeposited downstream.
- (3) *Terraces*: If river terraces occur, the relative stratigraphic ages have to be determined to identify suitable locations for collecting older and younger overbank/floodplain sediment samples from the terrace and current floodplain, respectively (Fig. 3.5.7). A stream or river terrace is produced by downcutting of the valley floor by the river or stream caused by uplift (rejuvenation). It is composed of either unconsolidated or indurated alluvium, depending on the age of the deposit.

3.5.1.2. Grain size of overbank and floodplain sediments

Overbank and floodplain sediments are deposited in layers during flood events in a low-energy environment on the floodplain of a stream or river (Ottesen *et al.*, 1989, 2010). Their grain size varies from *silt* to *clay* (*silty-clay*, *clayey-silt*), with a minor amount of fine sand, the proportion



Figure 3.5.5. A meandering river, Owens River, California, USA. Note the different generations of old meanders. (Source: http://www.seddepseq.co.uk/depositional_env/fluvial/meander/meander.htm).



Figure 3.5.6. Braided river. Waimakariri River, South Island of New Zealand (Source: https://upload.wikimedia.org/wikipedia/commons/3/35/Waimakariri01_gobeirne.jpg).



Figure 3.5.7. River terraces. Because of active rejuvenation, this river has two terraces (1. Oldest; 2. Intermediate), and the active floodplain (3. Youngest), which is comparatively narrow on the far side of the river, and much wider on the front side of the photograph (Source: Alecos Demetriades (IGME/IUGS-CGGB), FOREGS Geochemical Atlas of Europe project, sampling site: N25E13F4L - 22.021°E, 37.041°N).

of which may increase in some cases depending on catchment basin lithology and fluvial characteristics. Normally fine sand is deposited near the main channel, while the grain size decreases to silt-clay away from the main river valley (Moody *et al.*, 1999; Lecce and Pavlowsky, 2004; Walling *et al.*, 2004). Overbank and floodplain sediments are completely devoid of coarse-grained sand and gravel, which indicate medium- and high-energy environments, respectively. However, in the case of overbank sediment, which is collected from second-order streams of <100 km² in area, apart from a minor amount of fine sand, there may occur some clasts >2 mm. Locally, some organic debris may occur (*e.g.*, roots, wood, leaves) in both overbank and floodplain sediment sequences.

Moreover, a comparison of the grain size distribution of more than a hundred overbank and active stream sediments samples, collected in the same experimental area (south of Orléans France), showed that the latter is unimodal with a maximum peak (66%) of the <2 to 0.2 mm fraction, whereas the overbank sediments are bimodal with two peaks: the first peak in the <20 to 0.002 mm fraction is at 27.5%, and the second peak at 22.4% (Salpeteur *et al.*, 2000). Clays are not only produced by the present day temperate climate accretion, as a large amount is inherited from the palaeoweathering processes. *For example*, lateritic weathering during the Tertiary period, *i.e.*, the material record of the geochemistry of their parent rocks. This fine-grained material is selectively removed from the soil profiles and mixed downstream with the detritus of numerous tributaries when storms occur. This explains the better representativity of overbank/floodplain sediment with respect to soil and stream sediment geochemical surveys, in terms of catchment basin geochemistry (Salpeteur *et al.*, 2000).

As a rule of thumb, the grain size in the field can be estimated by the following practical method, after slightly wetting the overbank/floodplain sediment (FAO, 2006; Haslinger *et al.*, 2014):

- *Clay*: soils fingers, is cohesive (sticky), is formable, has 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.

3.5.2. Overbank and floodplain sediment samples to be taken

In the Global Geochemical Reference Network project, two layer-based samples of overbank and floodplain sediment are to be collected from the second- and third- or higher-order drainage basins with an area of <100 km² and 1000 to 6000 km², respectively (refer to Section §2.5 in Chapter 2 of this Manual). The overbank/floodplain sediment sample from the top (surface) layer may be affected in some cases by anthropogenic activities, as shown in Figure 3.5.4. The bottom overbank/floodplain sediment sample should be taken from the deepest possible layer, as the objective is to collect a pristine sample. As has already been shown in Figure 3.5.4, pristine conditions in this particular overbank/floodplain sediment sequence began to occur at a depth of 104 cm, and definitely in the layer below 195 cm depth.

Overbank sediment samples, representing the fine-grained sediments (silt, clay) of the small second-order drainage basin (<100 km²), are collected from its floodplain near the confluence point of the small, second-order, stream with the main, third-order, river, according to the Strahler (1957, 1969) stream magnitude order classification (see Figs. 2.5 & 2.8 in Chapter 2 of this Manual).

Floodplain sediment samples, representing the fine-grained sediments (silt, clay) of the large third- or higher-order drainage basin (1000 to 6000 km²), are collected from its alluvial plain near its outlet with the sea, or lake, or confluence point with a higher-order branch of a river.

The following layer-based overbank and floodplain sediment samples are taken:

- (a) Routine sample site of a normal 160x160 km grid cell:
- 2 – 3 kg of (a) *Top* overbank and floodplain sediment samples (0-20 cm) are collected from the surface layer, which may occur at the air/earth interface or below the surficial litter in the case of catchment basins that were not inundated by floods for prolonged periods. The maximum sampling range (thickness) of the *Top* overbank and floodplain sediment sample must not exceed 20 cm, *i.e.*, the upper 20 cm of the surficial layer are sampled. If the surface layer is less than 20-cm thick, then the *Top* overbank and floodplain sediment samples are collected from the entire layer, and the depth range is noted on the field observations sheet.
 - 2 – 3 kg of *Bottom* overbank and floodplain sediment samples are collected from the very bottom layer (lowermost 20 cm, >100 cm depth). The *Bottom* overbank and floodplain sediment samples should be collected from the deepest possible layer, as the aim is to reach pristine conditions. Again, a 20-cm thick section of a single *Bottom* overbank and floodplain sediment layer is sampled. If the thickness of the single *Bottom* overbank and floodplain sediment layer is less than 20 cm, then the entire layer is sampled, and the depth range is noted on the field observations sheet.
- (b) Duplicate field site of a duplicate grid cell (at least one in each country): At least one site out of twenty will be selected for collection of a set of duplicate field overbank and floodplain sediment samples (*i.e.*, ≈5% duplication of the sample sites) in each country. However, countries with less than 20 GTN grid cells should collect field duplicate overbank and floodplain sediment samples from at least one random site. The field duplicate sample site is selected at a distance of 5 to 50 metres away from the routine sampling site. The samples collected at the duplicated field site consist of **additional** *Top* and *Bottom* overbank and floodplain sediment samples, according to the sampling scheme summarised in (a) above.

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

3.5.2.1. Identifiers of overbank and floodplain sediment samples

The identifiers of the *Top* and *Bottom* overbank sediment samples are ‘K’ and ‘N’, respectively:

(a) Routine overbank sediment sample site (e.g., GTN grid cell N26E14):

- *Top* overbank sediment sample: N26E14**K1**
- *Bottom* overbank sediment sample: N26E14**N1**

Note: Number ‘1’ represents the 1st sample site in GTN grid cell N26E14.

(b) Duplicate overbank sediment field site (e.g., GTN grid cell N27E12):

- Routine *Top* overbank sediment sample: N27E12**K3**
- Duplicate *Top* overbank sediment sample – Duplicate: N27E12**K3D**
- Routine *Bottom* overbank sediment sample: N27E12**N3**
- Duplicate *Bottom* overbank sediment sample – Duplicate: N27E12**N3D**

Note: Number ‘3’ represents the 3rd sample site in GTN grid cell N27E12, and ‘D’ denotes the duplicate *Top* and *Bottom* overbank sediment samples.

The identifiers of the *Top* and *Bottom* floodplain sediment samples are ‘F’ and ‘L’, respectively:

(c) Routine floodplain sediment sample site (e.g., GTN grid cell N26E14):

- *Top* floodplain sediment sample: N26E14**F1**
- *Bottom* floodplain sediment sample: N26E14**L1**

Note: Number ‘1’ represents the 1st sample site in GTN grid cell N26E14.

(d) Duplicate floodplain sediment field site (e.g., GTN grid cell N27E12):

- Routine *Top* floodplain sediment sample: N27E12**F3**
- Duplicate *Top* floodplain sediment sample – Duplicate: N27E12**F3D**
- Routine *Bottom* floodplain sediment sample: N27E12**L3**
- Duplicate *Bottom* floodplain sediment sample – Duplicate: N27E12**L3D**

Note: Number ‘3’ represents the 3rd sample site in GTN grid cell N27E12, and ‘D’ denotes the duplicate *Top* and *Bottom* floodplain sediment samples.

3.5.3. Equipment for overbank and floodplain sediment sampling

3.5.3.1. Equipment to be provided by the Project Coordinator

The following equipment must be purchased or made centrally, and provided to all sampling teams in each participating country:

- 300x600x0.04 mm certified trace element free plastic bags, *e.g.*, Rilsan^{®2}, or similar type.
- Plastic strip locks for securing the sample bags (attention: the plastic strip 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).
- 6x10 cm white cards for writing the sample number on both sides.
- 7.5x11.5 cm zip-lock plastic bags for holding the 6x10 cm white cards.
- Plastic laminated scalebar for ‘photographs’ (see Fig. 3.3 in Chapter 3), and
- Black permanent drawing ink markers (ONLY black coloured allowed).

Instead of strong certified trace-element free plastic bags for packing the overbank and floodplain sediment samples, two other types of bags can be used, and purchased by the Project Coordinator and distributed to all participating countries. These are:

- 125x250 mm wet-strength Kraft³ paper bags with a plastic-coated aluminium tin-tie, which can be twisted to seal the bag, or
- 254x431 mm polyester bags with nylon cord drawstring.

Whatever the decision, the same type of sample bags must be used by all countries throughout the Global Geochemical Reference Network project.

3.5.3.2. Equipment to be purchased by each participant

Each participating country must purchase the following equipment, and for all its sampling teams:

- Stainless-steel spade with an unpainted wooden handle is preferred. If this is not available, then an unpainted steel spade with an unpainted wooden handle is the next option. However, if these cannot be found and painted spade and varnished wooden handle are purchased, the paint/varnish must be removed by sandblasting prior to sampling (see Fig. 3.1 in Chapter 3); sandpapering either the spade or wooden handle will not remove completely the paint/varnish.
- Unpainted mattock cutter (if mattock cutter is painted, the paint must be removed by sandblasting prior to sampling); the wooden handle must be unpainted (if varnished, it must be removed by sandblasting - not sandpapering - see Figure 3.1 in Chapter 3).
- Stainless steel knife.
- Metal-free white or colourless plastic scoop or stainless-steel scoop.
- Stainless-steel geological hammer either pointed-tip or chisel-end (preferable).
- Leather gloves.
- 10x magnifying lens (loupe).
- Hard bristle brush for cleaning plastic scoop, and geological hammer.

² TUB-EX: <http://www.tub-ex.com> – sales@tub-ex.com

³ The Kraft paper bags need to be constructed using waterproof glue, otherwise the bags will fall apart when wet.

- Cotton-lint or white cotton rags for cleaning sampling equipment.
- Wooden folding 2-m long measure (alternate colours every 10 or 20 cm), or plastic tape with alternate colours every 10 cm.
- 30x60 cm sturdy plastic bags for packing sample bags, 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 sturdy carton boxes for packing sample bags in the field, and subsequent transportation to the sample preparation laboratory.
- Strong PVC packing tape.
- 6 mm natural sisal rope.
- Heavy-duty cutter knife with replacement blades.
- Global Positioning System (GPS) for recording sample site coordinates, or a tablet with a GPS and digital topographical maps; or a mobile telephone with GPS; it is strongly recommended to have a backup GPS receiver.
- Extra batteries for GPS or battery charger with rechargeable batteries.
- Topographical maps, preferred scale 1:50,000 (a must in case electronic digital devices fail, *e.g.*, GPS).
- A plastic roamer or map ruler for extracting coordinates from 1:50,000 topographical maps in case GPS fails.
- An orienteering compass (a must in case GPS fails).
- Digital camera or a mobile telephone with a macro facility for field documentation (minimum 5 megapixels).
- Extra batteries for the digital camera.
- 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 or external hard drive) for backup of field data and digital photographs.
- USB cable to download photographs to a laptop computer daily.
- Threshold scintillometer to measure natural radioactivity (Total, Th, U, K); the scintillometer must be calibrated at least once a year before the field campaign at a certified national facility.
- Extra batteries for the threshold scintillometer.
- Field observations sheets.
- Waterproof case to hold field observation sheets.
- Writing pens.
- HB pencils, pencil sharpener and rubber (back-up in case the pens fail to write in the field).
- First-aid kit.
- Rope or wading pole as river conditions are not the safest, 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 1: The use of an auger for sampling overbank and floodplain sediment is strongly NOT recommended, as each site in the Global Geochemical Reference Network project is unique and, thus, very significant for obtaining the required three-dimensional information that can only be obtained from a vertical profile.

3.5.4. Overbank and floodplain sediment sampling procedure

3.5.4.1. Sample site selection

During the desk study, the 1:50,000 scale topographical⁴ and geological maps (refer to Section §2.5 of Chapter 2 in this Manual) are studied to find a suitable second-order small drainage basin (<100 km²) from where the overbank sediment will be collected. The third-order drainage basin (1000-6000 km²) is the one that has as a tributary the selected second-order drainage basin (see Figs. 2.5 & 2.8 in Chapter 2). The exact position of the sampling site is located, however, in the field, after a careful study of exposed overbank and floodplain sediment sections according to the following criteria (Figs. 3.5.7 & 3.5.8):

- The selected **overbank sediment sampling site** in the second-order stream must be well above the confluence point with the third-order river or trunk river. The reason for this condition is to ensure that there is no influence by the third-order river during flood conditions.
- The selected **floodplain sediment sampling site** in the third- or higher-order stream must be well above the high-tide level. The reason for this condition is to ensure that there is no marine influence on the deposited floodplain sediments. Similarly, the selected **floodplain sediment sampling site** with its outlet in endorheic lakes must be well above the highest water level of the lake to ensure that there is no lacustrine influence on the deposited floodplain sediments. Likewise, in case the floodplain sediment sampling site on the third-order stream is a tributary to a fourth-order stream, the site must be well above the confluence point.
- It is important to be certain that the overbank/floodplain sediment sequence corresponds to transported sediment that has been preserved in a depositional environment, and not *in situ* material on weathered bedrock.
- Select a suitable exposed section with many overbank/floodplain sediment layers of fine-grained material, *e.g.*, silt, silty clay, clayey silt, clay, which is deposited in a low energy environment (Fig. 3.5.9).
- The overbank/floodplain sediment must be devoid of pebbles and coarse- to medium-grained sand, which indicate high to medium energy environments, respectively.
- Sampling of older terraces is also appropriate to obtain pristine or pre-industrial overbank/floodplain sediment (Figs. 3.5.7 & 3.5.8). Such sampling is done *above the present inundation zone* to avoid material draped during recent floods.
- Selecting a sample site near or within an open cluster of established (mature) trees will increase the likelihood that the land surface is at a ‘natural’ level (no massive recent erosion or major land rehabilitation).
- Avoid possible contamination by selecting a sample site that is at least:
 - 100 m upstream of asphalted roads (particularly major roads), railway lines, bridges, buildings, and dams.
 - 50 m upstream of agricultural fields, paddocks, and high-voltage power lines, and

⁴ If topographical maps are not available, orthophotographs or satellite photographs can be used.

- 25 m upstream of fences.
- Avoid sites adjacent to dirt roads or ditches (minimum distance 10 m).
- Avoid sites that are disturbed by human activities such as camping sites (*e.g.*, presence of fireplaces, cans and/or bottles), graded areas (*e.g.*, areas from which the sediments were removed, and the remaining sediments cannot be classified), levelled fields (for irrigation), mines (active or abandoned), landfills, and rehabilitated sites. It is stressed that every single contaminated site will seriously influence the generated geochemical results.
- Avoid locally atypical sites.
- In case a suitable exposed section of overbank and floodplain sediment is not found, then a suitable site should be located on the floodplain of the second- and third- or higher-order catchment basins, respectively, according to the criteria described above, and a pit dug (Fig. 3.5.10).

Difficult cases for overbank sediment sampling: Remember that overbank sediment is collected from second-order streams of <math><100\text{ km}^2</math> in area. This means that in some cases, the field sampling team must understand fluvial geomorphology, and locate suitable sites for sampling overbank sediment even in difficult terrains such as those shown in Figures 3.5.11 and 3.5.12. In the Mediterranean region, there were much wetter periods in the past (*e.g.*, Finné, 2014) with active channel downcutting, and deposition of overbank sediments, as can be observed in Figures 3.5.7 to 3.5.9, 3.5.11 and 3.5.12. The bed load of this second-order stream (Fig. 3.5.11), made of gravel and boulders, indicates its high energy. However, in the recent past, more tranquil climatic conditions prevailed, and overbank sediment was deposited at the side of the channel during not so intense flood incidents (Figs. 3.5.11 & 3.5.12 – See also Annexe A3.5.1).



Figure 3.5.8. Exposed floodplain sediment section, site N26E13F2 (21.535°E, 38.340°N), Thrace, Hellas. In this case, the exposed section is along the riverbank. On the left-hand side there is a lower floodplain sediment deposit, and below it a more recent deposit. Photograph: Alecos Demetriades (IGME/IUGS-CGGB), FOREGS Geochemical Atlas of Europe project (Salminen *et al.*, 2005).

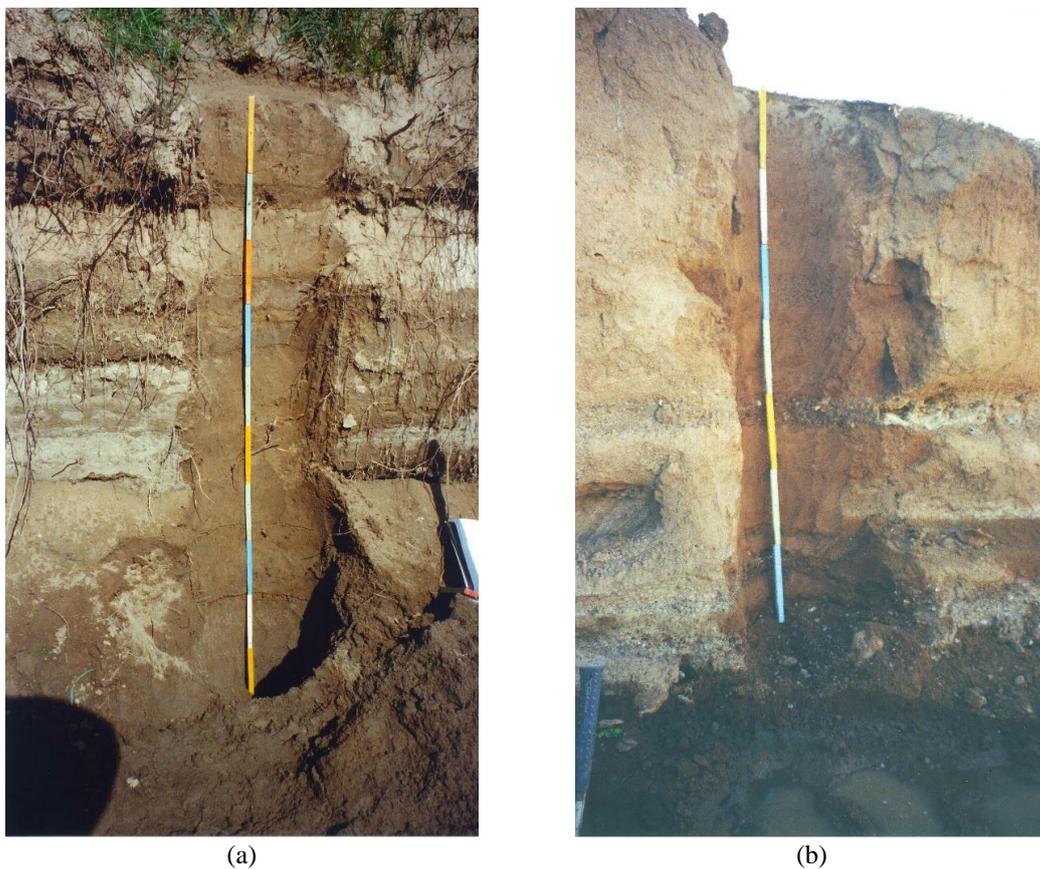


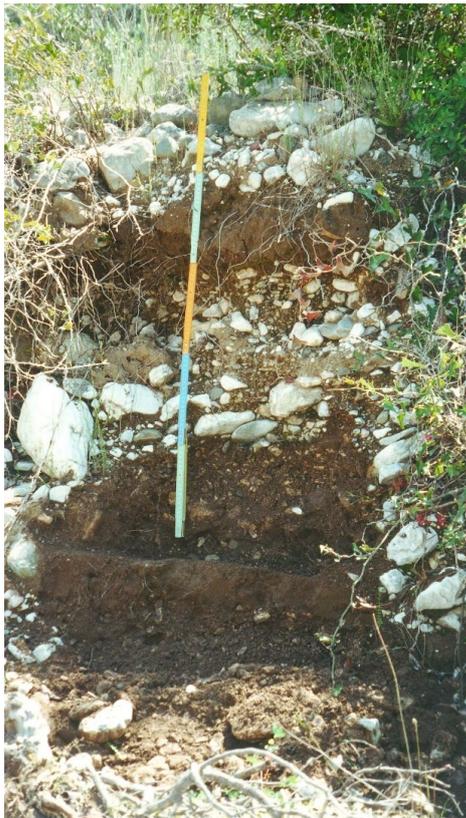
Figure 3.5.9. Overbank sediment sections with many fine-grained layers. (a) Site N27E12K1 (21.62°E, 39.96°N), Epiros, Hellas, and (b) Site N26E13K1 (22.45°E, 38.90°N), Sterea Hellas, which has three coarse-grained sandy pebbly layers in-between the fine-grained sediment sequence, and at the base occurs what seems to be the local base level bottom load deposit with coarse-grained sand and gravel. Photograph: Alecos Demetriades (IGME/IUGS-CGGB), FOREGS Geochemical Atlas of Europe project (Salminen et al., 2005).



Figure 3.5.10. Digging a pit on the floodplain for the collection of the floodplain sediment sample, NW Peloponnese, Hellas. It is noted that this is not a suitable site for the collection of the top floodplain sediment sample because it is cultivated. In this case, only the bottom sample was collected from the pit, and the top sample from a nearby undisturbed site. Photograph: Alecos Demetriades (IGME/IUGS-CGGB), FOREGS Geochemical Atlas of Europe (Salminen et al., 2005).



Figure 3.5.11. Bedload of a high-energy second-order stream (N25E13K2, 21.79°E, 37.40°N), Peloponnese, Hellas. At first glance, the situation appears to be hopeless. However, on closer look suitable sites were found for both recent and old overbank sediment. Hence, the reason for the sampling to be carried out by well-trained field personnel (see Figure 3.5.12). Photograph: Alecos Demetriades, FOREGS Geochemical Atlas of Europe project (Salminen et al., 2005).



(a)



(b)



(c)

Figure 3.5.12. Second-order stream (N25E13K2, 21.79°E, 37.40°N), Peloponnese, Hellas: (a) Stream bank section, which may be classed as a terrace deposit with layers of fine-grained overbank sediment (silty clay to clayey silt), and layers of coarse sand and pebbles (medium-energy environment), and layers of gravel (high-energy environment); (b) A recent overbank sediment layer deposited in a low-energy environment at the side of the active channel; (c) on closer study, it is a fine-grained (silty clay to clayey silt) overbank sediment, similar in texture with the overbank sediment layers occurring in (a). Photographs: Alecos Demetriades (IGME/IUGS-CGGB), FOREGS Geochemical Atlas of Europe project (Salminen et al., 2005).

Desert and semi-arid terrains: Overbank and floodplain sediments, as they normally occur in Arctic, Temperate, Mediterranean and semi-arid environments, are not easily found in desert terrains. However, even in desert and semi-arid terrains, there are occasional flash floods, which can deposit overbank and floodplain sediments (Fig. 3.5.13). According to Jim Bogen (co-author), there is evidence of flood events, and the occurrence of overbank and floodplain sediments in the Mojave Desert (Fig. 3.5.14) and Death Valley in California (USA), and in the Australian desert near Alice Springs. Similarly, Ignace Salpeteur (co-author) stresses that during the late Quaternary period, a more humid climate alternated with dry periods. Thus, it is possible to find palaeo-overbank and palaeo-floodplain sediments, *for example*, in the central pediplain of Saudi Arabia (Salpeteur and Sabir, 1989) and southern Mauritania.



Figure 3.5.13. (a) Dry stream with sandy bedload, and (b) Overbank sediment of clayey-silt, Gocheganas Nature Reserve, Namibia (17.214°E, 22.812°S). Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



Figure 3.5.14. Layers of overbank/floodplain sediment exposed in Afton Canyon, Mojave River, Mojave Desert, United States of America. Note the elevated terraces on both sides of the canyon (Source: <https://pubs.usgs.gov/of/2004/1007/river.html>).

3.5.4.2. Sampling procedure for overbank/floodplain sediment

Important Note 2: The same procedure is used for sampling overbank and floodplain sediments. In the following description, the following notation will be used ‘overbank/floodplain sediment’ from thenceforth.

Top and bottom layer-based overbank/floodplain sediment samples are taken at each site, either from cutting a vertical section at the stream/riverbank (Fig. 3.5.15) or from digging a pit on the floodplain (Fig. 3.5.10):

- A Top overbank/floodplain sediment sample is collected from 0-20 cm (excluding humus where present and surface litter (Fig. 3.5.15) – this is a case when the stream/river has not flooded for many years), and
- A Bottom overbank/floodplain sediment sample from the very bottom layer (lowermost 20 cm) of the exposed profile, just above the water level of the stream/river (Fig. 3.5.15); in this case, the bottom layer for sampling is approximately 10 cm thick (above the blue-grey clayey layer); hence, the whole layer is sampled, and the depth range of the sample interval is recorded on the field observations sheet).

In both cases, SINGLE overbank/floodplain sediment layers are sampled. If the thickness of the Top and Bottom overbank/floodplain sediment layers is less than 20 centimetres, the thinner layer is sampled, and its thickness is noted on the field observations sheet.



Figure 3.5.15. Overbank sediment section, S33E180, Cape Farms (18.610533°E, 33.684647°S), Cape Town, South Africa, field-training course on the occasion of the 35th International Geological Congress in Cape Town; the bottom sample is collected from the 15-cm thick overbank sediment layer above the grey layer (reducing conditions - gleying), which is below the stagnant water level, and the top sample is taken from the surface layer after removing the grass. Photograph: Alecos Demetriades (IGME/IUGS-CGGB).

Ideally, the Bottom overbank/floodplain sediment sample should be collected directly above the local base level gravel bed (Fig. 3.5.9b). Since this is not always possible, the deepest possible single overbank/floodplain sediment layer is sampled, because the objective is to reach a layer, which is not affected by human activities (a pristine layer).

The Top and Bottom overbank/floodplain sediment samples are collected from a SINGLE site, and a SINGLE layer. In difficult cases, the Top and Bottom overbank/floodplain sediment samples may be collected from different but close locations in the same catchment basin (Figs. 3.5.11 & 3.5.12; see Annexe A3.5.1). Again, each sample is taken from the same single site (NO field composites), and single layers of top and bottom overbank/floodplain sediment.

At each overbank/floodplain sediment sample site:

- (i) Switch on the GPS, or notebook or laptop computer with GPS (Fig. 3.5.16a), to obtain the WGS1984 decimal degree coordinates of the sample site. It is important to switch on the GPS upon arrival at the site, and to allow enough time for the signal to settle.
- (ii) Write the numbers of *Top* and *Bottom* overbank/floodplain sediment samples with a black permanent ink marker on the plastic trace element free Rilsan[®] bag (or Kraft paper bag; Fig. 3.5.16b).
- (iii) Write the numbers of Top and Bottom overbank/floodplain sediment samples on both sides of the small white card, and place each card in the small zip-lock bag and seal it (Figs. 3.5.16c, d).
- (iv) Clear the litter and surface humus (if present) to begin with a spade, and a mattock cutter if necessary (Fig. 3.5.15).
- (v) Cut a vertical section through the exposed overbank/floodplain sediment sequence (Figs. 3.5.17, 3.5.18 & 3.5.19) down to the local base level gravel bed, if possible (Fig. 3.5.9b), or down to the water level of the stream (Fig. 3.5.15), with an unpainted steel or stainless-steel spade, thus uncovering a clean vertical surface for sampling. The vertical face should be cut back at least 50 cm from the exposed bank face to uncover a clean section.
- (vi) Mark the overbank/floodplain sediment layers with the aid of a stainless-steel knife (Figs. 3.5.9, 3.5.15, 3.5.17c, d & 3.5.19a, b).
- (vii) **Photographic documentation:** At this stage, place an alternate coloured-section wooden measure on the face of the pit (Figs. 3.5.17c, d & 3.5.19a) and the plastic laminated scalebar (Fig. 3.3 in Chapter 3), and then take at least four digital photographs: (i) the sample number of the top sample (Fig. 3.5.17a); (ii) landscape upstream from sampling site (Fig. 3.5.17b), and (iii & iv) site photograph with natural light and fill-in flash (Figs. 3.5.17c, d). Additional close-up photographs can be taken to show the textural characteristics of the overbank/floodplain sediment layers.
IMPORTANT: *As a safety precaution, always photograph first the sample number of the Top overbank/floodplain sediment sample (Fig. 3.5.17a), and last the bagged samples with the sample number (Fig. 3.5.17e).*
- (viii) Mark the location of the sample site on the 1:50,000 topographical map (Fig. 3.5.20) or digital map.
- (ix) Record the general observations on the field observations sheet (Fig. 3.5.19c – refer to Appendix 1 for the Field observation sheet), leaving the grain size to be completed after the collection of the Top and Bottom overbank/floodplain sediment samples.
- (x) First, collect the Bottom overbank/floodplain sediment sample using a geological hammer and a white plastic scoop, and store the sample in a certified trace element free plastic Rilsan[®] bag (or Kraft paper bag) – Fig. 3.5.21. This procedure avoids

cleaning the surface of the bottom layer from fallen Top sample material if the latter is taken first.

- (xi) Upon collecting the Bottom overbank/floodplain sediment sample of about 2–3 kg weight (Fig. 3.5.21b), the numbered small card in the zip-lock bag is placed on top of the sample (Fig. 3.5.16d).
- (xii) Twist the top of the trace-element free plastic sample bag, and seal it securely with a plastic strip lock (Fig. 3.5.21c – in this case, twist the plastic-coated aluminium tin-tie).
- (xiii) For safety during transportation of the sample, place it in an ordinary plastic bag, and seal it securely with a plastic strip lock (Figs. 3.5.21d, e).
- (xiv) Clean thoroughly the sampling equipment with a hard bristle brush and cotton-lint or white cotton rag.
- (xv) Second collect the Top overbank/floodplain sediment sample using exactly the same procedure as that of the Bottom sample (Figs. 3.5.22).
- (xvi) Store both samples in a strong carton or plastic box for transportation to the next location or to the Survey base, and finally to the sample preparation laboratory.
- (xvii) Measure the natural radioactivity with a threshold scintillometer, which is held at knee height (Fig. 3.5.23), and record the measurements of Total, Th, U and K on the field observations sheet.
- (xviii) Record the grain-size of the Bottom and Top overbank sediment samples, and digital photograph numbers on the field observations sheet.
- (xix) If a pit is dug below the exposed section in order to reach the lowest possible overbank sediment layer (Figs. 3.5.17c, d; 3.5.18b, c), or local base level gravel bed, the pit must be covered after sampling (Fig. 3.5.17e).

Duplicate field samples: Duplicate Top and Bottom overbank/floodplain sediment samples are collected randomly at least at every 20th sampling site (*i.e.*, ≈5% duplication of the sample sites) in each country. However, countries with less than 20 GTN grid cells should collect duplicate field Top and Bottom overbank/floodplain sediment samples from at least one random site. The duplicate field 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 and Bottom overbank/floodplain sediment samples.

Important Note 3: Overbank/floodplain sediment samples from the lower layer must not be collected below the uppermost level of the fluctuating groundwater where obvious signs of reducing conditions are observed (greyish sediment – see Fig. 3.5.15). In the lower reaches of the floodplain of large rivers, the groundwater level near the main channel of the river may be very near the surface. In such cases, the top floodplain sediment should be collected from the recent alluvial deposits, and the bottom can be taken from another site further away from the main channel or even from terraces (see Fig. 3.5.7).

Important Note 4: If it is not possible to sample an exposed vertical overbank/floodplain sediment sequence with the aid of a spade, follow the same procedure by selecting a suitable sample site on the floodplain (*e.g.*, inside meander, or depression) and dig a pit down to the required depth using the mattock cutter and spade (Fig. 3.5.10). In this case, after collecting the Bottom and Top overbank/floodplain sediment samples, using the procedure described above, the dug-up sediment is returned to the pit, the two samples are placed on the surface together with the sample number (Fig. 3.5.17e), and the last site digital photograph is taken to show that the pit was filled in, and landscape returned to its original state.

3.5.4.3. Photographic documentation of overbank/floodplain sediment sampling procedure

The following set of photographs shows the sampling procedure for overbank and floodplain sediments.



(a)



(b)



(c)



(d)

Figure 3.5.16. (a) GPS switched on upon arriving at the sampling site for recording the coordinates. (b) Writing overbank/floodplain sediment sample number on the white paper bag with a blue permanent ink marker; this was during the FOREGS Geochemical Mapping of Europe project (Salminen, Tarvainen *et al.*, 1998; Salminen *et al.*, 2005). Since then, in other multinational geochemical mapping projects, such as GEMAS (EGS-GWG, 2008), only black permanent ink markers are allowed. For the Global Geochemical Reference Network project, the same strict specifications that ONLY black permanent drawing ink markers are allowed, and which must be provided centrally by the Project Coordinator. (c & d) Sample numbers of Top and Bottom overbank/floodplain sediment samples written on both sides of a small white card, and each card is placed in a small self-sealed plastic zip-lock bag. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)



(c)



(d)



(e)

Figure 3.5.17. Photographic documentation of sampling site: (a) Floodplain sediment sample number. (b) Landscape photograph looking upstream from the sampling site. (c) Floodplain sediment profile with natural light. (d) Floodplain sediment profile with fill-in flash, and (e) Pit filled-in and collected floodplain sediment samples placed on top together with the sample number as proof that the landscape was returned to its original state. Photographs: Alecos Demetriades (IGME/IUGS-CGGB), Sample site on Squamish River (N34W58F1 (123.158571°W, 49.710402°N), Squamish Community, Vancouver, Canada. Young Earth Scientists field course on the occasion of the RFG2018 conference, 22 June 2018, Vancouver. The reason for including these photographs in the Manual is the grey floodplain sediment layers indicating reducing conditions (gleying), which should be avoided from sampling if, of course, this is possible (the same condition applies to the grey bottom overbank sediment layer in Figure 3.5.15).



Figure 3.5.18. (a) Cutting a vertical profile in the exposed section of the overbank/floodplain sediment sequence; note the alternate layers of fine-grained overbank sediment and sand with gravel, denoting low and high energy environments, respectively. (b) and (c) Digging a pit at the base of the exposed section to locate other lower fine-grained overbank sediment layers. (d) Placing the wooden measure on the face of the overbank sediment sequence. It is noted that due to the prevailing dry conditions in the eastern Attiki region, this particular river has not flooded for many years, and is continuously downcutting its valley to reach the base level, thus exposing the overbank/floodplain sediment sequence. Photographs: Alecos Demetriades (IGME/IUGS-CGGB), FOREGS Geochemical Atlas of Europe project, Lavreotiki peninsula, Attiki (N26E14F6; 24.055°E, 37.755°N), Hellas (Salminen et al., 2005).



(a)

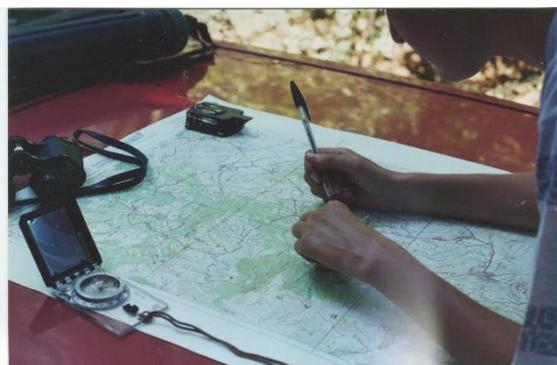


(b)



(c)

Figure 3.5.19. (a) The exposed top and bottom fine-grained layers. (b) Marking the floodplain sediment layers with the aid of a stainless-steel knife, and (c) Recording the field observations. Photographs: Alecos Demetriades (IGME/IUGS-CGGB), FOREGS Geochemical Atlas of Europe project, Lavreotiki peninsula, Attiki (N26E14F6; 24.055°E, 37.755°N), Hellas (Salminen et al., 2005).



(a)



(b)

Figure 3.5.20. Marking the sample site on the 1:50,000 topographical map. Photographs: Alecos Demetriades (IGME/IUGS-CGGB), FOREGS Geochemical Atlas of Europe project (Salminen et al., 2005).



(a)



(c)



(b)



(d)



(e)

Figure 3.5.21. (a & b) Sampling the top 20 cm of the **Bottom** floodplain sediment layer by digging with a pointed-tip geological hammer, collecting the sediment in the white plastic scoop, and placing each scoop of floodplain sediment in the Kraft bag. (c) Folding the top of the bag and sealing it by twisting the plastic-coated aluminium tin-tie. (d & e) Placing the Kraft bag in a plastic bag for safety during transportation and sealing it with a plastic-coated tin-tie. Photographs: Alecos Demetriades, FOREGS Geochemical Atlas of Europe project, Lavreotiki peninsula, Attiki (N26E14F6; 24.055°E, 37.755°N), Hellas (Salminen et al., 2005).



(a)



(c)



(b)



(d)



(e)

Figure 3.5.22. (a & b) Sampling the top 20 cm of the **Top** floodplain sediment layer by digging with a pointed-tip geological hammer, collecting the sediment in the white plastic scoop, and placing each scoop of floodplain sediment in the Kraft bag. (c) Folding the top of the bag and sealing it by twisting the plastic-coated aluminium tin-tie. (d & e) Placing the Kraft bag in a plastic bag for safety during transportation, and sealing it with a plastic-coated tin-tie. Photographs: Alecos Demetriades (IGME/IUGS-CGGB), FOREGS Geochemical Atlas of Europe project, Lavreotiki peninsula, Attiki (N26E14F6; 24.055°E, 37.755°N), Hellas (Salminen et al., 2005).



Figure 3.5.23. Taking the natural radioactivity readings by holding the scintillometer at knee level, and recording the measurements on the field observations sheet. Photograph: Alecos Demetriades (IGME/IUGS-CGGB), FOREGS Geochemical Atlas of Europe project, Lavreotiki peninsula, Attiki (N26E14F6; 24.055°E, 37.755°N), Hellas (Salminen et al., 2005).

3.5.4.4. Photographs to be taken at each overbank/floodplain sediment sampling site

Refer to Figure 3.5.17 where the required field digital photographs are shown in the order that should be taken. The last digital photograph is that of the field observations sheet as a safety precaution in case it is damaged (see example below and Figure 3.5.19c).



Global Geochemical Reference Network field observations sheet

Field Observations Sheet

FLOODPLAIN SEDIMENT

TOP Sample ID : N34W58F1 Date: 22/6/2018
 BOTTOM Sample ID: N34W58L1 Country: CANADA
 Organisation: YES NETWORK Sampler: ALL
 GTN Coordinator if different from above: _____

SAMPLE SITE LOCATION Region: SQUAMISH VANCOUVER Map sheet: _____

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

East West: 123.15871° North South: 49.710402°

Altitude: 8 metres above mean sea level

DESCRIPTION OF CATCHMENT BASIN

Approximate size of catchment basin _____ km²

Landscape / topography: FLAT

Land use: Agriculture Pasture, grassland, fallow field
 Forest Wetland
 Non-cultivated, moorland, etc.; Other, specify WOODLAND nearby

Predominant bedrock lithology within catchment basin _____

SITE DESCRIPTION

River width: 7 m depth: >2 m
 Depth of observed ground water table (cm): _____

Grain size range of TOP sample: sand-silt; silt-clay; clay
 Abundance of clasts >2 mm in % (Top sample): <2 %
 Sediment moisture on day of sampling: Dry; Medium; Wet

Grain size range of BOTTOM sample: sand-silt; silt-clay; clay
 Abundance of clasts >2 mm in % (Bottom sample): <2 %
 Sediment moisture on day of sampling: Dry; Medium; Wet

Sampling interval (Note: Sample SINGLE horizons only)

TOP sample: 0-20 cm; Other, specify: from 0 to 8 cm
 BOTTOM sample: from 28 to 33 cm

Possible sources of contamination, specify: Nearby dirt road & railway line
 Distance to minor road: 15 m; Distance to major road: _____ m
 (dirt)

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

REMARKS (any unusual observations)

Top sample has oxidation-reduction features. Sandy layer with small pebbles occurs below top layer. Bottom sample collected from a thin silty-clay layer. Directly below occurs coarse-grained sand with a large proportion of variable-size pebbles (bed load material).

Photographs: 4
P6220001, 2, 3, 4, 5

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Note: All hyperlinks were checked on the 20th of February 2022.

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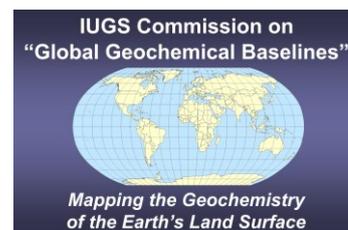
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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

**Annexe A3.5.1
Overbank and Floodplain Sediment Sampling:
Profiles**

Alecos Demetriades^{1,5}, Juan Pablo Lacassie Reyes^{2,5}, Felipe Astudillo^{2,5},
Pablo Sebastian Oliva Vicentelo^{2,5}, Paula Adánez Sanjuan^{3,5},
Adrián Pérez Avila^{4,5}, Gloria Prieto Rincón^{4,5}

¹ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

² Servicio Nacional de Geología y Minería, Valdivia, Chile

³ Instituto Geológico y Minero de España, Madrid, Spain

⁴ Servicio Geológico Colombiano, Bogotá, Colombia

⁵ IUGS Commission on Global Geochemical Baselines

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Introductory notes

In this Annexe, overbank and floodplain sediment profiles are presented from the Chilean part of Tierra del Fuego (Lacassie *et al.*, 2020), Colombia, Cyprus and Spain. In the main body of this Chapter there are overbank/floodplain sediment profiles from the Hellenic Republic.

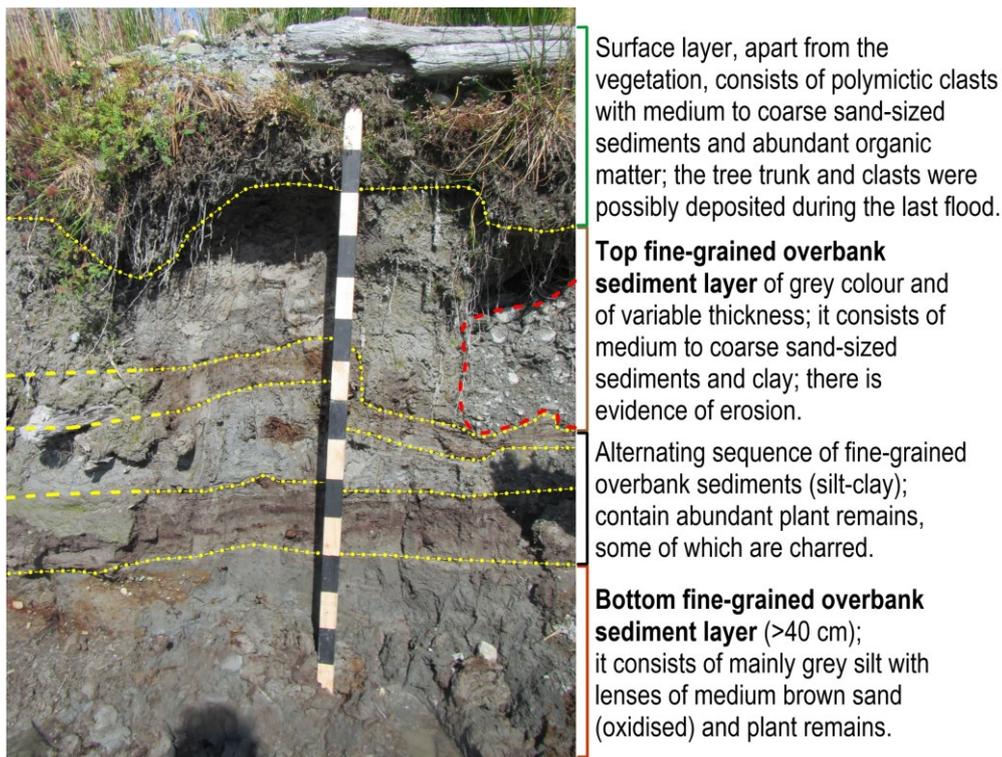
The Cypriot floodplain sediment sequences show some of the problems that may be encountered during sampling. Due to the downcutting of the valleys, the floodplain sediment sequences needed to be studied carefully and top and bottom samples were collected from different but nearby sites.

Reference

Lacassie, J.P., Astudillo, F., Johnson, C. & Oliva Vicentelo, P.S., 2020. Reconnaissance Survey of the Chilean Part of Tierra del Fuego, a Sub-Antarctic Terrain, as a Contribution to the IUGS Manual of Standard Methods for Global Geochemical Baselines and Regional Geochemical Surveys. 2020 Annual Report, IUGS Commission on Global Geochemical Baselines, Appendix 4, 55–75; https://www.globalgeochemicalbaselines.eu/datafiles/file/IUGS-CGGB_2020_Annual_Report_Final.pdf.

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A3.5.1.1. Overbank sediment profiles, Tierra del Fuego, Chile



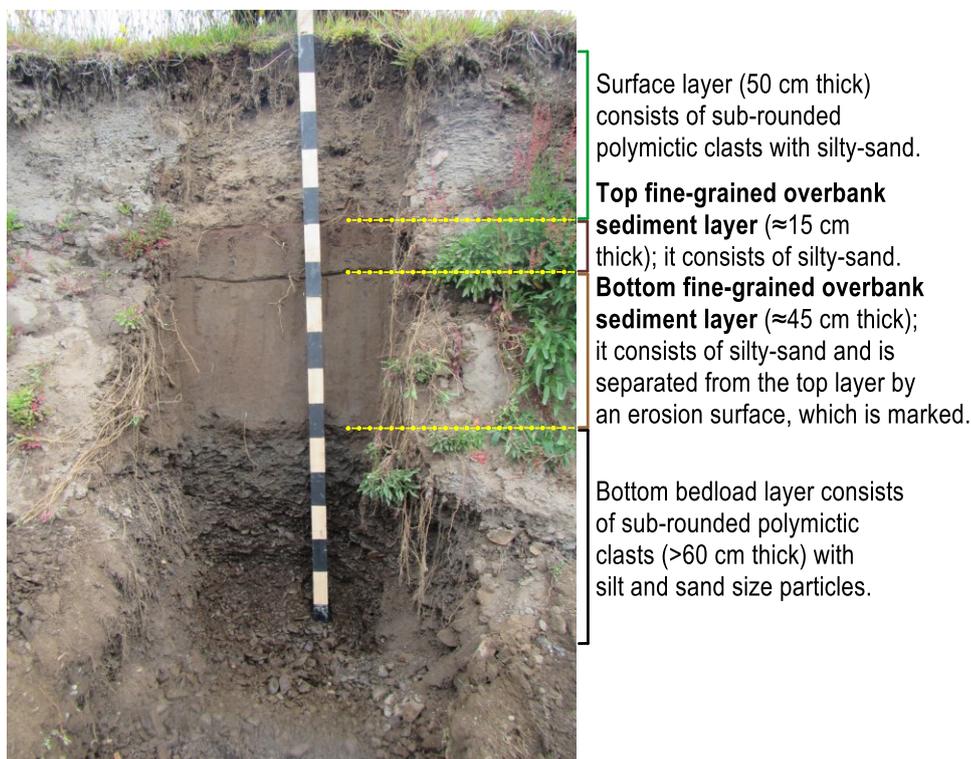
Surface layer, apart from the vegetation, consists of polymictic clasts with medium to coarse sand-sized sediments and abundant organic matter; the tree trunk and clasts were possibly deposited during the last flood.

Top fine-grained overbank sediment layer of grey colour and of variable thickness; it consists of medium to coarse sand-sized sediments and clay; there is evidence of erosion.

Alternating sequence of fine-grained overbank sediments (silt-clay); contain abundant plant remains, some of which are charred.

Bottom fine-grained overbank sediment layer (>40 cm); it consists of mainly grey silt with lenses of medium brown sand (oxidised) and plant remains.

Figure A3.5.1.1. Field site JP-761 (68.812544°W, 54.560516°S). Close-up of the overbank sediment profile. The alternate colour wooden scale-bar is divided into 10 cm sections. The red dotted-line marks an erosion hollow and deposition of polymictic clasts (pebbles-sand-silt). **Note:** Layers affected by gleying should be recorded on the field observations sheet because the speciation and solubility of many elements affected by redox relationships is difficult to interpret. Photograph: Felipe Astudillo, Servicio Nacional de Geología y Minería, Valdivia, Chile (SNGM).



Surface layer (50 cm thick) consists of sub-rounded polymictic clasts with silty-sand.

Top fine-grained overbank sediment layer (≈15 cm thick); it consists of silty-sand.

Bottom fine-grained overbank sediment layer (≈45 cm thick); it consists of silty-sand and is separated from the top layer by an erosion surface, which is marked.

Bottom bedload layer consists of sub-rounded polymictic clasts (>60 cm thick) with silt and sand size particles.

Figure A3.5.1.2. Field site JP-765 (68.726130°W, 54.227522°S). Close-up photograph of overbank sediment profile. The alternate colour wooden scale-bar is divided into 10 cm sections. Photograph: Juan Lacassie (SNGM).

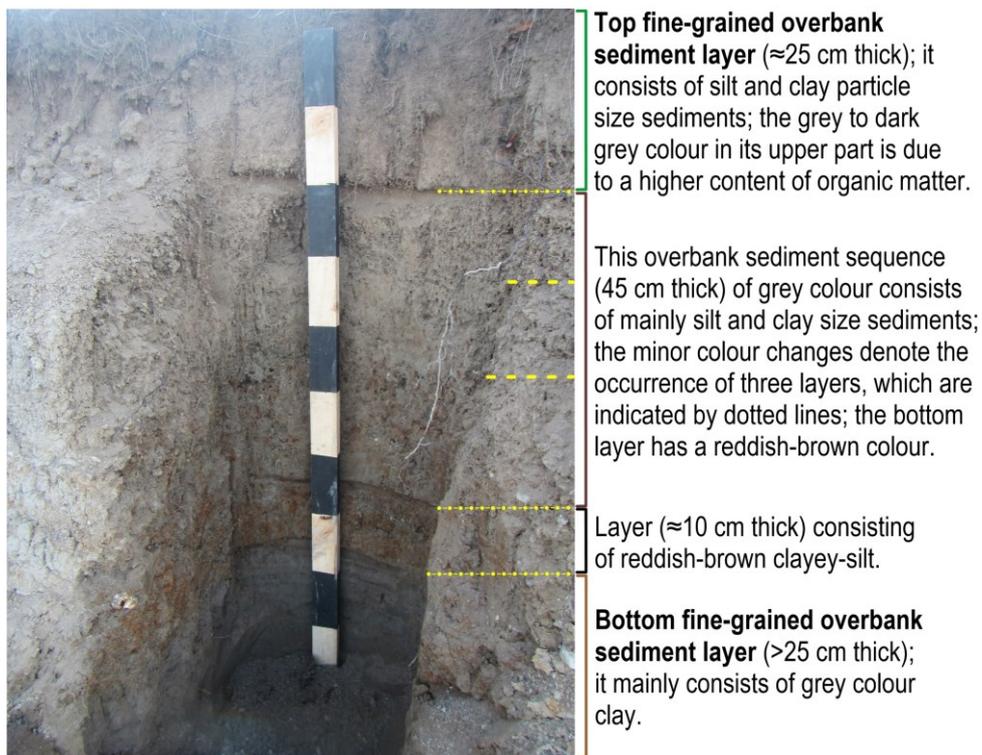


Figure A3.5.1.3. Field site JP-766 ($68.693970^{\circ}W$, $53.547565^{\circ}S$). Close-up of the overbank sediment profile on Río Chico. The alternate colour wooden scale-bar is divided into 10 cm sections. Refer to Note in Figure A3.5.1.1 for the Bottom blue-grey colour layer. So, in this case the 10-cm thick layer overlying the Bottom fine-grained, blue-grey layer should be sampled. Photograph: Felipe Astudillo (SNGM).

A3.5.1.2. Floodplain sediment profiles, Tierra del Fuego, Chile

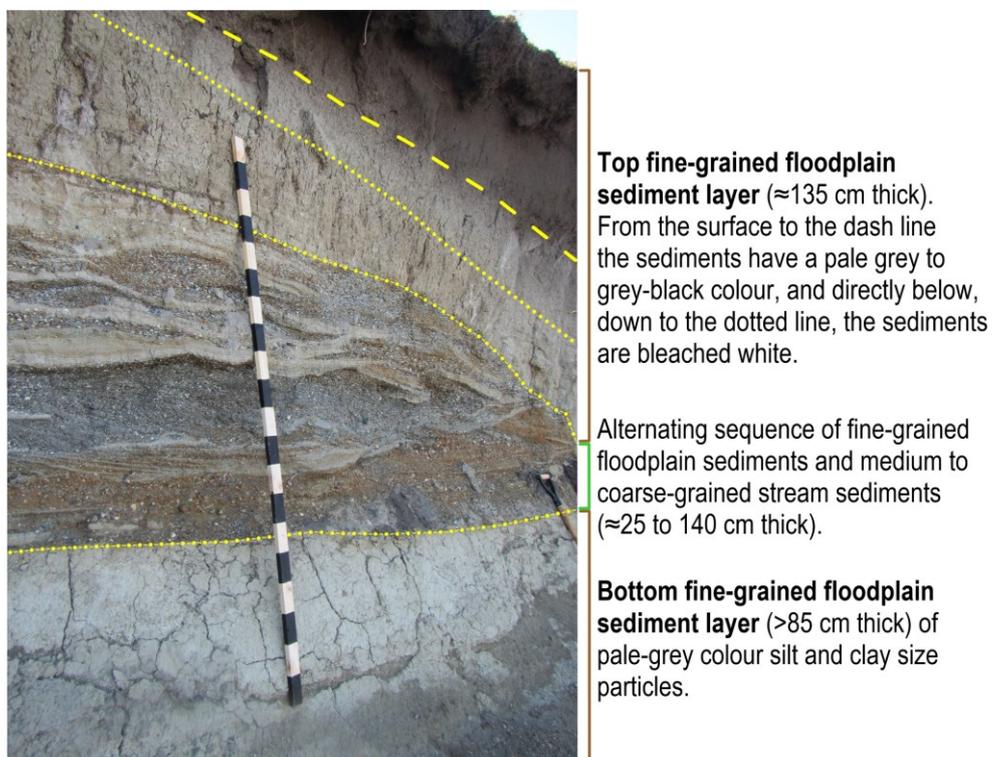


Figure A3.5.1.4. Field site JP-759 ($69.901037^{\circ}W$, $52.849004^{\circ}S$). Close-up photograph of the floodplain sediment profile. The alternate colour wooden scale-bar is divided into 10 cm sections. Photograph: Felipe Astudillo (SNGM).

A3.5.1.3. Overbank sediment profiles, Colombia



Figure A3.5.1.5. Overbank sediment profiles, Low-density Geochemical Mapping of Colombia: **(a)** Aracataca River (74.231°W, 10.95183333°S), Ciénaga Grande Santa Marta, Ciénaga, Magdalena, Caribbean Region. **(b)** Dagua River (76.68654722°W, 3.686675°S), Valle del Cauca, Pacific Region, Western Colombia. Photographs: Adrián Pérez Avila, Servicio Geológico Colombiano (SGC).

A3.5.1.4. Floodplain sediment profiles, Colombia

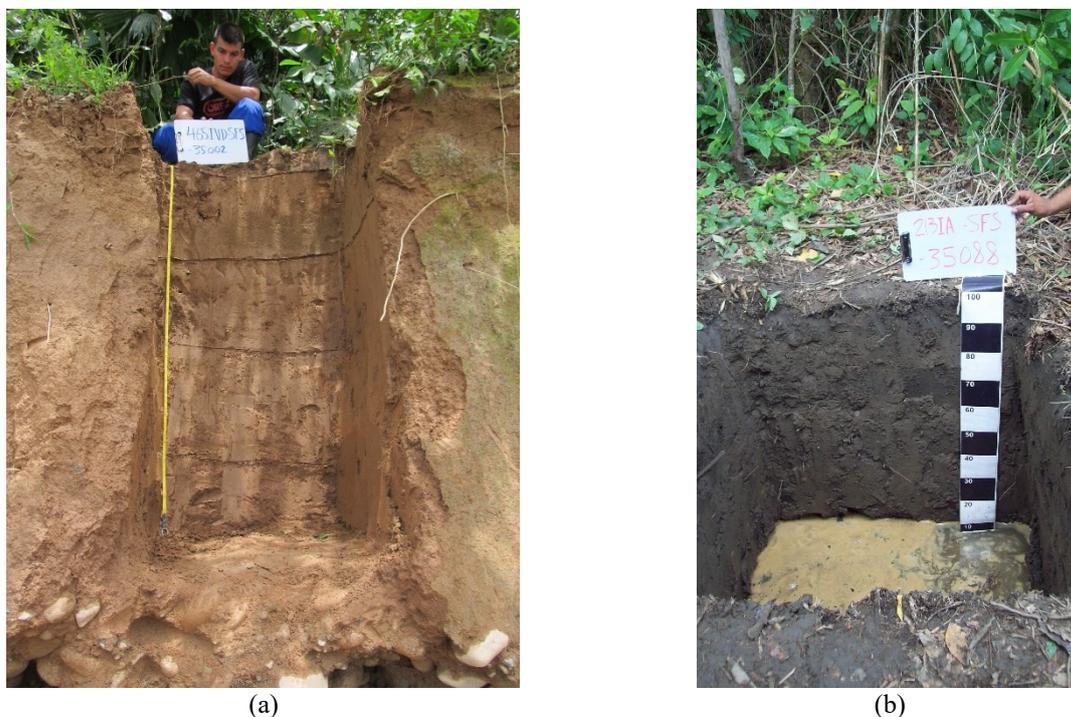


Figure A3.5.1.6. Floodplain sediment profiles, Low-density Geochemical Mapping of Colombia: **(a)** San Miguel River, tributary of Amazon River (76.97436667°W, 0.271380556°S), Putumayo, South-East Colombia, near to the Ecuador Border. **(b)** Cravo Sur River (72.08465833°W, 5.256952778°S), Orinoco River basin, Casanare, Eastern Colombia. Photographs: Adrián Pérez Avila (SGC).



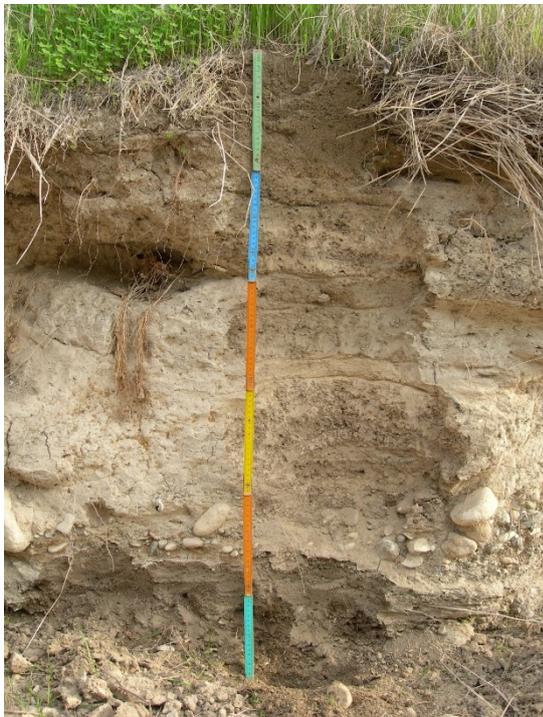
(a)



(b)

Figure A3.5.1.7. Floodplain sediment profiles, Low-density Geochemical Mapping of Colombia: (a) Roque River of Magdalena River basin ($73.93119444^{\circ}W$, $7.884108333^{\circ}S$), Serrania San Lucas, Bolivar, North Colombia. (b) Zulia River ($72.51006111^{\circ}W$, $8.245944444^{\circ}S$), Puerto Santander, Norte de Santander, North-East Colombia, Venezuela border. Photographs: Adrián Pérez Avila (SGC).

A3.5.1.5. Floodplain sediment profiles, Cyprus



(a)



(b)

Figure A3.5.1.8. Floodplain sediment profiles, Cyprus: (a) CYFP065 ($32.32844015^{\circ}E$, $34.91868153^{\circ}N$), and (b) CYFP036 ($32.38632217^{\circ}E$, $34.84335838^{\circ}N$), where there are alternate layers of gravel (bedload), and fine-grained floodplain sediments. Photographs: Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) and IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).



(a)



(b)

Figure A3.5.1.9. Floodplain sediment profiles, Cyprus. **(a)** From top to bottom: Three fine-grained floodplain sediment layers overlying a pebbly-sandy layer underlain by a fine-grained floodplain sediment layer (CYFP070 – 32.58569621°E, 35.17359554°N). **(b)** From top to bottom: Fine-grained floodplain sediment layer is at the surface, and below it there is a thick sequence of gravel-sand overlying a thin fine-grained floodplain sediment layer, underlain by medium grained pebbly-sandy layer followed by a fine-grained floodplain sediment and a bottom pebbly-sandy layer (CYFP093 – 32.38293209°E, 34.84913947°N). Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)

Figure A3.5.1.10. Floodplain sediment sample site CYFP017 (33.02761286°E, 34.66321255°N), Cyprus: **(a)** Bottom sample was collected first, and after clearing the vegetation and riverbank face **(b)** The top sample was taken. It is noted that in difficult cases, such as this one, the top and bottom overbank and floodplain sediment samples can be collected from different nearby sites. What is required is to study carefully the overbank/floodplain sediment sequence. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)

Figure A3.5.1.11. Floodplain sediment sample site CYFP022 (32.38756332°E, 35.04002401°N), Cyprus. The Top and Bottom floodplain sediment samples were collected from two nearby sites after studying the exposed sections: (a) Top sample site, and (b) Bottom sample site – the floodplain sediment sample was collected directly above the gravel bed, which is considered to be the base level of this catchment basin. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)

Figure A3.5.1.12. Floodplain sediment sample site CYFP027 (32.39492329°E, 34.83084008°N), Cyprus. The Top and Bottom floodplain sediment samples were collected from two nearby sites after studying the exposed sections: (a) Top sample site, and (b) Bottom sample site – the floodplain sediment sample was collected above the gravel bed, which is considered to be the base level of this catchment basin. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)

Figure A3.5.1.13. Floodplain sediment sample site CYFP080 (32.39649769°E, 35.03868915°N), Cyprus. The Top and Bottom floodplain sediment samples were collected from two nearby sites after studying the exposed sections: (a) Top sample site, and (b) Bottom sample collected directly above the gravel bed, which is considered to be the base level of this catchment basin. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).



(a)



(b)

Figure A3.5.1.14. Floodplain sediment sample site CYFP056 (32.80336926°E, 35.07273659°N), Cyprus. The Top and Bottom floodplain sediment samples were collected from two nearby sites after studying the exposed sections: (a) Top sample site, and (b) Bottom sample collected directly above the gravel bed, which is considered to be the base level of this catchment basin. Photographs: Alecos Demetriades (IGME/IUGS-CGGB).

A3.5.1.6. Overbank sediment profiles, Spain



(a)



(b)

Figure A3.5.1.15. Overbank sediment profiles in Spain: (a) Adaja River ($4.987508^{\circ}W$, $40.563325^{\circ}N$), and (b) Majones River ($0.883845^{\circ}W$, $42.64258^{\circ}N$). Photographs: Paula Adánez Sanjuan, Instituto Geológico y Minero de España, Madrid, Spain (IGME).

A3.5.1.7. Floodplain sediment profiles, Spain



(a)



(b)

Figure A3.5.1.16. Floodplain sediment profiles in Spain: (a) Besós River ($2.193414^{\circ}E$, $41.487622^{\circ}N$), and (b) Guadarrama River ($3.946772^{\circ}W$, $40.266259^{\circ}N$). Photographs: Paula Adánez Sanjuan (IGME).



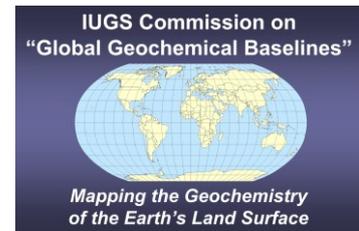
(a)



(b)

Figure A3.5.1.17. Floodplain sediment profile in Spain, Tinto River (6.774904°W, 37.304628°N): The two photographs show the same floodplain sediment section in (a) Its original state, and (b) After cleaning the face to expose the floodplain sediment layers. Note the oxidised floodplain sediments, which are derived from the Iberian Pyrite Belt mining activities. These two photographs show the work that must be done in such difficult cases to expose the floodplain sediment sequence for study and sampling. Photographs: Paula Adánez Sanjuan (IGME).

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 4

Sample Preparation and Storage

Daniela Mackovych^{1,3}, Pavol Lučivjanský¹, Alecos Demetriades^{2,3}

¹ State Geological Institute of Dionyz Stur, Regional Centre, Spiska Nova Ves, Slovakia

² Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

³ IUGS Commission on Global Geochemical Baselines

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4.1. Introduction

The preparation of samples collected for the Global Geochemical Reference Network project should be prepared in a single, experienced and well-equipped facility. Demetriades (2014, p.2) stressed the significance of all stages of a geochemical mapping project, and particularly sample preparation: “*Sampling is the costliest leg of the survey, and undoubtedly the most difficult to repeat if it is not carried out properly. The next step that must be performed correctly is **sample preparation**. Any mistakes made during sampling and **sample preparation** are difficult to trace and correct afterwards. As sampling and **sample preparation** affect project success, both must be carried out by well-trained personnel, and supervised by an experienced applied field geochemist and chemist, respectively. Laboratory analysis of samples is another costly part of the geochemical survey, and a stage of considerable concern. If samples, however, have been collected and **prepared properly**, they can be reanalysed until the results are of acceptable quality. Finally, data processing, map plotting, and interpretation, provided the previous stages of sampling, **sample preparation**, and analysis have given reliable results, are processes that can be repeated, depending on the skills of the applied geochemist.*”

The Geoanalytical laboratory of the State Geological Institute of Dionyz Stur (Spisska Nova Ves, Slovakia) has the necessary equipment, professional experience and expertise to carry out the sample preparation of all sample types to be collected during the Global Geochemical Reference Network project. The laboratory has previously prepared the samples for two pan-European geochemical projects, the FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005; Sandström *et al.*, 2005) and GEMAS – Geochemical Mapping of Agricultural and grazing land Soil (Reimann *et al.*, 2014; Mackovych and Lucivjansky, 2014).

Since national restrictions for sending unprepared samples abroad may complicate the centralised sample preparation, direct negotiation with each country may be necessary at the start of the project, and before the sampling is completed. In the worst-case scenario where the sample preparation is to be carried out in the country of origin, the procedures described herein must be strictly followed and supervised by the Laboratory Committee.

4.2. Sample preparation equipment

The sample preparation laboratory should have the following equipment and packing materials:

- Temperature-controlled oven
- Unglazed porcelain mortar and pestle
- Jaw crusher
- Agate pulveriser with agate balls or agate rings (pulverisette)
- Sieving machine
- 0.063 mm sieve with nylon mesh fabric
- 0.150 mm sieve with nylon mesh fabric
- 2.0 mm sieve with nylon mesh fabric
- Polyvinyl chloride (PVC) sieve frame
- Rotary divider (splitter)
- Nylon brush
- Silica sand (to clean agate bowl and balls)
- Acetone
- Deionised water
- Vacuum cleaner
- Powder-free single-use gloves
- Masks with filter
- White laboratory coat
- White laboratory hat

- Laboratory shoes
- 100 ml polyethylene bottles (PE) with colourless caps for analytical samples
- 200 ml PE bottles for archived samples
- Self-stick waterproof laboratory labels
- Black permanent ink marker
- Heavy-duty cardboard boxes for packing samples
- Computer and computer program for archiving samples

4.3. Cleaning of sample preparation equipment

The sample preparation laboratory must be clean and dust-free. All sample preparation equipment must be thoroughly cleaned before sample preparation commences. Dust generated during the processing of samples should be vacuumed away through a dedicated filter system. All sample preparation equipment must be thoroughly cleaned after each sample is packed to avoid contamination between samples.

4.4. Inspection of samples received

All sample sets received must be inspected, and catalogued and a 'Bar code' or 'quick response' (QR) code' assigned for each sample for tracking the progress of its preparation.

4.5. Randomisation of samples and insertion of control samples

Before starting the preparation of each sample set, the leading applied geochemist or Quality Control Committee of the Global Geochemical Reference Network project prepares a list of random numbers and sends it to the head of the sample preparation laboratory for implementation. This random list will allow the insertion of splits of the field routine-replicate samples (DUPA & REPA; Fig. 4.1) and their corresponding splits of field duplicate-replicate control samples (DUPB and REPB), project standard splits (secondary reference samples, SRMs) per batch of 20 samples, and a solid blank sample split per batch of 50 samples. Table 4.1 shows the insertion of 11 quality control samples in a randomised batch of 100 samples. Ideally, the randomisation of samples should be done when all global project samples are collected. If, however, it is decided to analyse collected samples, then they should be analysed in large, randomised batches of a few thousand samples (*this action is not recommended*).

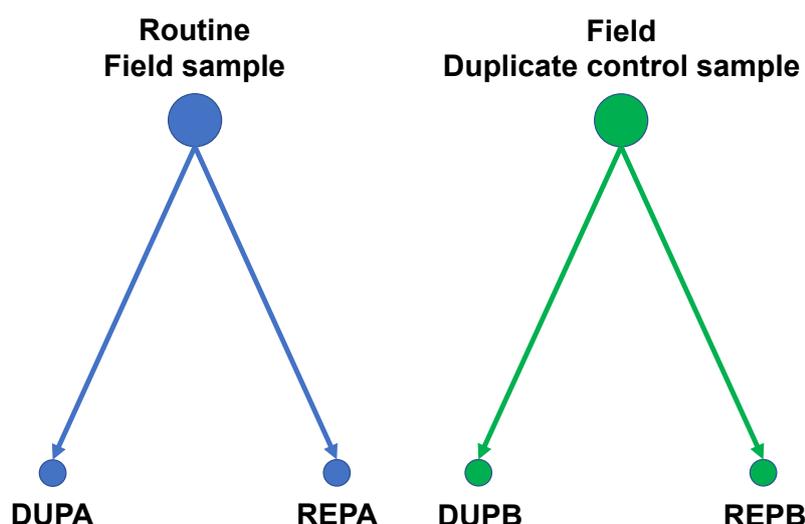


Figure 4.1. Diagram showing the relationship between the field duplicate pair (DUPA and DUPB) and the laboratory replicate pair (REPA and REPB). Slightly modified figure from Johnson (2011, Fig. 5.2, p.64). Drawn with Microsoft™ PowerPoint by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) and IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).

Table 4.1. Example of a random number list for sample number allocation to be used in the Global Geochemical Reference Network project: (a) Random number list showing the insertion of field duplicate (DUPA & DUPB) and laboratory replicate (REPA & REPB) pair sample splits, aliquots of two Global Geochemical Reference Network project SRMs (SRM 1 & SRM 2), and two aliquots of the solid Blank reference material (Blank 1A and 1B); the empty cells are then filled with routine Global Geochemical Reference Network project samples in consecutive numerical 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	
38		44		100		61	
10		91		73		99	
86		79		60		96	
98		68		16		77	
3		65		6		35	
76		89		58		97	
9		52		12		66	
78		27		1		83	
50		42		19		54	
24		62		31		11	
30		40		26		46	
5		94		20		15	
67		70		29		49	
71		56		95		28	
85		25		22		17	DUPA
32		84		92		21	REPA
93		47		69		75	DUPB
55		90		48		13	REPB
72		53		39		41	SRM 1A
80		2		4		88	SRM 1B
34		45		81		7	SRM 2A
82		43		63		74	SRM 2B
14		51		18		87	Blank 1A
33		36		23		57	Blank 1B
1				26		51	
2				27		52	
3				28		53	
4				29		54	
5				30		55	
6				31		56	
7	SRM 2A			32		57	Blank 1B
8				33		58	
9				34		59	
10				35		60	
11				36		61	
12				37		62	
13	REPB			38		63	
14				39		64	
15				40		65	
16				41	SRM 1A	66	
17	DUPA			42		67	
18				43		68	
19				44		69	
20				45		70	
21	REPA			46		71	
22				47		72	
23				48		73	
24				49		74	SRM 2B
25				50		75	DUPB
							76
							77
							78
							79
							80
							81
							82
							83
							84
							85
							86
							87
							Blank 1A
							88
							SRM 1B
							89
							90
							91
							92
							93
							94
							95
							96
							97
							98
							99
							100

4.6. Sample preparation

Figure 4.2 shows the homogenisation and splitting into subsamples of all sample types that are to be collected during the Global Geochemical Reference Network project. The subsample splits in the 100 and 200 ml bottles of each sample type are weighed, and their weight recorded.

The inset in Figures 4.3 to 4.8 shows the balanced field duplicated-replicated sample design to explain the ‘*additional splitting of duplicated field samples*’, which are to be collected during the Global Geochemical Reference Network project. This is the balanced quality control of sampling and analysis scheme by duplicate-replicate sample splits, using analysis of variance (ANOVA), which was followed by the FOREGS Geochemical Atlas of Europe project (Sandström *et al.*, 2005). It is strongly recommended that this balanced quality control scheme is used in the Global Geochemical Reference Network project.

4.6.1. Preparation of rock samples

The rock sample preparation procedure is shown in Figure 4.3. Rock chip samples are first broken down into smaller fragments in a jaw crusher, completely pulverised in an agate planetary mill to a grain size of <0.063 mm, homogenised and split into two equal portions. The first portion is homogenised and split into five 200 ml PE bottles, then archived for future use (Fig. 4.2).

The second portion is homogenised and split into ten 100 ml PE bottles for submission to the analytical laboratories (Fig. 4.2).

Homogenisation and splitting into subsamples of all sample types collected for the Global Geochemical Reference Network project

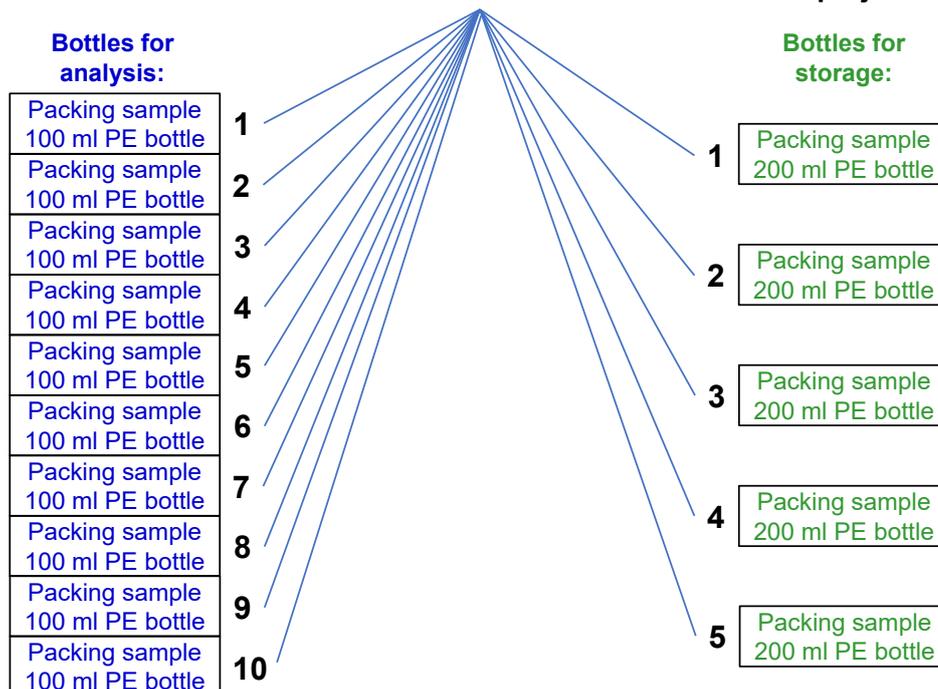


Figure 4.2. Diagram showing the homogenisation and splitting into subsamples of all sample types that are to be collected during the Global Geochemical Reference Network project. Ten 100 ml subsamples of each sample type are prepared for the analytical laboratories, and five 200 ml subsamples for storage. Drawn with Microsoft™ PowerPoint by Alecos Demetriades (IGME/IUGS-CGGB).

4.6.2. Preparation of residual soil samples

The residual soil sample preparation procedure is shown in Figure 4.4. Residual soil samples are dried in temperature-controlled ovens at <math><40^{\circ}\text{C}</math>, hammered to reduce agglomeration (if needed), disaggregated in an unglazed porcelain mortar (if needed) and sieved through a 2 mm nylon mesh fabric. Each sample is then homogenised and split into two equal portions using a rotary divider. The first portion, after homogenisation is split into five 200 ml PE bottles and archived for future studies (Fig. 4.2).

The second portion, following homogenisation, is split into ten 100 ml PE bottles for submission to the analytical laboratories (Fig. 4.2).

4.6.3. Preparation of humus samples

The humus sample preparation procedure is shown in Figure 4.5. The humus samples are dried at ambient room temperature. After removing large roots and rock fragments, the samples are disaggregated in an unglazed porcelain mortar and pestle and then sieved by hand through a 2 mm nylon mesh fabric. Each sample is then split into two equal portions using a rotary divider. The first portion, after homogenisation, is split into five 200 ml PE bottles and archived for future use (Fig. 4.2).

The second portion is pulverised in an agate planetary mill to a grain size of <math><0.063\text{ mm}</math>, homogenised and split into ten 100 ml PE bottles for submission to the analytical laboratories (Fig. 4.2).

4.6.4. Preparation of stream sediment samples

The stream sediment sample preparation procedure is shown in Figure 4.6. Stream sediment samples are either wet sieved or dry sieved in the field to <math><0.150\text{ mm}</math> grain size. In the case of

seasonal streams, the stream sediment maybe moist and as it cannot be sieved in the field, the sieving is carried out in the laboratory after drying.

All stream sediment samples upon arrival in the laboratory are dried in temperature-controlled ovens at $<40^{\circ}\text{C}$, disaggregated manually in a porcelain mortar, and sieved to <0.150 mm with a nylon mesh fabric. Afterwards, the <0.150 mm fraction is homogenised and split into two equal portions using a rotary divider. The first portion is homogenised and split into five 200 ml bottles and archived for future use (Fig. 4.2).

The second portion is pulverised in an agate mill to a grain size of <0.063 mm, homogenised and split into ten 100 ml bottles to be submitted to the analytical laboratories (Fig. 4.2). It is noted that pulverised parts of stream sediment samples, which do not pass through the <0.063 mm nylon mesh screen are returned to the agate mill, and are repeatedly pulverised until they pass through the screen.

4.6.5. Preparation of overbank sediment samples

The overbank sediment sample preparation procedure is shown in Figure 4.7. Overbank sediment samples are dried in temperature-controlled ovens at $<40^{\circ}\text{C}$, disaggregated manually in a porcelain mortar, and sieved through a 2 mm nylon mesh screen. Subsequently, the <2 mm fraction is homogenised and split into two equal portions. The first portion, after homogenisation, is split into five 200 ml portions using a rotary divider, and the samples are archived for future use (Fig. 4.2).

The second <2 mm portion is homogenised and split into ten 100 ml PE bottles for submission to the analytical laboratories (Fig. 4.2).

4.6.6. Preparation of floodplain sediment samples

The floodplain sediment sample preparation procedure is shown in Figure 4.8. The floodplain sediment sample preparation procedure is the same as that of the overbank sediment samples. Floodplain sediment samples are dried in temperature-controlled ovens at $<40^{\circ}\text{C}$, disaggregated manually in a porcelain mortar, and sieved through a 2 mm nylon mesh screen. Subsequently, the <2 mm fraction is homogenised and split into two equal portions. The first portion, after homogenisation, is split into five 200 ml PE bottles using a rotary divider, and the samples are archived for future use (Fig. 4.2).

The second <2 mm portion is homogenised and split into ten 100 ml PE bottles for submission to the analytical laboratories (Fig. 4.2).

4.7. Sample storage and management

The archived samples in the 200 ml PE bottles for long term storage must be stored in a secure and clean storeroom (Fig. 4.2). The PE bottles with the samples should have hand-written labels using a black permanent ink marker, as well as a specialised '*Bar or QR code Tracking System*' to allow them to be quickly located.

The 10 splits of each sample type, prepared for sending to the analytical laboratories, will not necessarily be used immediately. Unused sample sets for analysis, which have been randomised and include the quality control samples, should be safely stored in a permanent clean facility, and be ready for despatch to a specified laboratory when the need arises.

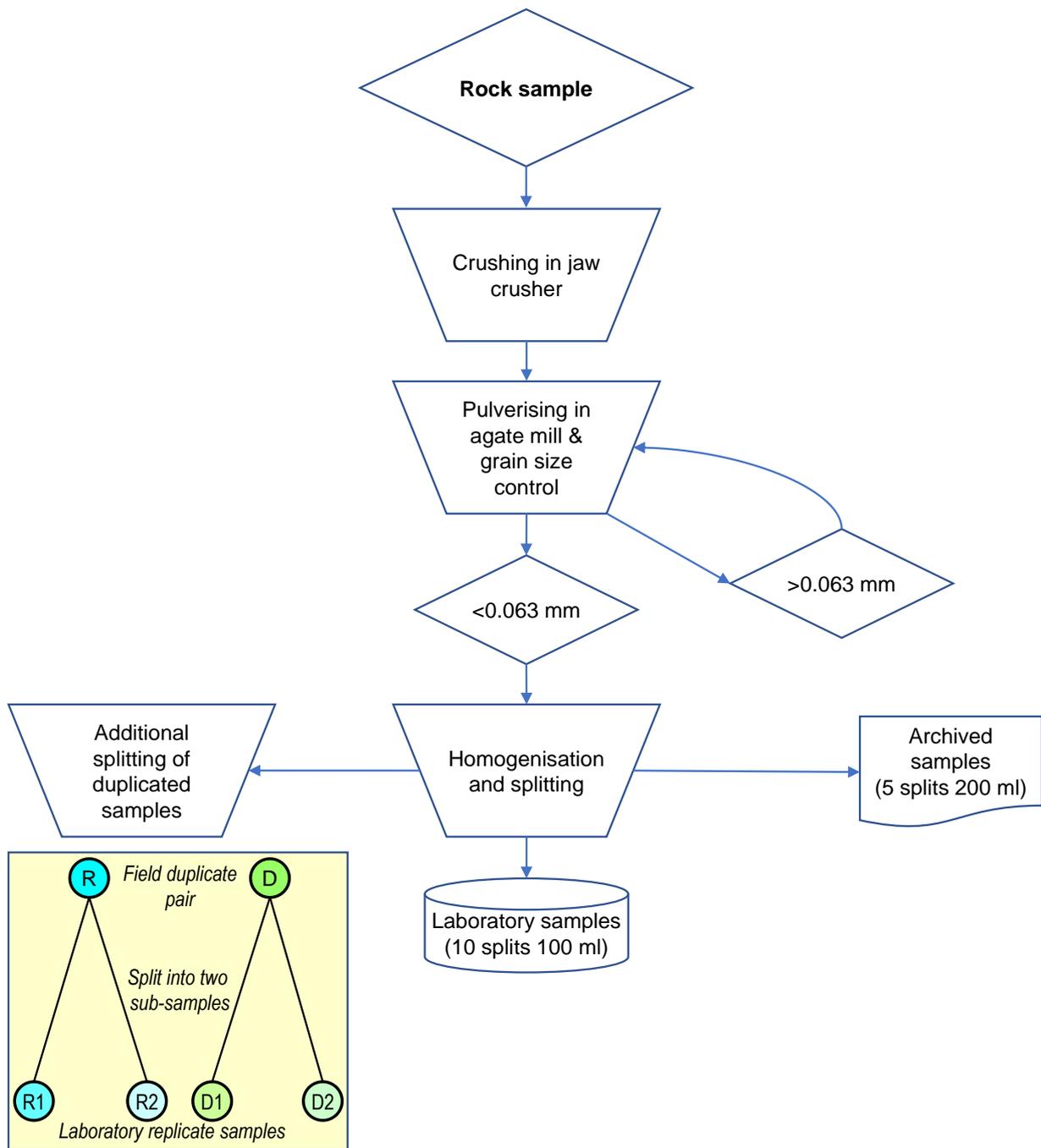


Figure 4.3. Rock sample preparation procedure. Yellow-colour inset shows the additional splitting of field duplicate sample pairs in a balanced design. Notation: R = Routine field sample; D = Field duplicate sample; R1 & R2 and D1 & D2 are the laboratory replicate splits of the routine and field duplicate samples, respectively. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Microsoft™ PowerPoint.

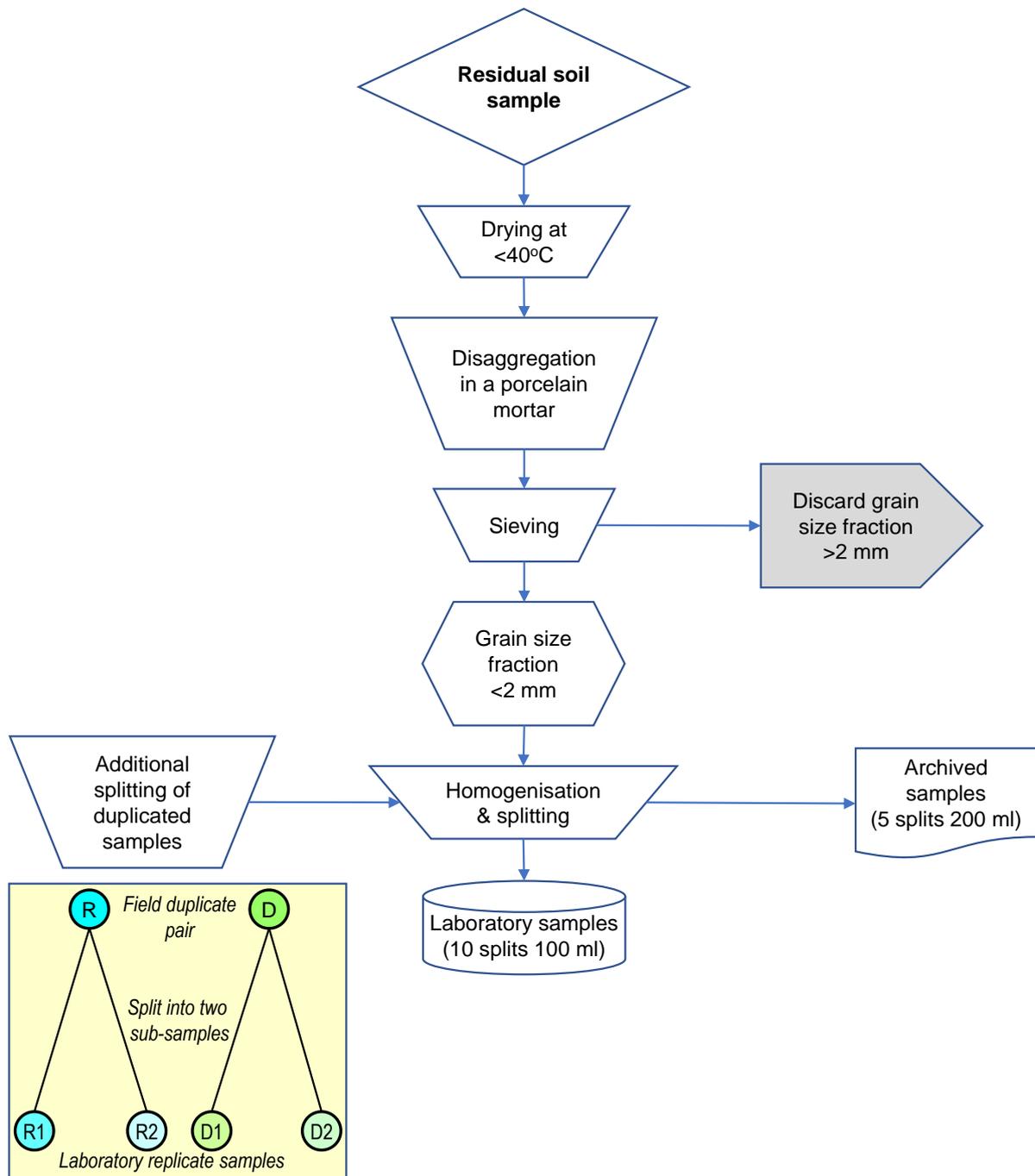


Figure 4.4. Residual soil sample preparation procedure (after Sandström et al., 2005, Fig. 4, p.86, with minor modifications). Yellow-colour inset shows the additional splitting of field duplicate sample pairs in a balanced design. Notation: R = Routine field sample; D = Field duplicate sample; R1 & R2 and D1 & D2 are the laboratory replicate splits of the routine and field duplicate samples, respectively. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Microsoft™ PowerPoint.

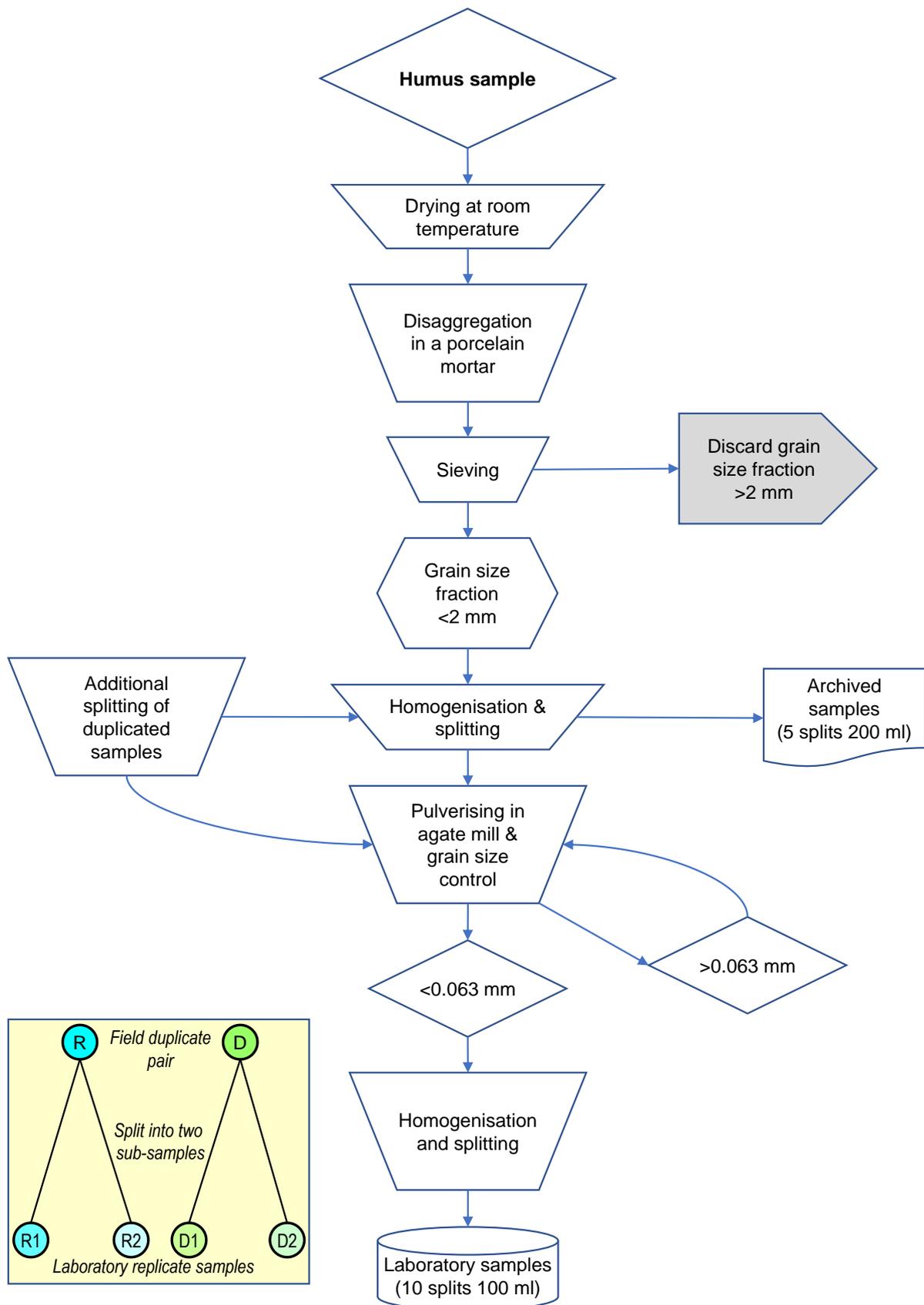


Figure 4.5. Humus sample preparation procedure (after Sandström et al., 2005, Fig. 5, p.87, with minor modifications). Yellow-colour inset shows the additional splitting of field duplicate sample pairs in a balanced design. Notation: R = Routine field sample; D = Field duplicate sample; R1 & R2 and D1 & D2 are the laboratory replicate splits of the routine and field duplicate samples, respectively. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Microsoft™ PowerPoint.

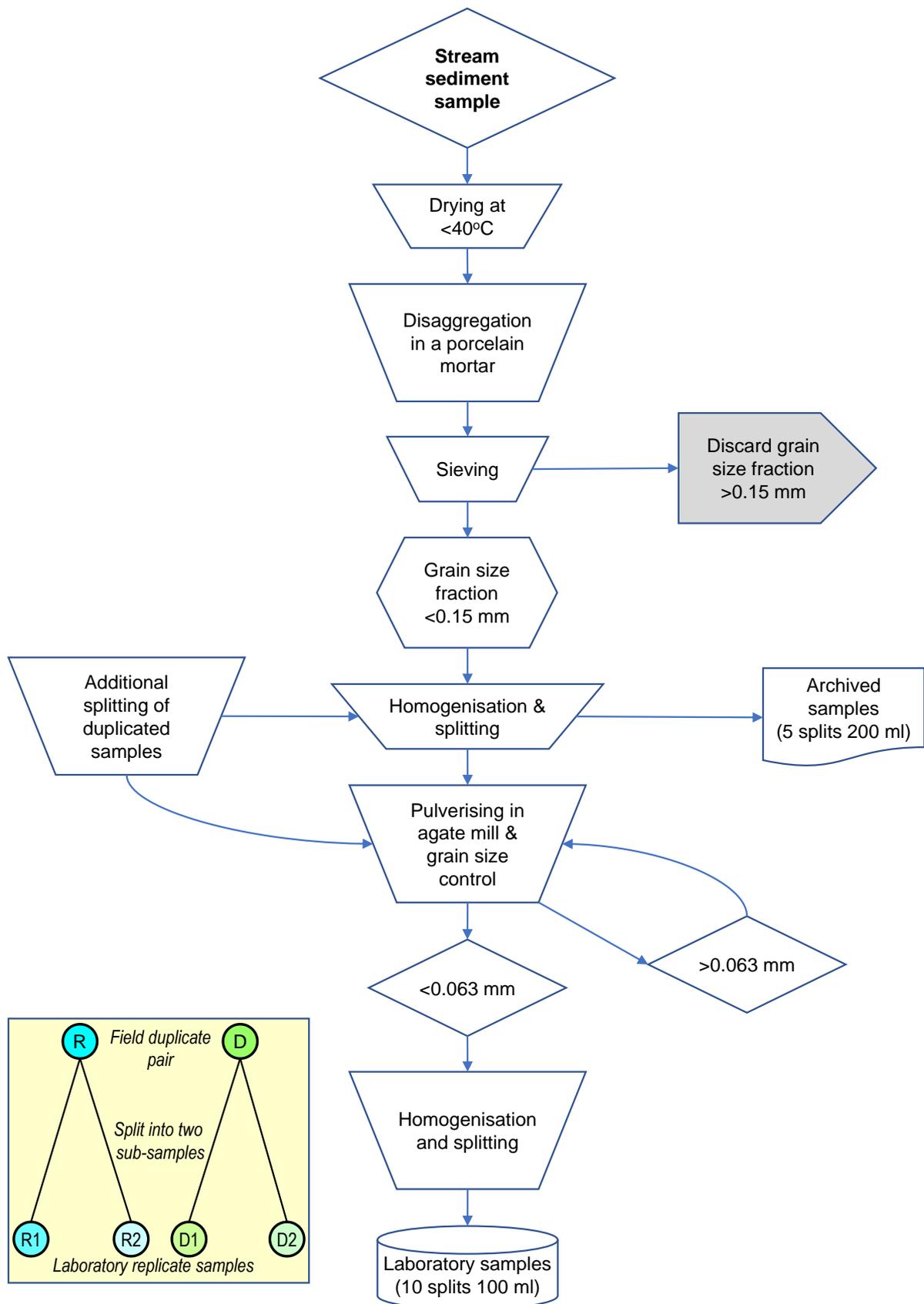


Figure 4.6. Stream sediment sample preparation procedure (after Sandström et al., 2005, Fig. 2, p.84, with minor modifications). Yellow-colour inset shows the additional splitting of field duplicate sample pairs in a balanced design. Notation: R = Routine field sample; D = Field duplicate sample; R1 & R2 and D1 & D2 are the laboratory replicate splits of the routine and field duplicate samples, respectively. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Microsoft™ PowerPoint.

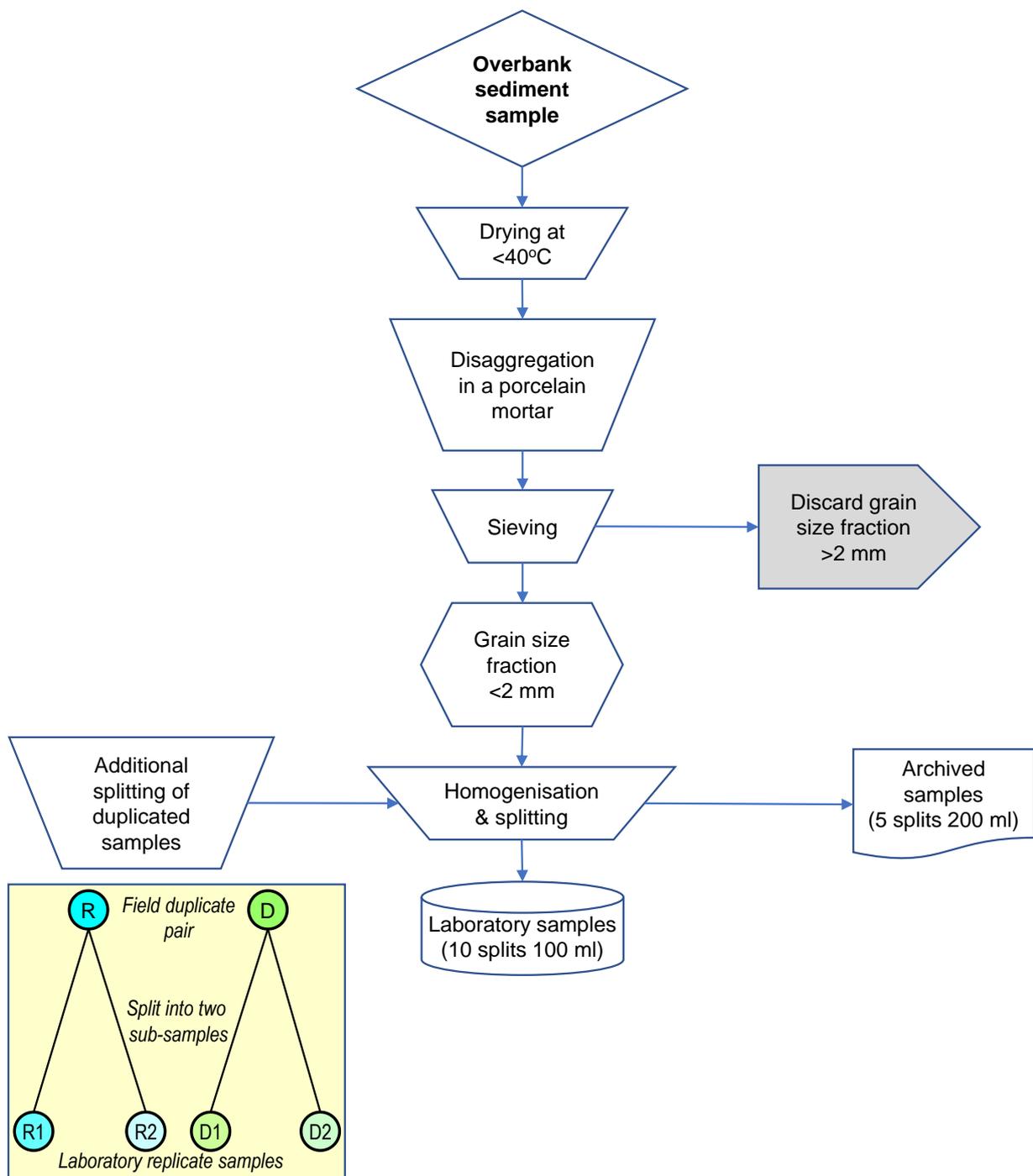


Figure 4.7. Overbank sediment sample preparation procedure. Yellow-colour inset shows the additional splitting of field duplicate sample pairs in a balanced design. Notation: R = Routine field sample; D = Field duplicate sample; R1 & R2 and D1 & D2 are the laboratory replicate splits of the routine and field duplicate samples, respectively. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Microsoft™ PowerPoint.

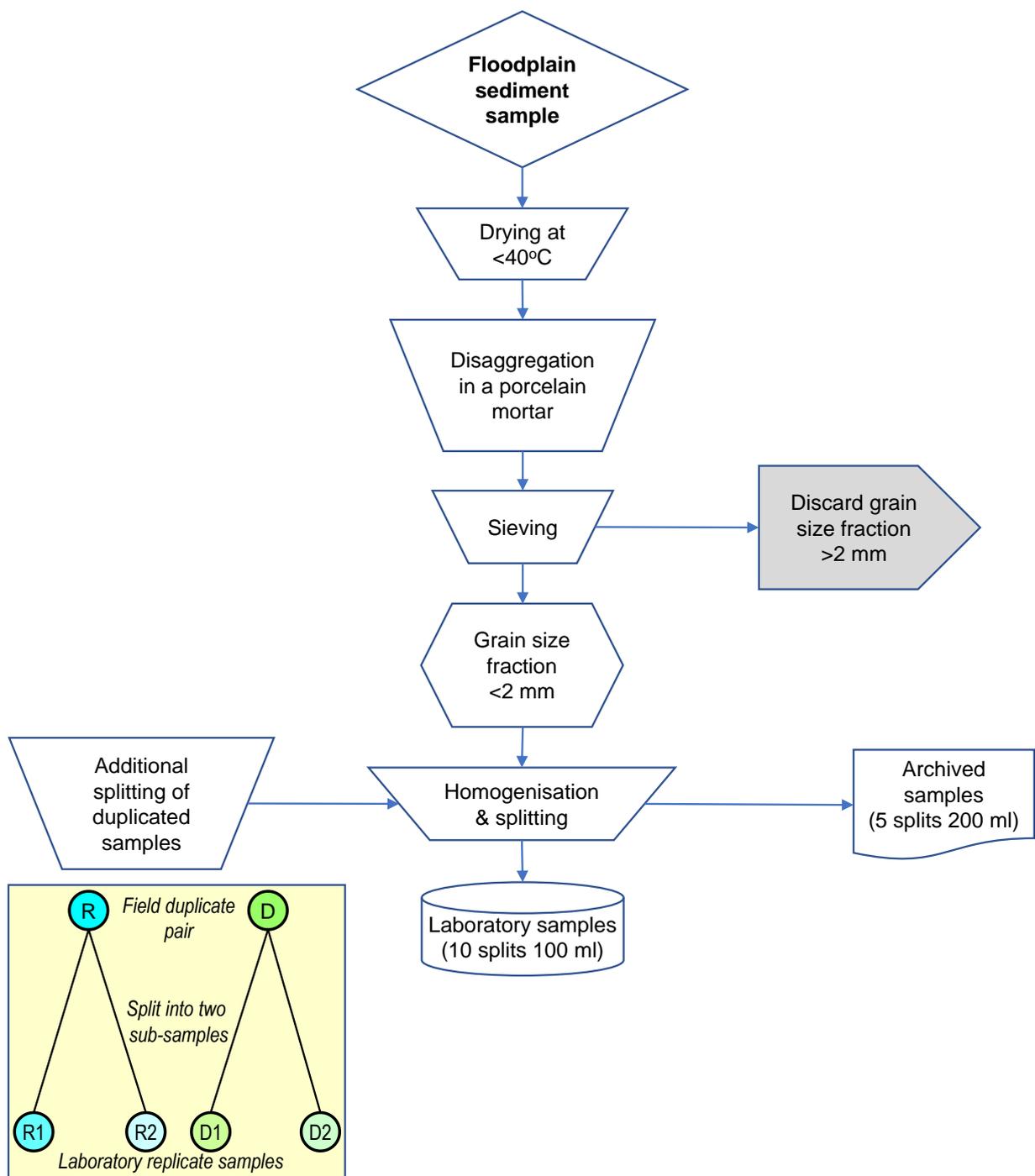


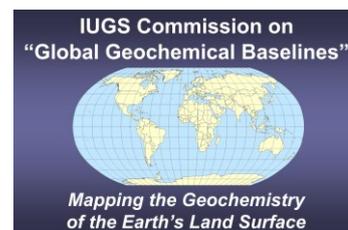
Figure 4.8. Floodplain sediment sample preparation procedure (after Sandström et al., 2005, Fig. 3, p.85, with minor modifications). Yellow-colour inset shows the additional splitting of field duplicate sample pairs in a balanced design. Notation: R = Routine field sample; D = Field duplicate sample; R1 & R2 and D1 & D2 are the laboratory replicate splits of the routine and field duplicate samples, respectively. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Microsoft™ PowerPoint.

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Note: All hyperlinks were checked on the 11th of February 2022.

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**International Union of Geological Sciences
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Chapter 5

**Development of Reference Materials for
External Quality Control**

Pavol Lučivjanský, Daniela Mackových

State Geological Institute of Dionyz Stur, Regional Centre, Spiska Nova Ves, Slovakia

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5.1. Introduction

Reference materials (RMs), whether Primary Reference Materials (PRMs) or Secondary Reference Materials (SRMs), are important tools in implementing several aspects of measurement quality of laboratory results, and are used for method validation, calibration, measurement uncertainty estimation, training, and for internal and external quality control purposes.

Preparation of any reference material requires a thorough knowledge of the type of material and its properties. Further, expertise in the selection of appropriate and sensitive methods for carrying out homogeneity tests, stability tests and material characterisation, and good command of the statistical methods necessary for the correct processing and interpretation of experimental data.

The procedure for the preparation of an SRM for external quality control is similar to that for PRM. The difference between a PRM and an SRM is that the former is subject to rigorous ring testing for its certification.

For the Global Geochemical Reference Network project, the following Secondary Reference Materials should be prepared for each of the recommended sample media:

- Rock
- Residual soil
- Stream sediment
- Overbank/Floodplain sediment, and
- Blank solid sample.

For rock, residual soil, stream sediment, and overbank/floodplain sediment, at least five SRMs for each sample type must be prepared with different major and trace element concentrations. The two solid blank project reference samples should be made from fine-grained kaolin tailings from two different kaolin plants, and if possible, from two different countries (Schermann, 1990). Alternatives to kaolin are quartz (need to manage silicosis risk) or feldspar ‘wash’, or even corundum. The risk and cost/benefit analysis of these materials should, however, be considered.

The recommended minimum amount for each SRM must be at least 1000 kg (refer to Chapters 8 & 10).

5.1.1. Definitions

The following definitions are according to ISO Guide 35 (ISO, 2017a, p.2):

Reference Material (RM): *Material, is sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process.*

Certified Reference Material (CRM): *Reference Material characterised by a metrologically valid procedure for one or more specified properties, accompanied by an RM certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability.*

In applied geochemistry, the term **Primary Reference Material (PRM)** is used and is synonymous with CRM, *i.e.*, it is an internationally certified standard with recognised and accepted elemental concentrations (Johnson, 2011, p.64).

Secondary Reference Material (SRM): *Generally, an in-house reference sample, is developed for internal use by projects, and is kept ‘blind’ to the analyst (Johnson, 2011, p.64). It is for ‘internal use’ by the project, and is referred to as an ‘external’ reference material because it is used by the applied geochemist to assess the quality of the analytical results generated by the*

laboratory, and it is kept ‘*blind*’ to the analyst. Laboratories usually have their own in-house secondary reference materials (Thompson *et al.*, 2006; ISO, 2014; Gowing and Hayr, 2020).

5.2. Planning preparation of Reference Materials

Detailed planning of each activity is needed to prepare the RM. The preparation project begins by defining the RM type. A key criterion in the selection and specification of an RM is that its chemical and mineralogical composition should be as close as possible to the actual samples to be analysed in the project, as well as to be available in a sufficient quantity. Knowledge of the analytical procedures commonly used in the analysis of these sample types is required. The RM (bottles) being prepared should contain a sufficient amount of material for single and/or multiple measurements.

Key steps in RM preparation are:

- Material specification
- Material acquisition
- Material processing
- Homogenisation, sub-division and packaging
- Homogeneity test
- Stability test
- Characterisation / Value Assignment
- Documentation / Information, and
- Storage of material.

5.3. Collection of RM sample

The first task is to obtain a sufficient amount of material for:

- The homogeneity test
- The stability test
- Level test (*e.g.*, concentration above the detection limit (DL) for the majority of elements)
- Organisation of interlaboratory comparisons (IC) – characterisation of assigned values, and
- Control analyses for the planned number of analyses of elements in collected reference samples.

By ‘*sufficient amount of material*’ is meant that there should be enough material to last for the duration of the Global Geochemical Reference Network project, and an adequate amount to be leftover for at least another run of the project.

5.4. Preparation of RM

The sample preparation scheme of the relevant RM will depend on the type of material and the required parameters of interest in the project.

For the preparation and testing of the RM is necessary for the laboratory to have the suitable equipment and environmental conditions, such as a clean environment, which ensures that the reference material is not contaminated during its preparation. Further, if certain components of the material have dangerous properties, it is necessary to take the appropriate measures to avoid endangering the health of the personnel handling the material.

5.5. Processing of RM

The collected material (soil, sediment) contains water, which is removed by drying at ambient or elevated temperature (maximum 40°C), depending on the parameters of interest, as some RM volatile components may be partly lost. After drying the soil or sediment sample, it is necessary to crush, disintegrate, grind and reduce the particle size to <2 mm by sieving with a nylon screen to improve the homogeneity of the material.

The sieved samples with the desired grain size (<2 mm) are homogenised in a tilting mixer for 24 hours. During homogenisation, the material is checked for lumps.

Rock reference materials following crushing should be pulverised in agate mills to <0.075 mm.

It is important to record all the preparation stages of RMs, and the type of equipment used.

5.6. Packaging, labelling, distribution

After the RM has been homogenised, it is necessary:

- To select a type of packaging that protects the reference material during storage, transport and handling, *i.e.*, the selection of packaging considers the type of prepared material.
- To label the packed material with the name of the test material and the name of the preparation laboratory.
- To maintain material homogeneity, and
- To avoid segregation of finer particles in the processing of soil or sediment during sub-division.

The sub-division of a bulk material should be completed in the shortest possible time to minimise the chances for the matrix to revert to heterogeneity.

Although it is probably not so relevant to the sort of standard reference materials used in geochemistry, tracking of standards is a requirement of accreditation organisations (*e.g.*, ISO 17025 (ISO, 2017b)), and the date of preparation is one thing they like to track. Therefore, the date of preparation should be on the label of each reference material.

5.7. Homogeneity test and statistical treatment of homogeneity data

As most RMs are prepared as batches of ‘units’ (*e.g.*, bottles or vials), all units must be of the same chemical composition within the stated uncertainty for each determinand (ISO, 2017a). The homogeneity of the prepared material is verified by a homogeneity test on a selected and sufficient number of units. The measurement is performed on those determinands that are of interest to the project. The choice of methodology shall ensure that the method is validated and has a sufficient level of repeatability.

According to ISO Guide 35 (ISO, 2017a), analytical test procedures that have little or no sample preparation (so-called non-destructive methods) can show better accuracy than those requiring extensive multi-stage sample preparation.

Homogeneity has two aspects, between-unit homogeneity and within-unit homogeneity. The *between-unit homogeneity* reflects changes in measurement results in each unit of material. The *within-unit homogeneity* is expressed as the minimum quantity of subsample that is representative of the whole unit. The results of the homogeneity test verify, whether the between-unit variance of the measured values of the monitored determinands of the test material is not statistically significant compared to the within-unit variance, and whether the within-unit variance is statistically significant compared to the variance of the method used.

The recommended number of units, from the multi-unit batches comprising a stock of ‘*n*’ - individual units, to perform the homogeneity test should be three times the cubed root of ‘*n*’

(ISO, 2014). *Example*: For the preparation of 1000 units, 10 units or more are sufficient, depending on the matrix of the test material. Stratified random sampling is recommended for selecting ‘*n*’ units from the entire set of prepared packages. Random samples should be determined using random number generation software.

Measurements are carried out under optimal repeatability conditions, *i.e.*, throughout the day, on the same instrument, by the same operators, against the same calibration standards, to minimise the potential impact of the measurement equipment’s instability.

The selection of determinands for the homogeneity test must be carried out in such a way that the tested determinands represent the largest possible number of determinands to be tested in an organised project.

For the assessment of homogeneity, the procedures given in ISO Guide 35 (ISO, 2017a), according to one-way or two-way analysis of variance are used. The calculated F-test result must be less than the appropriate critical value for the selected degrees of freedom and at the 95% level of confidence.

The test and evaluation of homogeneity are carried out directly after packaging the test material in the final form.

The following procedure is appropriate for carrying out the homogeneity assessment:

- Random selection of ‘*m*’ samples from the final package where $m \geq 10$.
- Preparation of two test portions from each sample by the most appropriate method, which minimises differences between test portions.
- Measure 2 ‘*m*’ test aliquots for the whole series in random order under repeatability conditions, and
- Calculate the arithmetic mean, \bar{x} , from the measurement results, the within-unit standard deviation, S_w , and the between-unit standard deviation, S_s (Thompson *et al.*, 2006; ISO, 2014, 2015, 2017a).

Replicate measurements are performed in random order or reverse order so that drift measurements can be distinguished from any trend in the batch of samples.

Graphic analysis reveals outliers, trends or systematic effects. Another possibility for identifying outliers is the Cochran outliers test (Thompson *et al.*, 2006). The measured determinands should be evaluated to be sufficiently homogeneous in the prepared RM. To use an RM, the between-unit standard deviation must be no more than one-third of the interlaboratory reproducibility standard deviation.

5.7.1. Within-unit homogeneity

The simplest method for testing significant within-unit heterogeneity is similar to the between-unit homogeneity study, with the difference being that the variance of interest is a member within-unit, between subsamples. From one RM unit, ‘*m*’ test portions are taken over the expected value of the minimum sample quantity, and each is processed and measured $n_w \geq 1$ times. Within-unit heterogeneity testing should provide at least 5 degrees of freedom for the within-unit term, *e.g.*, $m \geq 6$ subsamples per unit shall be taken. Where a repeat analysis is performed on each subsample, analysis of variance should be used followed by an F-test for significant between-subsample variance. In a single RM unit with aliquots measured multiple times, a single-factor ANOVA may be used (ISO, 2017a).

The minimum amount of sample can be determined by an experimental study from a within-unit homogeneity test with different weights of the sample intake. It is permissible to set the minimum amount of sample, based on experience or from the laboratory sampling used, which has reached acceptable precision in an interlaboratory characterisation.

5.8. Stability test

In preparing the RM, it is necessary to assess whether the stability test is necessary for all relevant properties, *i.e.*, if the conditions of packaging, storage and transport are met, to examine whether the published data in the literature for a given matrix type show stability. Experimental studies are not necessary if stability information of very similar materials stored under the same storage conditions is obtained. In principle, if there is a presumption that some form of stability assessment is necessary, approaches to confirm stability in the form of short-term and long-term stability tests should be applied (ISO, 2014, 2016, 2017a).

Tests must be performed on a sufficient number of units (usually at least two units) to ensure confidence in the stability of all prepared units. Units for the stability study are normally selected randomly from a set of packaged units.

When choosing the methodology, it is considered that the method has sufficiently reliable repeatability and good sensitivity. The measurement of samples must be performed randomly so that it is possible to distinguish the trend caused by the effect of measurement from the instability of the properties of the monitored samples.

The procedures are given in ISO Guide 35 (ISO, 2017a) and can be used to assess stability. The results of the stability test can contribute to the evaluation of uncertainty.

5.9. Characterisation and value assignment

Matrix reference materials such as soil and sediment samples are in most cases characterised through the implementation of interlaboratory comparisons (IC). According to ISO 17034 (ISO, 2016), the characterisation of an RM can be accomplished by several strategies. A variant of the procedure using two and more methods of demonstrable accuracy, and in several competent laboratories, should be used for soil and sediment RM samples. Care must be taken in interlaboratory comparisons that at least two different measurement principles are used. The organiser of an IC must define the objectives of the procedure, *i.e.*, the various goals include method validation, proficiency testing and RM characterisation. To ensure reliable assigning property values of RM, the IC organiser must inform participants that the interlaboratory comparison procedure will focus on characterising RM properties.

Interlaboratory comparison participants are expected to have validated methods, are competent enough, *i.e.*, they are accredited to perform the tests for a given matrix type (ISO, 2017b), and to have good Proficiency test results (ISO, 2017a). An important aspect of a good evaluation of RM property values is that which has a sufficient number of independent data sets. The IC organiser shall provide participants with all necessary information, and test instructions, such as study objective, number of samples, number of replicates, interlaboratory comparison schedule, method of reporting results according to prepared forms, *etc.*, which are given in more detail in ISO Guide 35 (ISO, 2017a).

Prior to the statistical processing of data sets, results from each participating laboratory should be checked for completeness by visual inspection and graphically, assessed for basic errors, procedural errors, and evaluated for technical errors that may have arisen from the procedures used. Appropriate statistical procedures should be applied to the data set to determine outliers (ISO, 2016, 2017a).

An effective way to determine the RM property value is to use the mean of the laboratory averages from the results of the organised interlaboratory comparison (IAEA, 2003; ISO, 2017a).

5.10. Assigned uncertainty

The value of the component properties of an individual RM unit may be affected in principle by the RM characterisation process, between-unit variance, and changes in property values of RM during transportation and storage. Adding measurement uncertainty to the RM property, better confidence in the validity of the measured result is ensured. According to the measurement

uncertainty documents (Pauwels *et al.*, 1998; Linsinger *et al.*, 2001; ISO, 2017a; Ramsey *et al.*, 2019), the combined standard uncertainty of the reference material - U_{RM} can be expressed as a positive square root of the sum of the squares of each type of uncertainty - relationship:

$$U_{RM} = [u_{char}^2 + u_{bb}^2 + u_{lts}^2 + u_{sts}^2]^{1/2} \quad (1)$$

Where:

u_{char} = uncertainty calculated from interlaboratory comparison

u_{bb} = uncertainty calculated from the inhomogeneity of the sample

u_{lts} = uncertainty regarding the instability of the test sample in the long-term stability test

u_{sts} = uncertainty regarding RM instability in the short-term stability test.

If, calculating the value of the RM component, the average of the data sets shows a normal distribution, the standard deviation of the mean of all data sets may be used as u_{char} - relationship (ISO, 2017a):

$$u_{char} = \frac{S_{Xp}}{\sqrt{p}} \quad (2)$$

Where:

S_{Xp} = standard deviation of the mean

Xp = total arithmetic mean of laboratory averages

\sqrt{p} = square root of data set (total number of laboratories).

5.11. Documentation and information

5.11.1. Expiry date

Each prepared RM should have a specified expiration date. Its determination should be based on experience with RMs having the same matrix and property values and information.

5.11.2. Storage and transportation of RM

The prepared RM should be stored under conditions that do not alter its properties. The normal temperature for soil, sediment and rock is ambient. The stored RM samples should be kept away from heat, light, and moisture, and the packages must be securely sealed. The RM long-term storage area should be monitored for changes in storage conditions, and it is also necessary to assess the continued fitness-for-purpose of the material.

5.11.3. Documentation and usage of RM

Documentation from RM preparation should be available, containing all necessary information and instructions for its use (ISO, 2014, 2016):

- Name and description of RM
- Batch number
- Date of preparation
- Expiration date
- Instructions for use, handling, storage conditions
- Reference values of tested parameters
- Minimum amount of material - minimum weight, and
- Security measures, risks if necessary.

The unit of packaging should be clearly labelled with the RM name, batch number, date of preparation, expiry date and package size. In addition to this information, in the case of an

inquiry or when preparing a new batch of RM, it is good to keep information on the origin and method of RM preparation and the type of packaging. Additional information on moisture, grain size, procedures used for homogeneity test, stability test and way of characterisation of the property values of the RM should be available to users.

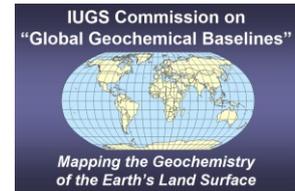
When using an RM for quality management, information is needed on how to proceed if the RM is stored for a long time. As RM sedimentation and separation may occur, the unit should be thoroughly shaken before use and visually inspected for material change, and clumping. If the RM values are reported as content per dry weight of the sample, the conditions to ensure the calculation of the moisture content of the sample shall be indicated.

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Note: All hyperlinks were checked on the 30th of January 2022.

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 6

Geoanalytical Methods and Requirements

Manfred Birke^{1,5}, Gwendy E.M. Hall^{2,5}, George Morris^{3,5},
Anna Ladenberger^{3,5}, Alecos Demetriades^{4,5}

¹ Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany

² Geological Survey of Canada, Ottawa, Ontario, Canada

³ Geological Survey of Sweden, Uppsala, Sweden

⁴ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

⁵ IUGS Commission on Global Geochemical Baselines

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6.1. Introduction

Progress in geochemical mapping, since it began in the 1950s, has been due principally to the development of new and improved instrumental techniques, providing better sensitivities for more elements more rapidly. Analytical requirements for the compilation of a global geochemical database, designed to facilitate firstly the establishment of the Global Geochemical Reference Network and secondly international geochemical mapping, need the best of the existing analytical techniques. Because the data are required for long-term reference purposes and comparisons, some special considerations need attention that should be attended to by the project's Laboratory Committee.

Most geochemical mapping has been undertaken to assist in discovering mineral deposits. Geochemical surveys carried out in the 1950s were considered a new method of prospecting to enable the mining industry to locate unexposed mineralisation, *e.g.*, Cu, Pb-Zn or Ni, usually within a geographically restricted area. The work was, therefore, narrowly focused and, at best, semi-quantitative analytical techniques were used (Lakin *et al.*, 1952; Ward, 1963; Stanton 1966; Levinson, 1974, 1980). National mapping programmes, which began 15 to 20 years later, expanded the approach started by the mining industry to provide information about a wider range of elements of possible economic interest (see Table 2-2, p.24-25, in Darnley *et al.*, 1995). Since the mid-1970s national regional geochemical atlas programmes have begun to add elements primarily because of their environmental significance (*e.g.*, Webb *et al.*, 1978; BGS, 1978, 1991, 1992, 1993, 1999, 2000; Thalmann, 1984; Fauth *et al.*, 1985; Xie *et al.*, 1985; Lahermo *et al.*, 1990; Koljonen, 1992; Lis and Pasieczna, 1995; Kadūnas *et al.*, 1999; Ottesen *et al.*, 2000, 2010; Halamić and Miko, 2009; Caritat and Cooper, 2011; Xie *et al.*, 2012; Andersson *et al.*, 2014; Smith *et al.*, 2014).

In general, however, the elements determined, and the analytical methods selected, have been chosen according to the presumed principal mineral potential of the region under investigation. Emphasis on mineral exploration considerations has influenced the types of samples collected, sample preparation, the analytical methods employed and the way they have been used. Cost-effectiveness, judged from a mineral exploration viewpoint, has been a prime consideration, and the quality of obtained geochemical data was not always a priority. This has not prevented large and unique data sets with important environmental implications from being acquired.

For both industry and national geological surveys, the cost was often and still is a limiting factor in the design of projects with the necessity to counterbalance sampling density, the comprehensiveness and quality of the data to be obtained, against the size of the area to be explored. This drawback has been overcome with the availability of low-cost multi-element analytical techniques, as has been shown in continental-scale geochemical projects carried out in Australia, China, Europe and the United States of America (Table 6.1). The data are still not, however, compatible because of different sampling, sample preparation and analytical techniques.

Table 6.1. Continental-scale projects carried out in Australia, China, Europe and the United States of America (USA) with project acronyms, sampling media collected, and analytical methods used.

Country	Australia ¹	China ¹	Europe ²			USA ¹	
Project	NGSA	CGB	FOREGS			GEMAS	NASGLP
Sampling medium	Sediment/Soil ³	Sediment/Soil ³	Soil ⁴	Sediment ⁵	Humus	Soil ⁶	Soil ⁷
Element							
Ag	TOT, AR, MMI	DCA	TOT	/	/	AR, MMI	MA
Al	XRF, AR, MMI	WD-XRF	XRF	WD-XRF	/	WD-XRF, AR, MMI	MA
As	TOT, AR, MMI	/	TOT, AR	WD-XRF, AR	/	WD-XRF, AR, MMI	AAS

<i>Country</i>	<i>Australia¹</i>	<i>China¹</i>	<i>Europe²</i>			<i>USA¹</i>	
<i>Project</i>	<i>NGSA</i>	<i>CGB</i>	<i>FOREGS</i>			<i>GEMAS</i>	<i>NASGLP</i>
<i>Sampling medium</i>	<i>Sediment/Soil³</i>	<i>Sediment/Soil³</i>	<i>Soil⁴</i>	<i>Sediment⁵</i>	<i>Humus</i>	<i>Soil⁶</i>	<i>Soil⁷</i>
Au	FA, AR, MMI	AR	/	/	/	AR, MMI	/
B	AR	DCA	/	/	/	AR	/
Ba	TOT, AR, MMI	XRF	WD-XRF, AR	WD-XRF, AR	TOT	WD-XRF, AR, MMI	MA
Be	TOT, AR	MA	TOT	TOT	/	AR	MA
Bi	TOT, AR, MMI	MA	TOT	/	/	WD-XRF, AR, MMI	MA
Br	/	WD-XRF	/	/	/	WD-XRF	/
C	/	COMB	/	/	/	EA	/
Ca	XRF, AR, MMI	XRF	WD-XRF	TOT	/	WD-XRF, AR, MMI	MA
Cd	TOT, AR, MMI	/	TOT	TOT	TOT	AR, MMI	MA
Ce	TOT, AR, MMI	/	TOT	TOT	/	XRF, AR, MMI	MA
Cl	XRF	XRF	/	/	/	WD-XRF	/
Co	TOT, AR, MMI	MA	TOT, AR	TOT, AR	TOT	WD-XRF, AR, MMI	MA
Cr	TOT, AR, MMI	/	WD-XRF, AR	WD-XRF, AR	/	WD-XRF, AR, MMI	MA
Cs	TOT, AR, MMI	MA	TOT	TOT	/	WD-XRF, AR, MMI	MA
Cu	TOT, AR, MMI	MA	TOT, AR	TOT, AR	TOT	WD-XRF, AR, MMI	MA
Dy	TOT, AR, MMI	/	TOT	TOT	/	MMI	/
Er	TOT, AR, MMI	/	TOT	TOT	/	MMI	/
Eu	TOT, AR, MMI	/	TOT	TOT	/	MMI	/
F	ISE	/	/	/	/	WD-XRF	/
Fe	XRF, AR, MMI, TIT	XRF, MA, CAL	WD-XRF, AR	WD-XRF, AR	/	WD-XRF, AR, MMI	MA
Ga	TOT, AR, MMI	XRF	TOT	WD-XRF	TOT	WD-XRF, AR, MMI	MA
Gd	TOT, AR, MMI	/	TOT	TOT	/	MMI	/
Ge	TOT, AR	MA	/	/	/	AR	/
Hf	TOT, AR	MA	TOT	TOT	/	WD-XRF, AR	/
Hg	AR, MMI	/	TOT	TOT	TOT	AR, MMI	AR
Ho	TOT, AR	/	TOT	TOT	/	/	/
I	/	AFC	TOT	/	/	ED-XRF	/
In	AR	MA	TOT	/	/	AR, MMI	MA
K	XRF, AR, MMI	XRF	/	WD-XRF	/	WD-XRF, AR, MMI	MA
La	TOT, AR, MMI	/	TOT	TOT	TOT	WD-XRF, AR, MMI	MA
Li	AR, MMI	MA	/	TOT	/	AR, MMI	MA
Lu	TOT, AR	/	TOT	TOT	/	/	/
Mg	XRF, AR, MMI	MA	WD-XRF	WD-XRF	/	WD-XRF, AR, MMI	MA

<i>Country</i>	<i>Australia¹</i>	<i>China¹</i>	<i>Europe²</i>			<i>USA¹</i>	
<i>Project</i>	<i>NGSA</i>	<i>CGB</i>	<i>FOREGS</i>			<i>GEMAS</i>	<i>NASGLP</i>
<i>Sampling medium</i>	<i>Sediment/Soil³</i>	<i>Sediment/Soil³</i>	<i>Soil⁴</i>	<i>Sediment⁵</i>	<i>Humus</i>	<i>Soil⁶</i>	<i>Soil⁷</i>
Mn	XRF, AR, MMI	XRF	WD-XRF, AR	WD-XRF, AR	/	WD-XRF, AR, MMI	MA
Mo	TOT, AR, MMI	/	TOT	TOT	/	XRF, AR, MMI	MA
N	/	COMB	/	/	/	EA	/
Na	XRF, AR	MA	WD-XRF	WD-XRF	/	WD-XRF, AR	MA
Nb	TOT, AR, MMI	/	TOT	TOT	/	WD-XRF, AR, MMI	MA
Nd	TOT, AR, MMI	/	TOT	TOT	/	MMI	/
Ni	TOT, AR, MMI	/	TOT, AR	TOT, AR	TOT	WD-XRF, AR, MMI	MA
P	MMI, XRF	XRF	WD-XRF	WD-XRF		WD-XRF, AR, MMI	MA
Pb	TOT, AR, MMI	/	TOT, AR	TOT, AR	TOT	WD-XRF, AR, MMI	MA
Pd	FA, MMI	/	/	/	/	AR*, MMI*	/
Pr	TOT, AR, MMI	/	TOT	TOT		MMI	/
Pt	FA, MMI*	/	/	/	/	AR*, MMI*	/
Rb	TOT, AR, MMI	XRF	WD-XRF	WD-XRF	TOT	WD-XRF, AR, MMI	MA
Re	AR	/	/	/	/	/	/
S	XRF	XRF	AR	AR	/	EA, WD-XRF, AR, MMI	MA
Sb	TOT, AR, MMI	/	TOT	TOT	/	WD-XRF, AR, MMI	MA
Sc	TOT, AR, MMI	/	TOT	/	/	WD-XRF, AR, MMI	MA
Se	AR, MMI	/	/	/	/	AR, MMI	AAS
Si	XRF	XRF	WD-XRF	WD-XRF	/	WD-XRF	/
Sm	TOT, AR, MMI	/	TOT	TOT	/	MMI	/
Sn	TOT, AR, MMI	/	WD-XRF	WD-XRF	/	WD-XRF, AR, MMI	MA
Sr	TOT, AR, MMI	MA	WD-XRF	WD-XRF	TOT	WD-XRF, AR, MMI	MA
Ta	TOT, AR*, MMI	MA	TOT	TOT	/	WD-XRF, AR, MMI	/
Tb	TOT, AR, MMI	/	TOT	TOT	/	MMI	/
Te	AR, MMI*	/	TOT	TOT	/	AR, MMI	MA
Th	TOT, AR, MMI	/	TOT	WD-XRF	/	WD-XRF, AR, MMI	MA
Ti	MMI, XRF	XRF	WD-XRF	WD-XRF	/	WD-XRF, AR, MMI	MA
Tl	AR, MMI	MA	TOT	TOT	/	AR, MMI	MA
Tm	AR	/	/	/	/	/	/
U	TOT, AR, MMI	/	TOT	WD-XRF	/	WD-XRF, AR, MMI	MA
V	TOT, AR, MMI	/	TOT, AR	WD-XRF, AR	/	WD-XRF, AR, MMI	MA

Country	Australia ¹	China ¹	Europe ²			USA ¹	
Project	NGSA	CGB	FOREGS			GEMAS	NASGLP
Sampling medium	Sediment/Soil ³	Sediment/Soil ³	Soil ⁴	Sediment ⁵	Humus	Soil ⁶	Soil ⁷
W	TOT, AR, MMI	MA	WD-XRF	TOT	/	WD-XRF, AR, MMI	MA
Y	TOT, AR, MMI	/	WD-XRF	TOT	/	WD-XRF, AR, MMI	MA
Yb	TOT, AR, MMI	/	TOT	TOT	/	MMI	/
Zn	TOT, AR, MMI	/	WD-XRF, AR	WD-XRF, AR	TOT	WD-XRF, AR, MMI	MA
Zr	TOT, AR, MMI	XRF	WD-XRF	WD-XRF	/	WD-XRF, AR, MMI	/
Bulk Properties							
CEC	/	/	/	/	/	STU	/
Clay content	LPSA	/	/	/	/	MIRS	/
EC	POT	/	/	/	/	/	/
LOI	CAL	GRAV, CAL	/	/	/	COMB	/
Mag Sus	/	/	/	/	/	SUS	/
Mineralogy	VNIRS	/	/	/	/	MIRS	XRD
pH	Field, POT	/	/	/	/	POT	/
Sand content	LPSA	/	/	/	/	MIRS	/
Silt content	LPSA	/	/	/	/	MIRS	/
TC	/	/	/	/	/	/	EA
TIC	/	/	/	/	/	/	XRD
TOC	/	/	LECO	IR		EA	CAL
Grain size 0.002	/	/	LPSA	/	/	/	/
Grain size 0.06	/	/	LPSA	/	/	/	/
Grain size	/	/	LPSA	/	/	/	/
GrainsSortIndex	/	/	CAL	/	/	/	/

¹ Caritat *et al.* (2018); ² Salminen *et al.* (2005) and Sandström *et al.* (2005); ³ Mixed sampling of outlet (floodplain) sediment and soil; ⁴ Residual soil; ⁵ Stream and Floodplain sediment (kept separate); ⁶ Agricultural and Grazing land soil (kept separate); ⁷ Soil. *All values below detection limit.

Notation: AAS = Atomic Absorption Spectrometry; AFC = Alkaline Fusion Spectrophotometry; AFS = Atomic Fluorescence Spectrometry; AR = *Aqua regia*; CAL = Calculated; COMB = Combustion; DCA = Direct Current Arc; Emission Spectrometry; EA = Elemental Analyser; FA = Fire Assay; Field = Field pH test kit; GRAV = Gravimetry; IR = Non-dispersive infrared carbon analyser; ISE = Ion Specific Electrode; LPSA = Laser Particle Size Analyser; MA = Multi-Acid digestion (it is a four-acid digestion that includes HF); MIRS = Mid InfraRed Spectroscopy; MMI = Mobile Metal Ion[®]; POL = Polarography; POT = Potentiometry; STU = Silver-Thiourea extraction; SUS = Susceptibility meter; TIT = Titrimetry; TOT = Total digestion (fusion then digestion by HF + HNO₃ after fusion); VNIRS = Visible Near InfraRed Spectroscopy; XRD = X-Ray Diffraction; XRF = X-Ray Fluorescence Spectrometry; ED-XRF = Energy Dispersive X-ray Spectrometry; WD-XRF = Wavelength Dispersive X-ray Spectrometry; Grain size 0.002 = <0.002 mm (clay particle size); Grain size 0.06 = <0.06 to 0.002 mm (silt particle size); Grain size D50% = particle size when the cumulative percentage reaches 50%.

The analytical requirements to arrive at a comprehensive and satisfactory Global Geochemical Reference Network database need to be considered under two headings:

- Requirements for the Global Geochemical Reference Network, described in Chapter 3, and
- Additional requirements for national and international organisations engaged in the production of regional geochemical survey data.

National and regional geochemical surveys must be tied into the Global Geochemical Reference Network so that geochemical map data at any scale can be followed continuously across borders, from one jurisdiction to another (refer to Chapter 8 in this Manual). To achieve

this, the Global Geochemical Reference Network and regional geochemical surveys must be tightly linked, methodologically and spatially, through:

- Shared secondary reference materials (SRMs).
- Common sampling points and sample media, and
- Matching analytical requirements.

There is a potential difficulty in that a small number of countries have already conducted a substantial amount of geochemical mapping to their own unique national or regional specifications. In some respects, these may differ from the recommendations contained in this Manual, which have been prepared to supply a common global perspective, and a standard for future geochemical surveys. Where the differences apply principally to analytical requirements, and original sample material has been retained, then it should be possible to reconcile differences by reanalysis. If original sample material has not been kept, or there are major differences in the types of sample material collected, a percentage of the original sample sites should be resampled according to these internationally standardised methods. There are serious difficulties in trying to reconcile data based on significantly different sample media (see Chapters 3 and 8 in this Manual). Actions must be determined on a case-by-case basis and cannot be further considered here. This work should be carried out by the project's Laboratory, Quality Control and Data Management Committees.

6.2. Global Geochemical Reference Network analytical requirements

Samples which are to form part of a Global Geochemical Reference Network justify the greatest care and attention in all respects at all times. Data must be comparable. The analytical requirements for Global Geochemical Reference Network samples are governed by the following requirements, bearing in mind that some are not attainable in the short term for all elements, depending upon the sample media:

- (1) All elements in the periodic table, except H, O, Tc, Po, At, Fr, Ac, Pa and inert gases other than Rn, plus total loss-on-ignition should be determined (see Fig. 6.1).
- (2) The total amount of each element present is the most fundamental (and reproducible) quantity in any sample. Direct measurement techniques, *e.g.*, X-ray fluorescence (XRF) or Instrumental Neutron Activation Analysis (INAA), or total extraction procedures using strong acid digestions and ICP-MS finish should, therefore, be employed as a priority. Accuracy is very important; the use of standard reference materials is discussed below (see Section §6.2.1).
- (3) Analytical methods that have detection limits significantly below the anticipated abundance of each element in the various specified sample media should be employed. Methods with insufficient sensitivity to produce reportable values for any given element in at least 80% of the samples cannot be considered satisfactory. It should be noted that the average abundance of a few elements (*e.g.*, Ag, Au, Bi, Hg) in various media is not well-established.
- (4) High analytical precision is essential, and preferably significantly better than natural geochemical variation. The use of methods providing low detection limits gives the best assurance of good precision for trace elements. For all elements, however, it is the combined errors and uncertainties of site, sampling, preparation, and analysis that affect the significance of the data.
- (5) The analytical accuracy must also be good, preferably better than that achieved in most national regional geochemical surveys.

- (6) Non-destructive methods of analysis should be used where the above requirements can be met, to allow the use of large sample weights and reduce sample wastage, and
- (7) The amounts of the principal natural and anthropogenic gamma-emitting isotopes in the rock, residual soil, overbank and floodplain sediment samples should be determined, as a component of the geochemical baseline data.

It should be noted that samples from the Global Geochemical Reference Network sites could have the supplementary function of being used to study and monitor the dispersion of degradation products of organic contaminants in the environment, *e.g.*, from pesticides and herbicides, solvents and plastic containers.

It is recommended that an evaluation of the best methods for the specific analytical requirements relating to the Global Geochemical Reference Network, should be determined by the Geoanalytical Committee of the [Association of Applied Geochemists](#) in collaboration with the project's Laboratory Committee. From this evaluation, specific laboratories can be invited to participate in the analysis of samples collected for the Global Geochemical Reference Network. Analytical schemes used in the pan-European continental-scale projects are described in Section §6.3. Recognising that the requirements, concerning the desired detection limits for some elements in some sample media, are beyond the capabilities of existing analytical procedures, every encouragement should be given to the appropriate authorities to sponsor the requisite research and development, which will enable the requirements to be met in the not-too-distant future.

H																	He		
Li	Be											B	C	N	O	F	Ne		
Na	Mg											Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac	Lanthanide series																
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
			Th	Pa	U	Actinide series													

	List 1 elements		Other elements
	List 2 elements		Elements not to be determined

Figure 6.1. Recommended list of elements for the Global Geochemical Reference Network project.

6.2.1. Use of standard reference materials

Analytical bias, both interlaboratory and batch-to-batch within a laboratory, must be reduced to a minimum to generate globally comparable data. This can be achieved by selecting the best analytical methods and using standard procedures in conjunction with routine monitoring of data quality. Primary (PRMs) and secondary (SRMs) reference materials must be prepared and used in these procedures (refer to Chapters 5, 7 & 8 in this Manual). The [Canadian 'STSD'](#) and Chinese 'GSD' (Xie *et al.*, 2007) series of PRMs are internationally recognised stream sediment

samples, well documented with recommended values of many elements. However, the quantities are not enough to be used in the Global Geochemical Reference Network project, and SRMs of each recommended sample type (rock, residual soil, stream sediment and overbank/floodplain sediment), with different element concentrations, must be prepared in large quantities to be used not only for the global project but also in national regional geochemical surveys (see Chapter 5).

Primary reference materials (PRMs) can be used for the selection of optimum analytical methods prior to the initiation of a geochemical mapping project. The preferred analytical method will be that which yields analytical data closest to the recommended values.

A set of PRMs should be inserted in each batch of 100 samples during routine multi-element analysis (approximately 4% of the total), *i.e.*, usually at a rate of four PRMS at the start and end of each analytical batch (refer to Section §8.5 of Chapter 8 in this Manual). The analytical bias between different national geochemical surveys can be determined in this way and if necessary, the results from PRMs in each batch can be utilised for levelling data to an international standard reference level.

The number of SRMs inserted into a batch of 100 samples should be a minimum of two if the active project is collecting 1000s of samples (refer to Section §8.5 of Chapter 8). If the project is collecting 100s of samples then this should be increased to four. If the number of samples collected is small (<100) then 1 in 20 samples and 1 in 10 samples should be an SRM. In Chapter 4, the quality control scheme requires the insertion of four SRMs in each batch of hundred samples of the Global Geochemical Reference Network project (see Table 4.1). It is stressed that the number of different SRMs submitted in an entire analytical batch of samples must be sufficient to produce satisfactory regression analysis plots (see Chapter 8 in this Manual).

The standard deviation of the determined values with the recommended values of PRMs and SRMs can be used to monitor the between-batch, between-method, between-map or between-laboratory bias. If the PRM and SRM data, obtained during any part of the work, are outside tolerance limits, then determinations should be repeated (Wisconsin Department of Natural Resources, 1996; EA, 1999, 2003a, 2003b, 2013; Eurachem, 2002; Ellison *et al.*, 2003; 2019; Forbes, 2012; Magnusson and Örnemark, 2014; ISO, 2020a;).

6.2.2. Proposed arrangements for reference sample analysis

Because of the importance of establishing an internally consistent Global Geochemical Reference Network data set for each sample medium, it is strongly recommended to minimise or eliminate the problems that can arise in the inter-laboratory comparability of data, by engaging a small number of laboratories on this task, each selected for its demonstrated and recognised expertise in a particular method of analysis. Interlaboratory collaboration and cross-checks, using the same reference materials, should be installed.

If possible, a single laboratory should be responsible for one type of analysis performed on one sample type, collected worldwide, as has been done in the FOREGS Geochemical Atlas of Europe project (Salminen *et al.*, 2005; Sandström *et al.*, 2005). It is also desirable that where possible some elements should be determined by more than one analytical method to cross-check results.

It is discussed and recommended in Chapter 2 of this Manual that samples should be collected worldwide from approximately 7356 Global Terrestrial Network (GTN) grid cells of 160x160 km. From each GTN grid cell, samples shall be collected from either 5 or 8 random sites, following the principles outlined in Chapters 2 and 3. The media sampled will be as follows, and they are all mandatory:

- Rock
- Residual soil (top and C horizon)
- Humus

- Stream or lake sediment
- Stream water
- Overbank sediment (top and bottom)
- Floodplain sediment (top and bottom).

In an ideal landscape, from each quadrant of a 160x160 km grid cell seven sample types will be collected, *i.e.*, five solid sample types, plus humus (if available), and stream water (if available). In total, between 25,000 and 36,000 samples of each type will be collected. Because humus and stream water samples will not be obtained in arid areas, there will be smaller numbers of these media. Lake sediments will be collected from less than 8% of the world's surface. In order to apply ANOVA statistical procedures, it has been recommended that samples from each site should be analysed separately (see Chapter 7), because the cost of sample collection, particularly from remote areas, is substantial and the value of the additional information provided is considerable.

It is, therefore, recommended that each sample type should be sent to a designated receiving laboratory, which would coordinate all work on that particular sample type. Logically this laboratory could be responsible for applying one analytical technique, *for example*, XRF, INAA, ICP-AES or ICP-MS, on this particular sample type or possibly on all sample types. This laboratory would be responsible for distributing splits of the samples to other participating laboratories responsible for other analytical techniques. In this way, laboratories accepting responsibility for certain methods could be responsible, ultimately, for handling up to 72,000 samples of a given sample medium. Allowing for replication of analyses, the total number of analyses could be of the order of 5% greater than the number of sample sites for that particular sample medium. This volume of work is not considered excessive in terms of the number of samples commonly processed by production-orientated laboratories, given that samples will be received over several years. Even under ideal circumstances, with high priority and adequate funding, it is estimated that sample collection would take at least five years, provided all countries agree to participate in the Global Geochemical Reference Network project.

6.2.3. National and international geoanalytical requirements

The production of geochemical maps at scales commonly ranging from 1:1 million to 1:50,000 is normally the responsibility of national organisations. In addition to providing a global overview, the prime reason for the establishment of the Global Geochemical Reference Network is to make it possible for researchers to compare and relate geochemical phenomena anywhere in the world.

It is proposed that a split of analysed reference samples from each grid cell in the Global Geochemical Reference Network should be retained in the country or region of origin, for ongoing reference purposes and quality control of subsequent geochemical work in that country. These sample splits will serve as secondary reference materials. As analytical data for these reference samples become available, a copy will be forwarded to the responsible national earth science institutes in the countries of origin. The existence of reference data and materials relevant to every region will make it possible for neighbouring countries to compare and connect the results of their detailed geochemical survey work and contribute to part of a single international database.

Recommended field sampling methods to encourage greater commonality for regional geochemical surveys are given in Chapters 2 and 3 in this Manual. Concerning the analytical requirements for these surveys, it is assumed that many countries will wish to develop and use their in-house analytical capabilities. Those not in a position to do so should, as an alternative, provide specifications for the work to be carried out by others, but these specifications should be compatible with recommended international procedures and employ the locally available reference materials.

The existence of international recommendations regarding the selection of sample media and analytical methods is not intended to suggest that organisations should not choose what they consider to be the optimum sample type, sample spacing or analytical method for their own particular purposes. However, it is strongly recommended that whenever other sample media or analytical methods are chosen by a country, these should be linked to the Global Geochemical Reference Network, by sampling at the same sites as are used for the Global Geochemical Reference Network and using the global project's secondary reference materials to establish a known relationship between their national analytical procedures and those recommended for international use.

It is recommended above that for the Global Geochemical Reference Network is desirable, ultimately, to obtain data for almost the entire periodic table. It is unlikely that many countries will see a need to make detailed maps for the complete list. Nevertheless, given the heterogeneous collection of data in existing data sets, it is highly desirable that a common range of elements of known economic and environmental importance should be determined in every country by internationally agreed standard methods. If some of the necessary facilities are lacking, rather than accept inferior data, consideration should be given to having some of the work undertaken in an internationally recognised laboratory. The recommended elements to be determined are grouped into 'analytical packages' (Fig. 6.1):

- List 1 elements, for economic and environmental purposes, including a group of major elements and a group of minor, trace and ultra-trace elements (total 55 determinands) that should be determined in any new geochemical mapping project, and
- List 2 elements that could usefully be added depending upon the funding of the project and the availability of laboratory facilities (total of 24 determinands).

Analytical precision will depend upon the method used and the element determined. Generally speaking, the relative standard deviation (RSD) for the major elements should be less than 3%, the RSD for minor and trace elements should be less than 10%, and the RSD for certain trace and ultra-trace elements should be less than 20%.

6.2.4. Need for independent quality control

Communication between laboratory and field staff is of paramount importance. Users of analytical data must always check the validity of the results reported and those generating the analytical data should be aware of the purposes for which the data are being utilised.

Blind confidence should not be placed upon any laboratory's quality assurance and control programme. An external quality assurance and control procedure must be installed by the Quality Control Committee of the Global Geochemical Reference Network project.

Laboratory quality assurance and control programmes may not always suit the types of sample matrices submitted or are rigorous enough to satisfy requirements close to detection limits. Normally, laboratories evaluate a new method by its application to well-characterised PRMs, available commercially from a number of organisations such as [CANMET Canada](#); [NIST](#) (formerly the U.S. National Bureau of Standards), the [United States Geological Survey Geochemical Reference Materials](#), [International Association of Geoanalysts](#), [LGC Geological materials](#), Institute of Geophysical and Geochemical Exploration, China (Xie *et al.*, 2007). They then standardise their own internal controls (SRMs) against these for frequent insertion in sample batches. For regional geochemical mapping, and especially the Global Geochemical Reference Network project, the organisations responsible should develop and standardise their own bulk control samples (SRMs), the matrices of which are typical of those found in the region under study. Replicate data for these control samples will allow computation of precision and accuracy

of the methods used, and also to level the results of disparate data sets (refer to Chapter 8 in this Manual). To assess the relative magnitude of analytical variability (precision) versus the spatial geochemical variability and bias introduced during sampling, replicate analyses of the survey samples should be carried out and Analyses of Variance determined (see Chapter 7 in this Manual).

6.3. Analytical schemes used in multinational continental-scale projects

The Geochemical Atlas of Europe of the Forum of European Geological Surveys (FOREGS presently EuroGeoSurveys), known as the FOREGS Atlas is widely regarded as a pilot for the Global Geochemical Reference Network project as it is the first multi-national and multi-media project in which 26 countries participated (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006), and followed the recommendations of Darnley *et al.* (1995) for the development of an internally consistent “*global geochemical database for environmental and resource management*”. Such a continental-scale project demands special requirements for chemical analysis, which have already been mentioned in Section §6.2. Nevertheless, it is important to stress that the accuracy of the European data set was essential since one of the objectives, according to Darnley *et al.* (1995), is for the results to be used to ‘*normalise*’ or to ‘*level*’ other geochemical data at national and international scales (refer to Chapter 2 in this Manual and its two Annexes). The methods used in this project are also likely to become standard operating procedures (SOPs) for the Global Geochemical Reference Network project, and hence should be reproducible in various laboratories throughout the world. Because of the stringent requirements regarding sensitivity and elemental coverage, the most sophisticated instrumental methods have to be utilised. This may restrict some skilled but poorly equipped national laboratories from participating fully in the global project in the future.

The material of this Section was extracted from the FOREGS Analytical Committee’s report prepared by Sandström et al. (2005), and modified for the purposes of this Manual.

Total element concentrations are most relevant for the geochemical interpretation of data. For solid materials, this means that the silicate matrix either needs to be fully decomposed by mixed acid digestion before instrumental analysis, or a solid sampling technique such as X-ray fluorescence needs to be used. However, to address the needs of national and European level environmental authorities, information on leachable concentrations of the elements was also considered to be important. In environmental chemistry, a slightly unscientific and non-specific term, ‘*near total*’, is often used to describe the maximum concentration of an element that can be liberated from a material in its natural environment. *Aqua regia* digestion is commonly used for simulating this process in the laboratory. Unfortunately, almost every laboratory has its own standard operating procedure for *aqua regia* digestion. For this project, an *aqua regia* leach was adopted to determine the leachable concentrations of the elements in sediment and soil samples. Errors introduced by a diversity of leaching procedures were avoided by having only one laboratory perform the extractions and analyses. The method used was validated against standard methods according to normal validation procedures in accredited laboratories.

6.3.1. Participating laboratories and analytical techniques

Nine laboratories were involved in the FOREGS Atlas project (Table 6.2). All solid samples collected by the 26 participating countries were shipped to the Slovakian State Geological Institute of Dionyz Stur (SGUDS), which was in overall charge of sample preparation, homogenisation, sub-sampling, and sample distribution to the analytical laboratories and archiving of the excess sample material (see Chapter 4 ‘Sample Preparation and Storage’). To ensure data homogeneity, and to avoid any bias between laboratories or analytical methods, each laboratory was nominated to take responsibility for carrying out analysis by a particular

analytical technique or techniques on all samples of a certain type. Some determinands were measured by more than one technique, *e.g.*, a range of trace elements in samples of soil and sediment were determined both by XRF and ICP-MS after mixed acid digestion. The laboratories and actual methods used were selected through careful consideration of a few quality issues and are listed in Table 6.3.

Table 6.2. European Geological Survey laboratories participating in the FOREGS Geochemical Atlas of Europe project.

<i>Laboratory</i>	<i>Acronym</i>
Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany	BGR
British Geological Survey, Keyworth, Nottingham, United Kingdom	BGS
Bureau de Recherches Géologiques et Minières, Orleans-Cedex, France	BRGM
State Geological Institute of Dionyz Stur, Bratislava, Slovak Republic	SGUDS
Geological Survey of Finland, Espoo, Finland	GTK
Mining and Geological Survey of Hungary, Budapest, Hungary	MBFSZ
Geological Survey of The Netherlands, Utrecht, The Netherlands	TNO
Geological Survey of Norway, Trondheim, Norway	NGU
Polish Geological Institute, Warszawa, Poland	PGI

Table 6.3. Summary of analytical methods used for each sampling medium in the FOREGS Geochemical Atlas of Europe project.

<i>Topsoil and Subsoil samples</i>		<i>Stream and Floodplain Sediment samples</i>	
<i>Laboratory</i>	<i>Method</i>	<i>Laboratory</i>	<i>Method</i>
SGUDS	Sample Preparation	SGUDS	Sample Preparation
TNO	Granulometry/TOC	SGUDS	TOC
BGR	WD-XRFS	BGS	XRFS
GTK	ICP-MS	BRGM	ICP-MS
PGI	AR/ICP-AES	GTK/PGI	AR/ICP-AES
MBFSZ	Hg analyser	MBFSZ	Hg analyser
<i>Stream Water samples</i>		<i>Humus samples</i>	
<i>Laboratory</i>	<i>Method</i>	<i>Laboratory</i>	<i>Method</i>
BGR	ICP-QMS / ICP-AES	SGUDS	Sample preparation
BGS	IC / DOC analyser	TNO	ICP-MS
BGS	DOC analyser	MBFSZ	Hg analyser
NGU	Hg analyser		

6.3.2. Sample preparation

Refer to Chapter 4 in this Manual.

6.3.3. Analytical methods used in the European Global Terrestrial Network

6.3.3.1. Analysis of stream water samples

6.3.3.1.1. Determination of anions

Anions were determined on stream water samples that were unfiltered and unpreserved but had been stored after sampling at between 1 and 8°C prior to analysis. Stream water samples were analysed for major and trace anions, *i.e.*, fluoride, chloride, nitrite, bromide, nitrate, orthophosphate and sulphate, by ion chromatography (IC). The determinations were made on a

Dionex 4000i Ion Chromatograph using an AS14 analytical column with both conductivity and UV/visible absorbance detection. The method is accredited by the United Kingdom Accreditation Service (UKAS) according to the requirements of BS EN ISO 17025 (ISO, 2017).

The stream water samples were filtered to $<0.45\ \mu\text{m}$ before analysis. After chromatographic separation, all the anions were measured using the conductivity detector. Nitrite, bromide and nitrate were also determined using the UV/visible absorption detector, and data for these anions were taken from this detector because of its better sensitivity.

For all anions, the accuracy of the method was better than $\pm 10\%$, the bias was within $\pm 3\%$ and the precision at the 95% confidence interval was better than 5% at concentrations an order of magnitude above the quantification limit. Quantification limits (QL) for all anions are given in Table 6.4.

6.3.3.1.2. Determination of dissolved organic carbon

Dissolved organic carbon (DOC) was determined on stream water samples that were filtered to $<0.45\ \mu\text{m}$ on collection but were otherwise unpreserved. Stream water samples were analysed using a Shimadzu TOC 5000 analyser with associated ASI 5000 auto-sampler. The method is accredited by the United Kingdom Accreditation Service according to the requirements of BS EN ISO 17025 (ISO, 2017).

Stream water samples were acidified and sparged prior to analysis to remove inorganic carbon. DOC was then determined by thermal combustion of the sample and the evolved CO_2 was measured by non-dispersive infra-red (NDIR) detection.

The accuracy of the method was better than $\pm 5\%$, the bias was within $\pm 2\%$, and the precision at the 95% confidence interval was better than 6% at concentrations an order of magnitude above the quantification limit at 0.5 mg/l.

6.3.3.1.3. Determination of major cations, metals and other inorganic elements

Stream water samples were filtered to $<0.45\ \mu\text{m}$, acidified to 1% v/v with nitric acid and stored at a temperature of $<8^\circ\text{C}$. The samples were analysed by both inductively coupled plasma quadrupole mass spectrometry (ICP-QMS) and inductively coupled plasma atomic emission spectrometry (ICP-AES), using Perkin Elmer Sciex ELAN 5000A and Spectro Flame M instruments, respectively, in accordance with the German norms DIN 38406-29 (ICP-MS) and DIN 38406-22 (ICP-AES) (DIN, 1988, 1996).

The primary chemicals used to prepare the calibration and quality control standards and reagents were of analytical reagent grade. Multielement standard solutions for calibration were prepared from Claritas SPEX/Certiprep stock solutions. International certified reference materials (NIST 1640, NIST 1643d and SLSR-4) were included in every batch of 20 samples. Indium was used as an internal standard.

The accuracy of the methods for all determinands was better than $\pm 10\%$, the bias was within $\pm 3\%$, and the repeatability at the 95% confidence interval was better than 5% at concentrations an order of magnitude above the quantification limit. Quantification limits for all cations and trace elements are given in Table 6.4.

6.3.3.1.4. Determination of mercury

Stream water samples were filtered to less than $0.45\ \mu\text{m}$ and preserved in the field using potassium dichromate dissolved in HNO_3 . The samples were analysed for mercury by a cold vapour atomic absorption (CV-AAS) technique using a CETAC M-6000A Hg Analyser. The method is accredited according to NS-EN ISO/IEC 17025 (ISO, 2017).

The method is based on the reduction of Hg ions in solution to atomic Hg vapour using stannous chloride (SnCl_2) as a reducing agent. The Hg/ SnCl_2 emulsion is introduced into the top of a gas-liquid separator and is detected by CV-AAS.

The accuracy of the method was estimated to be ± 1 to 2%, without any systematic bias. Within batch precision at the 95% confidence interval was estimated to be about 1%, and long-term precision better than 8%. The quantification limit was 0.01 $\mu\text{g/l}$.

Table 6.4. Summary of all elements and other determinands in the FOREGS Geochemical Atlas of Europe (after Sandström et al., 2005) for each sampling medium, including the analytical method and laboratory responsible for analysis with the limit of quantification, and the Upper Continental Crust abundance for comparison. Units are denoted by superscripts: ^amg/kg; ^b%; ^c $\mu\text{g/l}$; ^dmg/l; ^e $\mu\text{g/g}$; ^fmS/m; ^gmm; ^h μm

Element	Soil samples		Sediment samples		Humus	Stream water samples	Upper Continental Crust abundance (mg/kg)	Source
	Total	Aqua regia	Total	Aqua regia				
Ag	0.01 ^a	/	/	/	/	0.002 ^c	0.053	Rudnick and Gao (2003)
Al / Al ₂ O ₃	0.05 ^b	/	0.1 ^b	/	/	0.1 ^c	81,505	Rudnick and Gao (2003)
As	0.2 ^a	5 ^a	1 ^a	5 ^a	/	0.01 ^c	5.7	Hu and Gao (2008)
B	/	/	/	/	/	0.01 ^c	47	Hu and Gao (2008)
Ba	5 ^a	1 ^a	3 ^a	1 ^a	1 ^a	0.005 ^c	628	Rudnick and Gao (2003)
Be	2 ^a	/	0.02 ^a	/	/	0.005 ^c	1.9	Hu and Gao (2008)
Bi	0.5 ^a	/	/	/	/	0.002 ^c	0.23	Hu and Gao (2008)
Ca / CaO	0.01 ^b	/	0.05 ^b	/	/	0.001 ^d	25,657	Rudnick and Gao (2003)
Cd	0.01 ^a	/	0.02 ^a	/	0.1 ^a	0.002 ^c	0.06	Hu and Gao (2008)
Ce	0.15 ^a	/	0.02 ^a	/	/	0.002 ^c	63	Rudnick and Gao (2003)
Co	3 ^a	1 ^a	2 ^a	1 ^a	0.1 ^a	0.005 ^c	15	Hu and Gao (2008)
Cr	3 ^a	1 ^a	3 ^a	1 ^a	/	0.01 ^c	73	Hu and Gao (2008)
Cs	0.5 ^a	/	4 ^a	/	/	0.002 ^c	4.9	Hu and Gao (2008)
Cu	0.01 ^a	1 ^a	1 ^a	1 ^a	0.3 ^a	0.005 ^c	27	Hu and Gao (2008)
Dy	0.1 ^a	/	0.02 ^a	/	/	0.002 ^c	3.9	Rudnick and Gao (2003)
Er	0.1 ^a	/	0.02 ^a	/	/	0.002 ^c	2.3	Hu and Gao (2008)
Eu	0.05 ^a	/	0.02 ^a	/	/	0.002 ^c	1	Rudnick and Gao (2003)
Fe / Fe ₂ O ₃	0.01 ^b	2 ^a	0.01 ^b	2 ^a	/	1 ^c	39,176	Rudnick and Gao (2003)
Ga	0.2 ^a	/	1 ^a	/	0.1 ^a	0.002 ^c	18.6	Hu and Gao (2008)
Gd	0.1 ^a	/	0.02 ^a	/	/	0.002 ^c	4	Rudnick and Gao (2003)
Ge	/	/	/	/	/	0.005 ^c	1.3	Hu and Gao (2008)
Hf	0.2 ^a	/	0.05 ^a	/	/	0.002 ^c	5.3	Rudnick and Gao (2003)
Hg	0.0001 ^c	/	0.0001 ^c	/	0.0001 ^c	/	0.05	Rudnick and Gao (2003)
Ho	0.02 ^a	/	0.02 ^a	/	/	0.002 ^c	0.83	Rudnick and Gao (2003)
I	2 ^a	/	/	/	/	0.01 ^c	1.4	Rudnick and Gao (2003)
In	0.01 ^a	/	/	/	/	0.002 ^c	0.066	Hu and Gao (2008)
La	0.01 ^a	/	0.02 ^a	/	0.1 ^a	0.002 ^c	31	Rudnick and Gao (2003)
Li	/	/	0.05 ^a	/	/	0.005 ^c	41	Hu and Gao (2008)
Lu	0.02 ^a	/	0.02 ^a	/	/	0.002 ^c	0.36	Hu and Gao (2008)
Mg / MgO	0.01 ^b	/	0.1 ^b	/	/	0.001 ^d	14,955	Rudnick and Gao (2003)
Mn / MnO	0.001 ^b	10 ^a	0.01 ^b	10 ^a	/	0.05 ^c	774	Rudnick and Gao (2003)
Mo	0.1 ^a	/	0.05 ^a	/	/	0.002 ^c	0.6	Hu and Gao (2008)
Na / Na ₂ O	0.01 ^b	/	0.2 ^b	/	/	0.005 ^d	24,259	Rudnick and Gao (2003)
Nb	0.1 ^a	/	1 ^a	/	/	0.002 ^c	11.6	Hu and Gao (2008)
Nd	0.15 ^a	/	0.02 ^a	/	/	0.005 ^c	27	Rudnick and Gao (2003)
Ni	2 ^a	2 ^a	1 ^a	2 ^a	0.3 ^a	0.005 ^c	34	Hu and Gao (2008)
P ₂ O ₅	0.001 ^b	/	0.01 ^b	/	/	/	655	Rudnick and Gao (2003)
Pb	3 ^a	3 ^a	1 ^a	3 ^a	0.5 ^a	0.005 ^c	17	Rudnick and Gao (2003)
Pr	0.1 ^a	/	0.02 ^a	/	/	0.002 ^c	7.1	Rudnick and Gao (2003)

Element	Soil samples		Sediment samples		Humus	Stream water samples	Upper Continental Crust abundance (mg/kg)	Source
	Total	Aqua regia	Total	Aqua regia				
Rb	2 ^a	/	1 ^a	/	0.2 ^a	0.002 ^c	94	Hu and Gao (2008)
S	/	50 ^a	/	50 ^a	/	/	62	Rudnick and Gao (2003)
Sb	0.02 ^a	/	0.02 ^a	/	/	0.002 ^c	0.75	Hu and Gao (2008)
Sc	0.5 ^a	/	/	/	/	/	14	Hu and Gao (2008)
Se	/	/	/	/	/	0.01 ^c	0.09	Rudnick and Gao (2003)
SiO ₂	0.1 ^b	/	0.1 ^b	/	/	0.01 ^d	311,405	Rudnick and Gao (2003)
Sm	0.1 ^a	/	0.02 ^a	/	/	0.002 ^c	4.7	Rudnick and Gao (2003)
Sn	2 ^a	/	1 ^a	/	/	/	2.2	Hu and Gao (2008)
Sr	2 ^a	/	1 ^a	/	1 ^a	0.001 ^d	320	Rudnick and Gao (2003)
Ta	0.05 ^a	/	0.05 ^a	/	/	0.002 ^c	0.92	Hu and Gao (2008)
Tb	0.02 ^a	/	0.02 ^a	/	/	0.002 ^c	0.7	Rudnick and Gao (2003)
Te	0.02 ^a	/	/	/	/	0.005 ^c	0.027	Hu and Gao (2008)
Th	0.1 ^a	/	1 ^a	/	/	0.002 ^c	10.5	Rudnick and Gao (2003)
Ti / TiO ₂	0.001 ^b	/	0.005 ^b	/	/	0.01 ^c	3836	Rudnick and Gao (2003)
Tl	0.01 ^a	/	0.02 ^a	/	/	0.002 ^c	0.55	Hu and Gao (2008)
Tm	0.02 ^a	/	0.02 ^a	/	/	0.002 ^c	0.37	Hu and Gao (2008)
U	0.1 ^a	/	1 ^a	/	/	0.002 ^c	2.6	Hu and Gao (2008)
V	0.5 ^a	1 ^a	2 ^a	1 ^a	/	0.05 ^c	106	Hu and Gao (2008)
W	5 ^a	/	0.05 ^a	/	/	0.002 ^c	1.4	Hu and Gao (2008)
Y	3 ^a	/	0.02 ^a	/	/	0.002 ^c	21	Rudnick and Gao (2003)
Yb	0.05 ^a	/	0.02 ^a	/	/	0.002 ^c	2.34	Hu and Gao (2008)
Zn	3 ^a	1 ^a	1 ^a	1 ^a	1 ^a	0.01 ^c	75	Hu and Gao (2008)
Zr	3 ^a	/	1 ^a	/	/	0.002 ^c	193	Rudnick and Gao (2003)
EC	/	/	/	/	/	/	f	
HCO ₃ ⁻	/	/	/	/	/	/	d	
Br ⁻	/	/	/	/	/	/	0.01 ^d	
Cl ⁻	/	/	/	/	/	/	0.1 ^d	
F ⁻	/	/	/	/	/	/	0.05 ^d	
NO ₃ ⁻	/	/	/	/	/	/	0.04 ^d	
SO ₄ ²⁻	/	/	/	/	/	/	0.3 ^d	
DOC	/	/	/	/	/	/	c	
TOC	b	/	b	/	/	/	/	
Grain size 0.002 ^g	b	/	/	/	/	/	/	
Grain size 0.06 ^g	b	/	/	/	/	/	/	
Grain size D50% ^h	b	/	/	/	/	/	/	
GrainsSortIndex	unitless	/	/	/	/	/	/	

Units: ^amg/kg; ^b%; ^cµg/l; ^dmg/l; ^eµg/g; ^fmS/m; ^gmm; ^hµm

Colours: Refer to Table 6.2 for laboratory acronyms.

ICP-MS	GTK	BGR	BRGM	TNO
ICP-AES	PGI	BGR		
XRF	BGS	BGR		
IC	BGS			
CV-AAS	MFGI			

6.3.3.1.5. Selection of stream water data

Data for the major cations (Ca, Mg, Na and K) and some of the more abundant trace elements (Sr, Mn and Al), as well as Si and total P, were taken from the ICP-AES data set. All other trace element data were obtained from the ICP-MS data set. A range of trace elements was analysed by both ICP-AES and ICP-MS. The data were compared to ensure that there was good agreement between the two data sets. The ICP-MS data were generally selected for publication because of the better sensitivity of this instrumental method. All cation and trace element data determined by ICP techniques were considered to be of acceptable quality, except for Ag. Contamination, probably arising from the poor quality of the acid preservative used in a few countries, was the likely cause of the poor quality of Ag data.

Major anion data determined by IC, as well as the TOC data, were all considered to be of good quality. Because of the variable length of time between collection of the stream water samples and analysis in the laboratory, there is evidence that nitrite and phosphate, which are relatively unstable, may have been lost from solution. Data for nitrite and phosphate are not considered, therefore, to be acceptable for publication. The detection limits for bromide and phosphate were also not sufficiently sensitive for this study, and less than 10% of the samples contained concentrations of these anions above quantifiable levels.

Because of contamination, caused by inappropriate sample bottles being used in some countries, the mercury data were, unfortunately, not accepted for publication. *Hence, it is very important for the Project Manager of the Global Geochemical Reference Network project to ensure that the centrally purchased stream water sample bottles are certified trace element free, and to be distributed to all participating countries.*

Data for major cations determined by ICP-AES and anions determined by IC were checked for accuracy by calculating an ionic charge balance and also by checking the ratio of conductivity to total dissolved solids (TDS). Unfortunately, the major anion in most water samples was bicarbonate, which was determined by each country in the field. The quality of the bicarbonate data was highly variable, including errors in the analytical determination, errors in reporting units and some data were also not available. Nevertheless, a few rules and additional checks were established and applied to the stream water data set that enabled a thorough check on the overall quality of the analyses. *This is another standardisation problem that should be addressed by all participating countries: the same field instruments and the same chemical reagents must be used, and most importantly all field sampling teams must be trained in their use.*

Further details of the full range of elements determined are given in Table 6.4.

6.3.3.2. Analysis of stream and floodplain sediment samples

6.3.3.2.1. Determination of TOC

Determination of total carbon content in stream and floodplain sediment <0.063 mm samples was carried out by a pyrolysis technique with non-dispersive infrared detection using a Dohrmann-Rosemount DC-190 (USA) carbon analyser, with a 183-boat sampling module and a Fuji model 3300 direct non-dispersive infrared gas detector. The method has been validated against USEPA methods 415.1 and 9060 (USEPA, 1997, 2004) and ISO 10694 (ISO, 1995).

Well-mixed samples were treated with 50% HNO₃, and organic compounds were decomposed by pyrolysis in the presence of oxygen at a temperature of 800°C.

The uncertainty of the method was estimated to be ±10% and was mainly limited by sample heterogeneity.

6.3.3.2.2. Determination of mercury

Determination of total mercury was carried out using a cold vapour atomic absorption technique (CV-AAS), involving preconcentration on a gold amalgam before detection with an Advanced Mercury Analyser (AMA-254, ALTEC) instrument.

The analysis was performed directly on solid <0.063 mm samples without any sample preparation. Mercury is liberated from the sample during programmed temperature elevation to 850°C and amalgamated with gold to concentrate the determinand. Mercury vapour is then released from the amalgam by heating and detected using atomic absorption spectrometry.

The uncertainty of the analysis was typically better than $\pm 10\%$, or better than 5% in the case of higher concentrations. The quantification limit of Hg was 0.0001 $\mu\text{g/g}$.

6.3.3.2.3. Total multielement determination by XRF

A range of elements was determined by wavelength dispersive X-ray fluorescence spectrometry (WD-XRFS) and energy dispersive polarised X-ray fluorescence spectrometry (ED(P)XRFS). The instruments used were Philips PW1480 and PW2400 WD-XRFs, with W and Rh anode X-ray tubes respectively, and a Spectro X-LAB 2000 ED-XRF with a Pd anode X-ray tube.

Samples (<0.063 mm) were prepared by mixing with a binder and pressed into powder pellets before analysis by both instrumental techniques. For the WD methods, secondary radiation is collimated onto a diffraction crystal and its intensity at selected peak and background positions in the X-ray spectrum is measured using a detector mounted onto a goniometer. The net intensity, corrected for background, spectral interference and instrument drift, is calibrated against known synthetic standards and certified reference materials (CRMs). For the ED(P)XRFS method, five different secondary/polarisation targets are used to give optimal coverage of 52 elements from Na to U; all elements are measured to improve the accuracy of the corrections on the analytes of interest. Rather than being diffracted, the whole of the emitted X-ray spectrum is detected simultaneously using a Si(Li) detector. The acquired spectrum is deconvoluted and then evaluated using a calibration prepared by the instrument manufacturer. In general, data for lighter elements are taken from the WD-XRF instrument, and data for the heavier elements from the ED(P)XRFS instrument.

In practice, concentrations of MgO, P₂O₅, K₂O, CaO, TiO₂, V, Cr, MnO, Cs, Ba, La and Ce were obtained by using the ED technique. The WD technique was used for all other elements. Further details of the full range of elements determined are given in Table 6.4.

The accuracy of the method for all determinands was better than $\pm 5\%$, and the repeatability at the 95% confidence interval was better than 5% at concentrations an order of magnitude above the limit of quantification. Quantification limits for all determinands are given in Table 6.4.

6.3.3.2.4. Total multielement determination by ICP-MS

In addition to XRF analysis, a range of major and trace elements were also determined by quadrupole ICP-MS using a VG Elemental (UK) model PQ3 instrument equipped with a water-cooled sample introduction system, a PlasmaScreen torch, a high-efficiency interface device AutoRange Plus, a simultaneous detector system and PlasmaLab ICP-MS Software Suite.

Prior to analysis, the stream and floodplain sediment samples were decomposed by sintering with sodium peroxide (1 g of <0.063 mm sample and 3 g flux) at a temperature of 480°C. After cooling, the sinter was dissolved in 60 ml of deionised water and 20 ml of 50% nitric acid. Rhodium was used as an internal standard. Nowadays, indium is commonly used as an internal standard because of its lower cost.

At concentrations an order of magnitude above the quantification limit, the uncertainty of the method was between 5 and 10%, depending on the element. Quantification limits are given in Table 6.4.

6.3.3.2.5. Acid leachable multielement determination by ICP-AES

In addition to the total element concentrations, the acid leachable portion of selected elements was analysed after a hot *aqua regia* leach by ICP-AES, using a J-Y 70 Plus Geoplasma ICP-AES instrument.

Stream and floodplain sediment samples were digested in *aqua regia* by weighing 1 g of <0.063 mm sample in a polyethylene tube and adding 6 ml HCl and 2 ml HNO₃. The samples were left for 15 minutes at room temperature before heating in an aluminium block at 95°C for 60 minutes. After cooling, the samples were filtered and made up to 50 ml in a polyethylene flask.

Based on monitoring samples, the relative standard deviation of the measurements was typically between 3 and 7% for concentrations exceeding three times the quantification limit of the particular element. Quantification limits for all reported elements are given in Table 6.4.

6.3.3.2.6. Selection of stream and floodplain sediment data

A wide range of total multielement data determined by both ICP-MS and XRF methods were available. Data quality, including results of CRMs and ANOVA data for duplicate-replicate analyses, was assessed on an element-by-element basis. If only one of the two techniques were sufficiently sensitive to permit the determination of a particular element at the background levels found in the samples, then this technique was automatically selected. If both techniques were sufficiently sensitive, the data from the technique with the best precision, based on the ANOVA duplicate analyses, were selected. The actual method selected for reporting each element is given in Table 6.4.

The quality of the ANOVA data for the ICP-AES analysis of the *aqua regia* solutions was also assessed. For a few elements, the analytical variation exceeded that of the geochemical variation, and the data for these elements were not considered suitable for publication. Those elements with acceptable data quality are given in Table 6.4. *Aqua regia* data were also used for total S, for which no data were available by any other technique.

6.3.3.3. Analysis of residual soil samples

6.3.3.3.1. Determination of particle size distribution

Particle size (grain size) distribution between 0.1 and 2000 µm was measured by a Laser Particle Sizer (LPS) technique using a Malvern Mastersizer 2000 instrument (Malvern, UK) equipped with a Hydro 2000G sample dispersion accessory. The method is based on the correlation between the angles of light scattered from particles in a laser beam and the size distribution of these particles.

Latex spheres with unique known grain sizes traceable to NIST (Malvern Quality Audit Standard QAS2002) were used to calibrate the Laser Particle Sizer.

Samples were sieved to <2 mm, followed by the removal of organic matter and shells by oxidising the sample with 10 ml 30% H₂O₂ and heating to 70°C. Carbonates and iron oxides were removed by adding 10% HCl and heating. A suspension of the sample in Na₄P₂O₇·10H₂O was measured with a Laser Particle Sizer instrument.

The grain size distribution is expressed as the measured volume divided into 30 fractions, logarithmically spaced between 0.1 and 2000 µm. The software program is also able to calculate the different distribution classes (D (0.5), D (0.6), *etc.*).

6.3.3.3.2. Determination of TOC

The total organic carbon (TOC) content of <0.063 mm soil samples was analysed using a LECO SC-DR144 instrument coupled to a Mettler AT 400 analytical balance.

The method is based on the total combustion of the samples after the removal of the carbonate phase by hydrochloric acid. After combustion in a 99.99 % oxygen flow at 1350°C, the resulting CO₂ is passed through a water and halogen trap and detected with an infrared detector. Analytical grade CaCO₃ was used to construct a four-point linear calibration.

The detection limit for total carbon was estimated to be 0.01 wt% and the uncertainty was estimated to be better than ±5%.

6.3.3.3.3. Determination of mercury

Mercury in residual soil samples was determined by the method described in Section §6.3.3.2.2 of 'Stream and floodplain sediments'.

6.3.3.3.4. Total multielement determination by XRF

A range of elements was determined by wavelength dispersive X-ray fluorescence spectrometry (WD-XRFS) using Philips PW1480 and PW2400 WD-XRF instruments, with Cr and Rh anode X-ray tubes, respectively.

Residual soil samples were prepared by milling in an agate mortar to <40 µm (0.04 mm) particle size. Then 1000 mg per sample were mixed with 5.0 g lithium metaborate and 25 mg lithium bromide and fused at 1200°C for 20 minutes. Loss on ignition (LOI) was determined by heating to 1030°C for 10 minutes. For samples with a LOI greater than 20%, 2.5 g lithium metaborate and 2.415 g lithium tetraborate were used. Pt95-Au5 crucibles and a commercial automatic fluxer (Herzog 12/1500) were used for the fusion.

The calibration was carried out using 130 certified reference materials (CRMs) and corrections were made for matrix interferences. In addition to the routine laboratory quality control protocol, LUFA-B (a German residual soil reference sample) was analysed regularly throughout the batches of samples submitted for analysis.

6.3.3.3.5. Total multielement determination by ICP-MS

A range of rare earth elements (REE) and other trace elements was determined on residual soil samples using a Perkin-Elmer Sciex Elan 5000 inductively coupled plasma mass spectrometer.

Two sample digestion methods were used depending on the elements to be analysed in order to optimise the elemental recovery and detection limits. In the main method, 0.2 g of the <0.063 mm soil sample was weighed into a Teflon dish and the organic material totally decomposed by evaporating the sample to dryness with 5 ml of 65% nitric acid, followed by the addition of 10 ml of 40% hydrofluoric and 4 ml of 70% perchloric acid and evaporated on a hot plate. The residue was dissolved in 20 ml of 8 mol/l nitric acid and 1 ml of 30% hydrogen peroxide before filtration. The filtrate was saved, and the filter paper was ashed in a platinum crucible. The residue was then fused with 0.2 g of lithium metaborate, and 0.02 g of sodium perborate followed by dissolution in 5 ml of 0.8 mol/l nitric acid. The solutions were combined and made up to 100 ml in 1.8 mol/l nitric acid. Measurement of these digests was carried out using a Perkin Elmer Sciex Elan 5000 inductively coupled plasma-mass spectrometer.

A simple cold dissolution method was used for selected elements: As, Cd, Cs, Cu, Mo, Ni, Pb and Sn. In this method, 0.1 g of the <0.063 mm soil sample was weighed into a plastic test tube and 1.5 ml of nitric acid and 0.5 ml of hydrofluoric acid were added. The test tube was closed with a stopper, agitated and allowed to stand at room temperature for 48 h. Deionised water (8 ml) was then added and the solution was allowed to stand for a further 48 h. The test tubes were then agitated and centrifuged, and the solution was filtered. The solution was diluted before analysis using a Perkin Elmer Sciex Elan 6000 inductively coupled plasma-mass spectrometer.

A reagent blank and two CRMs (Slovakian Residual Soil 982 and River Clay 981) were included as monitoring samples in every batch of 40 samples. In addition, CRMs were included

within each batch of 80 samples for the main digestion method (syenite SY-2) and within each batch of 40 samples for the cold dissolution method (San Joaquin Soil NIST 2701).

At concentrations an order of magnitude above the quantification limit, the uncertainty of the method was between 1 and 10%, depending on the element. Quantification limits are given in Table 6.4.

6.3.3.3.6. Acid leachable multielement determination by ICP-AES

The acid leachable metal content of soil samples was determined by the same method described above for sediment samples (refer to Section §6.3.3.2.5).

6.3.3.3.7. Selection of residual soil data

A wide range of total multielement data determined by both ICP-MS and XRFS methods were available. Data quality, including results of CRMs and ANOVA data for duplicate analyses, was assessed on an element-by-element basis. If only one of the two techniques were sufficiently sensitive to permit the determination of a particular element at the background levels found in the samples, then this technique was automatically selected. If both techniques were sufficiently sensitive, the data from the technique with the best precision, based on the ANOVA duplicate analyses, were selected. The actual method used for each element is given in Table 6.4.

The quality of the ANOVA data for the ICP-AES analysis of the *aqua regia* solutions was also assessed. For a few elements, the analytical variation exceeded that of the geochemical variation, and the data for these elements were not considered suitable for publication. Those elements with acceptable data quality are given in Table 6.4. *Aqua regia* data were also used for total S, for which no data were available by any other technique.

6.3.3.4. Analysis of humus samples

6.3.3.4.1. Determination of mercury

Mercury in humus was determined by the method described above for sediments (refer to Section §6.3.3.2.2).

6.3.3.4.2. Total multielement determination by ICP-MS

Humus samples were analysed for total element content by inductively coupled mass spectrometry. Two instruments were used: a Fisons Plasmaquad PQ2 ICP-MS during the early stages of the project and later an Argilent 7500i ICP-MS instrument. The calibration regime for both instruments was very similar.

Samples were extracted with nitric acid prior to analysis. Extraction with mild nitric acid was considered the most effective leaching method for environmental geochemical surveys to distinguish between elements, specifically Pb, Cd and Zn, derived from anthropogenic sources and elements derived from the natural background. The weak nitric acid digestion used was expected to dissolve mainly the adsorbed, exchangeable and carbonate-bound phases in the sample material.

Samples (400 mg of <0.063 mm) were placed in 50 ml polypropylene centrifuge tubes and 40 ml 4.5% sub-boiled HNO₃ was added. The tubes were placed in an ultrasonic bath for 90 minutes and then centrifuged at room temperature at 3000 rpm for 30 minutes prior to analysis.

The estimated relative standard deviation was better than 5% for most of the anthropogenic sourced elements and always better than 10% for the elements reported. This estimate is valid, however, only for a well-homogenised reference sample; the sampling uncertainty was significant for the humus samples.

6.4.3.4.3. Selection of humus data

The quality of the ANOVA data for Hg and the ICP-AES analysis of the *aqua regia* solutions was assessed. For a few elements, the analytical variation exceeded that of the geochemical variation, and these elements were not considered suitable for publication. Those elements with acceptable data quality are given in Table 6.4.

6.3.4. Quality assurance and control

Sampling and sample preparation are the most critical processes contributing to the overall uncertainty budget (Demetriades, 2014). The methods and quality control measures employed for sampling have been discussed earlier in this Manual (see Chapter 3). The methods employed for sample preparation are described in Chapter 4. A special homogeneity test protocol was established for the project to demonstrate the quality of sample preparation.

Approximately one per cent of the prepared samples were split into four sub-samples, two pressed pellets prepared from each sub-sample, and each pellet analysed twice by XRF for ten major and trace elements in order to control the ‘between-bottle’ homogeneity and ‘within-bottle’ homogeneity.

Uncertainty in chemical analysis, although often significantly less than that associated with sampling and sample preparation, is nevertheless essential to understand and control. All the participating laboratories listed in Table 6.2 were selected on the basis that they had established quality control systems in place, they regularly participated in international proficiency testing schemes for the methods for which they were responsible, and their estimated analytical uncertainty and sensitivity for all determinands was likely to be acceptable.

For the project, additional quality measures were used to provide extra assurance that the overall quality of data was up to the high standards required. For all solid sample analyses, two reference materials (ISE 921 and ISE 982) were analysed at regular intervals (between 1 and 2%, depending on the method) to monitor long-term stability and to enable the comparison of data from different methods and different laboratories. About 8% of the solid samples were also used for inter-laboratory comparison, *e.g.*, about 50 soil samples were analysed by WD-XRF at BGS for comparison with the original BGR WD-XRF and GTK ICP-MS data.

To assess the precision of the chemical analysis relative to the variation due to sample preparation and sampling, duplicate samples were taken and repeat measurements were made. Approximately 5% of all sites were sampled in duplicate. The duplicate samples were prepared independently of each other and analysed randomly along with all other samples, with each duplicate sample also analysed in duplicate to allow estimation of sampling uncertainty by the balanced ANOVA statistical interpretation method (Fig. 6.2).

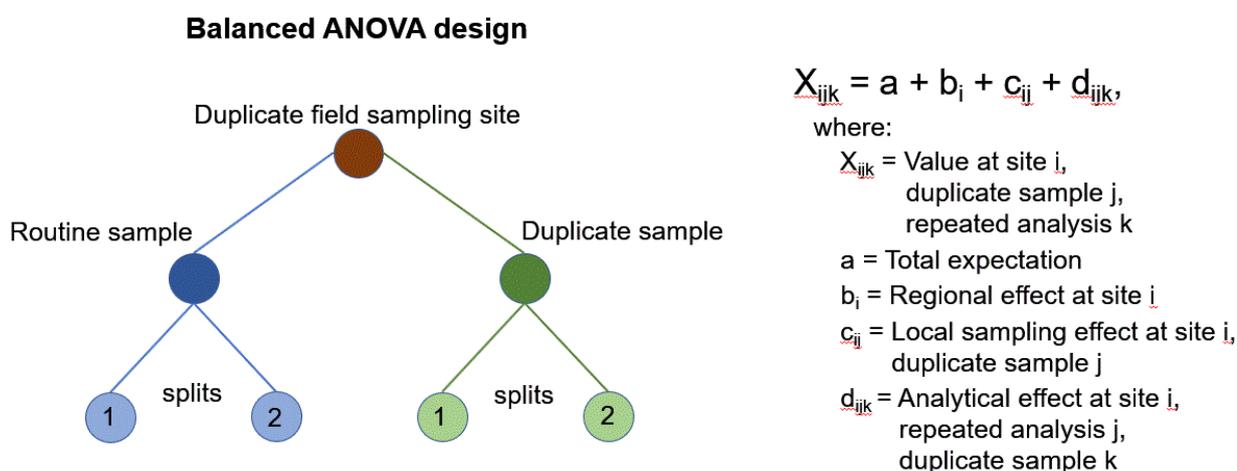


Figure 6.2. FOREGS Atlas quality control of sampling and analyses by replicates using a balanced ANOVA design (modified from Sandström et al., 2005, Fig. 1, p.83).

6.3.5. Additional methods used in European continental-scale projects

To show the significance of collecting and analysing the Global Geochemical Reference Network samples in a short time to establish a homogeneous and comparable database worldwide, the analytical methods used in another two European multi-national continental-scale projects are described below, and their detection limits compared with those of the FOREGS Geochemical Atlas of Europe.

6.3.5.1. Analytical methods used in the European Groundwater Geochemistry project

The material of this Section was mainly extracted from Birke et al. (2010), and Reimann and Birke (2010), and modified for the purposes of this Manual.

The reasons for selecting bottled mineral water to assess the geochemistry of European groundwater geochemistry are given in Reimann and Birke (2010).

The bottled mineral water samples were analysed by ICP-AES, ICP-QMS, IC, titration and photometric methods in the laboratories of the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) in Hannover Germany.

After adjusting the bottled mineral water samples to room temperature, pH (SenTix 81, glass electrode) and electrical conductivity (WTW TetraCon 325) were measured (WTW Multiline P4 electrode) with a precision of 0.01 for both parameters.

6.3.5.1.1. ICP-QMS analyses

Sample preparation (acidification and transfer to polypropylene (PP) tubes) and the ICP-QMS analysis were carried out using cleanroom procedures (class 10,000 cleanroom) in the BGR laboratories. Disposable polyethylene (PE) gloves (all other gloves contain toxic elements, *e.g.*, Zn) were used for all work in the cleanroom.

The water samples were analysed by inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS) using an Agilent 7500ce instrument. The instrument is equipped with a standard peristaltic pump, a Micro Mist concentric nebuliser, a Peltier-cooled spray chamber, the Plasma Forward Power, the Shield Torch System, and a Collision/Reaction Cell system. An autosampler (ASX 520, Cetac Technologies) was employed to introduce the analytes into the plasma of the ICP-MS. Sample introduction was done with a Micro Mist concentric nebuliser and Scott-type quartz glass spray chamber.

Details of the instrument settings and scanning conditions are given in Table 6.5. The analyses were conducted according to the German norm DIN 38406-29 (DIN, 1996).

Hydrogen was considered to be useful as a reaction gas only for Se. Helium was used as the collision gas for Ag, As, Co, Cr, Cu, Fe, Ga, Ge, Mo, Ni, Sc, Ti and Zn. No cell gas was used for the other elements.

Normally the analysis of iodine by ICP-MS requires special sample treatment and elimination of polyatomic interferences, in addition to keeping iodine in solution. But, for bottled mineral water, which has weakly acidic to acid pH, iodine can be measured directly. For the determination of iodine in this study, however, the samples were acidified with 1% ultrapure HNO₃. The instrument was calibrated with iodate. It was also attempted to stabilise iodine at basic pH, but the measurements were not reproducible.

Within the framework of the Geochemical Atlas of Germany (Birke *et al.*, 2006), ten water samples from different sources were acidified with 1% ultrapure HNO₃, and stored in fluorinated ethylene propylene (FEP) bottles for three years at low temperature (<4°C) and measured at different times. The measured iodine concentrations were reproducible over the entire three years. It has been reported that acidification can result, however, in the formation of elementary iodine, which can be adsorbed on the bottle walls and instrument tubing. But it has been verified that when HNO₃ is used for acidification, the iodine is oxidised to the iodate; this can occur at

different rates, and for this reason, there are no commercial certified standards for iodine. Water samples with high iodine concentrations were immediately reanalysed at several dilutions to test the stability of the measurement. After the measurement of a high iodine concentration, the water samples were reanalysed using the following procedure to exclude the possibility of a memory effect. A newly cleaned sample input system (tubing, sampler and skimmer cones, spray chamber) was used for each measurement. Each polypropylene (PP) tube was used only once.

Table 6.5. Instrument settings and scanning conditions of the Agilent 7500ce (ICP-MS) (from Birke *et al.*, 2010, Table 2, p.220).

Tuning Parameters	
Plasma forward power	1550 W
Reflected power	1 W
Sampling depth	8 mm
Cool gas flow	15 l/min
Carrier gas flow	0.72 l/min
Makeup gas flow	0.28 l/min
He collision gas flow	5.1 ml/min He 5.3
H ₂ reaction gas flow	4.2 ml/min H ₂ 5.3
Spray chamber	Scott/Duran
Spray chamber temp	10°C
Nebuliser	MicroMist
Sample uptake	0.4 ml/min
Oxide CeO156/Ce140	0.8 – 1.0 %
Doubly charged Ce140/70	1 – 3 %
Acquisition Parameters	
Points per mass	1
Repetitions	3
Scans/repetition	100
Stabilisation sample	60 sec
Stabilisation no gas	15 sec
Stabilisation H ₂	15 sec
Stabilization He	15 sec
Total acquisition time	165 sec
Rinse time (intelligent) for Sb, Tl, U	30 – 90 sec

It is known that interference corrections must be used for the numerous mass overlaps of the various REE oxides. The collision cell conditions that were used cannot eliminate these overlaps. A correction algorithm similar to that of Hall *et al.* (1995, 1996) was used to correct for the influence of BaO on the peaks for ¹⁵¹Eu and ¹⁵³Eu. The correction was made for each analytical sample batch to take into consideration the rate of BaO formation (0.8–1.0 %). Appropriate settings for the Agilent mass spectrometer were selected so that REE oxide formation was minimised. It is known that many of the REEs require 3 to 4 such corrections to obtain accurate results.

Table 6.6 shows that the analytical methods used in the European Groundwater Geochemistry project (Birke *et al.*, 2010; Reimann and Birke, 2010), approximately eight years after the FOREGS Geochemical Atlas of Europe project (Sandström *et al.*, 2005), have lower detection limits, because of improvements in the technology of analytical instruments.

Table 6.6. Analytical methods and detection limits used in (a) the European Groundwater Geochemistry (EGG) project, and (b) Stream water of the FOREGS Geochemical Atlas of Europe. For the EGG project there are three detection limits, i.e., Instrument detection limit (IDL), Reported detection limit (RDL) and Practical detection limit (PDL); the latter was estimated by a modified Thompson & Howarth (1976, 1978) method (Demetriades, 2011; see Chapter 7 in this Manual). Colour notation: Light Blue = lower detection limits (LDL) of European Groundwater Geochemistry project; Pale Brown = lower quantification limits of FOREGS Stream water; Pale Yellow = similar or better quantification limit of FOREGS Stream water (modified from Birke et al. (2010, Table 1, p.219-220) and Sandström et al. (2005, Table 3, p.89)).

Parameter	Unit	(a) European Groundwater Geochemistry project							(b) FOREGS Atlas Stream water	
		Analytical method	Isotope	Used gases	Instrument detection limit	Reported detection limit	Practical detection limit	Precision	Quantification limit	Analytical method
					IDL	RDL	PDL	(%)	QL	
Ag	µg/l	ICP-QMS	Min: 107-109	He GM ^a	0.001	0.002	0.002	13	0.002	ICP-MS
Al	µg/l	ICP-QMS	27	NGM ^b	0.2	0.5	0.2	5	0.1	ICP-MS
As	µg/l	ICP-QMS	75	He GM ^a	0.01	0.03	0.001	10	0.01	ICP-MS
B	µg/l	ICP-QMS	11	NGM ^b	0.1	2	0.2	4	0.01	ICP-MS
Ba	µg/l	ICP-QMS	137	NGM ^b	0.005	0.1	0.2 ^c	5	0.005	ICP-MS
Be	µg/l	ICP-QMS	9	NGM ^b	0.001	0.01	0.005	5	0.005	ICP-MS
Bi	µg/l	ICP-QMS	209	NGM ^b	0.0005	0.005	0.003	/ ^f	0.002	ICP-MS
Ca	mg/l	ICP-AES	/	/	0.005	0.01	/	/	0.001	ICP-AES
Cd	µg/l	ICP-QMS	114_cor	NGM ^b	0.001	0.003	0.002	29	0.002	ICP-MS
Ce	µg/l	ICP-QMS	140	NGM ^b	0.0005	0.001	0.0001	13	0.002	ICP-MS
Co	µg/l	ICP-QMS	59	He GM ^a	0.002	0.01	0.002	5	0.005	ICP-MS
Cr	µg/l	ICP-QMS	52	He GM ^a	0.01	0.2	0.014	7	0.01	ICP-MS
Cs	µg/l	ICP-QMS	133	NGM ^b	0.0005	0.002	0.004 ^c	3	0.002	ICP-MS
Cu	µg/l	ICP-QMS	Min: 63-65	He GM ^a	0.01	0.1	0.029	2	0.005	ICP-MS
Dy	µg/l	ICP-QMS	163	NGM ^b	0.0002	0.001	0.001	16	0.002	ICP-MS
Er	µg/l	ICP-QMS	166	NGM ^b	0.0002	0.001	0.0004	13	0.002	ICP-MS
Eu	µg/l	ICP-QMS	151_kor	NGM ^b	0.0002	0.001	0.001	18	0.002	ICP-MS
Fe	µg/l	ICP-QMS	56	He GM ^a	0.01	0.5	0.08	4	1	ICP-MS
Ga	µg/l	ICP-QMS	71	He GM ^a	0.0005	0.005	0.005	4	0.002	ICP-MS
Gd	µg/l	ICP-QMS	157	NGM ^b	0.0002	0.002	0.001	22	0.002	ICP-MS
Ge	µg/l	ICP-QMS	72	He GM ^a	0.005	0.03	0.02	6	0.005	ICP-MS
Hf	µg/l	ICP-QMS	178	NGM ^b	0.0001	0.002	0.001	28	0.002	ICP-MS
Hg	ng/l	AFS	/	/	1	5	/	/	/	
Ho	µg/l	ICP-QMS	165	NGM ^b	0.0001	0.001	0.0003	19	0.002	ICP-MS
I	µg/l	ICP-QMS	127	NGM ^b	0.01	0.2	0.09	15	0.01	ICP-MS
In	µg/l		/	/	/	/	/	/	0.002	ICP-MS
K	mg/l	ICP-AES	/	/	0.05	0.1	/	/	/	ICP-MS
La	µg/l	ICP-QMS	139	NGM ^b	0.0001	0.001	0.001	9	/	ICP-MS
Li	µg/l	ICP-QMS	7	NGM ^b	0.01	0.2	0.14	5	0.005	ICP-MS
Lu	µg/l	ICP-QMS	175	NGM ^b	0.00005	0.001	0.0002	16	0.002	ICP-MS
Mg	mg/l	ICP-AES	/	/	0.005	0.01	/	/	0.001	ICP-AES
Mn	µg/l	ICP-QMS	55	NGM ^b	0.005	0.1	0.111	2	0.05	ICP-MS
Mo	µg/l	ICP-QMS	95	He GM ^a	0.001	0.02	0.017	4	0.002	ICP-MS
Na	mg/l	ICP-AES	/	/	0.02	0.1	/	/	0.005	ICP-AES
Nb	µg/l	ICP-QMS	93	NGM ^b	0.001	0.01	0.001	15	0.002	ICP-MS
Nd	µg/l	ICP-QMS	146	NGM ^b	0.0001	0.001	0.001	18	0.005	ICP-MS
Ni	µg/l	ICP-QMS	60	He GM ^a	0.005	0.02	0.01	4	0.005	ICP-MS

Parameter	Unit	(a) European Groundwater Geochemistry project							(b) FOREGS Atlas Stream water	
		Analytical method	Isotope	Used gases	Instrument detection limit	Reported detection limit	Practical detection limit	Precision	Quantification limit	Analytical method
					IDL	RDL	PDL	(%)	QL	
P	mg/l	ICP-AES	/	/	0.01	0.01	/	/	/	/
Pb	µg/l	ICP-QMS	Sum:	NGM ^b	0.001	0.01	0.003	6	0.005	ICP-MS
Pr	µg/l	ICP-QMS	141	NGM ^b	0.00005	0.001	0.0002	15	0.002	ICP-MS
Rb	µg/l	ICP-QMS	85	NGM ^b	0.001	0.01	0.30 ^e	6	0.002	ICP-MS
Sb	µg/l	ICP-QMS	121	NGM ^b	0.001	0.01	0.0001	6	0.002	ICP-MS
Sc	µg/l	ICP-QMS	45	He GM ^a	0.001	0.02	0.001	23	/	/
Se	µg/l	ICP-QMS	78	H ₂ GM ^c	0.005	0.02	0.009	19	0.01	ICP-MS
Si	mg/l	ICP-AES	/	/	0.03	0.03	/	/	0.01	ICP-AES
Sm	µg/l	ICP-QMS	147	NGM ^b	0.0001	0.001	0.001	23	0.002	ICP-MS
Sn	µg/l	ICP-QMS	118	NGM ^b	0.001	0.02	0.003	12	/	ICP-MS
Sr	mg/l	ICP-AES	/	NGM ^b	0.001	0.001	/	/	0.001	ICP-AES
Ta	µg/l	ICP-QMS	181	NGM ^b	0.0005	0.005	0.002	/ ^f	0.002	ICP-MS
Tb	µg/l	ICP-QMS	159	NGM ^b	0.00005	0.001	0.0002	23	0.002	ICP-MS
Te	µg/l	ICP-QMS	126	NGM ^b	0.001	0.03	0.01	/ ^f	0.005	ICP-MS
Th	µg/l	ICP-QMS	232	NGM ^b	0.0001	0.001	0.0004	33	0.002	ICP-MS
Ti	µg/l	ICP-QMS	Min: 47-49	He GM ^a	0.005	0.08	0.04	52	0.01	ICP-MS
Tl	µg/l	ICP-QMS	205	NGM ^b	0.0005	0.002	0.001	6	0.002	ICP-MS
Tm	µg/l	ICP-QMS	169	NGM ^b	0.00005	0.001	0.0002	22	0.002	ICP-MS
U	µg/l	ICP-QMS	238	NGM ^b	0.00005	0.001	0.006 ^e	2	0.002	ICP-MS
V	µg/l	ICP-QMS	51	NGM ^b	0.01	0.1	0.02	6	0.05	ICP-MS
W	µg/l	ICP-QMS	182	NGM ^b	0.002	0.05	0.009	1	0.002	ICP-MS
Y	µg/l	ICP-QMS	89	NGM ^b	0.00005	0.001	0.002	7	0.002	ICP-MS
Yb	µg/l	ICP-QMS	172	NGM ^b	0.0001	0.001	0.001	17	0.002	ICP-MS
Zn	µg/l	ICP-QMS	Min: 66-68	He GM ^a	0.01	0.2	0.11	3	0.01	ICP-MS
Zr	µg/l	ICP-QMS	90	NGM ^b	0.0001	0.001	0.013	7	0.002	ICP-MS
Br ⁻	mg/l	IC	/	/	0.003	0.003	/	/	0.01	IC
HCO ₃ ⁻	mg/l	titration	/	/	2	2	/	/	/	/
Alkalinity	mg/l	titration	/	/	0.1	0.1	/	/	/	/
Cl ⁻	mg/l	IC	/	/	0.01	0.01	/	/	0.1	IC
F ⁻	mg/l	IC	/	/	0.003	0.003	/	/	0.05	IC
NH ₄ ⁺	mg/l	photometric	/	/	0.005	0.005	/	/	/	/
NO ₂ ⁻	mg/l	IC	/	/	0.005	0.005 – 0.1 ^d	/	/	/	/
NO ₃ ⁻	mg/l	IC	/	/	0.01	0.01 – 1.0 ^d	/	/	0.04	IC
PO ₄ ³⁻	mg/l	ICP-AES	/	/	0.02	0.02	/	/	/	/
SO ₄ ²⁻	mg/l	IC	/	/	0.01	0.01	/	/	0.3	IC
SiO ₂	mg/l	ICP-AES	/	/	0.05	0.05	/	/	/	/

Superscript notation: ^aHe gas mode; ^bno gas mode; ^cH₂ gas mode; ^ddependent on TDS; ^etoo large a concentration range and too many high values to reliably calculate PDL; ^finsufficient number of values above detection limit to estimate precision.

6.3.5.1.2. ICP-AES analyses

The acidified and non-acidified water samples were analysed using an ICP-AES (Spectro Ciros instrument) with radial plasma measurement according to DIN EN ISO 11885 (DIN, 1988, 1998, 2009). The wavelengths and detection limits are given in Table 6.7 for the analysed elements.

The detection limits were estimated from the calibration curves according to DIN 32645 (DIN, 1994).

Blank samples (0.15 M HNO₃ in deionised water) were measured for calibration of the instrument. A multielement standard solution containing the elements of Table 6.7 in 0.15 M HNO₃ was also used. This standard of known composition was analysed as part of each batch of samples.

6.3.5.1.3. Ion chromatography (IC)

A Dionex ICS 3000 ion chromatograph, equipped with a conductivity detector, an AS 19 column and a self-regenerating suppressor using a KOH eluent, was used for the determination of F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻ and SO₄²⁻ in nonacidified water samples, according to DIN EN ISO 10304-1 (DIN, 1995). The detection limits of this method are given in Table 6.6.

6.3.5.1.4. Photometric analyses

Ammonium ion was analysed photometrically using a Thermo Unicam UV 300 spectrometer according to DIN 38406-5 (DIN, 1983) in samples that were not acidified. The detection limits estimated from the calibration curve, and calculated according to DIN 32645 (DIN, 1994), are given in Table 6.6.

Table 6.7. Wavelengths and instrument detection limits for elements analysed in groundwater samples by ICP-AES (from Birke et al., 2010, Table 3, p.220).

<i>Element</i>	<i>Wavelength (nm)</i>	<i>Instrument detection limit (mg/l)</i>
Al	167.078	0.003
B	249.678	0.01 as BO ₂
Ba	455.404	0.0005
Be	313.042	0.0005
Ca	317.933, 422.673	0.005
Cd	228.802	0.002
Co	228.616	0.003
Cr	267.716	0.003
Cu	324.754	0.003
Fe	259.94	0.003
K	766.49	0.05
Li	670.78	0.003
Mg	285.213, 279.079	0.005
Mn	257.611	0.001
Na	589.592	0.02
Ni	231.603	0.005
P	177.49	0.01 as PO ₄ ³⁻
Pb	220.351	0.02
Sc	361.364	0.001
Si	251.611	0.03 as SiO ₂
Sr	407.771	0.0003
V	311.071	0.003
Zn	213.856	0.003

6.3.5.1.5. Titration method

Alkalinity was determined on nonacidified water samples by titration with 0.05 M HCl. This was done with an automatic Metrohm titrator on a 50 ml water sample. The titration result was given as bicarbonate concentration (titration end-point 4.3 in acid pH range) or carbonate (titration end-point 8.2 in weakly basic pH range). The detection limit was 1 mg HCO₃⁻/l.

6.3.5.1.6. Atomic fluorescence spectrometry (AFS)

Atomic fluorescence spectrometry was used for the determination of mercury (Instrument PSA 10.035 Millennium Merlin 1631).

Elemental mercury vapour is generated from the sample by reduction with tin(II) chloride, and is purged from the solution by an argon carrier stream. The mercury vapour is detected by atomic fluorescence spectrometry.

The system uses continuous flow vapour generation, the mercury vapour is passed over a gold trap where the mercury is concentrated. After collection for a set time (25 sec), the mercury is then thermally desorbed from the gold into the atomic fluorescence detector.

The sample is stabilised by a mixture of potassium dichromate and nitric acid (5 g potassium dichromate in 1 litre HNO₃ (64%), 1 ml in 100 ml sample).

The linear dynamic range of this method is approximately 0.1 ng/l to 100 µg/l Hg.

Accuracy and precision were controlled continuously by using CRMs BCR 60 and BCR 61.

High purity MERCK reagents (suprapur) were used in all cases; prior to use, the tin(II) solution was purged for 24 hours with nitrogen.

6.3.5.2. Analytical methods used in the European Geochemical Mapping of Agricultural and grazing land Soil project

The material of this Section was extracted from reports of the GEMAS project (Geochemical Mapping of Agricultural and grazing land Soils), namely Reimann et al. (2009, 2011) and Birke et al. (2014), and modified for the purposes of this Manual.

6.3.5.2.1. Total element concentrations by XRF

The elements SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, SO₃, Cl, F, As, Ba, Bi, Ce, Co, Cr, Cs, Cu, Ga, Hf, La, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn and Zr were determined by wavelength dispersive X-ray fluorescence spectrometry (WD-XRFS) using PANalytical PW2400 and AXIOS WD-XRFs, with Cr and Rh anode X-ray tubes, respectively.

The splits of all <2 mm samples were prepared for XRF analysis via milling to <0.063 mm particle size in a disk mill using agate vessels. Loss on ignition (LOI) was determined on all samples by slowly heating them to 1030°C and keeping the samples at this temperature for 15 minutes in a muffle furnace. Although LOI may be used as a proxy for TOC, it must be recognised that other components may be released, including free water, bound water, carbonate minerals, sulphate and sulphides. Depending on the value of LOI (above or below 25%), the samples for XRF determination were prepared, using different proportions of lithium metaborate and lithium bromide for the fused beads. The sample weight in each case was 1000 mg.

A 1000 mg aliquot of each soil sample with a LOI < 25% was mixed with 5.0 g lithium metaborate and 25 mg lithium bromide in Pt95-Au5 crucibles, and fused at 1200°C for 20 minutes in an automatic fluxer (HAG 12-1500). For soil samples with a LOI > 25%, weights of 2.5 g lithium metaborate and 2.415 g lithium tetraborate were used for the preparation of the fused beads. To correct for matrix and spectral interferences, calibration curves were constructed using 130 certified reference materials.

XRF is the method of choice when total element concentrations in a sample are to be determined. However, very light elements (like Li, Be, B), or trace elements with very low

concentrations (like Ag, Au, Se, Te) cannot be reliably determined by XRF (Reimann *et al.*, 2011).

Table 6.8 shows that the XRF instrument of BGR, used in the analysis of the GEMAS agricultural soil samples, has comparable detection limits to those of the FOREGS Geochemical Atlas of Europe. However, the estimation of the practical detection limit in the GEMAS project indicates that lower detection limits can be used. As the XRF results are censored, the estimated practical detection limits, in this case, verify the laboratory detection limits, and lower values cannot be assigned. *Hence, it is strongly recommended for the XRF instruments to be programmed to provide uncensored values.*

6.3.5.2.2. Hot aqua regia extraction and determination by ICP-AES & ICP-MS

A weight of 15 g of the sieved mineral soil samples (<2 mm) was digested in 90 ml aqua regia and leached for one hour in a hot (95°C) water bath. After cooling, the solution was made up to a final volume of 300 ml with 5% HCl acid. The sample weight to solution volume ratio is 1 g per 20 ml. The solutions were then analysed using a Spectro Ciros Vision emission spectrometer (ICP-AES) and a Perkin Elmer Elan 6000/9000 inductively coupled plasma mass spectrometer (ICP-MS). In addition to the project standards and duplicate sample splits that were unknown to the analyst, the laboratory inserted its own project standards and analytical replicates.

The hot aqua regia digestion method, used in the GEMAS project, owing to the combined use of modern ICP-MS and ICP-AES instruments, and the larger weight of 15 g soil compared to the 1 g used in the FOREGS project, achieved lower detection limits after approximately eight years from the FOREGS Geochemical Atlas of Europe project in which an ICP-AES instrument was used (Table 6.9). *It is, therefore, strongly recommended for the aqua regia extraction to use a larger weight.*

Table 6.8. XRF methods and detection limits used in (a) the European Agricultural and Grazing Soil (GEMAS) project, and (b) FOREGS Geochemical Atlas of Europe determined at Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) and British Geological Survey (BGS). For the GEMAS project, two detection limits are given, i.e., Instrument detection limit (IDL) and Practical detection limit (PDL); the latter was estimated by a modified Thompson & Howarth (1976, 1978) method (Demetriades, 2011; see Chapter 7 in this Manual). For the FOREGS project the Quantification limit (QL), and Upper Continental Crust abundance values are given for comparison. The precision at the 95% confidence level for the GEMAS project samples was estimated by two different methods. Colour notation: Light Blue = lower detection limits of GEMAS project soil samples analysed by XRF at BGR; Pale Brown = lower quantification limits of FOREGS sediment samples analysed by XRF at the British Geological Survey (BGS); Pale Yellow = similar or better quantification limit of FOREGS residual soil samples analysed by XRF at BGR (modified from Reimann *et al.* (2011, Table 2, p.19-20) and Demetriades *et al.* (2014, Table 6.1, p.50-51) and Sandström *et al.* (2005, Table 3, p.89)).

Parameter	BGR Lab	(a) GEMAS Agricultural (Ap) soil			(b) FOREGS Geochemical Atlas of Europe		Upper Continental Crust	
		Project replicates (N=104 pairs)			Soil samples	Sediment samples	Abundance	Source
		Practical	Precision %					
IDL	PDL	1	2	BGR QL	BGS QL			
<i>Values in wt.%</i>								
SiO ₂	0.1	0.01	1	0.4	0.1	0.1	66.6	Rudnick and Gao (2003)
TiO ₂	0.001	0.005	1	2	0.001	0.005	0.640	Rudnick and Gao (2003)
Al ₂ O ₃	0.05	0.04	1	1	0.05	0.1	15.4	Rudnick and Gao (2003)
Fe ₂ O ₃	0.01	0.01	1	1	0.01	0.01	5.60	Rudnick and Gao (2003)
MnO	0.001	0.0001	2.2	2	0.001	0.01	0.100	Rudnick and Gao (2003)
MgO	0.01	0.01	1	1	0.01	0.1	5.19	Rudnick and Gao (2003)
CaO	0.005	0.01	2	1	0.01	0.05	3.59	Rudnick and Gao (2003)
Na ₂ O	0.01	0.01	3	3	0.01	0.2	3.27	Rudnick and Gao (2003)
K ₂ O	0.005	0.001	2	2	/	/	2.80	Rudnick and Gao (2003)

Parameter	BGR Lab	(a) GEMAS Agricultural (Ap) soil			(b) FOREGS Geochemical Atlas of Europe		Upper Continental Crust	
		Project replicates (N=104 pairs)			Soil samples	Sediment samples		
		Practical	Precision %					
		IDL	PDL	1	2	BGR QL		
P ₂ O ₅	0.001	0.001	2	3	0.001	0.01	0.150	Rudnick and Gao (2003)
SO ₃	0.01	0.003	12	27	/	/	0.015	Rudnick and Gao (2003)
Cl	0.002	0.002	43	67*	/	/	0.037	Rudnick and Gao (2003)
F	0.05	0.04	50	341*	/	/	0.056	Rudnick and Gao (2003)
LOI ^a	0.01	0.04	7	1	/	/	/	/
S ^b	0.01	0.005	32	48	/	/	0.0062	Rudnick and Gao (2003)
C ^b	0.01	0.008	22	6	/	/	0.324	Wedepohl (1995)
TOC ^c	0.1	0.3	22	9	/	/	/	/
<i>Values in mg/kg</i>								
As	3	0.4	15	21	/	1	5.7	Hu and Gao (2008)
Ba	5	2	3	1	5	3	628	Rudnick and Gao (2003)
Bi	3	2	31	576*	/	/	0.23	Hu and Gao (2008)
Ce	20	7	15	33	/	/	63	Rudnick and Gao (2003)
Co	3	1	16	27	/	/	15	Hu and Gao (2008)
Cr	4	3	3	3	3	3	73	Hu and Gao (2008)
Cs	/	/	/	/	/	4	4.9	Hu and Gao (2008)
Cu	5	0.5	10	21	/	1	27	Hu and Gao (2008)
Ga	2	1	8	20	/	1	18.6	Hu and Gao (2008)
Hf	5	9	37	92	/	/	5.3	Rudnick and Gao (2003)
La	20	64	27	120	/	/	31	Rudnick and Gao (2003)
Mo	2	**	34	**	/	/	0.6	Hu and Gao (2008)
Nb	2	0.2	8	15	/	1	11.6	Hu and Gao (2008)
Ni	3	1	4	5	/	1	34	Hu and Gao (2008)
Pb	3	0.3	98	13	/	1	17	Rudnick and Gao (2003)
Rb	2	0.2	4	6	2	1	94	Hu and Gao (2008)
Sb	5	**	18	**	/	/	0.75	Hu and Gao (2008)
Sc	2	1	10	33	/	/	14	Hu and Gao (2008)
Sn	4	2	45	577	2	1	2.2	Hu and Gao (2008)
Sr	2	1	1	1	2	1	320	Rudnick and Gao (2003)
Ta	5	**	13	**	/	/	0.92	Hu and Gao (2008)
Th	5	3	21	54	/	1	10.5	Rudnick and Gao (2003)
U	3	7	31	126	/	1	2.6	Hu and Gao (2008)
V	5	2	3	5	/	2	106	Hu and Gao (2008)
W	5	**	22	**	5	0.05	1.4	Hu and Gao (2008)
Y	3	2	4	1	3	0.02	21	Rudnick and Gao (2003)
Zn	3	1	2	2	3	1	75	Hu and Gao (2008)
Zr	3	1	3	4	3	1	193	Rudnick and Gao (2003)
CEC ^d	0.1	0.04	6	9	/	/	/	/
pH CaCl ₂ ^e	0.1	0.1	1	3	/	/	/	/

^aGravimetric method; ^bLECO; ^cInfrared method; ^dAg thiourea method in meq/100g; ^epH-meter (Reimann *et al.*, 2011; Birke *et al.*, 2014)

* = too many values near DL to estimate reliable values of PDL and Precision

** = too few samples above detection to estimate PDL and Precision 2

DL = Detection limit

QL = Quantification limit

Table 6.9. Hot aqua regia digestion methods and determination of element concentrations by ICP-MS and ICP-AES and detection limits used in (a) the Geochemical Mapping of Agricultural and Grazing Soil (GEMAS) project, and (b) the FOREGS Geochemical Atlas of Europe. For the GEMAS project, two detection limits are given, i.e., Instrument detection limit (IDL) and Practical detection limit (PDL); the latter was estimated by a modified Thompson & Howarth (1976, 1978) method (Demetriades, 2011; see Chapter 7 in this Manual), and for the FOREGS project the Quantification limit (QL). Upper Continental Crust abundance values are given for comparison. The precision at the 95% confidence level for the GEMAS project samples has been estimated by two different methods. Colour notation: Light Blue = lower detection limits of GEMAS project soil samples analysed by a commercial laboratory; Pale Brown = lower quantification limits of FOREGS residual soil samples (modified from Reimann et al. (2009, Table 3, p.22-24) and Demetriades et al. (2014, Table 6.1, p.50-51) and Sandström et al. (2005, Table 3, p.89)).

Element	(a) GEMAS Agricultural soil (Ap) samples						(b) FOREGS Residual soil samples	Upper Continental Crust	
	Commercial Laboratory	Lab replicates (N=146 pairs)	Project replicates (N=104 pairs)			Lab replicates (N=146 pairs)			
			Practical	Practical	Precision %				
	IDL	PDL	PDL	1	2	1			
Ag	0.002	0.002	0.007	9	18	8	/	0.053	Rudnick and Gao (2003)
Al	100	104	4	6	8	3	/	81,505	Rudnick and Gao (2003)
As	0.1	0.065	0.005	8	10	4	5	5.7	Hu and Gao (2008)
Au	0.0002	0.002	0.0007	46	55	66	/	0.0015	Rudnick and Gao (2003)
Ba	0.5	0.88	1.3	7	8	5	1	628	Rudnick and Gao (2003)
Be	0.1	0.04	0.033	19	39	16	/	1.9	Hu and Gao (2008)
Bi	0.02	0.004	0.01	6	7	5	/	0.23	Hu and Gao (2008)
Ca	100	48	178	11	4	6	/	25,657	Rudnick and Gao (2003)
Cd	0.01	0.01	0.0086	8	9	9	/	0.06	Hu and Gao (2008)
Ce	0.1	1.21	1.2	6	14	4	/	63	Rudnick and Gao (2003)
Co	0.1	0.013	0.085	6	8	4	1	15	Hu and Gao (2008)
Cr	0.5	0.45	0.019	6	8	5	1	73	Hu and Gao (2008)
Cs	0.02	0.014	0.011	7	9	4	/	4.9	Hu and Gao (2008)
Cu	0.01	0.02	0.27	5	4	4	1	27	Hu and Gao (2008)
Fe	100	121	163	3	5	3	2	39,176	Rudnick and Gao (2003)
Ga	0.1	0.026	0.065	5	6	4	/	18.6	Hu and Gao (2008)
Ge	0.1	0.64	0.019	52	58	47	/	1.3	Hu and Gao (2008)
Hf	0.02	0.006	0.01	12	9.5	14	/	5.3	Rudnick and Gao (2003)
Hg	0.005	0.003	0.002	13	15	13	/	0.05	Rudnick and Gao (2003)
In	0.02	0.003	0.004	21	28	19	/	0.066	Hu and Gao (2008)
K	100	5.7	21	8	13	5	/	23,244	Rudnick and Gao (2003)
La	0.5	0.09	0.026	5	8.5	4	/	31	Rudnick and Gao (2003)
Li	0.1	0.04	0.28	6	8	4	/	41	Hu and Gao (2008)
Mg	100	3.1	64	5	6	3	/	14,955	Rudnick and Gao (2003)
Mn	1	14	2	6	7	8	10	774	Rudnick and Gao (2003)
Mo	0.01	0.01	0.018	9	17	7	/	0.6	Hu and Gao (2008)
Na	10	1.1	1.1	8	14	10	/	24,259	Rudnick and Gao (2003)
Nb	0.02	0.01	0.028	11	9	7	/	11.6	Hu and Gao (2008)
Ni	0.1	0.11	0.26	6	6.5	6	2	34	Hu and Gao (2008)
P	10	33	4.3	7	11	5	/	655	Rudnick and Gao (2003)
Pb	0.01	0.35	0.88	11	15	12	3	17	Rudnick and Gao (2003)
Pd	0.01	0.01	0.001	540	228	415	/	0.000526	Park et al. (2012)
Pt	0.002	0.0016	0.00007	131	89	76	/	0.000599	Park et al. (2012)
Rb	0.1	0.15	0.23	6	10	4	/	94	Hu and Gao (2008)
Re	0.001	0.0003	0.06	1079	100	1048	/	0.000198	Rudnick and Gao (2003)
S	200	4	3.3	8	7	46	50	62	Rudnick and Gao (2003)
Sb	0.02	0.003	0.0002	12	18	7	/	0.75	Hu and Gao (2008)
Sc	0.1	0.0006	0.05	5	7.5	5	/	14	Hu and Gao (2008)

Element	(a) GEMAS Agricultural soil (Ap) samples						(b) FOREGS Residual soil samples	Upper Continental Crust	
	Commercial Laboratory	Lab replicates (N=146 pairs)	Project replicates (N=104 pairs)			Lab replicates (N=146 pairs)			
		Practical	Practical	Precision %		Precision %			
	IDL	PDL	PDL	1	2	1			
Se	0.1	0.04	0.1	19	17	18	/	0.09	Rudnick and Gao (2003)
Sn	0.1	0.01	0.0056	8	14	20	/	2.2	Hu and Gao (2008)
Sr	0.5	0.4	0.65	9	6	8	/	320	Rudnick and Gao (2003)
Ta	0.05	0.005	0.004	65	84	73	/	0.92	Hu and Gao (2008)
Te	0.02	0.01	0.021	53	24	60	/	0.027	Hu and Gao (2008)
Th	0.1	0.02	0.0008	5	9	5	/	10.5	Rudnick and Gao (2003)
Ti	10	0.9	6.7	8	8	11	/	3836	Rudnick and Gao (2003)
Tl	0.02	0.0005	0.00009	9	11	10	/	0.55	Hu and Gao (2008)
U	0.1	0.04	0.015	5	5	5	/	2.6	Hu and Gao (2008)
V	2	0.09	0.07	8	10	5	1	106	Hu and Gao (2008)
W	0.1	0.01	0.0045	16	26	12	/	1.4	Hu and Gao (2008)
Y	0.01	0.04	0.053	4	9	3	/	21	Rudnick and Gao (2003)
Zn	0.1	0.26	1	4	5	5	1	75	Hu and Gao (2008)
Zr	0.1	0.02	0.07	12	8	8	/	193	Rudnick and Gao (2003)

6.4. Analysis of rock samples

Most routine chemical bulk analyses of rocks are currently made with instruments (the X-ray fluorescence spectrometer, and the inductively coupled plasma spectrometer), which permit the simultaneous or rapid successive determination of major and trace elements (Hooper, 1964, 1966; Welday *et al.*, 1964; Hooper *et al.*, 1976; Hall, 1992; Jarvis *et al.*, 1992; Montaser, 1998; Olesik, 2000; Gäbler, 2002).

X-ray fluorescence spectrometry (XRF) coupled with total acid digestion and inductively coupled plasma-mass spectrometry (ICP-MS) analysis is the technique of choice of most petrologists and geochemists for whole-rock analysis. The XRF method is described in detail in the FOREGS (Sandström *et al.*, 2005) and GEMAS atlases (Reimann *et al.*, 2011; Birke *et al.*, 2014) – refer to Sections §6.3.3.2.3, §6.3.3.3.4 and §6.3.5.2.1, respectively.

Fusion of a powdered sample with a suitable flux, usually lithium metaborate, lithium tetraborate or a blend of the two, is used to break down the mineral structures thereby eliminating sample heterogeneity, such as grain size and mineralogical effects of the various rock-forming minerals. Traditionally fusion methods have been predominantly used to determine the major elements in silicate rock, and pressed powder pellet is used for trace element analysis. More recently, the use of a single low dilution (2:1 flux:sample) fused bead has improved sensitivity allowing the analysis of major and trace elements at the same time (Johnson *et al.*, 1999).

As detection limits of the XRF technique are often higher for the reliable analysis of many trace elements, it is desirable, as already pointed out, to couple the analysis of the same powdered sample by XRF and ICP-MS. Unless Li and B are of interest, the same fusion technique can be used to break down mineral structures making for a much more precise determination of trace elements, which are often located in refractory and hard-to-dissolve minerals such as zircon. The resulting fused bead is then re-ground and dissolved in strong acid in the usual way before analysis on the ICP-MS instrument. If Li and B are of interest, the powdered sample can be dissolved directly in a blend of strong inorganic acids before analysis. This approach, however, often fails to dissolve the most refractory minerals, leading to the name ‘near-total digestion’ technique and, therefore, misses some of the important trace elements such

as Zr and the REEs. If boron is not of interest, a sodium borate flux can be used to fuse the sample (Bank *et al.*, 2016).

Recent developments in whole-rock analysis have focused on using laser ablation to introduce the sample into the ICP-MS directly from the same fused bead as analysed by XRF (Eggins, 2003; Yu *et al.*, 2003; Kurosawa *et al.*, 2007). This approach reliably achieves complete sample digestion and provides for complementary XRF and LA-ICP-MS analysis of a full suite of major and trace elements including the rare earth elements (REEs) from single sample preparation (Fedorowich *et al.*, 1993; Strnad *et al.*, 2007; Tanaka *et al.*, 2007; Liu *et al.*, 2013). This reduces sample supply, preparation time and handling, thereby decreasing the risk of error in the analytical routine (*e.g.*, Yu *et al.*, 2003; Yamasaki and Yamashita, 2016). While this approach is still developing, this will become a significant method in the future.

Some specially adapted techniques need to be applied to elements that are difficult to analyse with either XRF or bulk ICP-MS, *for example*, noble elements (Au), platinum group elements (PGM), mercury, carbon, sulphur and halogens.

Modern instrumental methods such as flame atomic absorption spectrometry (F-AAS) (Terashima, 1988; Tewari *et al.*, 1990; Ramesh *et al.*, 2001; Balaram *et al.*, 2012), graphite furnace atomic absorption spectrometry (GF-AAS) (Benedetti *et al.*, 1987), neutron activation analysis (INAA) (Keays and Scott, 1976; Nesbitt *et al.*, 1987), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Yan *et al.*, 1995), and inductively coupled plasma mass spectrometry (ICP-MS) (Hall and Bonham-Carter, 1988; Ely *et al.*, 1999; Pitcairn *et al.*, 2006) are commonly used for gold determination with low detection limits. The very low average gold concentration in non-mineralised rocks ranges between 0.0005 and 0.005 mg/kg and requires a separation (dissolution of gold from the geological samples), pre-concentration of gold and a correspondingly highly sensitive analytical method for its quantification (Pitcairn *et al.*, 2006). Accordingly, the determination of gold in rock samples with concentrations in the ultra-trace range (in the parts-per-trillion to parts-per-billion) is considerably more complex than in ore samples where fire-assay (FA) and cyanidation methods have been successfully used for centuries (Chow and Beamish, 1967; Vanloon and Barefoot, 1991; Marsden and House, 2006; Asamoah *et al.*, 2014).

Platinum-group elements (PGEs: Pt, Pd, Rh, Ir, Os, Ru) in rocks are best determined by fire assay with ICP-MS or HR-ICP-MS finish. Modern methods such as INAA and ICP-MS (including HR-ICP-MS) offer highly sensitive determinations for PGEs (Shazali *et al.*, 1987; Hall and Pelchat, 1994; Figueiredo *et al.*, 2000; Garuti *et al.*, 2000; Hann *et al.*, 2001; Morcelli *et al.*, 2004; Balaram *et al.*, 2006). Several geochemical studies have confirmed that fire assay with either ICP-MS or HR-ICP-MS is the best method for the determination of PGEs in geological samples (Jackson *et al.*, 1990; Kontas *et al.*, 1990; Flight *et al.*, 1994; Barfoot, 1998; Reddi and Rao, 1999).

The precise and accurate determination of REEs in geological materials is mainly achieved by using ICP-MS-based methods with multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) and isotope dilution thermal ionisation mass spectrometry (ID-TIMS). These techniques are superior in terms of analytical reproducibility compared with quadrupole ICP-MS (Baker *et al.*, 2002; Kent *et al.*, 2007). Other instrumental methods that are commonly used for the determination of REE are X-ray fluorescence spectrometry (XRF), instrumental neutron activation analysis (INAA) (Ravisankar *et al.*, 2006; Bounouira *et al.*, 2007; Alharbi and El-Taher, 2016) and HR-ICP-MS (Bradshaw *et al.*, 1989; Smirnova *et al.*, 2010; Balaram, 2018; Satyanarayanan *et al.*, 2018; Singh *et al.*, 2018).

Mercury (Hg) determination in rocks requires low-temperature aqua regia digestion followed by ICP-AES or ICP-MS finish with as low as a 1 mg/kg detection limit. For more than 40 years, total mercury has also been determined with a high level of sensitivity (detection limit: 0.005 mg/kg) directly on the rock powder (fine milled <0.04 mm) samples using flameless AAS (see Section §6.3.3.2.2).

An advantage of the XRF method is the measurement of halogens like chlorine, which is not possible with the classical ICP-MS technique. Otherwise, the analysis of halogens requires fusion techniques that allow the elements to be retained in solution, *for example*, KOH fusion followed by ion chromatography for fluorine analysis. In general, rocks can be analysed for fluorine and chlorine with a number of methods like ion-specific electrode (Rice, 1988; Yuchi *et al.*, 1988), ion-chromatography (Hall *et al.*, 1986; Kennedy *et al.*, 1983; Gent and Wilson, 1985), XRF (Langenauer *et al.*, 1992) or spectrophotometry (Fuge and Andrews, 1985; Hoffstetter *et al.*, 1991). Bromine and iodine can be determined by spectrophotometry (Fuge *et al.*, 1978); XRF (Ullmann and Tissue, 1983; Takeda *et al.*, 2011) or instrumental neutron activation analysis (Langenauer *et al.*, 1992).

Total carbon and sulphur can be analysed using infrared spectroscopy (Terashima, 1988). Automated, high-temperature combustion, carbon-sulphur-analysers utilise solid-state infrared absorption for the detection of total carbon and sulphur. In addition, secondary ion mass spectrometry (SIMS), nuclear methods (INAA, RNAA), and LA-ICP-MS can be used for the detection of low levels of sulphur in minerals and glasses (Ripley *et al.*, 2011).

Summing up, the following bulk analytical methods are recommended to obtain the basic set of major and trace elements in rocks for the purpose of geochemical mapping: XRF, lithium (meta)borate (LiBO₂) flux-fusion by ICP-MS, and FA by ICP-AES or ICP-MS for PGEs.

6.5. Determination of mineralogy by XRD

X-ray diffraction (XRD) is a powerful non-destructive technique for characterising all kinds of matter – ranging from fluids to powders and crystals. X-ray diffraction analysis is used, not only to identify the phase of an 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 (Ufer *et al.*, 2008a, 2008b, 2012a, 2012b; Waseda *et al.*, 2011; Lavina *et al.*, 2014).

The most effective quantitative methods, particularly those involving pattern modelling, are computationally intensive, and can be applied only with powerful analytical software (*e.g.*, [GSAS](#), [FullProf](#), [FULLPAT](#), [RockJock](#), [Profex](#) (Rietveld-Software BGMN), [AUTOQUAN](#) from GE Sensing & Inspection Technologies GmbH). The methods with the greatest chance of producing successful results generally involve the addition of a known amount of an internal standard and calculation of ratios of the areas of the standard peaks to those of the phases being determined.

The type and percentage of rock-forming minerals are characteristic of a rock type and are reflected in the content of the mineral-forming major, minor, trace and ultra-trace elements (Table 6.10). As soils and sediments are derived from the weathering and erosion of rocks, the determination of their mineralogy is important in the effective interpretation of geochemical patterns as has been shown by the “*Geochemical and Mineralogical Maps for Soils of the Conterminous United States*” (Smith *et al.*, 2014). It is, therefore, strongly recommended that the Laboratory Committee includes in the analytical procedures the determination of mineralogy in all sample types.

Table 6.10. Estimated average concentrations of elements in the most common rock-forming minerals (slightly modified after Wedepohl, 1969-78). Major elements >1%; Minor elements >0.1 to <1%; Trace elements >0.01 to <0.1%; Ultra-trace elements <0.001%.

Concentration	X%	0.X%	0.0X%	0.00X%	0.000X%
Minerals	Major elements	Minor elements	Trace elements	Ultra-trace elements	
Plagioclase	Ca, Na, Si, Al	Sr, K	Ba, Rb, Ti, Mn	V, Zn, Ni	Pb, Cu, Li, Cr, Co
Alkali feldspar	K, Na, Si, Al	Ca, Ba, Sr	Rb, Ti	Pb, Li, Mn	Zn, V, Cr, Ni, Co
Quartz	Si			Al, Ti, Fe, Mg, Ca	Na, Li, Ni, Zn, Ge, Mn
Amphibole	Si, Fe, Na, Mg, Al, Ca	Ti, K, Mn, Rb	Zn, Cr, V, Sr, Ni	Ba, Cu, Co, Pb	Li, B
Pyroxene	Al, Si, Fe, Mg, Ca	Ti, Na, Mn, K	Cr, V, Ni, Sr	Cu, Co, Zn, Li, Rb	Ba, Pb, Ga, B
Biotite	Si, Al, Fe, Mg, K	Ca, Na, Ba, Mn, Rb	V, Cr, Li, Ni, Ti	Cu, Sr, Co, Pb	B
Olivine	Si, Fe, Mg	Ni, Cr, Ti, Ca	Mn, Co	Zn, V, Cu, Sc	Rb, B, Ge, Sr, As, Ga, Pb
Spinels (including magnetite)	Ti, Al, Fe	Mg, Mn, V	Cr, Zn, Cu	Ni, Co	Pb, Mo

6.6. Particle size analysis

There are different methods for the determination of particle size (grain size) distribution (PSD) in soil and sediment samples. The Laboratory Committee should select the most appropriate, reproducible, cost- and time-effective method. The available and most used methods are:

- (i) Köhn pipette method is described in ISO 11277 (ISO, 2020b).
- (ii) Hydrometer analysis method is described in ASTM D7928-16 (ASTM, 2017).
- (iii) Hydrophotometer analysis (Jordan *et al.*, 1971).
- (iv) SediGraph particle size analysis (Coakley and Syvitski, 2010).
- (v) Laser diffraction analysis (LDA) (Agrawal *et al.*, 2010; ISO, 2020b), and
- (vi) Mid-infrared spectroscopy (MIRS) (Thomas *et al.*, 2021).

The Köhn pipette method is a very time-consuming procedure and in practice impossible for very large sample sets. Alternatives to the Köhn-pipette method are the Hydrophotometer and the SediGraph particle size analysis. Comparability of SediGraph results to those of ISO 11277 (ISO, 2020b) has been demonstrated by Müller *et al.* (2009). Further, Coates and Hulse (1985) compared the first four methods of particle size analysis on fine-grained sediments and concluded that the results of the Köhn pipette and Hydrometer analysis methods are comparable and have excellent reproducibility. They also found that the results of the SediGraph compare well with those of the Köhn pipette and Hydrometer at particle sizes finer than 16 µm, but tend to read low at coarser sizes. However, the first four methods are time-consuming and not suitable when thousands of samples need to be analysed. Usually, laser-based methods are used in the case of thousands of samples. Nevertheless, it should be thoroughly tested with soil and sediment samples from different morphoclimatic regions, because the laser diffraction method is

repeatable and characterised by a high-resolution. However, the measurement of soil particle size distribution can have limited reproducibility (Polakowski *et al.*, 2021).

Another method that can be used in the case of thousands of samples is mid-infrared spectroscopy, the results of which can be used to predict, apart from the particle size distribution (Janik *et al.*, 2011; Reimann *et al.*, 2012; Birke *et al.*, 2014), a large variety of soil properties, provided proper models for the soil and sediment samples under study are built and validated (Viscarra Rossell *et al.*, 2006; Janik *et al.*, 2009; Soriano-Disla *et al.*, 2014; Janik *et al.*, 2015a, b). The advantages and disadvantages of LDA and MIRS methods for particle size analysis of soil samples are discussed by Thomas *et al.* (2021).

Refer to Section §6.3.3.3.1 where the method used in the FOREGS Geochemical Atlas of Europe project for the determination of particle size distribution in soil samples is described.

6.7. Summary of recommendations

The analytical requirements for the purpose of producing internationally comparable geochemical baseline data are as follows:

- 1) Given the many applications of geochemical baseline data, a comprehensive multi-element approach is essential. Analytical requirements are considered in two categories:
 - (a) For the Global Geochemical Reference Network samples, and
 - (b) National or regional surveys conducted by national or international organisations.
- 2) Samples collected as part of the Global Geochemical Reference Network project should ultimately provide abundance data for at least 78 naturally occurring elements (excluding inert gases, except Rn, and some of the elements from the actinide series with atomic number >84, using methods with detection limits significantly below presently estimated crustal abundances.
- 3) Analytical requirements for national or regional surveys must be fully compatible with those that will be used for the establishment of the Global Geochemical Reference Network database. Where possible identical methods should be used but alternative multi-element schemes, based on the techniques of XRF, ICP-AES, ICP-MS, INAA, *etc.*, can be employed as long as the criteria of precision and accuracy are met, and the SRMs developed for the Global Geochemical Reference Network are included in the analytical batches (refer to Chapter 8 in this Manual). To portray the spatial distribution of elements as completely as possible, detection limits must be as low as possible.
- 4) A proposal is made for a standard list of elements to be determined; elements are grouped into List 1 (51 elements) and List 2 (20 elements) (see Fig. 6.1); Ru, Rh, Re, Os and Ir require the establishment of satisfactory methods and detection limits; Ra and Rn require radiometric methods.
- 5) For national geochemical surveys, if analytical facilities are insufficient to cover all List 1 elements initially, missing data should be added at a later date. List 2 is of lower priority, but potentially important.
- 6) To establish reproducible geochemical baseline data of permanent value, analytical methods should be employed that provide the total concentration of each element present. Sample decomposition, where required, must, therefore, be total.
- 7) Partial decomposition (partial extraction) methods have many variants in different laboratories and are difficult to standardise, so they are NOT recommended for any data

that may be used for international compilation or correlation. The only exception is hot *aqua regia* extraction, which is the method used for the estimation of statutory values, and a standardised method should be used by all geological survey laboratories.

- 8) The different options for the analysis of the Global Geochemical Reference Network samples are:
 - (a) All sample types are to be analysed in the same laboratory by the same analytical methods for the same suite of determinands. If this is not possible, then the second option is:
 - (b) In selected laboratories the same suite of determinands to be analysed by the same analytical methods on all samples of one sample type, *i.e.*, rock, residual soil, humus, stream sediment, stream water, overbank sediment, and floodplain sediment.

In both cases, strict internal and external quality control procedures must be followed, and the inclusion in the analytical batches of SRMs, developed for the Global Geochemical Reference Network project. The selected laboratories must be approved by the relevant project management committees, namely the Laboratory and Quality Control Committees (see Chapter 10 in this Manual). The laboratories should be selected on the basis that they are accredited and have established quality control systems in place, they regularly participate in international proficiency testing schemes for the methods for which they are responsible, and their estimated analytical uncertainty and sensitivity for all determinands are likely to be acceptable.

- 9) With respect to national and regional surveys, it is recommended that if more than 20% of the reportable values for any element determined fall below the detection limit, the results for that element should be considered unsatisfactory and alternative analytical methods should be considered.
- 10) Strict quality control, through the use of appropriate primary (PRMs) and secondary (SRMs) reference materials, is essential, and how standard reference materials have been used and the resulting quality control statistics must be reported by each laboratory. The laboratory must provide a full report with analytical results of each sample suite in the order analysed, together with the analytical batch number, date of analysis, results of blanks, and repeated analyses of samples. It is important for the approved laboratory to have installed its own internal quality control procedures, and should include primary reference materials (PRMs) usually at a rate of four PRMs at the start and end of each analytical batch (see Chapter 8 in this Manual). The applied geochemist in charge of the Global Geochemical Reference Network project, as well as the national project managers, should set up their own independent or external quality control procedures in collaboration with the Quality Control Committee (see Chapter 10 in this Manual).
- 11) The Canadian STSD and Chinese series GSD and GSS standard reference samples, are good reference materials for use as Primary Reference Materials (PRMs) in (a) international geochemical mapping, and (b) national geochemical surveys. However, for the Global Geochemical Reference Network project, it is considered imperative that large quantities of secondary reference materials (SRMs) for each sampling medium (rock, residual soil, stream sediment, overbank/floodplain sediment) should be developed. This is a mandatory prerequisite before the start of the project, because it is necessary to have adequate material not only until the completion of the global project, but there should be enough material for
 - (a) to be distributed to all countries for their regional geochemical surveys, and

(b) at least one repeat of the global project at a future date.

At least five SRMs of each sample medium with different element concentrations must be developed (refer to Chapter 8 in this Manual). For national surveys, primary (PRMs) and secondary reference materials (SRMs) should be used to monitor the analytical accuracy: PRMs to monitor the international or interlaboratory bias, and SRMs to monitor the routine between-batch bias within a laboratory.

- 12) The laboratories must provide the **uncensored values** of determined elements, as these are important for the estimation of the practical detection limit of each determinand (refer to Chapter 7 in this Manual), which may be different from the reported laboratory detection limit.
- 13) The laboratories must provide all the analytical results of each sample type, including the analytical reagent blanks, international and internal reference samples in the order analysed, together with the analytical batch numbers, date and time stamp for every analysis.
- 14) The Project Manager in collaboration with the Laboratory Committee should organise the contract with the laboratory or laboratories, which will be participating in the analysis of all sample types collected in the Global Geochemical Reference Network project. The contract should specify that:
 - (a) Primary reference materials (PRMs) should be included at a rate of four PRMs at the start and end of each analytical batch.
 - (b) Replicated analyses to be performed every twentieth sample.
 - (c) Depending on the number of samples in each analytical batch 2 to 10 reagent blank samples should be included, and
 - (d) The **uncensored values** of determined elements and parameters MUST be provided, and the other information included in bullet 13 above, as well as any problems encountered, and solutions given.

An important condition in the contract is if the Quality Control Committee discovers any analytical errors in the results, the laboratory will be obliged to reanalyse the batches in question, and if all results are considered unacceptable the laboratory will be required to reanalyse the complete sample suite.

- 15) Natural radioactivity of K, U, Th and Total is measured in the field using a portable threshold scintillometer, which should be calibrated at least once a year at a national facility, which is certified by the [International Atomic Energy Agency](#).

Finally, it is strongly recommended that the Laboratory Committee consults the extensive list of analytical methods, which were published in the special issue of the Journal of Geochemical Exploration entitled “*Geoanalysis*” (Hall, 1992). This is still a reference book for applied geochemists on the state-of-the-art at that time. It describes not only the capabilities and limitations of major methodologies, but the accuracy and precision expected, practicalities of usage, the suite of international reference samples available and discussions on data quality.

Other publications on analytical methods that should be consulted are by Fletcher (1981), Hall (1991), Finch *et al.* (1992), Giessmann and Grebb (1994), Balaram (1995, 2018, 2020), Jenkins and Snyder (1996), USEPA (1996), Hall and Pelchat (1997), Odegard *et al.* (1998), CEN (2002), Gäbler (2002), Krachler *et al.* (2002, 2007), Yu *et al.* (2003), Townsend and Poole (2005), Smirnova *et al.* (2010), Duyusen and Görkern (2011), McDonough (2014), He *et al.* (2015), Worsfold *et al.* (2019), Balaram *et al.* (2022) and Mnculwane (2022).

Attention is also drawn to the Geostandards Newsletter, which is currently called [Geostandards and Geoanalytical Research](#) and published by Wiley-Blackwell on behalf of the [International Association of Geoanalysts](#).

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Note: All hyperlinks were checked on the 23rd of January 2022.

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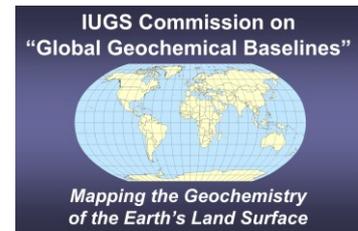
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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 7

Quality Control Procedures

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

¹ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

² GeoElementary, Derby, United Kingdom

³ Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Hellenic Republic

⁴ IUGS Commission on Global Geochemical Baselines

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7.1. Introduction

The analytical data that will be produced for the Global Geochemical Reference Network project are environmentally sensitive and important for the present and future generations of humankind because, apart from their use as reference data for levelling the more detailed national geochemical data sets, they will be used by many disciplines and for different purposes (Fig. 7.1). Consequently, they must be of proven quality and integrity.

To ensure the quality of generated geochemical data, a rigorous quality control and assurance procedure must be installed from the start of the project. The same quality control procedure should be in place for any geochemical survey at any mapping scale.

The quality control procedure for each generated geochemical data set should end with the estimation of sampling, analytical, and geochemical variance, and measurement uncertainty¹ (Ramsey, 1997, 1998; Ramsey and Argyraki, 1997; Ellison *et al.*, 2000; Ramsey and Ellison, 2007; Ellison and Williams, 2007, 2012; Demetriades, 2011; Majcen *et al.*, 2011; Ramsey *et al.*, 2019).

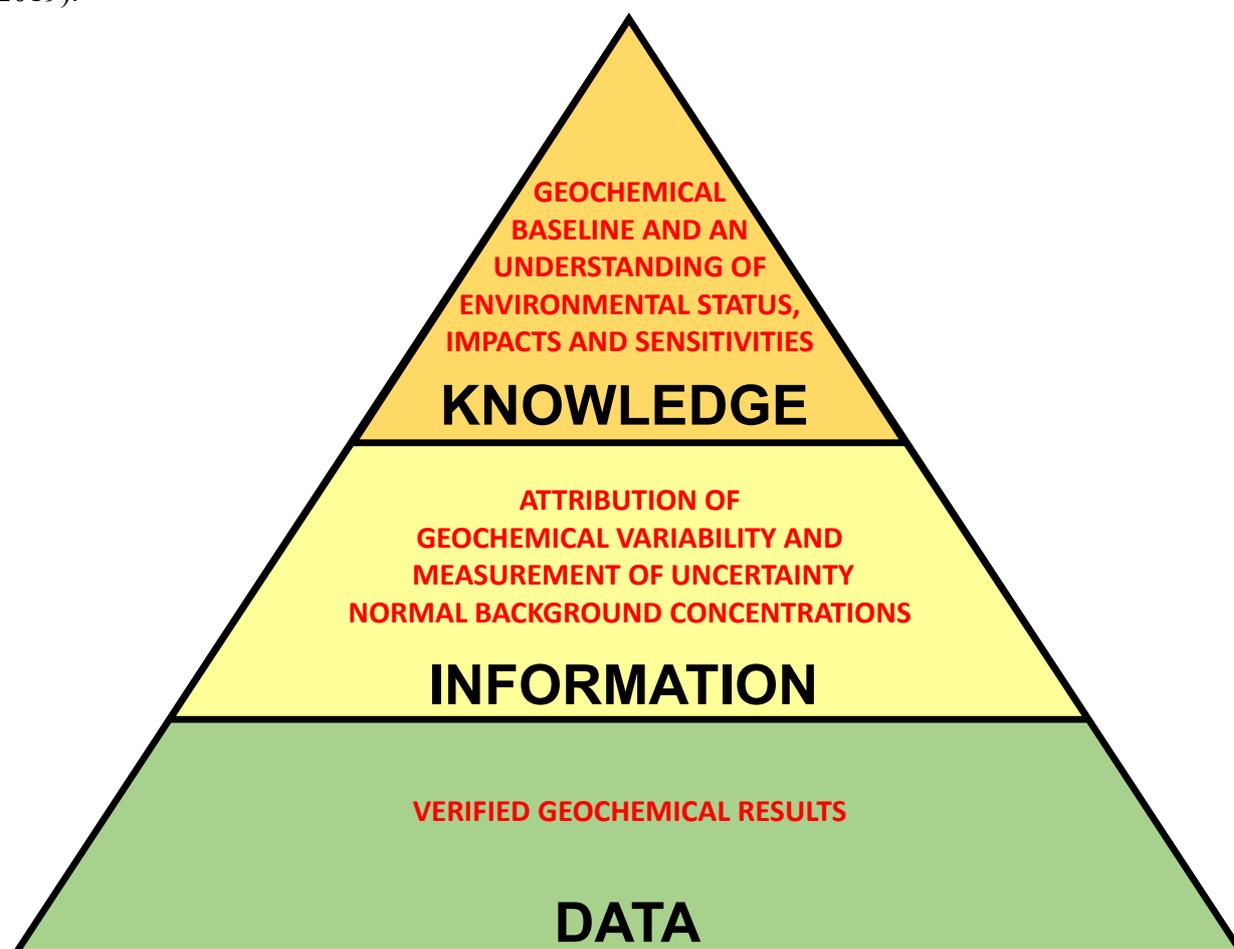


Figure 7.1. The triangular diagram shows how quality control procedures can contribute to two levels of the $DATA + INFORMATION = KNOWLEDGE$ equation. Quality control produces the $DATA$ set (verified geochemical results). This along with attribution of geochemical variability and measurement of uncertainty, plus other parameters such as threshold and normal background concentration determinations ($INFORMATION$) contribute to the $KNOWLEDGE$ of the geochemical baseline and an understanding of environmental status, impacts and sensitivities. Plotted by Christopher C. Johnson (GeoElementary/IUGS-CGGB) with Microsoft™ PowerPoint.

¹ Course on “Estimation of Measurement Uncertainty in Chemical Analysis”:
<https://sisu.ut.ee/measurement/uncertainty>

7.1.1. Obligations of leading applied geochemist

At present, 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 keeping 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 assure adequacy for intended applications, and the laboratory must be participating in a proficiency analytical testing programme. To put it simply, an accredited laboratory has the right ‘*internal*’² procedures in place to analyse samples. It is, therefore, the professional responsibility of the leading applied geochemist of the project to install his/her own independent ‘*external*’² quality control procedures to ensure that the results received are of a good standard and fit for the purposes of the project. Hence, *the project manager must ensure that there is in the team a professional applied geochemist with the skills to organise the project’s quality control procedure, and to check the quality and integrity of the analytical results received from the laboratory.*

It is important to remember that the analytical results of the Global Geochemical Reference Network project must be of high quality and integrity, as has already been stressed. Therefore, the leading applied geochemist must not rely on the ‘*element concentration numbers*’ given by the laboratory. He/she must ensure that these ‘*numbers*’ are meaningful, and are validated by his/her independent external quality control results. Consequently, the leading applied geochemist, upon receipt of the analytical results, must check them thoroughly to verify their quality and integrity.

For the Global Geochemical Reference Network project, it is proposed that there should be an international Quality Control Committee, which will organise the quality control procedure from sampling to sample preparation, and subsequently the randomisation of samples and insertion of project reference samples, and splits of routine and field duplicate samples.

Upon receipt of the analytical results, the Quality Control Committee studies the analytical report of the laboratory, before proceeding to check the quality of the project analytical results. Afterwards, proceeds in the arduous task of verification of the quality of the analytical data, using the project’s external quality control results, and the laboratory’s internal quality control results. If the leading applied geochemist, or the Quality Control Committee, is not satisfied with the quality of analytical results, then the laboratory is 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, and even an in-house laboratory.

When satisfied with the quality of the analytical results, an analysis of variance (ANOVA) is the final step of quality control for any geochemical mapping project. A procedure to estimate the geochemical, sampling and analytical variation, as well as measurement uncertainty, is performed by using the robust statistical method proposed by Ramsey (1998; Lee and Ramsey, 2001; Lyn *et al.*, 2007, Boon, 2009; Demetriades, 2011). 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 Global Geochemical Reference Network project, the estimation of measurement uncertainty of the analytical results of each determinand or measurand is of paramount importance, because it is a parameter that describes quantitatively the quality of geochemical results. Some laboratories nowadays report measurement uncertainty, but it is prudent for the leading applied geochemist or the Quality Control Committee to estimate

² An accredited laboratory has its own ‘*internal*’ quality control procedure installed. The applied geochemist for the verification of the integrity and quality of the analytical results should install his/her independent ‘*external*’ quality control procedure, which is unknown to the laboratory.

measurement uncertainty using the project's own independent quality control results. The requirement is that the combined sampling and analytical variances should be considerably smaller than the regional or spatial variability (geochemical variance) for the construction of a reliable geochemical map.

When satisfied with the quality of analytical results, then and only then the leading applied geochemist or Quality Control Committee should sanction the second step, which is the processing of geochemical data leading to map plotting.

As the generated data of the Global Geochemical Reference Network project are of interest to the whole geoscientific community, and not only, it is important to write a detailed quality control report for all the different geochemical data sets generated by different analytical methods and laboratories. Hence, the statement that *the generated Global Geochemical Reference Network project data must be legally defensible, according to international guidelines or national legislation. So, the first and foremost obligation of the Global Geochemical Reference Network project manager is the delivery of good quality geochemical data for multipurpose use.*

7.2. 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 §7.3). The assessment report of the quality of analytical data is an integral part of any geochemical project, and must be compiled and made available as an open file report.

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

7.3. Data checking

7.3.1. 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.

The first assessment of data quality will consist of simple and obvious procedures that involve looking at the analytical results, as they are received from the laboratory. This needs to be done systematically, 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 analytical results, and it is at this stage that the most obvious problems with the data can be identified.

At this point, something should also be done for 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 analytical data file, as received from the laboratory, should always be saved before any changes are made, and for data processing a work file should be prepared.

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

- Field duplicate samples: DUPA and DUPB.
- Field replicate samples: REPA and REPB.
- Project reference material³(s): REF1, REF2, REF3, REF4 and REF5 (in case more than one Project reference material has been prepared), and
- Project solid blank material: BLK1 and BLK2 (refer to Chapters 4 & 5 in this Manual).

Upon preparing different files of the quality control data, the leading applied geochemist or Quality Control Committee 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 (2011). Other open file quality control reports that should be consulted are by Reimann *et al.* (2009, 2011, 2012).

7.3.1.1. Laboratory reagent blank samples

Firstly, check the analytical results of the laboratory reagent blank samples, which should be all below the laboratory's lower detection limit (LDL) for all elements determined. The reagent blank is made-up of the same acids (plus deionised water), which are added to the solid⁴ 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 batch or batches analysed during that particular period. Once satisfied with this particular visual test, the verification of the quality of the analytical results can proceed.

7.3.1.2. Project solid blank materials

Secondly, check the analytical results of project solid blank materials. It is noted that the aliquots of solid blank materials are packed in the field, and go through the sample preparation procedure as the routine project samples, and their main purpose is to indicate contamination during sample preparation (Schermann, 1990).

If the solid blank material 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 material is kaolinite (Schermann, 1990), then the analytical results should be within the accepted limits, as estimated by the standardisation procedure (see Chapter 5 in this Manual). If the results deviate

³ Project reference materials are called Secondary Reference Materials (SRMs)

⁴ 'Solid' samples are the analysed aliquots of the collected rock, soil and sediment samples.

from the accepted limits, then most likely the aliquots of the solid blank material have been contaminated either during sample preparation or laboratory analysis. If the laboratory blank samples (e.g., reagent blank or pure silica sand) are below the lower detection limit in that particular analytical batch or batches, then the project solid blank material has been contaminated during sample preparation.

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, while a secondary reference material could give an indication of '*between batch*' contamination.

The results of the suspected batch or batches of contaminated routine samples (rock, soil, sediment) should be studied carefully to assess the extent of contamination, and examine if it can be corrected by applying a correction factor, otherwise, new samples should be collected.

7.3.1.3. Project blank water samples

The analytical results of filtered blank water samples (see Chapter 3.3 in this Manual) are checked to ensure that all values are below the lower detection limit. If not, then the filtered blank water samples may have been contaminated during sampling or acidification. The results of the suspected batch or batches of contaminated routine stream water samples should be studied carefully to assess the extent of contamination, and if it can be corrected by applying a correction factor, otherwise new samples should be collected.

7.3.1.4. 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 control chart 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 7.2. The X-axis shows the date of analysis or the laboratory batch, if batch numbers are 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 secondary reference materials (see Chapter 8 in this Manual). The AV will depend on the method of chemical extraction and analysis, *i.e.*, a partial method of extraction will yield a lower AV than a total extraction method. The AV used on the control chart must be that which has been determined by 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 of the reference material is, but the AV should be a good approximation of it. Defining limits of the secondary reference material are also plotted on the chart; in Figure 7.2, 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 with its internal reference materials. Using the secondary reference materials (SRMs) inserted in each sample batch, the applied geochemists can check accuracy for themselves by visual inspection of these plots.

Accuracy is a measurement of how close to a 'true' or 'accepted' value a result is. A scattering of results about the AV line is to be expected, though a consistent trend to a higher or lower value would be referred to as *analytical bias*.

Control charts are invaluable in detecting analytical shifts that can occur over time, as, *for example*, after the installation of a new X-ray tube in X-ray fluorescence spectrometry (XRFS) 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 (Johnson *et al.*, 2018; and Chapter 8 in this Manual).

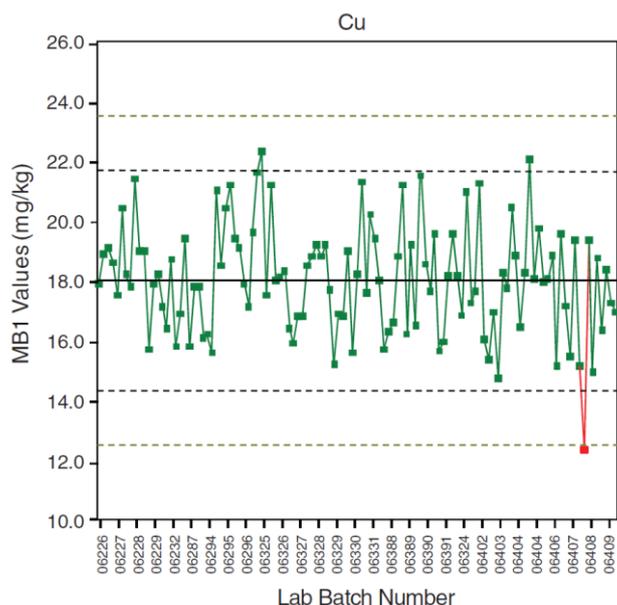


Figure 7.2. Example of a control chart plot using QI Analyst software for the BGS Moroccan secondary reference material MB1 (after Johnson et al., 2001, Fig. 2.4, p.10). The central solid line represents the accepted value (AV) of the secondary reference material; outer black and olive colour dashed lines are at $AV \pm 2SD$ and $\pm 3SD$, respectively. The red dot and line represent a batch that fails QC criteria. Source: Johnson (2011, Fig. 5.4, p.68).

The second example is a control chart of a project reference material (Fig. 7.3), which does not show the expected random variation of the individual sub-sample results about the accepted value (AV). It has many outliers, and even time trends. Such data cannot be accepted when the objective is to compare the analytical results among different countries (in this example, different cities); in this plot, problems (time trends) are shown even between two analytical batches of the same city.

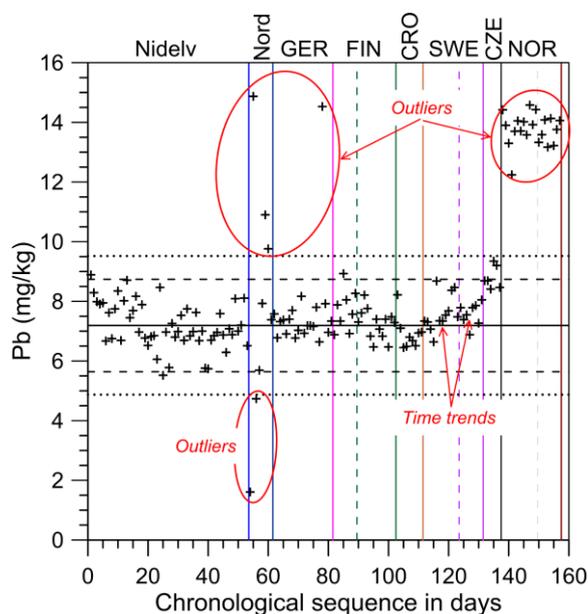


Figure 7.3. Example of a control chart for a secondary reference material used in the EuroGeoSurveys URGE I project. The central solid line represents the accepted value (AV); outer dashed lines are at $AV \pm 2SD$ and dotted lines at $AV \pm 3SD$. The secondary reference material was used in the urban 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 times, and dashed lines separate the two batches. Plotted by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) and IUGS Commission on Global Geochemical Baselines (IUGS-CGGB) with Golden Software's Grapher™ v20.

7.3.1.5. Precision

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

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 (Figs. 7.2 & 7.3), 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 (Fig. 7.4) and Thompson and Howarth plots (see Section §7.3.1.9), which are described below. Overall precision at the 95% confidence level can be also estimated quantitatively, based on the mean (\bar{x}) and standard deviation (SD) expressed as a percentage:

$$\text{Overall Precision, P (\%)} = \frac{1.96^5 * \text{SD}}{\bar{x}} * 100 \quad (1)$$

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

Substituting CV in Equation 1:

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

It should be noted that the calculation of the ‘*overall precision*’ by the above equations is an oversimplification because it estimates the average precision for a range of element concentrations, which are assumed to follow a normal Gaussian distribution about their mean (\bar{x}) concentration (Fletcher, 1981). However, it is well known that most geochemical distributions are multimodal. Hence, the reason for referring to this parameter as ‘*overall precision*’.

An important feature of precision is that it varies with concentration (Thompson and Howarth, 1976; Fletcher, 1981, 1986; Demetriades, 2011). At low concentrations, near to the detection limit precision is poor, and normally improves with increasing concentration.

Other methods for the estimation of precision are described below.

7.3.1.6. 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 (Fig. 7.2). 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 7.4 displays 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 the Cu results reflect actual between site variability. The Ni plot exhibits a few 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

⁵ The value for which $P = 0.05$, or 1 in 20, is 1.96 (Fisher, 1973). As the normal distribution is symmetric, $P(-1.96 < X < 1.96) \approx 0.95$, approximately 95% of the area under a normal distribution curve lies within roughly 1.96 standard deviations of the mean (JCGM 100, 2008, p.70). Due to the central limit theorem, 1.96 is used in the construction of the 95% confidence intervals (Dixon and Massey, 1969).

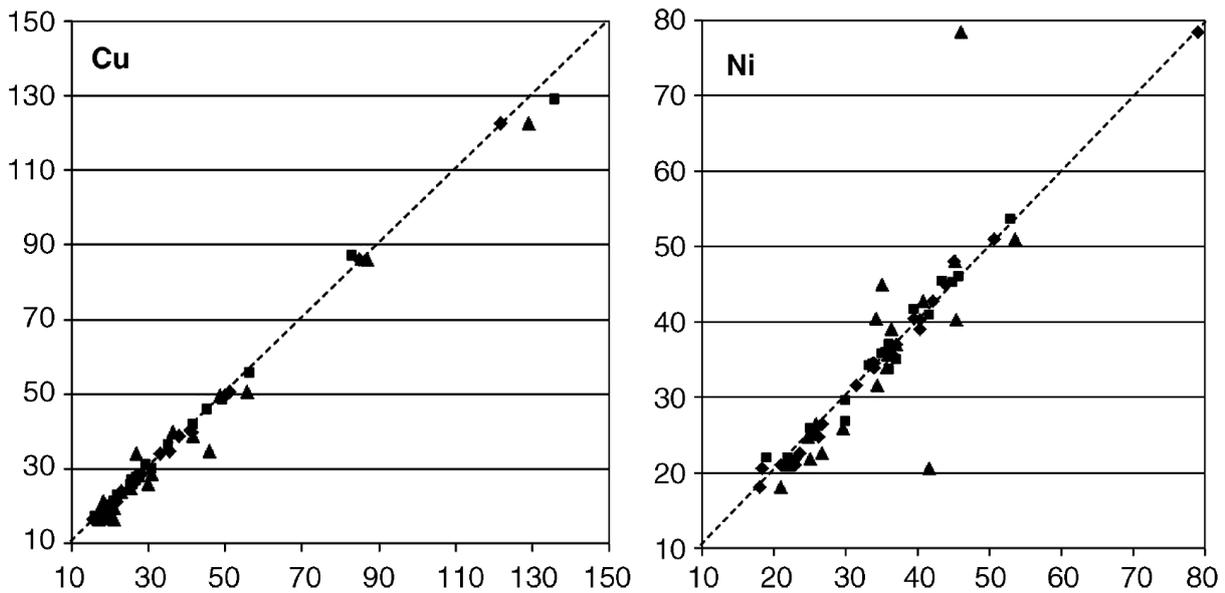


Figure 7.4. Duplicate-replicate plots for Cu and Ni for G-BASE urban soil (35-50 cm) from United Kingdom East Midlands. Axis units in mg/kg. Triangle = DUPA versus DUPB; Square = REPA versus DUPA; and Diamond = REPB versus DUPB (all x-axis versus y-axis). Notation: DUPA = Routine sample; REPA = Replicate split of routine sample; DUPB = Field duplicate sample; REPB = Replicate split of field duplicate sample. Source: Johnson (2011, Fig. 5.6, p.69).

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 a single or a small number of duplicate-replicate pairs are available, Thompson-Howarth plots (Thompson and Howarth, 1976, 1978; Thompson, 1983; AMC, 2002) described below, can be used.

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

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

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:

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

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

$$\text{Precision, P (\%)} = 1.96 * \frac{\sqrt{\text{Var}}}{\bar{x}} * 100 \quad (7)$$

Software for X-Y plots is readily available and Microsoft™ Excel or R routines provide satisfactory graphs (Reimann *et al.*, 2008). The BGS 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 suitably for publication. A Microsoft™ Excel workbook, ‘IUGS-CGGB_Chapter-7_DUPREPLOT.xlsm’ by Christopher C. Johnson is available (refer to the Supplementary material). See also worked example in Section §7.4.1.

7.3.1.7. Practical detection limit and analytical precision

The analytical precision can be calculated by another method as described below (Demetriades 2011, 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 (2011) 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 the 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 assumed to be 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 the 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, ($Y = B * X + A$), 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 the dependent variable?* Since both variables are derived from the grouping of the same analytical data set, they are subject to errors of the same order of magnitude. It is concluded, therefore, that the requirements of classical regression cannot be met. To overcome this situation Kermack and Haldane (1950) developed the reduced major axis line, which is the line of best-fit between a set of points (Fig. 7.5; Till, 1974). Essentially, is the best-fit line between the two regression lines of ($Y = B*X + A$) and ($X = B*Y + A$). Hence, errors of estimation are minimised.

7. Obtain from the reduced 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 the 95% confidence level (approximately at two standard deviations).

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

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

$$P_c \% = \frac{196 * \sigma_o}{X_{ci}} + 196 * k \quad (13)$$

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

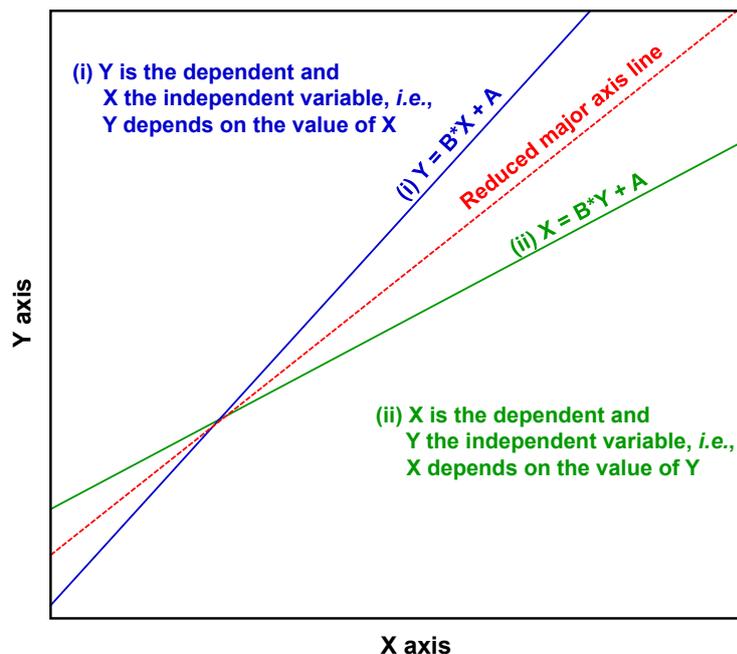


Figure 7.5. The reduced major axis line is the best fit line of Y on X and X on Y . Source: Demetriades (2011, Fig. 6.2, p.82, slightly modified).

10. Calculate the detection limit. The 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 incorrect 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 196k in the above expressions (refer to Fletcher, 1981, Fig. 2-5, p.32; see Fig. 7.6 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 remarkably close to instrument detection limits. For element concentrations that have a non-Gaussian distribution, their practical detection limits are normally quite different from those quoted by the analysts.

Ideally, the samples selected for replicate measurements should include extremely low, low, moderate, high, and exceedingly high concentrations of the determinands or measurands studied. However, this selection can only be made upon completion of the routine geochemical survey, 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 ‘IUGS-CGGB_Chapter-7_PDLPRECIS.xlsx’ by Alecos Demetriades is available (refer to the Supplementary material).

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 7.6, using the Be duplicate-replicate results from the *aqua regia* GEMAS grazing land soil data set (Reimann *et al.*, 2014). 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 196k in the above expressions. Beyond this limit, the curve reaches a plateau, and this is considered to be the overall precision. The practical detection limit (PDL), as 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 (Fig. 7.6), 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 value and N=94 pairs), and an overall precision of 18.4% at the 95% confidence level, and a precision equation (Fig. 7.6a):

$$P_c \% = \frac{5.86}{X_{ci}} + 18.4 \quad (14)$$

(b) PDL=0.046 mg Be/kg (without negative values and N=93 pairs), and an overall precision of 24.5% at the 95% confidence level, and a precision equation (Fig. 7.6b):

$$P_c \% = \frac{3.44}{X_{ci}} + 24.5 \quad (15)$$

where X_{ci} in both cases is any concentration of Be that one is interested to know its precision at the 95% confidence level. For example, a Be concentration of 5 mg/kg has a precision of 19.6% and 25.2% for (a) and (b), respectively. As Be concentrations approach the detection limit, the precision becomes poorer, e.g., for a Be concentration of 1.5 mg/kg, the precision for (a) is 22.3%, and for (b) is 26.8% at the 95% confidence level.

The reported laboratory's lower detection limit is 0.1 mg Be/kg, which is higher than the values estimated for the practical detection limit with and without negative values, i.e., 0.072 and 0.046 mg Be/kg, respectively (see Fig. 7.6). For elements, such as Be, where most of the values are extremely low, and near to the analytical method's lower detection limit, it is an advantage to estimate the practical detection limit, using actual recorded analytical 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 (refer to Chapter 8). Thus, losing many actual background values.

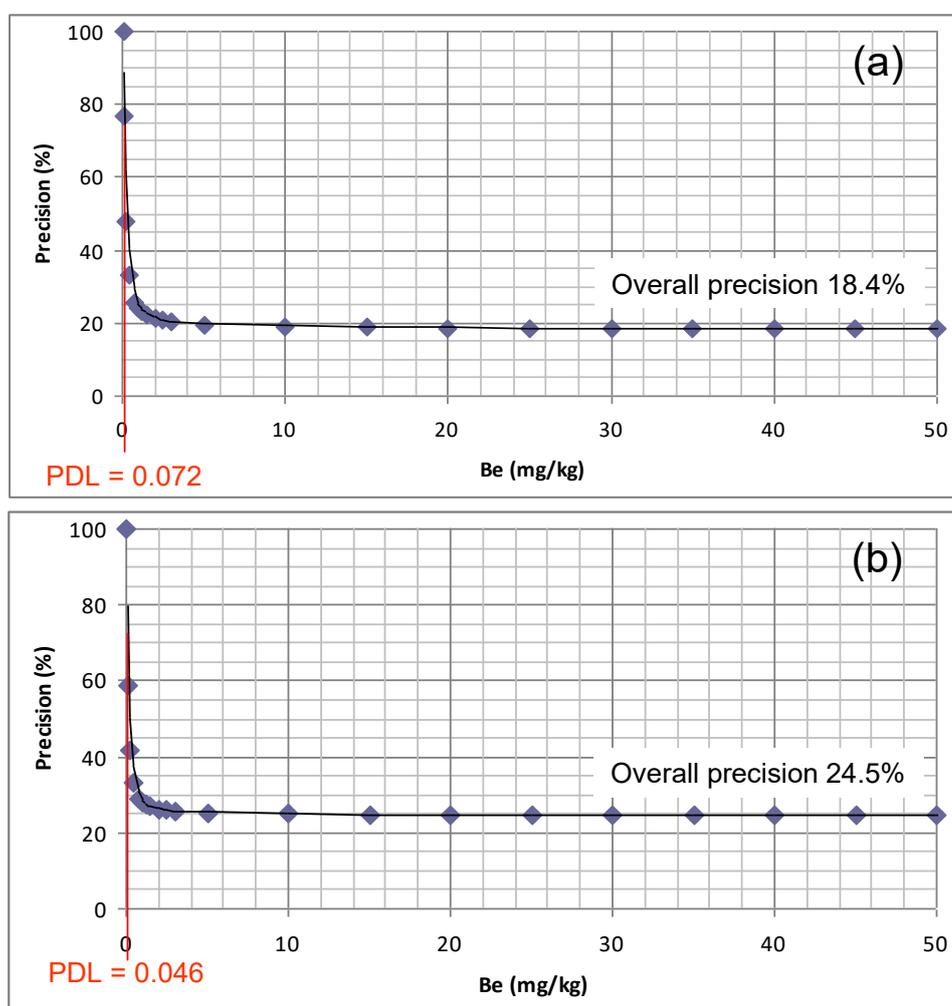


Figure 7.6. Variation of precision with concentration. Two examples of Be from the aqua regia GEMAS grazing land soil data set (Reimann et al., 2014) plotted with 'IUGS-CGGB_Chapter-7_PDLPRECIS.xlsx' Microsoft™ Excel file (see Supplementary material): (a) With negative values ($N=94$ pairs), and (b) With negative values removed ($N=93$ pairs). The former gives a PDL at 0.072 mg/kg and an overall precision of 18.4% at the 95% confidence level, and the latter a PDL at 0.046 mg/kg and an overall precision of 24.5% at concentrations beyond 50 mg Be/kg. Plotted by Alecos Demetriades (IGME/IUGS-CGGB).

7.3.1.8. Cumulative probability plot

According to Johnson (2011, p.68–69), replacing the value below the lower detection limit (LDL) 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, while 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 Figures 7.7 and 7.8 by cumulative probability plots, 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 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.

The first example in Figure 7.7 is from the FOREGS Geochemical Atlas of Europe topsoil survey (Salminen *et al.*, 2005), where Ni was determined by two different analytical methods. The second example in Figure 7.8 uses the As and Tl uncensored aqua regia analytical results from the EuroGeoSurveys project of Geochemical Mapping of Agricultural and Grazing land Soil of Europe (GEMAS; Reimann *et al.*, 2014). The third example in Figure 8.14 (Chapter 8) is from the British Geological Surveys' stream water survey where Al was determined by two different analytical methods. It is quite evident in these figures that the actual lower detection limit of Ni, As, Tl and Al is lower than that given by the laboratory.

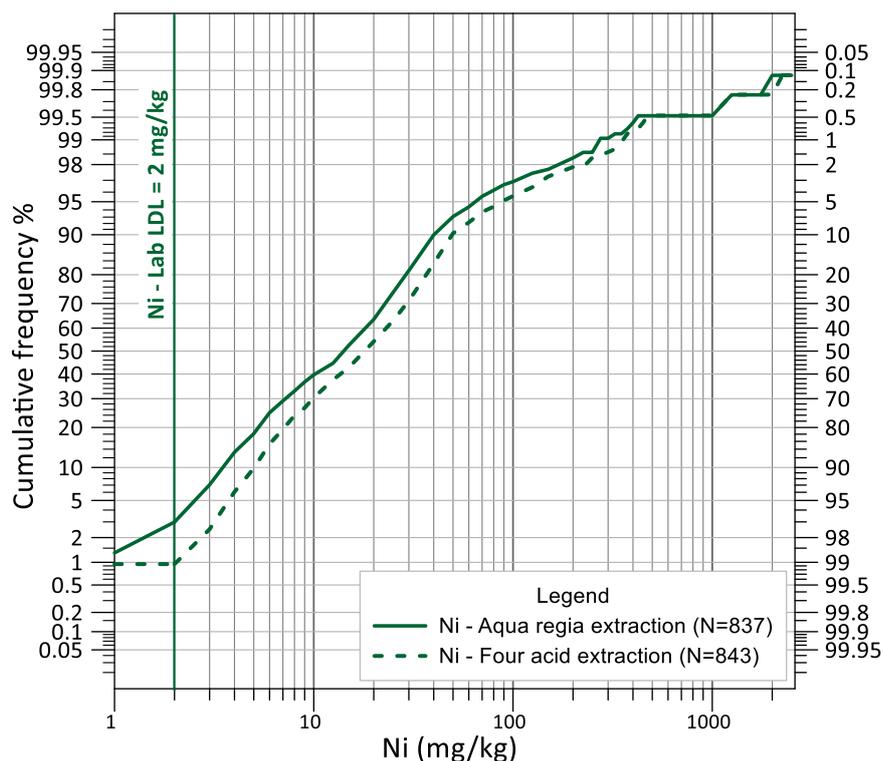


Figure 7.7. Cumulative probability plots of Ni indicating true detection limits for topsoil samples determined by two different analytical methods (data from the FOREGS Geochemical Atlas of Europe – Salminen *et al.*, 2005). Plotted by Alecos Demetriades (IGME/IUGS CGGB) with Golden Software's Grapher™ v20.

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 §7.3.1.7.

Reporting values below the cited LDL, as a single value MUST BE discouraged (AMC, 2001) **in favour of delivering the recorded values as measured by the analytical instrument.** Users of uncensored analytical 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 statutory guideline value a result will fall.

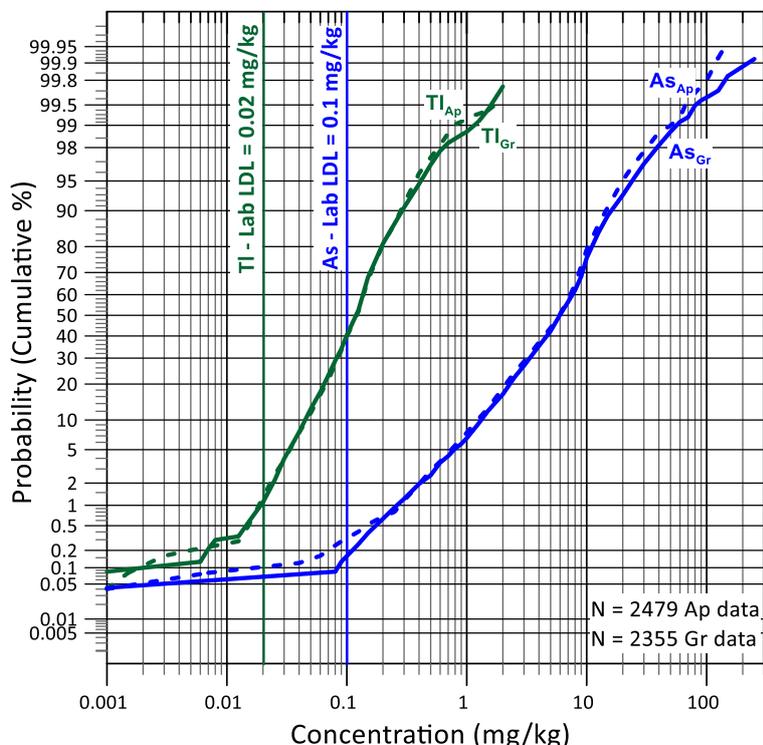


Figure 7.8. Cumulative probability plots indicating that the conservative laboratory lower detection limits (LDL) of hot aqua regia extractable As and Tl for the agricultural (Ap) and grazing land (Gr) soil samples of the EuroGeoSurveys project of Geochemical Mapping of Agricultural and Grazing land 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™ v20.

7.3.1.9. 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 precision of the analytical method (see Fig. 7.9).

The absolute difference between the two replicate analyses is plotted against the mean of the replicate results. On the graph, the fitness-for-purpose criteria are defined by the detection limit (herein 0.2 µg/l As) and 99th, 90th, and 50th percentile lines. In Figure 7.9, precision is generally good with only a small percentage of duplicate-replicate pairs plotting above the 90th percentile line. The example graph shown here was plotted using SigmaPlot software. Reimann *et al.* (2008, 2009, 2011, 2012) give examples of Thompson-Howarth plots generated using R.

The second Thompson and Howarth plot (Fig. 7.10) is a variant using normal linear axes. In this case, the 10% precision at the 95% confidence level is generally good as only 4 duplicate-replicate pairs plot above the 99th percentile line.

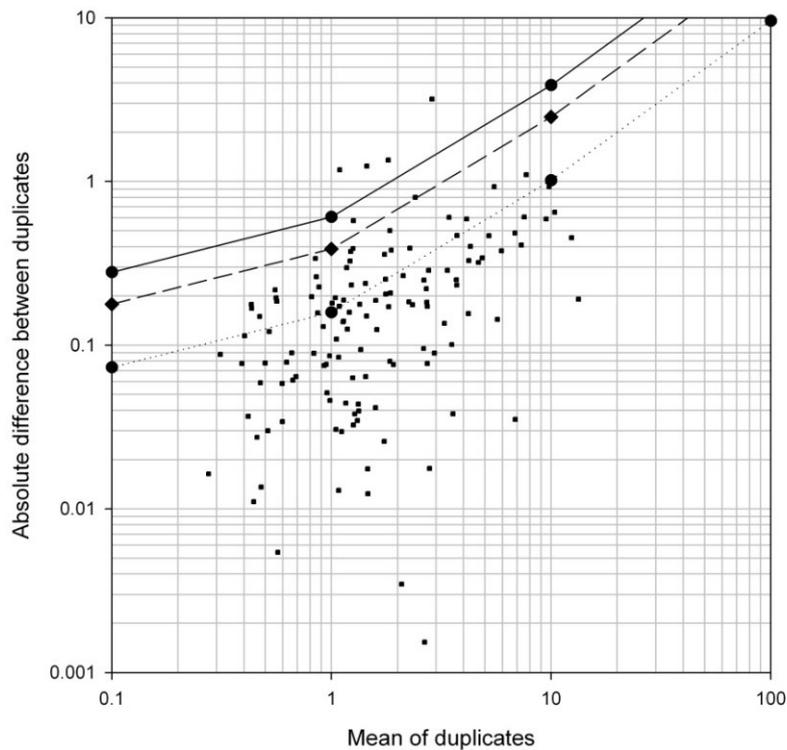


Figure 7.9. A logarithmic-scale Thompson-Howarth plot was used for visualising analytical precision. This is a plot of G-BASE stream water duplicates for As with probabilities calculated at 0.2 µg/l detection limit using SigmaPlot v10 software by E.L. Ander (BGS). See AMC (2002) for the rationale behind the Thompson-Howarth plot. Solid, dashed, and dotted lines represent 99th, 90th, and 50th per cent confidence levels, respectively. Source: Johnson (2011, Fig. 5.7, p.71).

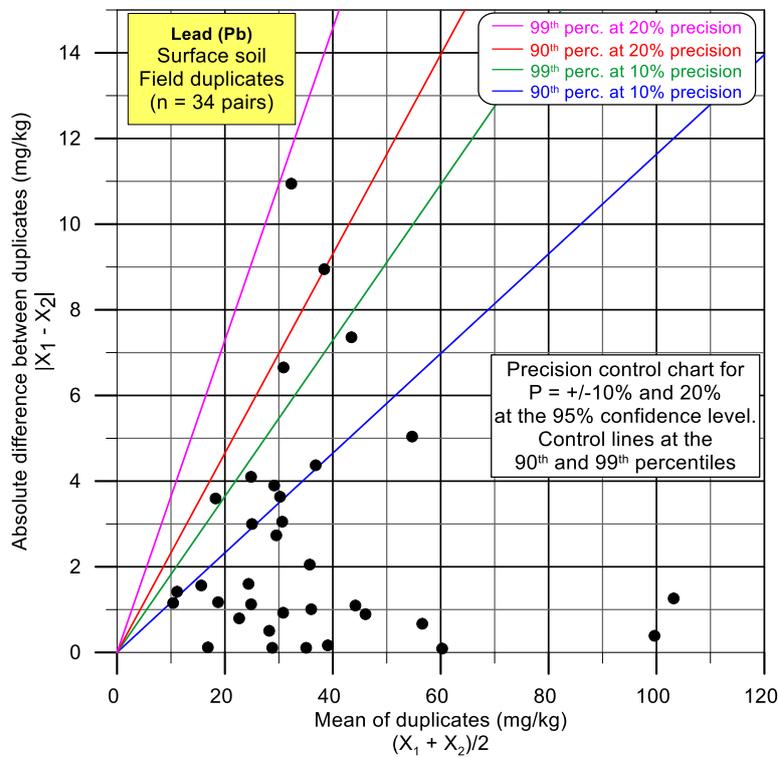


Figure 7.10. A normal linear scale Thompson and Howarth plot was used for visualising the precision of Pb. This is a plot from the results of the Hellenic Institute of Geology and Mineral Exploration's urban soil geochemistry project at Thrakomakædónæ, a suburb of Athens. Colour lines represent 10% and 20% precision at the 95% confidence level, and the 90th and 99th percentiles. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

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

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

The balanced RANOVA method proposed by Ramsey (1998), apart from estimating the geochemical, sampling and analytical variance, calculates measurement uncertainty, which is an essential parameter for the qualification of the determinands or measurands of any geochemical mapping project. 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 the:

“Parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand” (Ramsey and Argyraki, 1997, p.244; ISO/IEC, 2008, p.2 & 36; 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 into 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 intended use*’, 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, thereby decreasing the cost of analysis.

In the ‘*bottom-up*’ approach the random error from each 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, and volumetric additions.

The ‘*top-down*’ approach is intended to obtain a reliable estimate of the 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 is 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 (Argyrazi *et al.*, 1995). Thus, in this case, many laboratories ($N > 8$) are involved in the sampling and analysis by using 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 represent the typical composition of the target sites (it is stressed that this minimum concerns small projects, and definitely not the Global Geochemical Reference Network project).

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), and herein (Section §7.4). 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 variances and random components of measurement uncertainty (Fig. 7.11). 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) for the minimum number of sampling sites that should be duplicated. 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.

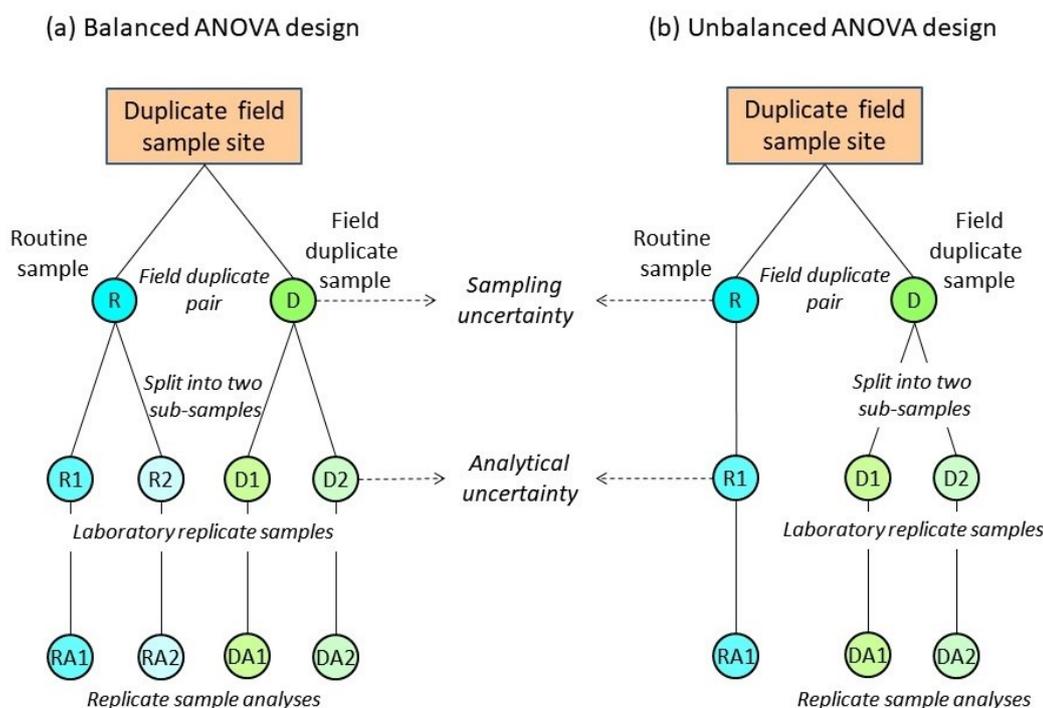


Figure 7.11. (a) Balanced and (b) unbalanced hierarchical geochemical sampling and analytical schemes for the estimation of geochemical, sampling, and analytical variance and random components of measurement uncertainty. Source: Demetriades *et al.* (2014, Fig. 6.4, p.56) slightly modified.

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 should 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_{smp} , and *analytical*, s^2_{anal} , *variances*. 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} , or *spatial variance*, 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. 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 out 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 element 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. In the case of the Global Geochemical Reference Network project, the duplicate field samples are taken within the selected drainage basin, and the distance between the routine and duplicate locations of each sample type (*i.e.*, rock, residual soil, stream sediment, stream water, overbank sediment, floodplain sediment) could vary from 10 to 50 metres.

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

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

Ramsey *et al.* (1992) proposed initially the term *technical variance*, s^2_{tech} , for the sum of the *sampling*, s^2_{smp} , and *analytical*, s^2_{anal} , *variance* of a particular determinand or measurand 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.*,

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

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:

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

It is a normal statistical procedure to increase the confidence interval of the uncertainty by multiplying by a *coverage factor* $k = 1.96$ (at the 95% confidence level) or 2.00 (at the 95.44% confidence level) to give the *expanded* or *extended uncertainty* U :

$$\text{expanded uncertainty, } U = k * u = 2.00 * s_{meas} \quad (20)$$

In the statistics of the normal gaussian distribution, the coverage factor is 1.96 for the 95% confidence interval, and 2.00 for the 95.44% confidence interval. These coverage factors apply to an entire population when the true values for the mean and standard deviation are known. However, in geochemical mapping, the values of mean and standard deviation are estimated from ‘samples’ of this entire population. Because of the extra uncertainty in the estimates of standard deviation, it is necessary to increase the coverage factor to achieve a stated level of confidence. Consequently, international guidance recommends a coverage factor of 2 (*i.e.*, 2.00) for the expression of measurement uncertainty at *approximately 95% confidence*, to allow for this extra uncertainty that arises from using estimates of standard deviation (JCGM 100, 2008; ISO/IEC, 2008). This more reliable coverage factor is generally calculated using a t-distribution for the numbers of measurement values typically used (as explained in Annex G of JCGM 100, 2008, p.70–78). Further, the choice of coverage factor is discussed in detail in other publications that should be consulted (Ellison and Williams, 2012), and the key principles for its selection are given by Ramsey *et al.* (2019). If anyone wants to understand this more deeply, Section §G6.6.6 in JCGM 100 (2008, p.77) should be consulted, where it is stated: “*Then, based on the discussion given in this annex, including that emphasizing the approximate nature of the uncertainty evaluation process and the impracticality of trying to distinguish between intervals having levels of confidence that differ by one or two percent, one may do the following:*

- *adopt $k = 2$ and assume that $U = 2u_c(y)$ defines an interval having a level of confidence of approximately 95 percent”.*

Whichever coverage factor is used, it is important to state its value and confidence level when reporting expanded uncertainty.

The *expanded or extended uncertainty* U , expressed as a percentage of the mean concentration of a particular determinand, gives the *relative expanded uncertainty* U' %:

$$\text{relative expanded uncertainty, } U' \% = \frac{(100 * 2.00) * s_{meas}}{\bar{x}} \quad (21)$$

where:

\bar{x} 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):

$$\text{relative sampling uncertainty, } U'_{samp} \% = \frac{(100 * 2.00) * s_{samp}}{\bar{x}} \quad (22)$$

$$\text{relative analytical uncertainty, } U'_{anal} \% = \frac{(100 * 2.00) * s_{anal}}{\bar{x}} \quad (23)$$

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_{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:

$$\text{relative expanded uncertainty, } U' \% = \left(\frac{100 * 2.00 * S_{meas}}{\bar{x}} \right) \div \sqrt{2} \quad (24)$$

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 materials, 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 limit 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 is 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, *for example*, 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 §7.3.1.5).

7.3.1.10.1. Calculation of standard and expanded uncertainty factor

It is well known that geochemical data generally follow a log-normal distribution (*e.g.*, Razumovsky, 1941; Ahrens, 1953, 1954a, 1954b; Chayes, 1954; Tennant & White, 1959; Vistelius, 1960; Shaw, 1961; Lepeltier, 1969; Sinclair, 1976, 1983, 1986; Reimann and Filzmoser, 2000; Buccianti *et al.*, 2006; Mateu-Figueras and Pawlowsky-Glahn, 2008; Zhao *et al.*, 2018), which can be seen in Figures 7.7 and 7.8. It is, therefore, advisable before embarking on the statistical treatment of the quality control results and analytical data from any geochemical mapping project, to check their statistical distribution. This can be done either by plotting a histogram or a cumulative frequency curve or both.

Figure 7.12 shows two graphs of Zn in topsoil samples of the FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005). The first (a) is a histogram with the fitted normal distribution curve exhibiting a positive skewness. The second (b) is a cumulative frequency curve depicting the existence of at least four log-normal populations. From these two graphs, it can be concluded that the cumulative frequency distribution is a much better and more powerful visualisation tool than the histogram because it shows more effectively the pictorial statistical distribution of a determinand or measurand.

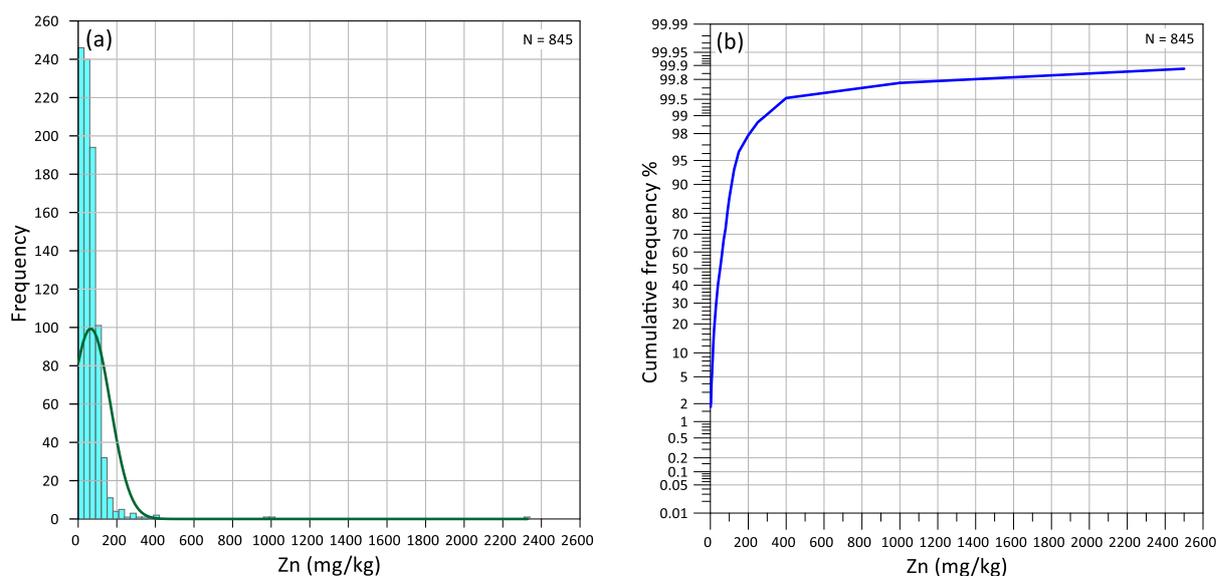


Figure 7.12. (a) Histogram of Zn distribution with fitted normal distribution curve, and (b) Cumulative frequency plot of Zn in topsoil samples determined by XRF, FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005). It is noted that most of the topsoil samples have Zn concentrations <400 mg/kg. Plotted by Alecos Demetriades (IGME/IUGS- CGGB) with Golden Software's Grapher™ v20.

Figure 7.13 shows the log-normal distribution of Zn in the routine and duplicate quality control topsoil samples from the same geochemical mapping project; (a) displays the linear and (b) the \log_e distribution. In both cases, the curves depict the existence of at least two log-normal populations.

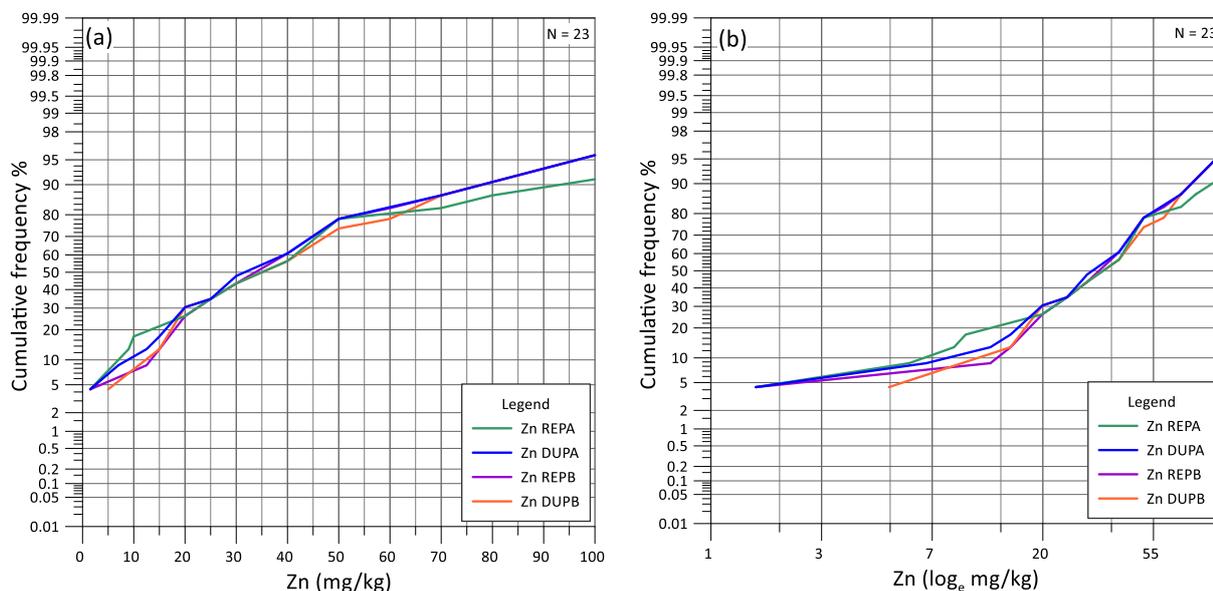


Figure 7.13. Cumulative frequency curves of Zn in routine and field duplicate topsoil samples determined by XRF, FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005). (a) Linear graph and (b) \log_e graph. Notation: DUPA = Routine sample; REPA = Replicate split of routine sample; DUPB = Field duplicate sample; REPB = Replicate split of field duplicate sample. Plotted by Alecos Demetriades (IGME & IUGS CGGB) with Golden Software's GrapherTM v20.

Ramsey and Argyraki (1997) already stated that the uncertainty interval of any concentration X_i (*e.g.*, the estimated mean for the site) becomes asymmetric (log-normal). However, they did not elaborate on the procedure that should be followed when expressing uncertainty to account for this asymmetry.

Ramsey *et al.* (2019) to accommodate this known asymmetry in the statistical distribution of geochemical data proposed the calculation of a *standard* ($^F u$) and an *expanded* ($^F U$) *uncertainty factor* by using natural logarithms. The reason for suggesting this transformation is that ANOVA assumes that the frequency distribution of a determinand (or measurand) is approximately normal, *i.e.*, Gaussian (Scheffé, 1959, 1999; Davis, 1973, 1986, 2002; Till, 1974; Reimann *et al.*, 2008), which is not the case of most geochemical statistical distributions, as has already been stated (see Figs. 7.7, 7.8, 7.12 & 7.13). Thus, according to Ramsey *et al.* (2019), it is more appropriate to express measurement uncertainty by using the *expanded uncertainty factor* ($^F U$), especially when the frequency distribution is approximately log-normal, a feature common at high values of sampling uncertainty. In such cases, the ANOVA is performed on the natural logarithms of the measurement values and, consequently, the results are not in the original units of elemental concentration.

To estimate the upper and lower confidence limits of the uncertainty interval about a determinand concentration value (X), Ramsey *et al.* (2019) proposed the multiplication and division of the measured concentration X by the *expanded uncertainty factor* ($^F U$), respectively.

The *standard uncertainty factor* ($^F u$) is calculated from the standard deviation (s_G) of \log_e -transformed determinand or measurand values [$s(\ln(X)) = s_G$], where $^F u = \exp(s_G)$.

The *expanded uncertainty factor* ($^F U$), using a *coverage factor* $k = 2.00$ at the $\approx 95\%$ confidence interval, can be calculated, according to Ramsey *et al.* (2019), in two ways, either:

$$(i) \quad \text{expanded uncertainty factor, } ^F U = \exp(2.00 * s_G) \quad (31)$$

Or, alternatively, because multiplying by k in log-space is the same as raising to the power of k in linear space, *i.e.*, ${}^FU = ({}^Fu)^k$, it can be calculated more simply as shown below:

$$(ii) \quad \text{expanded uncertainty factor, } {}^FU = ({}^Fu)^{2.00} \quad (32)$$

The upper and lower confidence limit for the expanded uncertainty interval about a determinand concentration X_i is calculated as follows:

- a) *Upper Confidence Limit (UCL)* at the 95% confidence level is estimated by the equation:

$$UCL = X_i * {}^FU$$

(Measured concentration X_i is *multiplied* by the Expanded uncertainty factor, FU) (33)

- b) and the *Lower Confidence Limit (LCL)* at the 95% confidence level is estimated by the equation:

$$LCL = X_i / {}^FU$$

(Measured concentration X_i is *divided* by the Expanded uncertainty factor, FU) (34)

Consequently, this confidence interval is not symmetrical about the measured concentration X_i in normal linear concentration space.

Finally, the *relative uncertainty*, u' , expressed as a fraction, can be calculated by the following expression:

$$\text{relative uncertainty, } u' = \sqrt{\exp(s_G^2) - 1} \quad (35)$$

which for modest values of u' (*for example*, <0.2 , which is the usual case according to Ramsey *et al.*, 2019) is approximately equal to s_G .

Worked examples for estimating all parameters discussed in this Section will be found in Section §7.4.

7.3.1.10.2. Interpretation of uncertainty statements for regulatory purposes

The main aim of the Global Geochemical Reference Network project is the establishment of the geochemical baseline of chemical elements and compounds in natural surficial materials against which future changes can be quantified, whether natural or human-induced. Further, the generated analytical data, apart from their use as reference data for levelling the more detailed national geochemical data sets, will be used by many disciplines and for different purposes, including possible compliance with international or national regulatory limits. Therefore, it is important to take uncertainty into account, especially in the interpretation for regulatory purposes. A full discussion is beyond the scope of the present Manual, and the interested reader should consult Ellison and Williams (2007, 2012). Ramsey *et al.* (2019, p.32) have given the basic principles to be followed for regulatory purposes, *i.e.*:

- “Decide whether the decision requires proof of compliance, proof of non-compliance, or a ‘shared risk’ approach, and set an appropriate level of confidence.
- For proof of compliance, the result and its uncertainty interval must be entirely within the permitted range.
- For proof of non-compliance, the result and its uncertainty interval must be entirely outside the permitted range.

- *For shared risk approaches, set a range for acceptable measurement results based on the permitted interval, adjusted to provide a specified probability of false acceptance and false rejection rates. More recent guidance gives useful details of the procedure (ISO/IEC, 2012)."*

For regulatory purposes, it is important to consult the specific international or national regulations applicable, as no general guidance can currently cover all cases.

7.4. Worked examples

For the worked examples, software packages and data sets are provided, and which can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<https://www.globalgeochemicalbaselines.eu/>) – Refer to Supplementary material.

7.4.1. Program for plotting X-Y diagrams

The following files should be downloaded from the [Publications](#) web page of the IUGS Commission on Global Geochemical Baselines (see Supplementary material):-

- IUGS-CGGB_Chapter-7_DUPREPLOT.xlsm: Microsoft™ Excel Workbook with a macro for plotting X-Y diagrams. The Workbook consists of two Worksheets. The first, "INFO" gives general information, author and instructions on how to use the macro routine; the test duplicate-replicate analytical results are included on this page and come from samples of topsoil from the FOREGS Geochemical Atlas of Europe project (Salminen *et al.*, 2005). The second worksheet, 'ControlData', contains the topsoil duplicate-replicate analytical results used for plotting the X-Y diagrams when running the macro.
- IUGS-CGGB_Chapter-7_DUPREPLOT_Output.xlsm: Microsoft™ Excel Workbook with the output of X-Y plots in different worksheets with the symbol of each element.
- IUGS-CGGB_Chapter-7_FOREGS_Topsoil_QC_XRF_data.xlsx: Example quality control data set from the FOREGS Geochemical Atlas of Europe project (Salminen *et al.*, 2005). The Microsoft™ Excel workbook contains the original balanced ANOVA quality control XRF topsoil data, which have been transferred to "DUPREPLOT" after cleaning, *i.e.*, deleting columns of determinands with many values below the analytical method's lower detection limit, such as F, Bi, Cu, Hf, La, Mo, Sb, Sn, Ta, U and W. It also includes other worksheets: (a) Lower_detection_limit; (b) Notation_of_Control-ID; (c) Legal_Notice, and (d) Reference.

To obtain a visual appreciation of the analytical laboratory's precision simple X-Y plots of duplicate-replicate pair results for each determinand or measurand are plotted. Two examples, Zn and Th, have been extracted from the 'IUGS-CGGB_Chapter-7_DUPREPLOT_Output.xlsm' Microsoft™ Excel file to show good and poor precision, respectively (Figs. 7.14 & 7.15). If all X-Y plots are studied in this output file, it will be observed that apart from Th, the elements As, Ce, Co, Cs, Ga, Nb, Ni, Pb, Sc and V show poor precision and, therefore, were rejected for further treatment. Consequently, this first step is important for apart from obtaining an appreciation of the analytical laboratory's precision, within-site variability can also be assessed, and poor data are rejected.

7.4.2. Program for the estimation of practical detection limit and precision

For the estimation of the practical detection limit and precision according to the method described in Section §7.3.1.7, a Microsoft™ Excel workbook 'IUGS-CGGB_Chapter-7_PDLPRECIS.xlsx' is available (see Supplementary material).

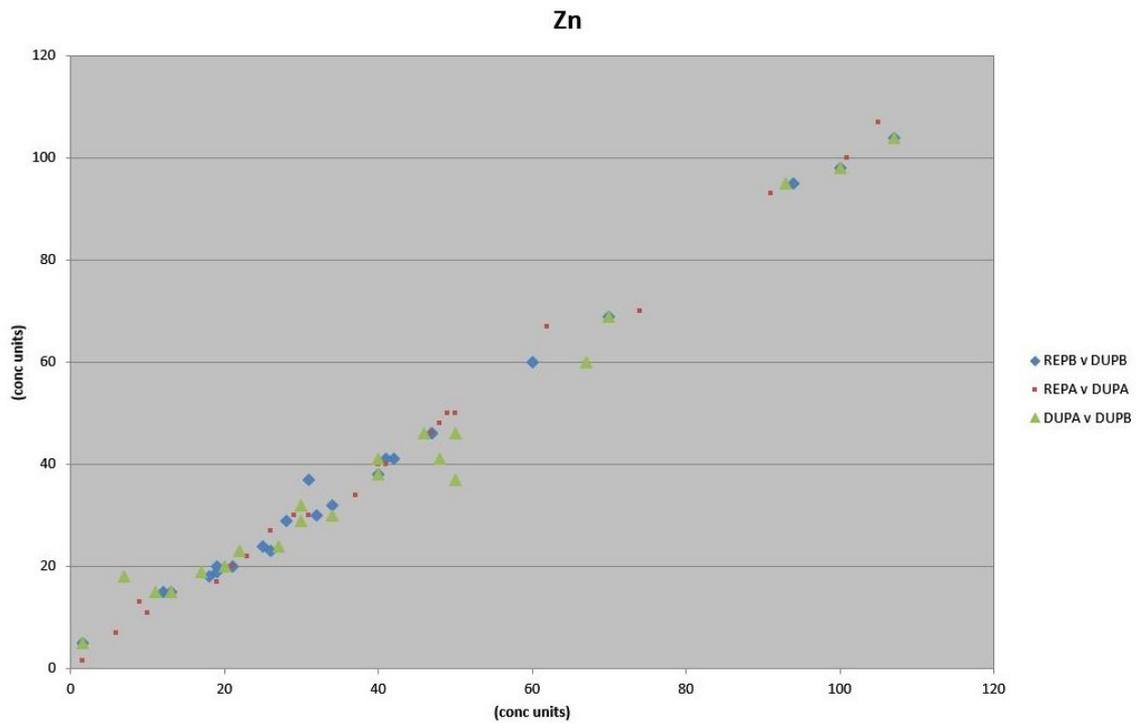


Figure 7.14. Duplicate-replicate plots for Zn from FOREGS Topsoil XRF quality control data (N=23 duplicated sites). It shows that the duplicate-replicate results are aligned close to the 1:1 gradient line. Plotted with 'DUPREPLOT.xlsm', a Microsoft™ Excel Workbook macro routine developed by Christopher C. Johnson. Axis concentration units in mg/kg. Notation: Blue diamond = REPB versus DUPB; Red square = REPA versus DUPA; Green triangle = DUPA versus DUPB; and (all X-axis versus Y-axis). Notation: DUPA = Routine sample; REPA = Replicate split of routine sample; DUPB = Field duplicate sample; REPB = Replicate split of field duplicate sample. Plotted by Christopher C. Johnson (GeoElementary/IUGS-CGGB) with Microsoft™ Excel.

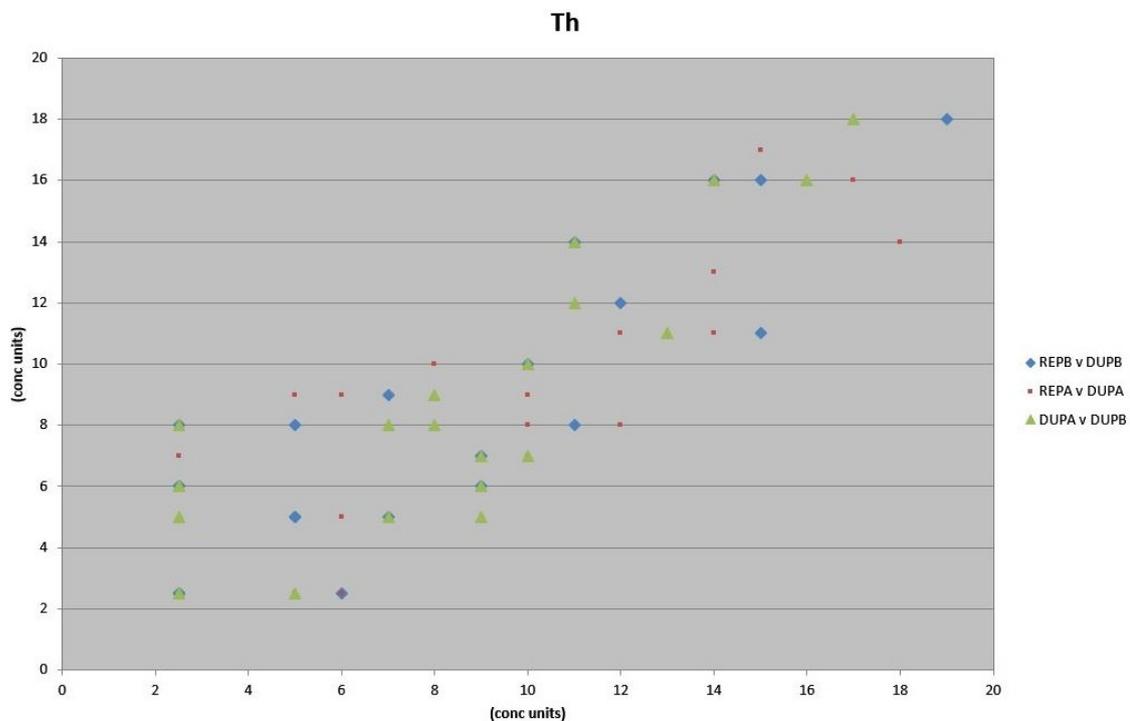


Figure 7.15. Duplicate-replicate plots for Th from FOREGS Topsoil XRF quality control data (N=23 duplicated sites). It shows a wide scatter of (i) Routine and field duplicate results (within site variability), and (ii) Duplicate-replicate results (analytical variability). Plotted with 'DUPREPLOT.xlsm', a Microsoft™ Excel Workbook having an embedded macro routine developed by Christopher C. Johnson. Axis concentration units in mg/kg. Notation: See Figure 7.14. Plotted by Christopher C. Johnson (GeoElementary/IUGS-CGGB) with Microsoft™ Excel.

The PDLPRECIS Microsoft™ Excel Workbook comprises the following worksheets:

- **Contents:** Description of included worksheets, as given below.
- **Read-Me:** Contains the procedure described in Section §7.3.1.7.
- **Citation:** How PDLPRECIS should be cited when used.
- **Important cautions:** These cautions are very significant. They must be read carefully and understood, otherwise the calculations performed within the ‘PDLPRECIS.xlsx’ worksheet for the estimation of practical detection limit and precision will give erroneous results.
- **GEMAS-Gr_Be_QC_data:** The worksheet contains an uncensored data set: (a) Be analytical results including one sample with a negative value, and (b) the same Be analytical results without the sample pair without the negative value. These Be quality control results are from the GEMAS grazing land soil (Gr) samples (Reimann *et al.*, 2009, 2014). The reason for their selection is because the Be analytical results are uncensored and, thus, suitable for the estimation of the practical detection limit. Here a question is raised: *Can the “PDLPRECIS” Worksheet be used for the estimation of the practical detection limit for censored or rather truncated data sets, i.e., data sets that the laboratory does not report values below its estimated lower detection limit.* Censored or truncated analytical results can be used for the estimation of the practical detection limit (PDL). The drawback here is if the value of the practical detection limit is lower than the laboratory detection limit. In such a case, the estimated PDL, cannot be used because of the laboratory’s truncation. However, the estimation of the PDL, even for censored or truncated analytical results by the laboratory, verifies the laboratory’s lower detection limit.
- Two worksheets: (i) **GEMAS-Gr_Be-1_PDLPRECIS** (with the Be negative value, N=94 pairs), and (ii) **GEMAS-Gr-Be-PDLPRECIS** (without the Be negative value, N=93 pairs): Worksheets with all the calculations leading to the estimation of (a) the practical detection limit; (b) precision and precision equation, and (c) a graph showing the distribution of precision with respect to concentration (see Fig. 7.6).
- **GEMAS-Ap_Be_Lab-replicate-data:** This worksheet contains the laboratory Be replicate analyses performed on the agricultural soil samples of the GEMAS project (Reimann *et al.*, 2009, 2014). The reason for selecting this data set is because it has 146 pairs of Be analyses.
- **GEMAS-Ap_Be_Lab_PDLPRECIS:** Contains all the calculations leading to the estimation of the practical detection limit, precision, precision equation, and graph showing the distribution of precision with respect to concentration.
- **Summary_Table:** The worksheet contains the estimated results of Be from the different PDLPRECIS worksheets.
- **CLEAN-PDLPRECIS_Worksheet:** It is a clean worksheet for copying the pair of duplicate-replicate results of any geochemical project. Up to 440 pairs of analyses can be handled, and the calculations are carried out automatically, provided the underlying instructions and cautions are observed. If the data set exceeds 440 pairs of analyses, the Worksheet can be modified according to the instructions given below.

The Microsoft™ Excel Worksheet performing the calculations leading to the estimation of practical detection limit and precision is annotated with instructions on how to use it, and to modify it, if necessary, according to the number of pairs of analyses. The most important procedures that must be followed exactly when using the ‘CLEAN-PDLPRECIS’_Worksheet are:

- a) Copying the analytical results: This must be done by selecting from the relevant Microsoft™ Excel Worksheet the range of analytical results and then using the ‘Copy’ command.
- b) Pasting the analytical results in the PDLPRECIS Worksheet: It is important to use the ‘Paste Special & Values’ command for the succeeding automated procedures to work properly.
- c) Deleting all zero values in Columns: G ‘ $(X1+X2)/2$ ’ (mean), and H ‘ $|X1-X2|$ ’ (absolute difference). These two columns have entries until line 444. So, if your data set has fewer pairs of sample values, the zeros below your data set must be deleted. This is a very important action, otherwise, in the next step, all lines with ‘zero’ values will be transferred to the top of the worksheet.
- d) Directly afterwards, you must ‘Sort’ the analytical results in Columns ‘A’ to ‘G’, with respect to their mean values, *i.e.*, Column G ‘ $(X1+X2)/2$ ’, which means you mark all columns from ‘A’ to ‘G’ and use the ‘Data/Sort’ command to order the mean values from ‘Smallest to Largest’.
- e) Delete all zero (0) or no values in Columns N, O, P, Q, R and S. This is a very important action for the Excel range commands in the calculations part of the Worksheet to work properly.
- f) Finally, if your data set has pairs of values exceeding 440 (= 11 groups of pairs x 40 groups), you must first extend the calculation of the mean ‘ $(X1+X2)/2$ ’, and absolute difference ‘ $|X1-X2|$ ’ in columns G and H, respectively. Secondly, you must extend the estimation of ‘Group Mean’ and ‘Group Median’ in groups of 11 pairs of values in columns I and J, respectively, and to number each group of 11 pairs in Column K, and enter the corresponding line number in Column L. Thirdly, modify Columns N, O, P, Q, R and S by increasing the entry lines according to the additional groups of 11 pairs of values, and fourthly, modify accordingly the range commands in the calculations part of the Worksheet. The last action, *i.e.*, modification of equations, should be tested by using the Be results to ensure that the range commands work properly.

7.4.3. Programs for 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-and-community/connect-with-others/through-interests/divisions/analytical/amc/software/>)⁶:

- **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 (Fig. 7.11a) and unbalanced (Fig. 7.11b) experimental designs. Output is expressed as standard uncertainty, expanded relative uncertainty, and Uncertainty Factor.
- **RANOVA3** 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 (Fig. 7.11a), and unbalanced experimental designs (Fig. 7.11). Output is expressed as standard uncertainty, expanded relative uncertainty, and Uncertainty Factor. Version 3 includes an option to calculate confidence intervals on uncertainties for balanced designs.

⁶ As new versions of software programs may be released from time to time, it is recommended to consult the web page of the Royal Society of Chemistry at regular intervals. The same applies to all recommended web pages with software programs.

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 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 **ROBCOOP4A** (Vassiliades, 2022). There are two variants to run on both 32- and 64-bit computers, and it is available for download from the Publications web page of the IUGS Commission on Global Geochemical Baselines' website together with test data sets.

7.4.3.1. Classical and robust balanced ANOVA

According to Ramsey (1998, p.102) the ROBCOOP4.EXE and, consequently the new version ROBCOOP4A.EXE program (Vassiliades, 2022) 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 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 an example (Salminen *et al.*, 2005).

Figures 7.16 and 7.17 are multiple-boxplots of the major and trace element XRF duplicate-replicate topsoil data sets, respectively. The multiple-boxplots can be plotted with any statistical software package. In this case, they were plotted with Golden Software's Grapher™ v20.

The major elements multiple boxplot plot displays outliers for Fe₂O₃, MnO, MgO, CaO, SO₃, F and LOI (Fig. 7.16), 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 (Fig. 7.17). 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 7.16, and Bi, Co, Cu, Mo, Sb, Ta and U in Figure 7.17 have more than 10% outlying values, which means that the classical and robust ANOVA will most likely give erroneous results with the ROBCOOP4A.EXE program.

Let us select CaO and Zn for a more detailed study. The multiple-boxplots (Fig. 7.18) and tabulated concentrations (Table 7.1) 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 analysis, CaO exceeds slightly the upper limit of 10%, while Zn is within the upper limit.

The other elements with outliers should be subjected to the same rigorous treatment before running the ROBCOOP4A.EXE program.

The output results of the ROBCOOP4A.EXE program for CaO and Zn are shown in Tables 7.2 and 7.3, respectively, and the pie charts in Figure 7.19 display the proportion of geochemical (spatial), sampling, and analytical classical and robust analysis of variance results.

Tables 7.2 and 7.3 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 (Fig. 7.19a).

For Zn again, the greatest contribution to measurement uncertainty in both classical and robust balanced ANOVA results is due to sampling (Table 7.3; Fig. 7.19b).

In both cases, the robust measurement variance out of the total is comparatively small, 2.40% for CaO and 0.93% 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 their intended use and the maps can be plotted, and the geochemical distribution interpreted (Fig. 7.20).

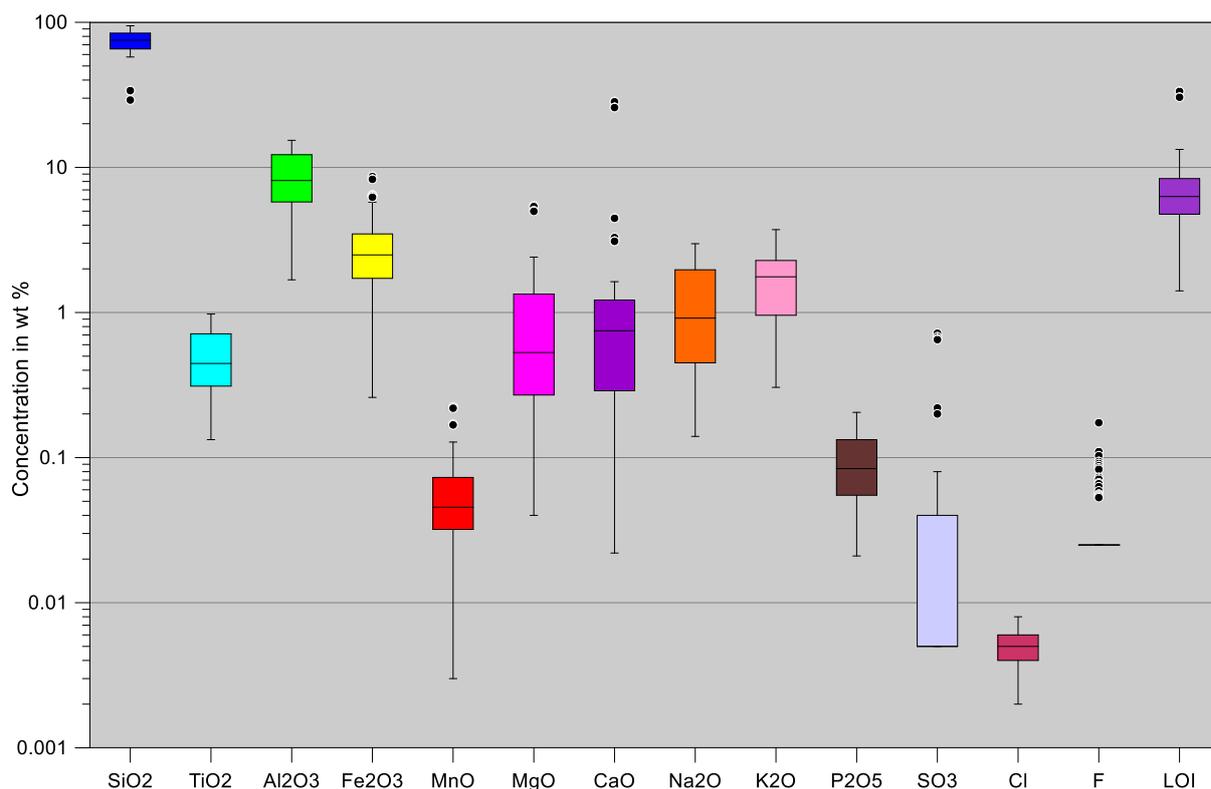


Figure 7.16. Multiple-boxplot of major element quality control data in European topsoil (N=23 duplicated sites). Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

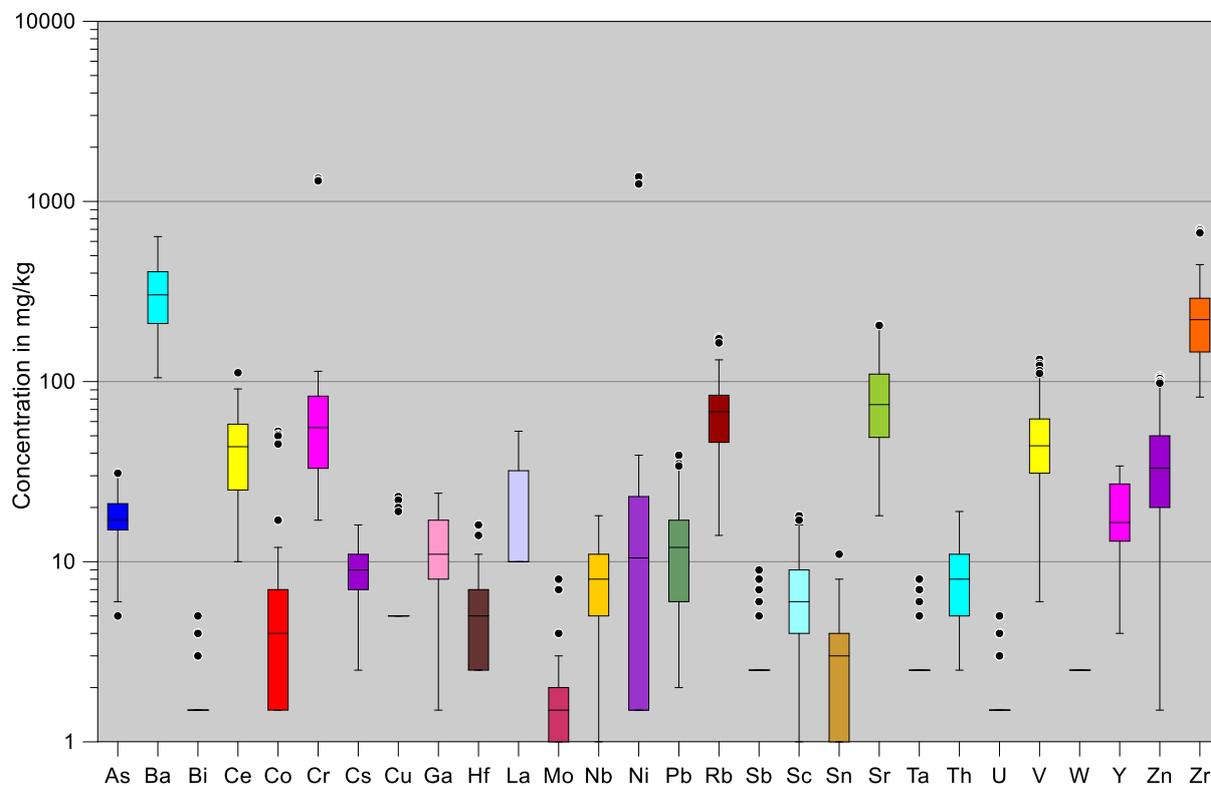


Figure 7.17. Multiple-boxplot of trace element quality control topsoil data (N=23 duplicated sites; Total number of sample splits, N=92) – FOREGS project (Salminen et al., 2005). Plotted by Alecos Demetriades (IGME & IUGS-CGGB) with Golden Software's Grapher™ v20.

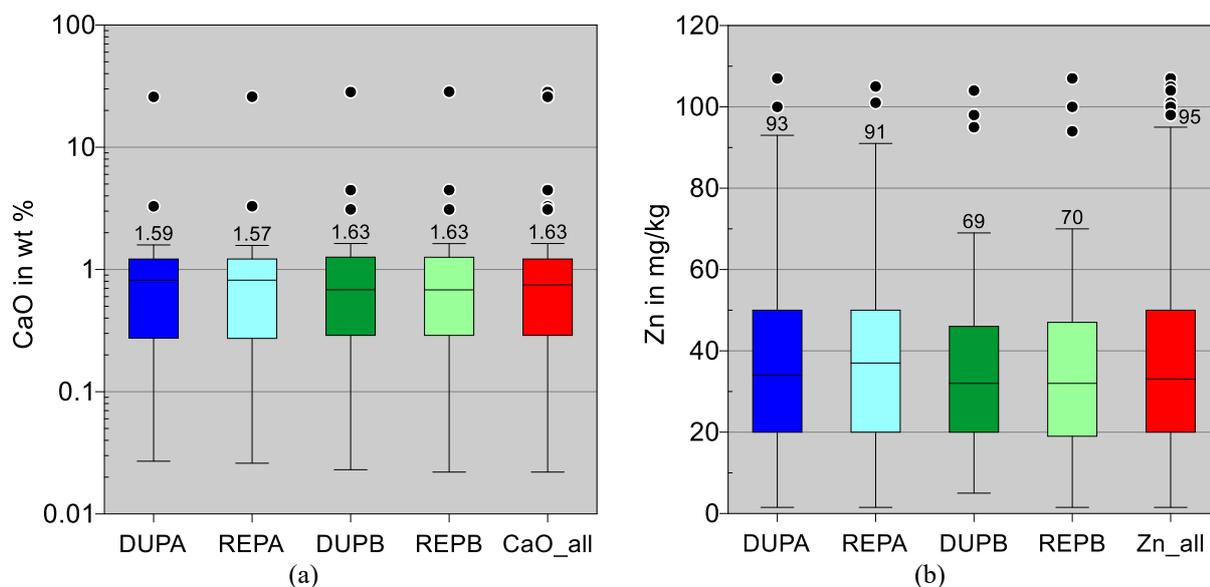


Figure 7.18. Multiple-boxplots of routine and field duplicate sample splits of (a) CaO and (b) Zn, FOREGS Topsoil QC data set ($N=23$ duplicated sites) (Salminen et al., 2005). The value of the upper whisker of all duplicate-replicate splits ($N=92$) is 1.63 wt% CaO, and 95 mg/kg Zn. Samples with values greater than these limits are considered outliers (see Table 7.1). Notation: DUDA = 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™ v20.

Table 7.1. CaO (wt%) and Zn (mg/kg) results of routine and field duplicate sample splits of FOREGS Topsoil samples (Salminen et al., 2005). 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. Notation: DUDA = Routine sample; REPA = Replicate split of routine sample; DUPB = Field duplicate sample; REPB = Replicate split of field duplicate sample.

Sample Number	CaO in wt%				Zn in mg/kg			
	DUDA	REPA	DUPB	REPB	DUDA	REPA	DUPB	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 7.2. Classical and robust analysis of variance results of CaO from the FOREGS Topsoil XRF data set (Salminen et al., 2005). Output as given by ROBCOOP4A.EXE program (Vassiliades, 2022). The coverage factor used in this case is 1.96 at the 95% confidence level. Note: The output is exactly as given by the program. In practice, the results should not be quoted with more than two or three significant figures to the right of the decimal point depending on the number of integers.

Element	CaO			
Number of duplicated sample sites	23			
<hr/>				
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			
<hr/>				
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 7.3. Classical and robust analysis of variance results of Zn from the FOREGS Topsoil XRF data set (Salminen et al., 2005) as given by the output of ROBCOOP4A.EXE program (Vassiliades, 2022). The coverage factor used in this case is 1.96 at the 95% confidence level. Note: The output is exactly as given by the program. In practice, the results should not be quoted with more than two or three significant figures to the right of the decimal point depending on the number of integers.

Element	Zn			
Number of duplicated sample sites	23			
<hr/>				
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			
<hr/>				
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			

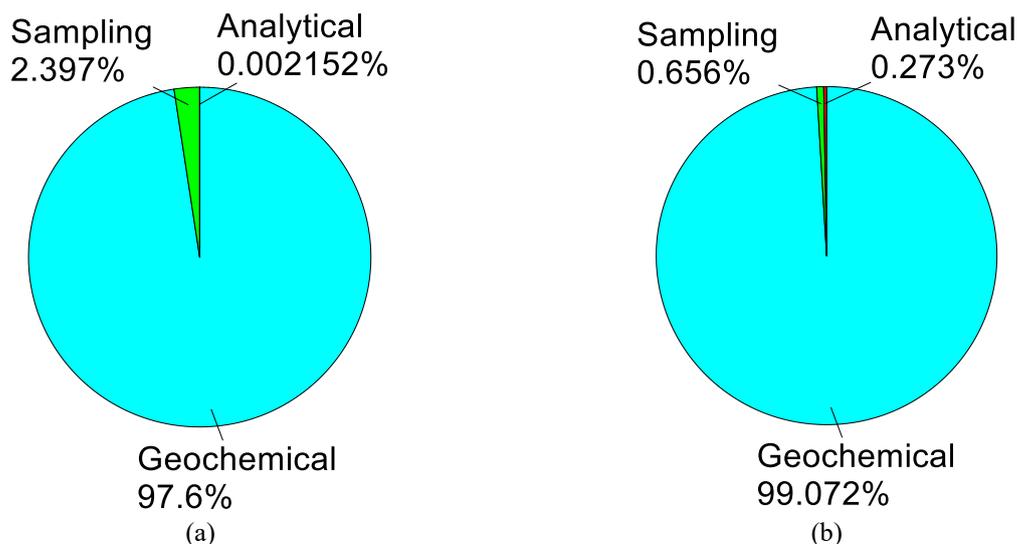


Figure 7.19. Pie charts of robust balanced ANOVA results for (a) CaO and (b) Zn in topsoil samples of the FOREGS Geochemical Atlas of Europe, determined by XRF (Salminen et al., 2005). Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

7.4.3.1.1. Use of expanded uncertainty factor

The example in Table 7.4 shows the advantage of using the expanded uncertainty factor ($^F U$) in comparison to the robust expanded relative uncertainty (U'). The former takes into account the positive skewness in the Zn topsoil analytical data (Figs. 7.12 & 7.20b - inset), and gives a much higher upper confidence limit (UCL) on the Zn concentration in comparison to the lower confidence limit (LCL), *i.e.*, the confidence interval from -23.5 to +36 mg/kg is asymmetrical around the measured value of 67 mg/kg Zn. While using the robust expanded uncertainty (U'), a symmetrical confidence interval of ± 8.4 mg/kg Zn on the measured value of 67 mg Zn/kg is given.

The notable difference between the two estimations is shown in the X-Y plot of Figure 7.21. Using the robust expanded relative uncertainty (U'), the UCL and LCL remain constant at $\pm 12.6\%$ on the Zn values through the entire concentration range. While the UCL and LCL, estimated by the expanded uncertainty factor ($^F U$) on the Zn values, allow for the asymmetry due to the positive skewness of the Zn concentrations (Fig. 7.12a). This feature is quite evident in Figure 7.21 as the upper and lower confidence limits become distinctly larger at higher Zn concentrations.

Table 7.4. Calculations using the Zn concentration of 67 mg/kg in topsoil sample N31E05T2 (see Tables 7.1 and 7.3) with respect to the robust expanded relative uncertainty ($U' = \pm 12.6\%$), and expanded uncertainty factor ($^F U = 1.54$). The much higher UCL for the $^F U$ approach better reflects the positive skewness of the underlying logarithmic frequency distribution (see histogram and cumulative frequency curve in Fig. 7.12). The coverage factor used in this case is 1.96 at the 95% confidence level. See Table 7.5 for the calculations and Figure 7.21. Notation: LCL = Lower confidence limit; UCL = Upper confidence limit; CI = Confidence interval.

Measurement uncertainty and factor at the 95% confidence level		Calculation of LCL	LCL (mg/kg)	Calculation of UCL	UCL (mg/kg)	CI around measured value (mg/kg)
Robust expanded relative uncertainty (U')	12.6%	$67 - (67 * 12.6\%)$ (Equation 26)	58.6	$67 + (67 * 12.6\%)$ (Equation 25)	75.4	± 8.44
Expanded uncertainty factor ($^F U$)	1.54%	$67 / 1.54$ (Equation 34)	43.5	$67 * 1.54$ (Equation 33)	103	-23.5, +36

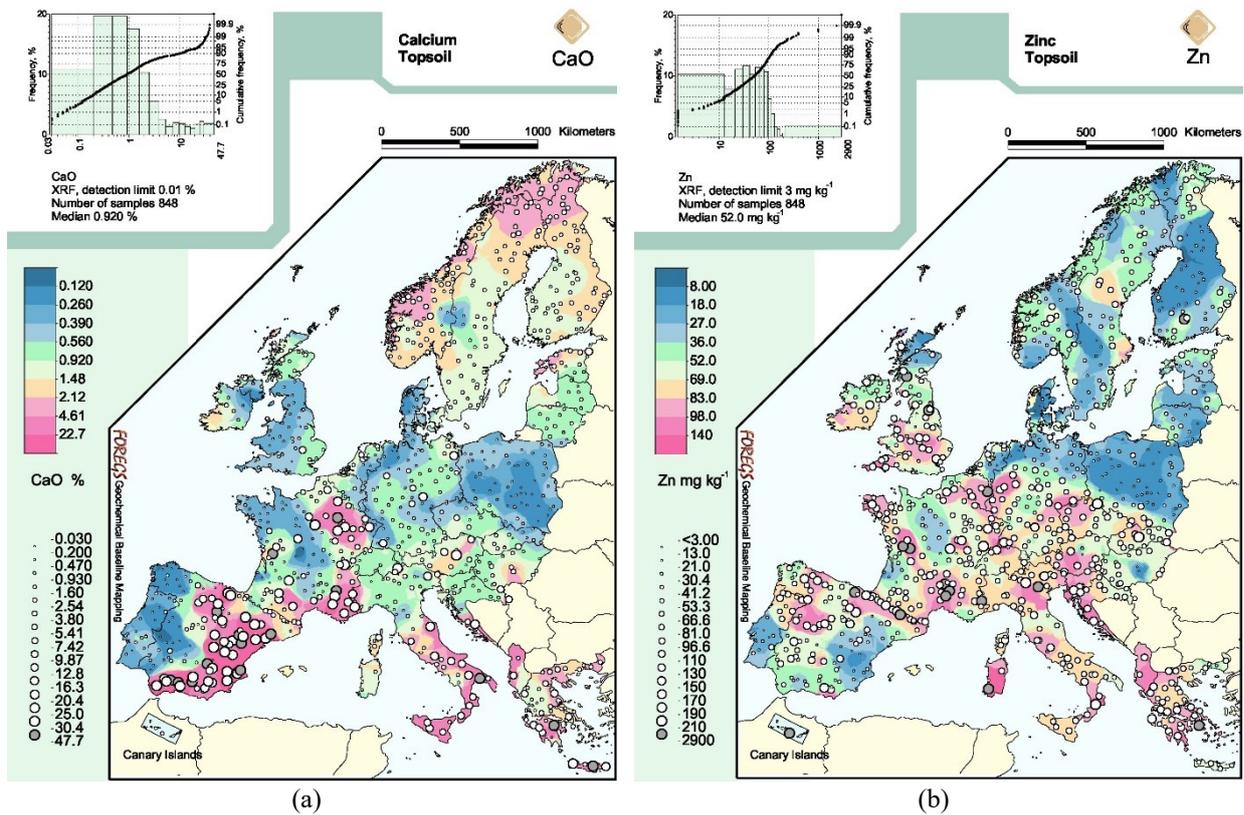


Figure 7.20. FOREGS Geochemical Atlas of Europe maps of topsoil (a) CaO and (b) Zn determined by XRF. Source: Salminen et al. (2005, p.158 CaO - http://weppi.gtk.fi/publ/foregsatlas/maps/Topsoil/t_xrf_cao_edit.pdf; p.513 Zn - http://weppi.gtk.fi/publ/foregsatlas/maps/Topsoil/t_xrf_zn_edit.pdf). It is noted that the number of topsoil samples analysed by XRF is 845 and not 848.

Table 7.5. Extract from the example used for plotting Figure 7.21 to show the calculations presented in Table 7.4 with respect to the Expanded uncertainty factor ($^F U$). The Microsoft Excel worksheet is provided in the Supplementary material (IUGS-CGGB_Chapter-7_FOREGS_Topsoil_LCL_&_UPL.xlsx). Numbers were rounded to the first decimal place <99.9 and nearest integer >100.

GTN Sample No.	Zn_i (mg/kg) ordered	Zn_i LCL (mg/kg) ($Zn_i / ^F U\%$)	Zn_i UCL (mg/kg) ($Zn_i * ^F U\%$)	E_i (mg/kg) ($Zn_i * U\%$)	$Zn_i - E_i$ (mg/kg)	$Zn_i + E_i$ (mg/kg)
	Zn_i	$Zn_i / 1.54$	$Zn_i * 1.54$	$E_i = Zn_i * 0.126$		
.....
N42E11T3	114	74.0	176	14.4	99.6	128
N25E13T1	115	74.7	177	14.5	101	129
N38W03T3	117	76.0	180	14.7	102	132
N32E07T1	118	76.6	182	14.9	103	133
N26E13T2	120	77.9	185	15.1	105	135
N30E06T4	130	84.4	200	16.4	114	146
N33E06T1	141	91.6	217	17.8	123	159
N29W02T5	142	92.2	219	18.0	124	160
N37W01T3	295	192	454	37.2	258	332
N31W01T5	314	204	484	39.6	274	354
N26E14T4	358	232	551	45.1	313	403
N27E05T1	396	257	610	50.0	346	446
.....

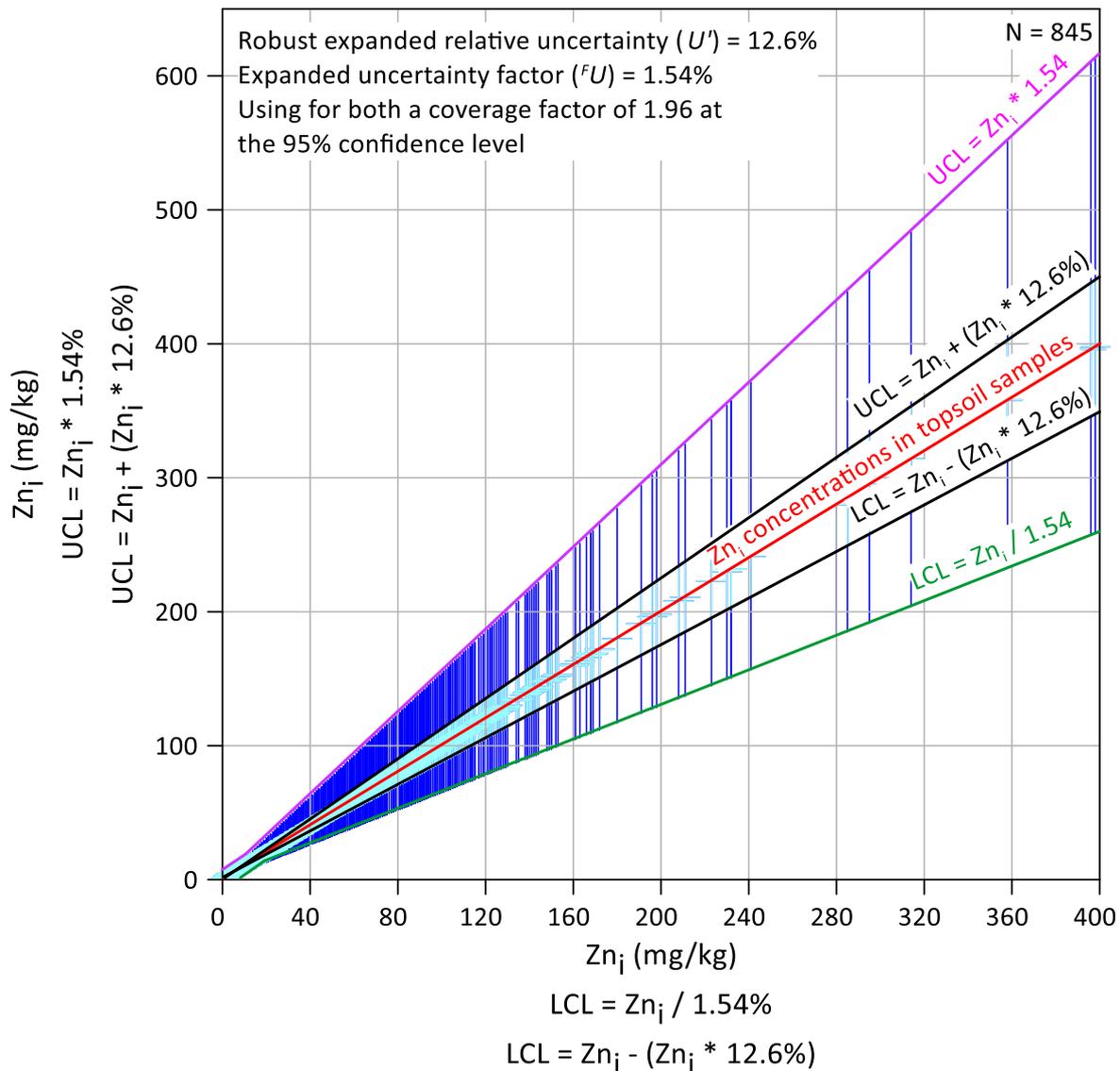


Figure 7.21. Composite high-low-close plot of Zn_i versus Zn_i concentrations in topsoil samples showing the upper (UCL) and lower (LCL) confidence limits estimated by the robust expanded relative uncertainty (U') and expanded uncertainty factor ($F'U$) on the Zn_i concentrations. The most notable feature is the exhibited asymmetry of the UCL and LCL on the Zn_i concentrations calculated with the use of the expanded uncertainty factor ($F'U$). It is noted that the plot shows Zn concentration values up to 400 mg/kg in the abscissa and 600 mg/kg in the ordinate. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

Supplementary material

The following files can be downloaded from the Publications web page of the IUGS Commission on Global Geochemical Baselines (<http://www.globalgeochemicalbaselines.eu/>):

- IUGS-CGGB_Chapter-7_DUPREPLOT.xlsm
- IUGS-CGGB_Chapter-7_DUPREPLOT_Output.xlsm
- IUGS-CGGB_Chapter-7_DUPREPLOT_ExcelMacroEMPTY.xlsm
- IUGS-CGGB_Chapter-7_PDLPRECIS_Clean_worksheet.xlsx
- IUGS-CGGB_Chapter-7_PDLPRECIS_Worked-example.xlsx
- IUGS-CGGB_Chapter-7_FOREGS_Topsoil_XRF_QC_data.xlsx
- IUGS-CGGB_Chapter-7_FOREGS_Topsoil_XRF_LCL_&_UCL.xlsx

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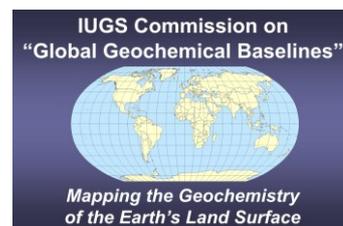
Note: All hyperlinks were checked on the 4th of February 2022.

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 8

**Data Conditioning Methods:
Generating Time Independent Geochemical Data**

Christopher C. Johnson¹, T. Robert Lister²

¹GeoElementary, Derby, United Kingdom

²British Geological Survey, Keyworth, Nottingham, United Kingdom

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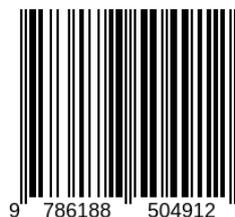
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8.1. Introduction

A geochemical project can generate data sets of varying sizes whether it be the results of twenty samples from an undergraduate university thesis or a national mapping programme completing chemical analyses of tens of thousands of samples. The former project may take a couple of weeks and the latter could span many decades. If data from a single long-duration programme or multiple smaller projects carried out over a long period are to be compared, or used to produce seamless geochemical maps, then strategies need to be adopted to mitigate any changes that may occur to the methodology over a long time. Figure 8.1 from the original Geochemical Atlas of Alaska¹ (Weaver *et al.*, 1983) illustrates the problem of combining disparate data sets. The prominent geochemical features visible relate to map sheet boundaries rather than any real natural geochemical variation. The results from the different map sheets need to be levelled such that a seamless geochemical map can be produced, irrespective of field campaign boundaries.

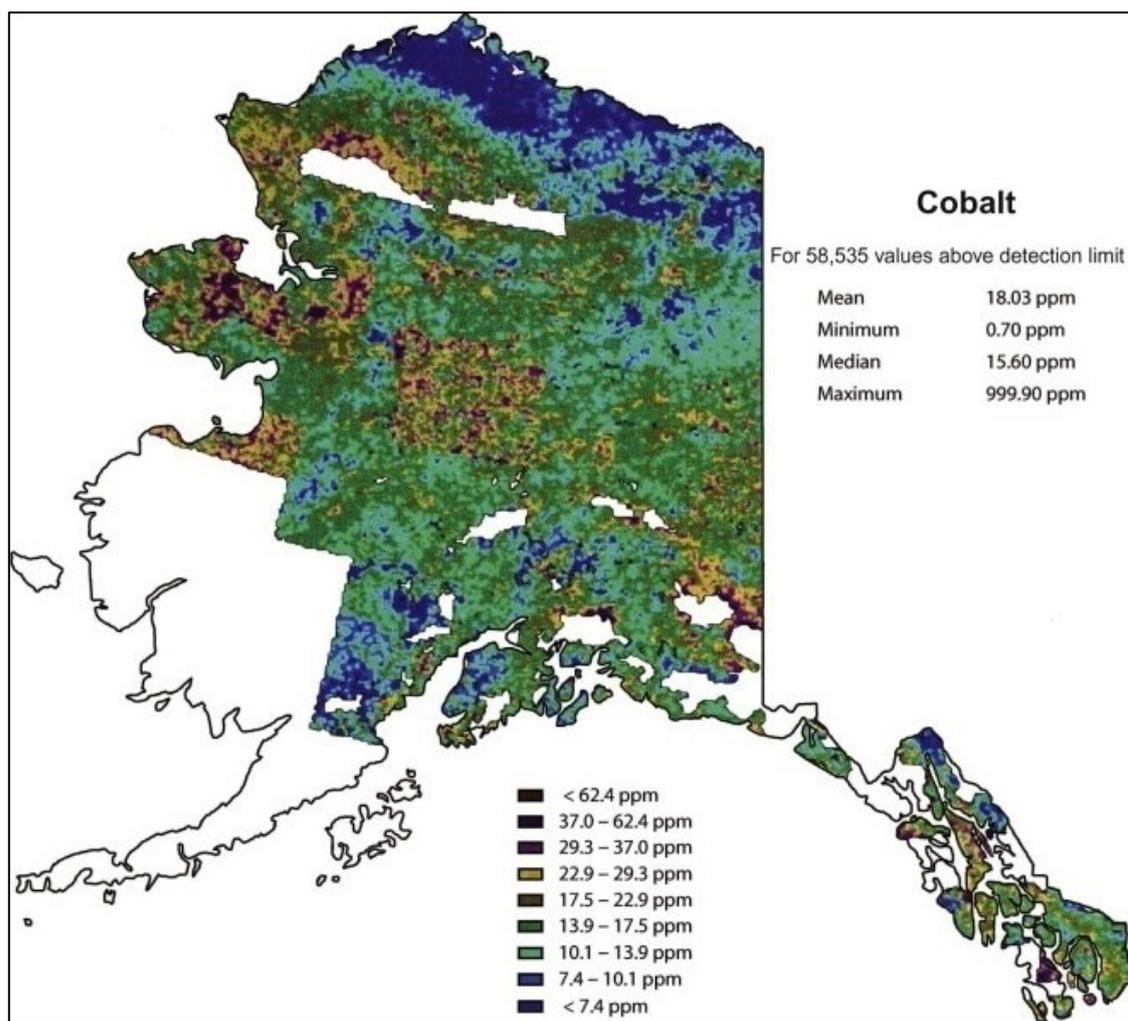


Figure 8.1. Cobalt distribution map from the original Geochemical Atlas of Alaska (Weaver *et al.*, 1983) modified by Smith *et al.* (2013, Fig. 4, p.172). Large blocks of unlevelled data, identifiable by their straight-edge boundaries (map sheet boundaries), show the effects of uncorrected bias in the analytical results.

This chapter discusses the strategies and methods available to make existing geochemical data sets more compatible and recommends how we should future proof our geochemical data. The primary method described is that of parametric data levelling with real examples from the British Geological Survey's (BGS) G-BASE project (Johnson *et al.*, 2005; Everett *et al.*, 2019).

¹ Subsequently updated and revised by Lee *et al.* (2016)

Before the advent of global recommendations to standardise methods of collecting and analysing geochemical samples (Darnley *et al.*, 1995), it was not easy to combine or compare the geochemical results generated by different projects and organisations at local through to global scales. Better coordination of procedures has meant that it is now easier to compare directly regional geochemical data sets from around the globe (*e.g.*, Reimann *et al.*, 2012). Hence, useful and meaningful variations in the distribution of chemical elements can be described and discussed with confidence. A particularly important part of the recommendations is the use of control samples in the chemical analysis. The primary and secondary reference materials (abbreviated to PRMs and SRMs and described in Chapter 5 of this Manual) can be used to level chemical results generated over a long time. It is necessary that the reference samples have been regularly submitted for analysis over the period the project lasts, and that the reference materials cover the range of concentrations for the elements being determined.

8.2. Data levelling

All the procedures applied to geochemical results after receipt from the analytical laboratory to make them fit for the purpose of their intended use are collectively referred to as *data conditioning* (Johnson *et al.*, 2018). The process of adjusting a set of results to combine it with another existing set to give a single seamless geochemical map is called *data levelling*. It should be noted that data conditioning includes procedures to assess whether data levelling is needed. Levelling is akin to data normalisation in which results, measured under different conditions, are adjusted to a notionally common scale or references. The more general term ‘*levelling*’ is preferred here as the process can be required whether or not the conditions of analysis are the same (see also Annexes A2.1 & A2.2 in this Manual).

It must be emphasised that, if the standard methods for sampling and analysis, as described in this Manual are used (see Section §8.2.1 below), the process required is initially one of inspection to see whether the results need levelling. It is only after exceptional circumstances that the results will need to be levelled.

Such exceptional circumstances may arise if there is a change during a project that spans many years. *For example*, the analytical method may change (including subtle changes to the extraction procedure) or the analytical instrument used for the analyses undergoes significant modification, like a replacement of an X-ray fluorescence tube. Upon the completion of a project that has spanned many years or even decades, a final levelling process to ensure the data fits with other international data sets may also be required. The high-resolution baseline geochemical mapping of the United Kingdom (UK) using stream sediment samples (the G-BASE project) spanned more than forty years during which time analytical methods improved and were changed. This has required several periods of levelling that are summarised in Table 8.1. The final phase of levelling was to ensure the UK stream sediment geochemical atlas (Everett *et al.*, 2019) is compatible with other national stream sediment data sets from around the globe.

8.2.1. Preparation of geochemical data prior to testing whether levelling is required

Before establishing whether a data set needs to be levelled relative to another, certain conditions need to be satisfied regarding the results:

- a) High-quality geochemical results have been received from the chemical laboratory and have been accepted as satisfactory. This is achieved by ensuring the analytical methodology (as described in Chapter 6 of this Manual) has been implemented, particularly concerning the inclusion of reference control samples (see Chapter 7 of this Manual).
- b) The control sample data are available as a supplement to the sample results and should also be stored in the geochemical database. All too often control samples are omitted

from geochemical data sets, so that users do not misuse the control data as ‘real samples’. But this omission makes it more difficult to undertake any levelling of the results many years in the future by those not involved in the original project.

Important note 1: Therefore, an important prerequisite, during the design of a project geochemical database, is that the control samples must be an integral part of the database.

- c) Note that it should be the laboratory’s responsibility to ensure the accuracy of results and that any observed analytical bias is removed before it is accepted by the applied geochemist. This can be verified by repeated analyses of primary reference standards and internal laboratory procedures to correct for analytical bias. The results received from a specific laboratory should be seen, therefore, as consistent and initially requiring no further levelling.

It will be the applied geochemist’s responsibility to routinely carry out checking of the results for any analytical bias. This is achieved by inserting a range of SRMs that are ‘blind’ to the analyst to provide results that can be used in the parametric levelling procedure described below. Sufficient quantities of PRMs and SRMs need to be available to service long contracts with an analytical laboratory or laboratories as the analytical requirements (that is, analytical method and laboratory) are likely to change over a long period of many decades.

Table 8.1. A summary of the levelling reference points for the British Geological Survey’s G-BASE stream sediment data.

<i>Reference Point</i>	<i>Date of first levelling</i>	<i>Method</i>
North Scotland DC-OES	1970s	Parametric levelling using internal reference materials relative to the first batch of results.
Wales XRFS	1993	All samples previously analysed by DC-OES levelled to the new XRFS method, using parametric levelling of internal reference materials repeatedly analysed by both methods. Some complete sample batches were also analysed by both methods to confirm the suitability of levelling.
United Kingdom geochemical atlas	2015	All stream sediment results were levelled to an international reference point using international reference materials.

8.2.2. Testing to see whether an analytical batch requires levelling

Testing to see whether a newly received batch of analytical results requires any levelling can be done by two methods:

- a) Plotting spatial data to generate geochemical images to inspect whether any artefacts can be seen between the boundaries of analytical batches, and
- b) Plotting X-Y graphs for each element for three or more reference standards against their accepted reference values to determine any deviation from a straight line of gradient 1. This is referred to as parametric data levelling.

The first method is most applicable if the new analytical batch is spatially adjacent to existing results. Generally, the process of data levelling will be investigated when complete map sheets or large regions have been sampled and analysed. It is when complete map sheet areas are plotted together that any problems arising between map sheet boundaries can be tested (see Figs. 8.1 & 8.2).

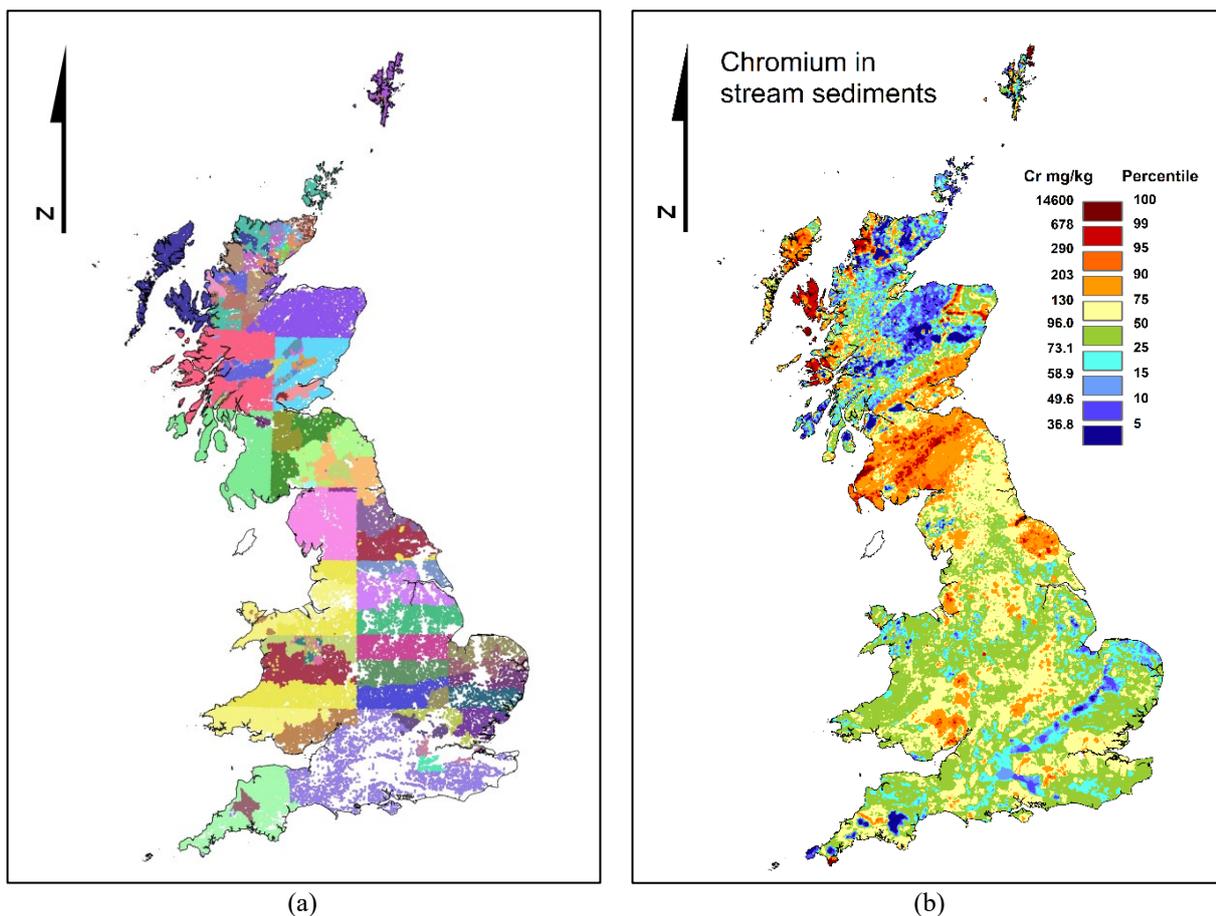


Figure 8.2. (a) A map of the United Kingdom showing the different G-BASE sampling campaigns from 1969–2013. Each colour represents a different year of sampling, which progressed from the north of Scotland to the south of England. This figure shows how most field campaigns were carried out within map sheet boundaries. (b) A map of chromium (Cr) in stream sediments (levelled data) showing no analytical bias associated with any of the map sheet boundaries or field campaigns.

8.2.2.1. Parametric levelling

The method of X-Y plots is referred to as *parametric*, which is a term in statistics that refers to the fact that independent variables (X and Y) can be defined by an equation. The simplest and most common of these is the parametric linear equation:

$$Y = B \cdot X + A$$

where ‘B’ is the gradient of the line, and ‘A’ is the intercept on the Y-axis at X equals zero concentration (Fig. 8.3).

Levelling adjusts the results to a common level, which in the subsequent real examples is the accepted element value for a secondary reference material (plotted as ‘Y’ on the X-Y plot). The two data sets being levelled can be referred to as *disparate* because, as a consequence of changes in methodology (planned or otherwise), the results contain an analytical bias that needs to be removed. The parametric linear equation is the simplest model to work with, and it may be necessary to logarithmically transform the data prior to levelling, and this can be determined from an initial X-Y plot. A good guide is, if when plotted without a logarithmic transformation the data ‘fan out’ at higher levels, then the data should be logarithmically transformed for reasons related to the homogeneity of variance and the subsequent numerical steps (Darnley *et al.*, 1995; see also Annexe A2.2 in this Manual).

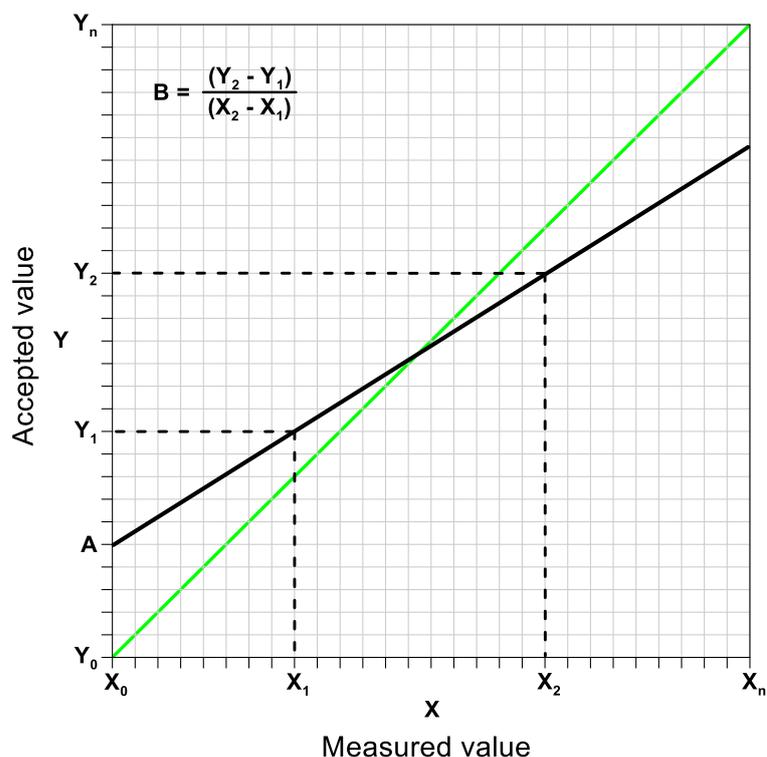


Figure 8.3. Parametric linear equation $Y = B \cdot X + A$ shown graphically. Note that A is the intercept on the Y -axis at $X_0 = \text{zero}$. The green line indicates the 45-degree (1:1) diagonal. Plotted with Golden Software's Grapher™ v20.

Firstly, the X-Y plots of the SRMs from the analytical batches to be levelled are plotted. Where 'X' is the measured value and 'Y' is the SRM accepted reference value, determined by taking the mean value of many earlier analyses (refer to Chapter 5 in this Manual; Heydorn, 2006). A selection of SRMs showing a good range of elemental values is required for each plot and each element determined has to be processed individually. This means a large number of plots are required, so it is useful to automate the process using graphical plotting software for the X-Y plots and regression analysis to determine 'B' and 'A'. This can be done in Microsoft™ (MS) Excel, but other software packages are available which can offer greater automated customisation and consistency, such as R–scripts (Reimann *et al.*, 2008). The more SRMs that are available the better the fit of the modelling.

Figure 8.4 shows various scenarios for how the X-Y plot may look. The situation shown in Figure 8.4a has points plotting on or close to the line of gradient 1 (*i.e.*, value of $B = 1$), and the regression line passes through the origin of the graph (*i.e.*, value of $A = 0$), referred to subsequently here as the *reference line*. In this instance, no levelling of the data is required. Figure 8.4f shows the scenario that may arise where no correlation - linear or non-linear - can be seen between the data sets to be levelled. In this instance, levelling using this procedure must be considered impossible. In cases of non-linearity some form of linearisation, polynomial or non-linear curve fitting might be considered but modelling of this complexity may bring into question the credibility of the modified results.

A generally straight line, parallel to the reference line, indicates a constant positive or negative shift in the results to be levelled (as shown in Figs. 8.4b & 8.4c). If the slope of the regression line is greater or lesser than that of the reference line combined with a positive or negative shift (scenarios shown in Figs. 8.4d & 8.4e), then a correction factor (determined by 'B') and constant (subtraction or addition determined by 'A') will be required to level the element concentration 'X'.

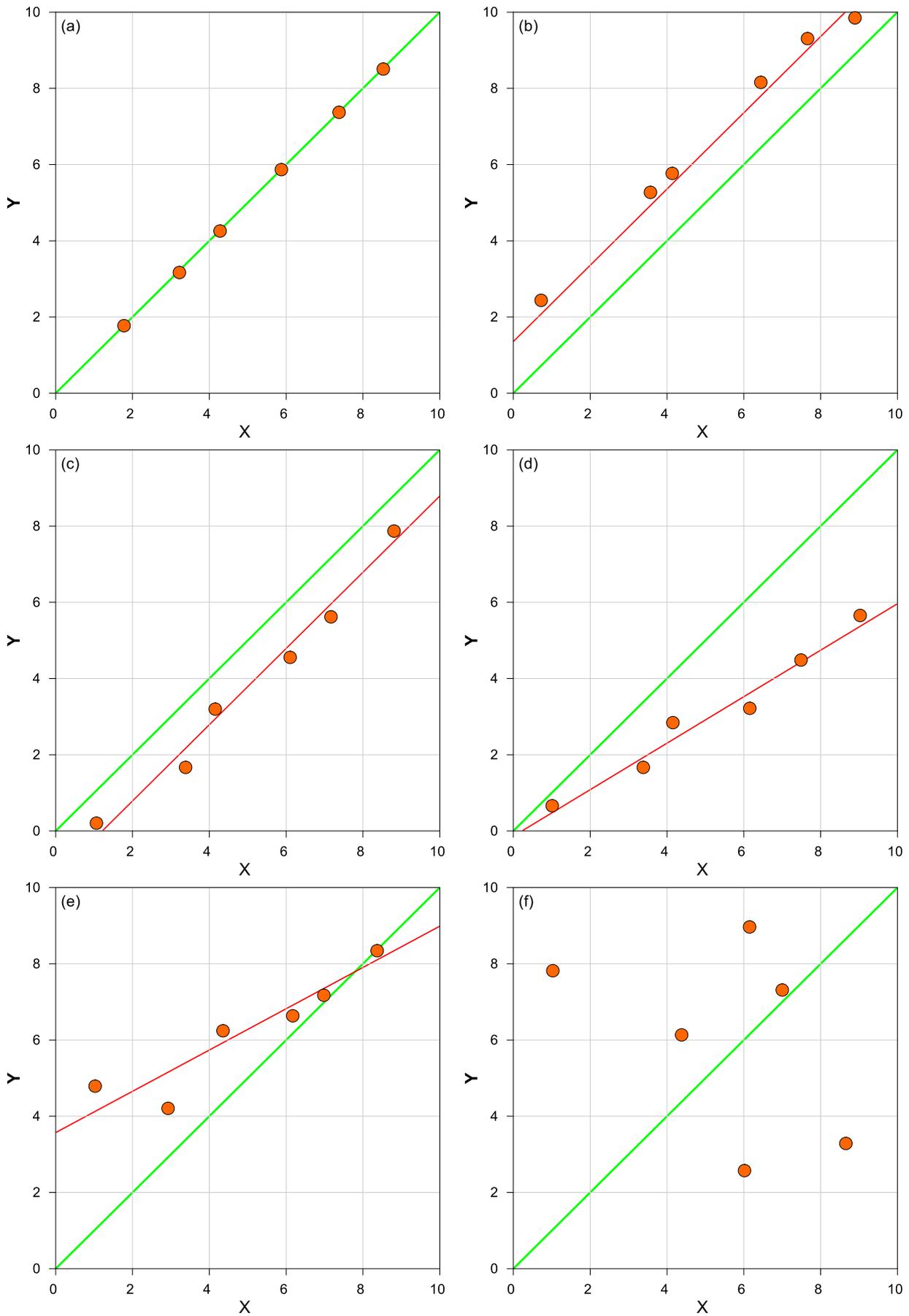


Figure 8.4. Various scenarios are shown by X-Y plots that may occur during parametric levelling. For descriptions of (a) to (f) see text. The green line indicates the 45-degree (1:1) diagonal. Plotted with Golden Software's Grapher™ v20.

8.3. Worked examples

8.3.1. Worked Example 1: Levelling stream sediment results for K₂O from the G-BASE central and eastern England area

The preceding discussion of the X-Y plotting procedure is best explained by using a real example taken from the BGS G-BASE project, as documented in detail in the G-BASE data conditioning procedures manual (Lister and Johnson, 2005). This example shows levelling arising out of routine inspection of control data before the preparation of a map sheet area sampled and analysed over several years. The data used in this example for K₂O results are given in Table 8.2, categorised by laboratory batch number.

Table 8.2. K₂O results of SRM S15B determined by WD-XRFS used for plotting the time series (Shewhart) chart of Figure 8.5. Note that the different aliquots of S15B are given regular sample numbers and are inserted in the analytical batches as routine samples not recognisable by the laboratory. The laboratory must provide the applied geochemist with the recorded results as extracted from the analytical instrument with the laboratory batch number and date of analysis. The colours denote the different batches analysed at different dates.

<i>Sample No.</i>	<i>SRM</i>	<i>Laboratory batch No.</i>	<i>Date</i>	<i>K₂O% WD-XRFS</i>
440022	S15B	10372-0010	26/6/2003	3.04
440687	S15B	10372-0225	6/7/2003	3.03
440822	S15B	10372-0260	7/7/2003	3.02
441087	S15B	10372-0341	12/7/2003	3.04
441622	S15B	10377-0052	22/7/2003	2.84
441887	S15B	10377-0109	25/7/2003	2.86
442128	S15B	10377-0196	29/7/2003	2.83
440287	S15B	10372-0102	9/10/2003	3.03
440422	S15B	10372-0150	13/10/2003	3.03
444022	S15B	10587-0022	25/12/2003	2.75
442422	S15B	10587-0026	25/12/2003	2.83
444217	S15B	10587-0064	28/12/2003	2.79
442928	S15B	10586-0190	15/1/2004	2.74
443196	S15B	10586-0280	23/1/2004	2.77
443417	S15B	10586-0346	28/1/2004	2.78
443668	S15B	10586-0417	2/2/2004	2.76
443947	S15B	10586-0509	16/2/2004	2.76
444617	S15B	10719-0109	27/5/2004	2.74
445087	S15B	10719-0373	16/6/2004	2.74
445622	S15B	10721-0097	2/7/2004	2.73
445828	S15B	10994-0048	27/12/2004	2.72
446447	S15B	10994-0323	19/1/2005	2.74
447028	S15B	10995-0074	9/2/2005	2.68

The British Geological Survey (BGS) carried out a high-resolution geochemical mapping programme of the United Kingdom (Johnson *et al.*, 2005) that commenced in 1969 and was finally completed in 2013, a span of 44 years. Figure 8.2a shows a map of the annual G-BASE field campaigns from 1969 to 2013, each colour representing a different field campaign year as the sampling progressed generally from north to south during the summer months. Within an annual field campaign, the 1000s of samples collected would have been analysed in more than

one analytical batch and these are not distinguished on the field campaign map. Figure 8.2a shows how the sampling campaigns were often carried out constrained by map sheet boundaries. Prior to the production of each map sheet geochemical atlas, data levelling was undertaken to give seamless geochemical maps and to avoid the analytical bias relating to map-sheet boundaries, as is seen in Figure 8.1. This was achieved by studying the results from the SRMs submitted blind to the laboratories for each element in turn to identify any analytical bias introduced during a field campaign or analytical batch. The G-BASE analytical batch consisted of 500 samples, comprising five batches of one hundred samples submitted from the field (field batch) and including two SRMs per hundred samples (Johnson *et al.*, 2018). The SRMs chosen for inclusion were selected to be of similar chemical composition to the samples being submitted and a number of different SRMs per laboratory batch were inserted to give a range of element concentrations to determine any analytical bias.

The data levelling was the last of the G-BASE data conditioning procedures (Lister and Johnson, 2005), performed before preparing the final atlas sheet data sets. The levelling proceeded as follows:

- a) **Gather the geochemical results for inspection.** Analytical batches for all the samples of the map sheet to be levelled are downloaded from the laboratory results database. From this, all the SRM results are extracted. The SRM samples, when submitted for analysis, were assigned normal sample numbers to be kept blind from the analyst and, thus, the SRM identity has to be reassigned, a process helped when the analytical results are merged with the field database (which identifies control samples).
- b) **Plot time series charts.** Time series charts (Shewhart plots) like that shown in Figure 8.5 (Table 8.2) are plotted for each SRM for every element determined. With more than forty elements and five SRMs, this gives two hundred time series charts. So, this plotting needs to be automated with a systematic naming convention for the computer plot files generated. Such software was not available for much of G-BASE's history and plots were done individually initially by hand and later in MS Excel.

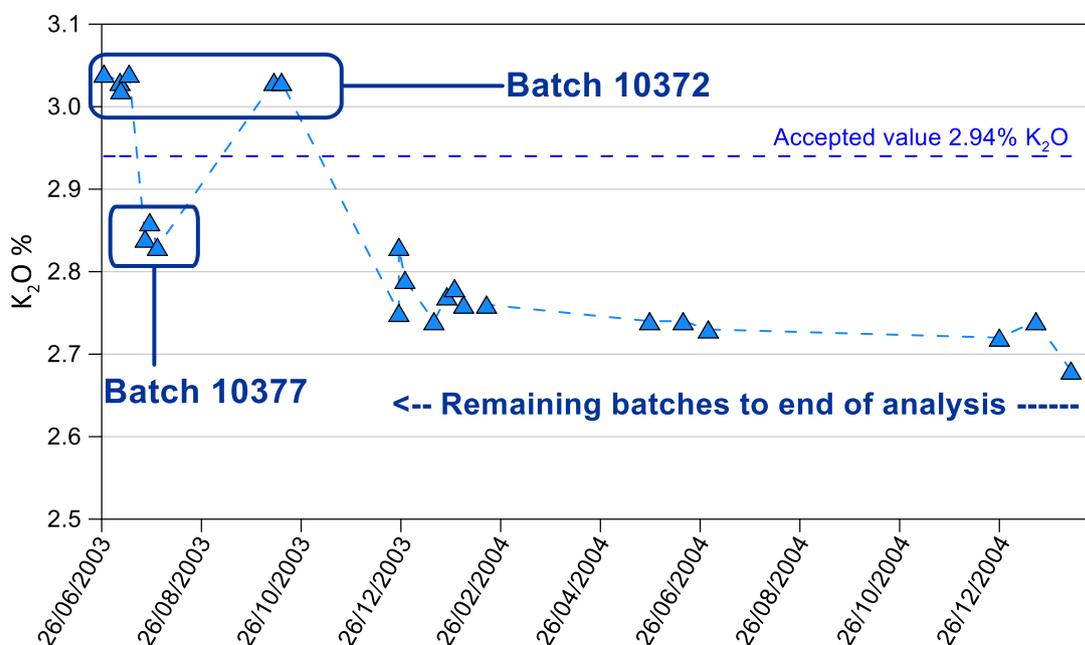


Figure 8.5. A time series (Shewhart) plot showing the K₂O% results (Y-axis) for secondary reference material S15B plotted against the date of analysis (refer to Table 8.2 for results). The blue dashed horizontal line represents the accepted value for SRM S15B. These results were generated when the BGS XRF laboratory was undergoing major changes during the latter half of 2003. Analytical differences can be seen in three groups, namely, batches 10372 and 10377 and the remaining batches. The chart indicates clearly some analytical bias between batches during 2003. Plotted with Golden Software's Grapher™ v20.

- c) **Look for significant changes in the time series charts.** Each chart is inspected for significant changes from a horizontal trend and if deviations are seen in several or more elements and for the different SRMs, then there is clearly an analytical problem introducing analytical bias. Figure 8.5 shows an example of this procedure. Further investigation revealed that in the second half of 2003 the XRF machine started to develop problems, which eventually led to the X-ray tube being replaced and the instrument being recalibrated. The laboratory batches affected are identified and the SRMs from these batches are used to level the results.
- d) **Make X-Y plots for the SRMs for each element requiring levelling.** For each affected laboratory batch X-Y plots are plotted and inspected with reference to Figure 8.4 to assess the nature of the levelling required or if indeed levelling can be done. In the worked example given here, three groups of affected samples are identified, namely, batch 10372, batch 10377 and batches from after 26/12/2003 (Fig. 8.5). X-Y plots for the three groups, tabulated in Table 8.3, are given in Figures 8.6 to 8.8 (prepared initially by using the MS Excel scatterplot graph option with inserted trend line and equation; the charts were subsequently plotted with Golden Software's Grapher v20 for this Manual). All three plots show a very close fit of the data to the regression line. The coefficient of determination, R^2 , is very close to 1.0. The closeness to the 45-degree (1:1) reference line on the X-Y plots shows the levelling to the results will be small but is subtly different for the different batches.

Table 8.3. Results for different SRMs were extracted from analytical batches before the commencement of levelling of the central and eastern England map sheets. The table below represents the batches identified on the Shewhart charts of Figure 8.6: (a) Laboratory Batch 10372 (Fig. 8.6). (b) Laboratory Batch 10377 (Fig. 8.7). (c) Laboratory batches after 26/12/2003 (Fig. 8.8), all charts plotted against (d) The Accepted SRM value.

SRM ID	(a) Batch 10372	(b) Batch 10377	(c) Batches after 26/12/2003	(d) Accepted SRM value
	X-axis K ₂ O % values in different batches			Y-axis values
S13	–	2.078	2.006	2.170
S13B	2.324	2.283	2.227	2.290
S15B	3.030	2.843	2.752	2.940
S23B	3.790	3.790	3.784	3.860
S58S	2.144	1.993	1.896	2.040

- e) **Apply the proposed correction factors.** The regression equations determined for each of the three groups of samples (given in Figs. 8.6 to 8.8) are used to correct the data from the respective analytical batches. All the results in the batch (control samples included) for every element identified as requiring correction. The following shows how the SRM sample S15B is corrected in each of the three groups given in this worked example. All the sample K₂O results from each analytical batch will be similarly corrected in a similar manner. It is stressed that this is a tedious procedure and must be carried out with the utmost care.

Batch 10372: K₂O = 3.030%, regression equation $Y = 1.0811 * (X - 0.2685)$;
corrected value = $(1.0811 * 3.030) - 0.2685 = 3.007\%$ K₂O

Batch 10377: K₂O = 2.843%, regression equation $Y = 1.0455 * (X - 0.0796)$;
corrected value = $(1.0455 * 2.843) - 0.0796 = 2.893\%$ K₂O

Batches after 26/12/2003 (from new, recalibrated X-Ray tube):

$K_2O = 2.752\%$, regression equation $Y = 1.0062 * (X + 0.0872)$;

corrected value = $(1.0062 * 2.752) + 0.0872 = 2.856\% K_2O$

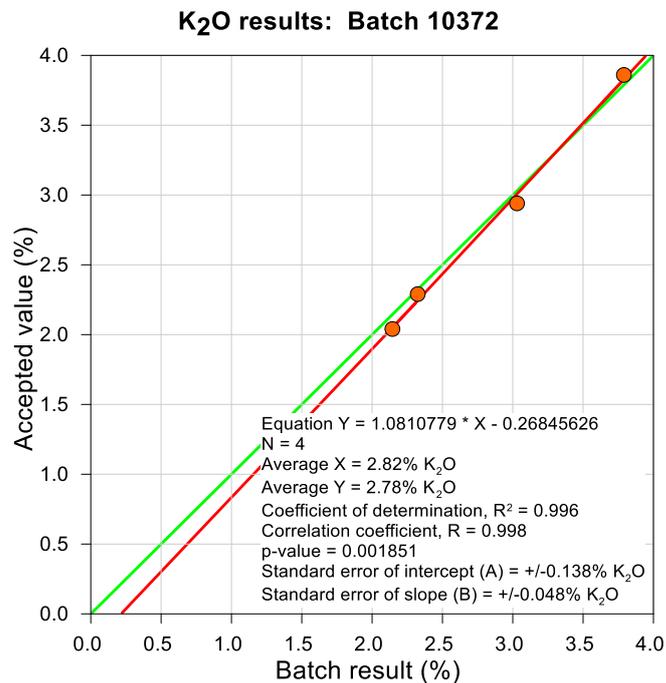


Figure 8.6. Regression analysis of the K_2O results for SRMs from laboratory batch 10372 (using results in Table 8.3a initially in MS Excel to plot X-Y values and fit a linear trend line and regression equation). The green line indicates the 45-degree (1:1) diagonal, and the red line is the fitted linear correlation line. R is the linear correlation coefficient, and R^2 is a statistical measure of how close the data are to the fitted regression line. Plotted with Golden Software's Grapher™ v20.

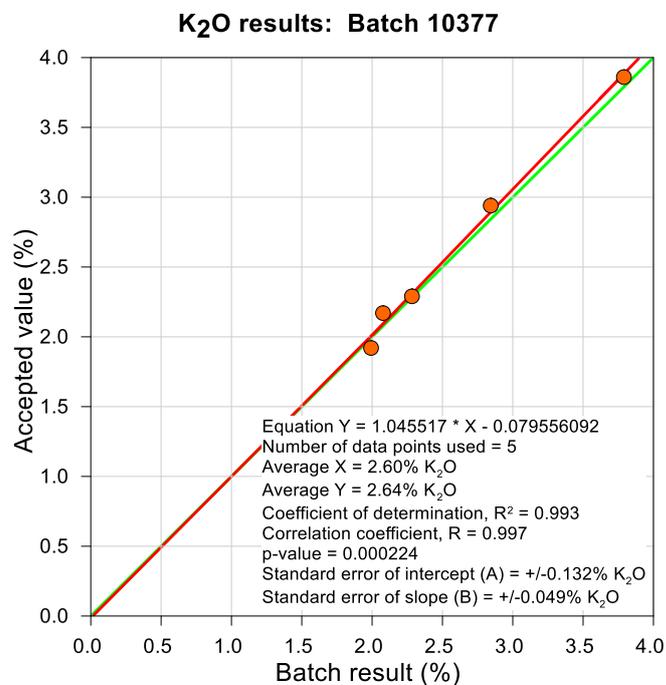


Figure 8.7. Regression analysis of the K_2O results for SRMs from laboratory batch 10377 (using results in Table 8.3b initially in MS Excel to plot X-Y values and fit a linear trend line and regression equation). The green line indicates the 45-degree (1:1) diagonal, and the red line is the fitted linear correlation line. R is the linear correlation coefficient, and R^2 is a statistical measure of how close the data are to the fitted regression line. Plotted with Golden Software's Grapher™ v20.

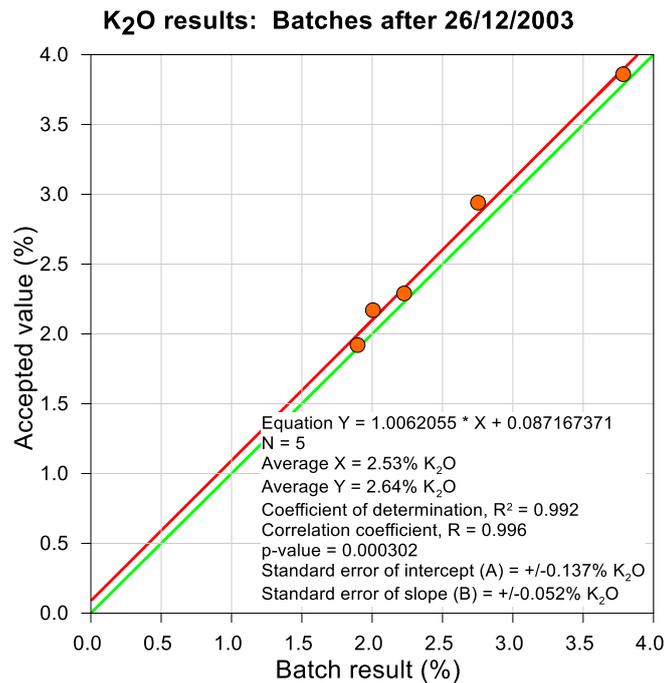


Figure 8.8. Regression analysis of the K₂O results for SRMs from all batches after 26/12/2003 (using results in Table 8.3c initially in MS Excel to plot X-Y values and fit a linear trend line and regression equation). The green line indicates the 45-degree (1:1) diagonal, and the red line is the fitted linear correlation line. R is the linear correlation coefficient, and R² is a statistical measure of how close the data are to the fitted regression line. Plotted with Golden Software's Grapher™ v20.

- f) **Replot the time series chart with the corrected results.** The time series chart can be replotted for each SRM and element. Figure 8.9 visually shows the extent to which the various batches have been corrected. The most significant change is the *ca.* 0.1% K₂O raising of concentrations for samples analysed after 26/12/2003 when the new XRF instrument was recalibrated.
- g) **Plot geochemical map sheets with corrected results.** Once the results for a map sheet area have been corrected by levelling to the satisfaction of the applied geochemist, the geochemical maps can be produced. Figure 8.10 shows the regional geochemical map of K₂O for the area covered by the worked example above. Here the changes are subtle such as the raising of areas to the next percentile level as shown within the red circle. For environmentally sensitive elements, such as As, this raising to a higher percentile level could have significant implications for the area affected. The impact of the levelling procedure shown here, arising from anomalies as seen in a time series chart, and caused by instrument recalibration, is not as striking as the changes observed when levelling across campaign/map boundaries as shown in Figure 8.1. Plotting the geochemical images is an important part of the iterative process to level the data. It is important to look at the images in the context of other parameters (*e.g.*, sampling campaign boundaries or analytical batches) that may cause analytical artefacts.

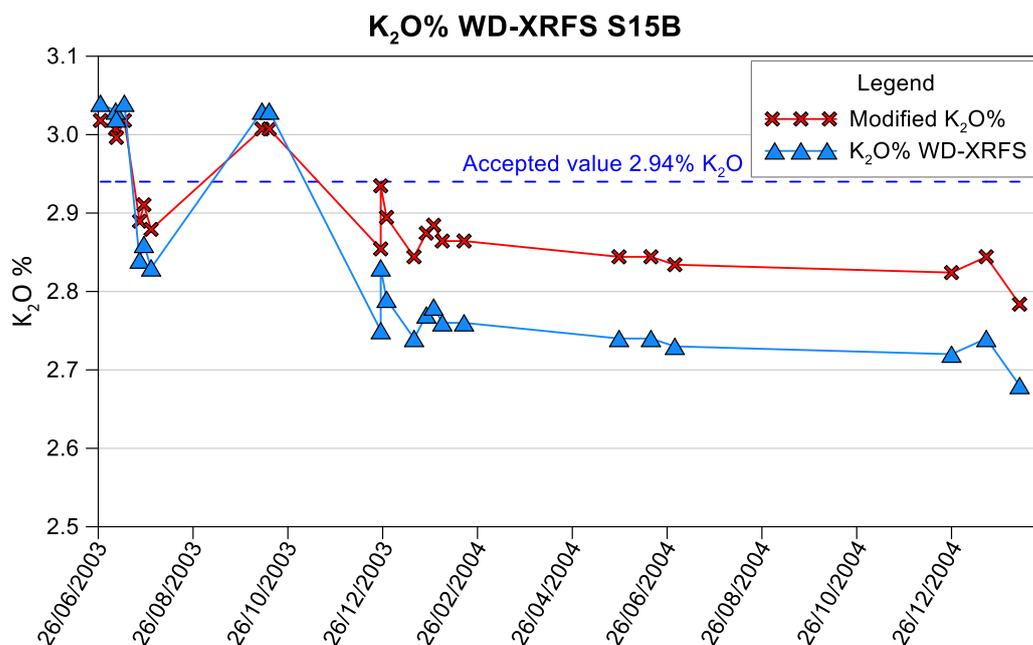


Figure 8.9. Time series plot (Shewhart plot) for SRM S15B for K₂O% showing the original and corrected results from Table 8.4 (from Johnson et al., 2018, Fig. 5.13, p.96). Plotted with Golden Software's Grapher™ v20.

Table 8.4. The original and modified K₂O% results of SRM S15B are displayed in the time series (Shewhart) plot of Figure 8.9. Note that SRM S15B was inserted as a routine sample in the analytical batches and blind to the laboratory. The results were subsequently extracted from the different batches, as indicated by the Laboratory No. and date. Refer to text for explanations.

Sample No.	SRM	Laboratory No.	Date	K ₂ O% WD-XRFS	Modified K ₂ O
440022	S15B	10372-0010	26/6/2003	3.04	3.02
440687	S15B	10372-0225	6/7/2003	3.03	3.01
440822	S15B	10372-0260	7/7/2003	3.02	3.00
441087	S15B	10372-0341	12/7/2003	3.04	3.02
441622	S15B	10377-0052	22/7/2003	2.84	2.89
441887	S15B	10377-0109	25/7/2003	2.86	2.91
442128	S15B	10377-0196	29/7/2003	2.83	2.88
440287	S15B	10372-0102	9/10/2003	3.03	3.01
440422	S15B	10372-0150	13/10/2003	3.03	3.01
444022	S15B	10587-0022	25/12/2003	2.75	2.85
442422	S15B	10587-0026	25/12/2003	2.83	2.93
444217	S15B	10587-0064	28/12/2003	2.79	2.89
442928	S15B	10586-0190	15/1/2004	2.74	2.84
443196	S15B	10586-0280	23/1/2004	2.77	2.87
443417	S15B	10586-0346	28/1/2004	2.78	2.88
443668	S15B	10586-0417	2/2/2004	2.76	2.86
443947	S15B	10586-0509	16/2/2004	2.76	2.86
444617	S15B	10719-0109	27/5/2004	2.74	2.84
445087	S15B	10719-0373	16/6/2004	2.74	2.84
445622	S15B	10721-0097	2/7/2004	2.73	2.83
445828	S15B	10994-0048	27/12/2004	2.72	2.82
446447	S15B	10994-0323	19/1/2005	2.74	2.84
447028	S15B	10995-0074	9/2/2005	2.68	2.78

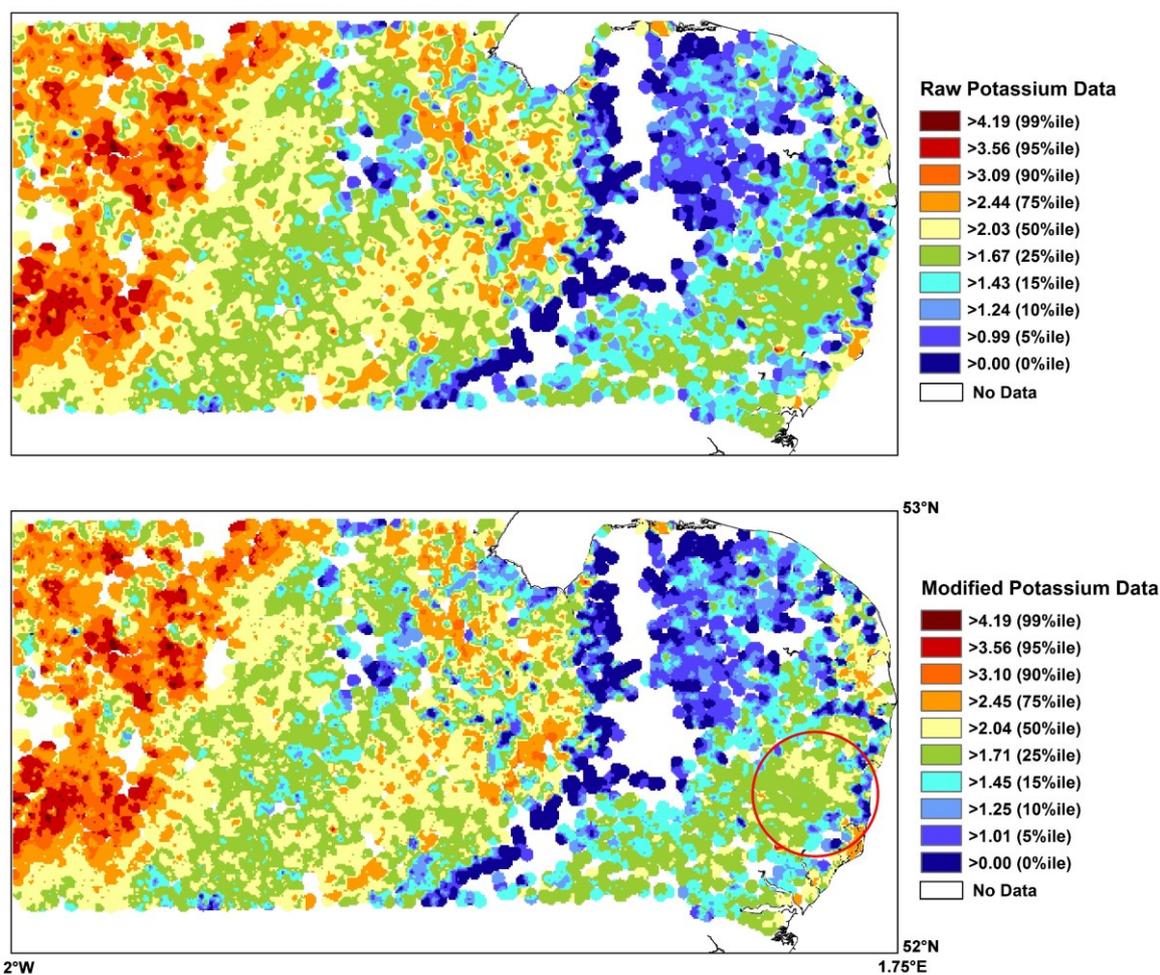


Figure 8.10. Percentile geochemical maps for K_2O in stream sediment samples from central and eastern England. The original results are shown on the top map, the bottom map includes the levelled results. The changes are subtle such as the raising of areas to the next percentile level as shown within the red circle (from Lister and Johnson, 2005, Fig. 39, p.43).

8.3.2. Worked Example 2: Levelling stream sediment results for lanthanum (La) from northern Scotland determined by DC-OES and ICP-MS

Regional geochemical mapping of northern Britain began in 1969 and the analyses of stream sediment samples were carried out by direct current optical emission spectroscopy (DC-OES). Lanthanum (La) was not in the original suite of elements analysed though it was added to the analytes determined several years into the project. Some thirty years later, excess material from these original stream sediment samples was analysed by inductively coupled plasma mass spectrometry (ICP-MS) and La was one of the reported analytes. In Figure 8.11, the area of northern Scotland where La in the stream sediment samples was determined by ICP-MS is put into the context of the large area of northern Britain where La was determined by DC-OES.

The results by the ICP-MS method were reported in two discrete laboratory batches, namely Consignment A and Consignment E.

To align the ICP-MS data to the existing error-controlled and conditioned DC-OES data, an alternative levelling methodology, using cumulative percentiles was employed.

- a) The percentiles of existing DC-OES data from the area to the south of the ICP-MS data area were estimated for the 5th, 10th, 20th, 30th, 40th, 50th, 60th, 70th, 80th, 90th and 95th percentiles. These were then plotted against the ICP-MS data for the same percentiles to determine levelling factors based on comparative percentile distributions over like

lithologies (Everett *et al.*, 2019). This was done independently for data from consignments A and E to give two separate regression equations. This is, therefore, an example of parametric data levelling using percentile values from old (accepted) data and new data to be levelled rather than based on reference material results. The percentile values determined are shown in Table 8.5.

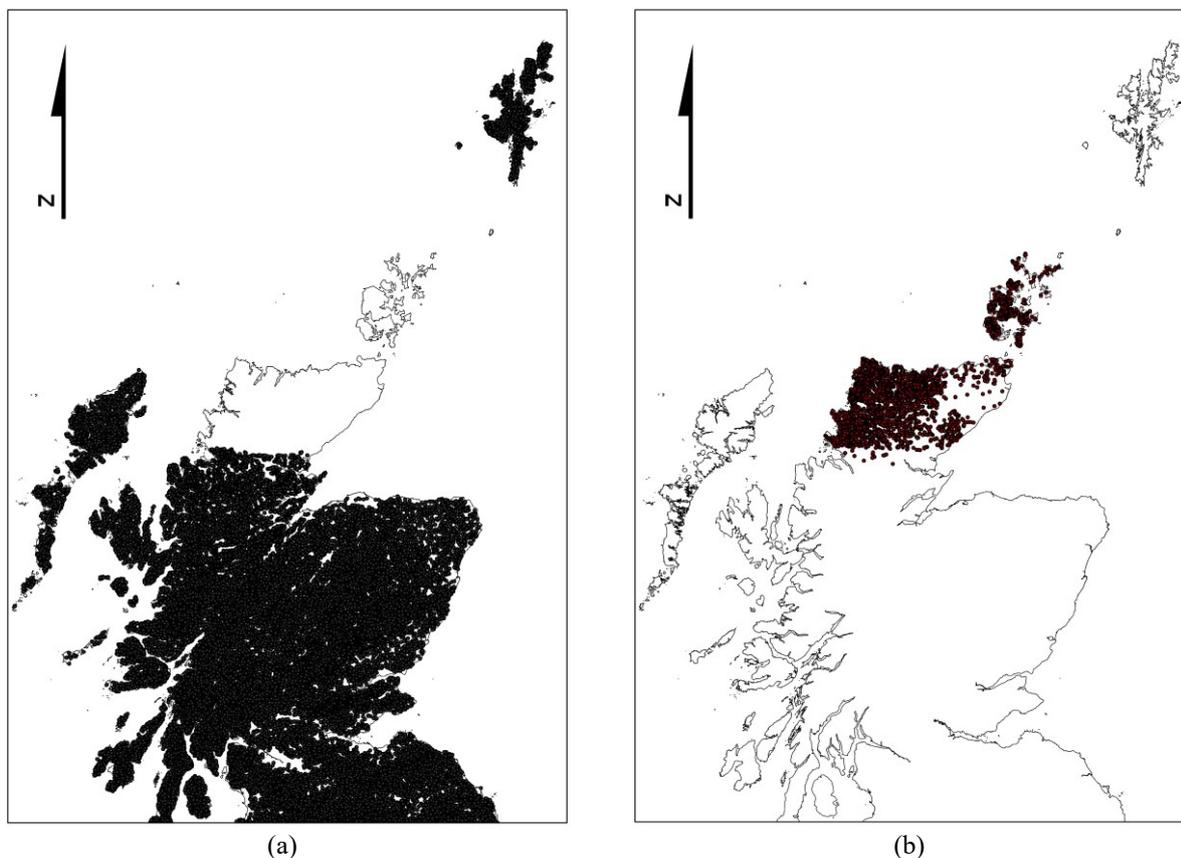


Figure 8.11. Map of northern Britain showing the areas where La has been determined in stream sediment samples by different analytical methods with a 30-year time gap (dark shading). (a) La was determined by DC-OES, and (b) La was determined by ICP-MS.

Table 8.5. Percentiles were calculated for the new ICP-MS La results (consignments A and E) and the original DC-OES results from northern Britain. Consignments A and E contained 2,822 and 1,824 samples, respectively. The original DC-OES data is for 64,530 samples.

Percentile	Consignment A ICP-MS La (mg/kg)	Consignment E ICP-MS La (mg/kg)	DC-OES La (mg/kg)
5	3	7	34
10	6	9	37
20	9	12	41
30	11	15	44
40	14	17	45
50	16	19	48
60	19	21.2	50
70	23	25	53
80	30	30	59
90	41	43.8	69
95	59	62.6	79

- b) X-Y plots of the data from Table 8.5 are shown in Figure 8.12 for the ICP-MS consignments A and E (prepared initially by using MS Excel scatterplot graph option with inserted trend line and equation; the charts were subsequently plotted with Golden Software's Grapher v20 for this Manual). From the regression equations, a correction factor was calculated to level the ICP-MS La results with respect to the DC-OES data.
- c) Where Y is the revised La result and X is the original ICP-MS, the levelling can be carried out for all the newly determined ICP-MS samples, namely:

Consignment A: $Y = 0.8089X + 33.831$

Consignment E: $Y = 0.8135X + 31.471$

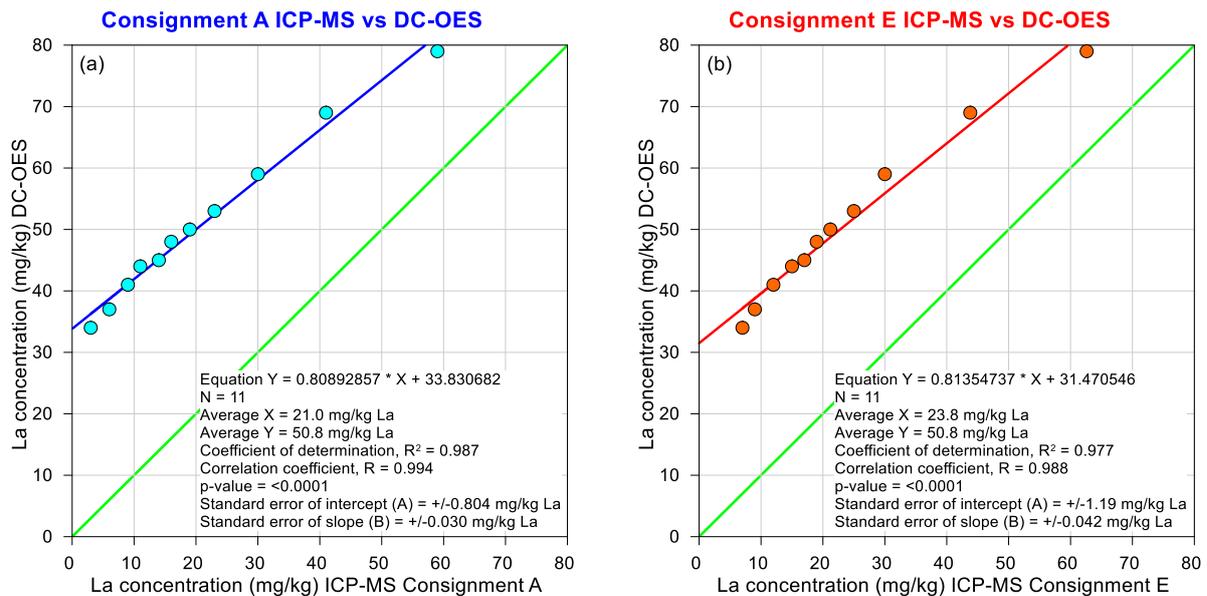


Figure 8.12. Regression analysis (X-Y plots) for the two ICP-MS consignments (A & E) comparing percentiles with the original DC-OES results from northern Britain (refer to Table 8.5). The green line indicates the 45-degree (1:1) diagonal, and the blue in (a) and red in (b) the fitted linear regression lines. R is the linear correlation coefficient, and R^2 is a statistical measure of how close the data are to the fitted regression line. Plotted with Golden Software's Grapher™ v20.

- d) The levelled data can be plotted as a seamless geochemical image (Figure 8.13) based on cumulative percentiles regressions of the two discrete batches of ICP-MS data against the pre-existing error controlled and conditioned DC-OES data.

The worked examples show a procedure to level data when no adequate control samples are available to use the more straightforward method given in Example 1. In such instances, it is necessary to try a range of levelling techniques and have a good understanding of the possible constraints associated with the results being merged. The percentile classification in Table 8.5 shows the higher concentrations of La resulting from the use of a 'total' analytical method (DC-OES) rather than a 'partial' method in which the sample requires a digestion process before its determination is done (ICP-MS). Furthermore, the levelling method assumes similar geological constraints on the distribution of La on either side of the boundary of the two sets of data. In this example, the seamless fit achieved across the joining boundary and the close resemblance of the La and uranium (U) geochemical distribution in northern Scotland (Everett *et al.*, 2019) is satisfactory evidence that the levelling procedure was appropriate.

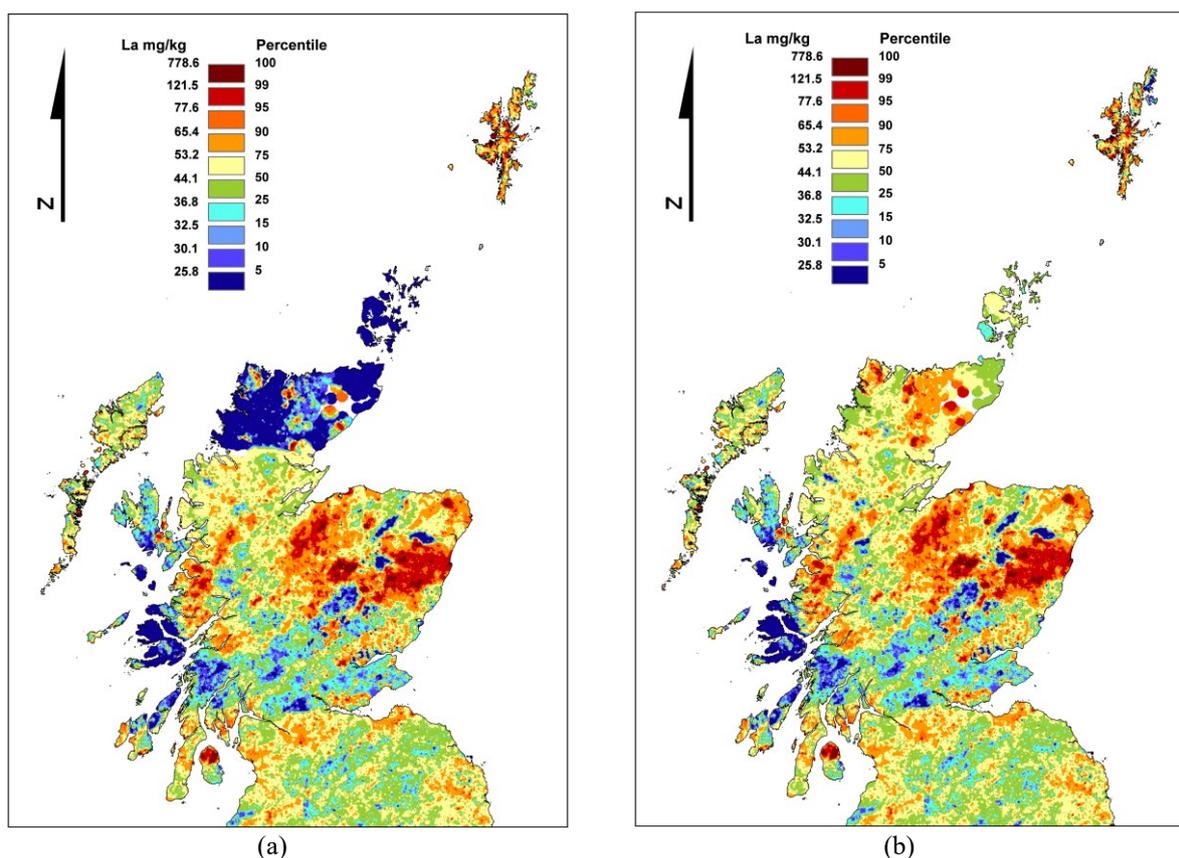


Figure 8.13. Lanthanum in stream sediment samples from northern Britain based on combined data sets from La determined by DC-OES and ICP-MS. Maps with (a) Unlevelled ICP-MS La results, and (b) Levelled ICP-MS La results.

Other levelling procedures are described in Darnley *et al.* (1995, Section §8.4, p.75-78), and more recently by Amor *et al.* (2019) in an example using lake-sediments from western Labrador and north-eastern Québec, Canada. Amor *et al.* (2019) describe a data set of 21,678 samples with disharmony in the original database arising from analyses employing digestions of differing strengths. Nearest-neighbour regression, quantile regression, and moving-median smoothing levelling methods are described by Amor *et al.* (2019). Another detailed example of quantile levelling is given by Daneshfar and Cameron (1998). Here the method is more refined using a weighted regression so the outer quantiles, which have the greater error, have less influence in estimating the regression coefficients. Note that the quantile is the value corresponding to a given fraction of the data and is an alternative expression for percentile when the result is expressed in fractions.

Apart from the normal statistical levelling methods discussed above, there are two additional methods in the literature, the first using geostatistics and the second the compositional nature of geochemical data. Lark *et al.* (2019) describe a multivariate geostatistical model, the linear model of coregionalisation (LMCR), to join the spatial distribution of two data sets, namely the English Representative Soil Sampling Scheme with 6620 samples (Church and Skinner, 1986) and the National Soil Inventory of England and Wales with a total of 5586 samples (McGrath and Loveland, 1992). Williams (2021) proposes a method for levelling multi-element geochemical data sets by levelling all elements and their covariances, simultaneously across all component map sheets by taking full account of the compositional nature of the data. The data sets used were the 28 elements determined by ICP-MS on 23,517 stream sediment samples, which are located in 34 separate Canadian 1:250,000 map sheets (Mackie *et al.*, 2017). It has been shown that this method is computationally feasible, requiring manageable execution time even for large numbers of elements and large numbers of component surveys.

Most likely other statistical or geostatistical levelling and normalisation methods of existing data sets will be published in the future, and the applied geochemist should be careful, as pointed out by Darnley *et al.* (1995, p.75), that these are ‘*geochemically blind*’ because they simply manipulate numbers.

8.4. Other strategies required to future-proof data over long periods

8.4.1. Improved lower detection limit

A significant problem in combining geochemical data sets generated several decades apart is dealing with changes in how missing, semi-quantitative and unreliable results are dealt with (Johnson *et al.*, 2018). This is particularly the case for the semi-quantitative (‘less than’) reporting of results falling below an analytical method’s lower detection limit (LDL).

Firstly, it is important to be aware of the distinction between *recorded* and *reported* results (AMC, 2001a, b). **Recording** of results is a listing of the data as produced by the analytical instrument, including negative values and results that may be below the laboratories cited LDL (uncensored analytical data). The **reporting** of results is a contractual matter between the analytical laboratory and the customer receiving the results. *For example*, the results may be edited by the laboratory, so all recorded results of an element that fall below the cited LDL are reported as ‘<LDL’ (censored data), and if a quantitative value is required for statistical analysis, a value ‘half the LDL’ may be substituted. This introduces a significant statistical bias at the lower end of the analyte’s data distribution. A similar analytical bias is introduced if results are rounded, say to the nearest mg/kg, giving a stepped data distribution. **A geochemical database must comprise entirely of recorded results** and not a mixture of recorded and reported data sets. Sufficient metadata needs to be attached to the data set so that, over a long period, the derivation of the reported results from the recorded results can be understood, reproduced or even modified. This helps to accommodate improvements to analytical precision, and results from areas produced over different periods may have different LDLs and methods of representing semi-quantitative data, described in the associated metadata.

An example from the BGS G-BASE programme is given in Figure 8.14 showing how the changes in the analytical method for the determination of Al in stream water samples greatly reduced the analytical bias at the lower concentrations of the Al data distribution (see other examples in Chapter 7 of this Manual). The change from the ICP-AES to ICP-MS analytical method resulted in a more than ten-fold improvement in the LDL. This meant that, over a long time, when all the results were put together into a single data set to plot a regional geochemical map, a strategy was required to produce a meaningful geochemical image (see Fig. 8.15). It is not possible to generate a seamless geochemical map for this situation, but a common percentile classification can be used for the higher Al results. However, the lower (below detection limit results) for the ICP-AES method have to be distinguished as a different classification on the map giving a non-seamless but honest representation of the results. The consequence is that the Al stream water results for Wales and northern England cannot be reported with the same high degree of resolution as the results for central and eastern England. A seamless map could be produced by using the poorer ICP-AES LDL for all the data giving a consistent lowest percentile class across the entire region. This would be at the expense of seeing meaningful patterns in the lower end of the Al data distribution in the central and eastern England area and degrading the high-quality modern data.

A similar non-seamless map would be generated using early geochemical results reported with less resolution, *for example*, to the nearest mg/kg, and later reported results with better resolution, say, *for example*, to one or more decimal places. A seamless geochemical map could be generated by reducing the precision of the later data (*i.e.*, rounding to 0 decimal places) but again this would result in the loss of recognition of meaningful element distributions. Alternatively, without any degradation of the data set with better precision, a careful choice of

percentile class thresholds can be used to minimise the effect of the ‘stepped’ data generated from the older and poorer analytical methodology.

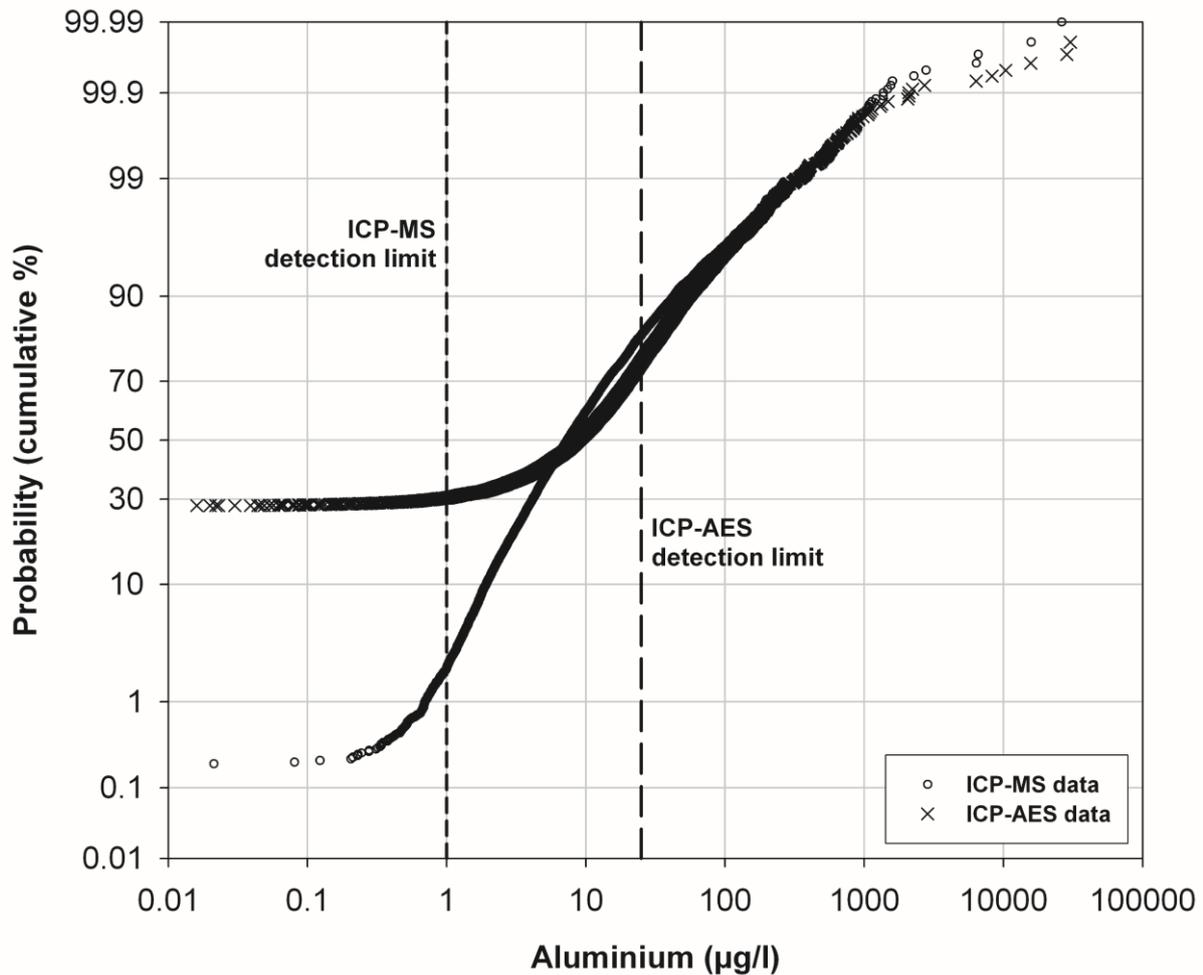


Figure 8.14. Cumulative probability plot indicating true detection limits for samples determined by two different analytical methods. Such plots can demonstrate that the real detection limits (i.e., the point at the lower end of the cumulative distribution curve where the curve becomes horizontal) are often much lower than those cited by the analyst (the cited detection limits are marked on the plot). Recorded data for 10,000 samples from part of central and eastern England (from Johnson et al., 2018, Fig. 5.5, p.88).

It should also be noted here that the analysts generally report more conservative LDLs than the real LDLs that can be determined from the distribution plots or estimated as the practical detection limit (see Chapter 7 of this Manual). From the cumulative probability plot shown in Figure 8.14, the real LDL for the two analytical methods is the point where the lower end of the curves becomes flat, and the data distribution is truncated. Figure 8.14 shows that there is a significant structure to be found in the results reported between the cited LDL and the real LDL and this emphasises the importance of using the *recorded* rather than the reported analytical results. In this example, the reported data (for both ICP-AES and ICP-MS) would have been given as less than (<) the cited LDL losing a lot of interesting distribution information at the lower concentrations of Al in stream water.

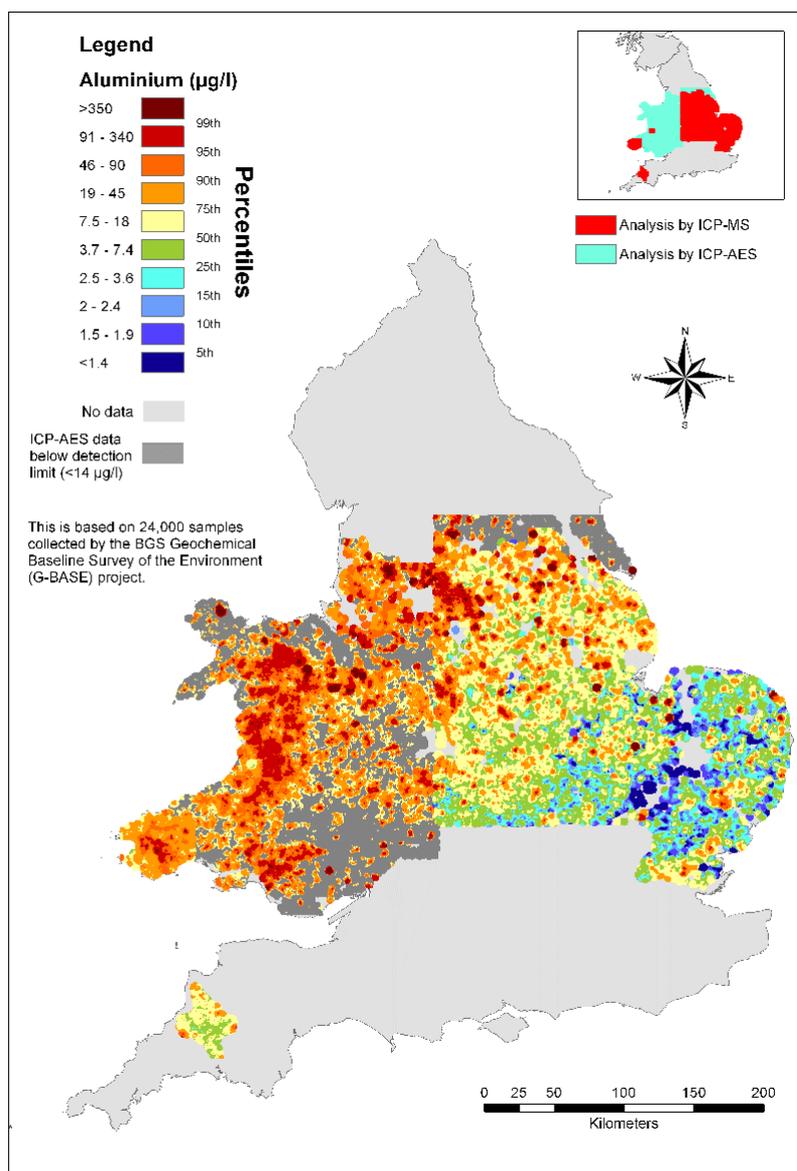


Figure 8.15. Aluminium in stream water samples from England and Wales from the G-BASE project illustrates how data sets with different lower detection limits can be combined (from Johnson et al., 2018, Fig. 5.14, p.98).

Important note 2: The laboratory MUST provide the applied geochemist with the *recorded* results as produced by the analytical instrument, including negative values (uncensored data). The geochemical database MUST NOT include a mixture of recorded and reported results.

Important note 3: Secondary Reference Materials (SRMs) of different chemical composition must always be introduced systematically in the analytical batches of geochemical surveys as their results can be used in the future for levelling disparate data sets. At least five different SRMs will be needed for each sample type to cover the concentration ranges of all elements. Hence, large quantities of each SRM are required to be made to cover the duration of long-running surveys such as the Global Geochemical Reference Network project, and enough material should remain for future use and for standardising new SRMs.

8.4.2. Monitoring changes to the geochemical baseline over long periods

It is important to distinguish between changes in the geochemical baseline arising from different methodologies used to quantify that baseline, and the real environmental changes that occur over time, both natural and anthropogenic. *For example*, the cessation of domestic coal burning has significantly reduced the airborne input of some metals to soil (Haygarth, 1994; McConnell and Edwards, 2008). Long term monitoring of key national sites is, therefore, an important part of future-proofing regional geochemical mapping programmes. This is something that is relevant to a wide range of environmental sciences and needs to be coordinated nationally between environmental institutions and organisations. In the United Kingdom, the Park Grass experiment at Rothamsted Research, Harpenden, Hertfordshire, was initiated in 1856 and is the longest-running experiment on permanent grassland in the world (Silvertown *et al.*, 2006). The experiment was originally designed to investigate the impacts of agriculture but has provided a soil sample archive that has helped to record changes to the geochemistry of the soil (*e.g.*, Zhao *et al.*, 1998; Warneke *et al.*, 2002; Blake *et al.*, 1999; Hartley *et al.*, 2013; Bowley *et al.*, 2017).

With the establishment of standards for the global geochemical baseline mapping of the environment since the mid-1990s (Darnley *et al.*, 1995) more long-term monitoring sites need to be established globally to monitor changes to the soil, stream sediment and stream water. This is particularly relevant to monitoring the changes caused by global-scale industrialisation and urbanisation and accompanying natural climate change. Only by adding a time dimension to the geochemical baseline can the long term future-proofing of global baseline data be achieved.

8.5. Recommendations

This chapter demonstrates the value of routinely and systematically including SRM samples in analytical batches to enable sets of geochemical results produced over a long period to be combined to yield seamless geochemical maps. Methods of chemical analysis will evolve during the lifetime of a long-running project to achieve better precision and accuracy in the measurement of the natural geochemical variability. This will generate some incompatibility with earlier data sets that can be rectified with the use of SRMs. If a national or a global geochemical data set has been rapidly generated, using standardised and consistent methodology throughout, no 'internal' levelling is necessary. It may well be used, however, in the context of other data sets of lesser quality, and in such cases, SRMs from the high-quality data set are still required for the levelling process.

A further very important consideration in any long-running geochemical survey is the financial budget. A fluctuating budget over the lifetime of a project will have an impact on the consistency of data quality. In the case of the BGS's G-BASE project, there were many changes to the annual budget over four decades. A limitless budget is a rare occurrence for any geochemical survey and the analytical scheme is usually a compromise to achieve the best value for the available budget. *The inclusion of a sufficient number of SRMs throughout a project's duration is an insurance policy that ensures the final product is universally applicable and defensibly consistent.* This is particularly important if data are to be applied in a legislative or regulatory context.

Regarding the data levelling procedure, it is recommended that:

- 1) **Sufficient time must be allocated for the data conditioning of the geochemical results.** The final part of this process is testing whether the results need to be levelled to make them consistent with earlier analytical batches or with other external data with which they may be combined or compared, provided the same SRMs have been used. It is our experience from over four decades of generating large regional geochemical baseline data sets, for many countries around the globe, that the data conditioning process is generally under-resourced and not understood by project managers who have no geochemical experience. Making geochemical maps and X-Y plots for a data set, which

may contain results for more than fifty elements, can be very time-consuming. Consistent and rapid output is best achieved by automating the plotting procedures using application software on standard formatted data files containing SRMs results and their accepted values (e.g., R scripts (Reimann *et al.*, 2008) or MS Excel macro routines) – see the example MS Excel file in the Supplementary material.

- 2) **The SRMs should be of a similar material to the sample types being determined.** In some analytical methods, high concentrations of elements can lead to interference in the determination of other elements so these control samples should experience the same interferences as the real samples. Any national or global geochemical survey should consider at the commencement of a large geochemical and long-running project the need to develop a set of SRMs (see Chapter 5 of this Manual). *Experience from past geochemical mapping projects would suggest that at least five different SRMs will be needed for each sample type to cover the concentration ranges of all elements (e.g., see the range of different SRMs used by the G-BASE project in Table 8.3).*
- 3) **A number of different SRMs should be routinely analysed in every batch of samples** so that the X-Y plots, such as those shown in Figures 8.6 to 8.8, provide a meaningful regression analysis over a range of concentrations for all the elements determined. The number of SRMs inserted into a batch of 100 samples should be a minimum of two if the active project is collecting 1000s of samples. If the project is collecting 100s of samples then this should be increased to four. If the number of samples collected is small (<100) then between 1 in 20 samples and 1 in 10 samples should be an SRM. The number of different SRMs (see point 2 above) submitted in an entire analytical batch of samples must be sufficient to produce satisfactory regression analysis plots.
- 4) **The process of submitting SRMs in batches of samples for analysis should be done independently of the analytical laboratory** with the SRMs being submitted to the laboratories in the guise of normal samples and hence ‘blind’ to the analyst. The analytical contract should include a requirement for the laboratory to routinely determine primary reference materials (PRMs) usually at a rate of four PRMs at the start and end of each analytical batch. This is a procedure the laboratory must do to confirm for itself, as well as to its customer, that the results generated are of acceptable quality. The results of the PRMs can also be used to ensure the final levelling of a completed data set is done to an international standard reference point (e.g., Everett *et al.*, 2018), provided that the same PRMs have been used throughout a long-running project.
- 5) **The geochemistry database storing the geochemical results needs to be carefully designed so it captures all versions of the geochemical results a project will generate.** A project will initially receive laboratory results that will be subjected to data conditioning to produce a project geochemical database, which may be subjected to one or more phases of levelling. It needs to be able to store the original results as received from the laboratory plus the results after they have been verified and conditioned to deal with missing or semi-quantitative results (Johnson *et al.*, 2018). Then for each phase of data levelling, database tables associated with version control need to contain the levelling factors determined by the parametric levelling. In this way, a single geochemical database can be used to access all the versions of the geochemical results from those received from the laboratory to the latest version of levelled data. Most importantly, control data (duplicates, replicates, blanks, PRMs and SRMs) and recommended levelling factors should also be included in the database so future researchers can carry out any further levelling independently of the originators of the original results. This will give a clear audit of any data modifications.
- 6) **National monitoring sites for all types of environmental samples should be set up and coordinated internationally for recording changes to the geochemical baseline over time.** As global geochemical baseline mapping becomes established and the recorded baselines covers many decades, applied geochemists must be in a position to

monitor changes to the baseline with time. The data levelling procedures described here to combine results collected over a long period assume that the geochemical baseline has remained the same. However, urbanisation and industrialisation do change the natural geochemical baseline (Johnson *et al.*, 2011), and more rapid climate change will also cause significant changes in the foreseeable future. It is, therefore, important that long-term national monitoring sites covering a range of environmental materials are set up and coordinated on a global scale. In this way, the process of levelling data between projects can be refined to include real changes to the geochemical baseline over time.

Supplementary material

The following MS Excel file can be downloaded from the [Publications](#) web page of the IUGS Commission on Global Geochemical Baselines:

- **IUGS-CGGB_Chapter-8_Examples.xlsx.**

The MS Excel file contains the data for plotting Figures 8.5, 8.6, 8.7, 8.8, 8.9 and 8.12.

The MS Excel file with the DUPREPLOT routine is included in the Supplementary material of Chapter 7.

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Note: All hyperlinks were checked on the 30th of January 2022.

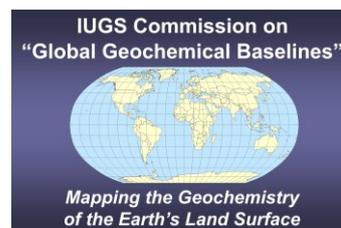
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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 9

Data Management and Map Production

Timo Tarvainen^{1,5}, Steven M. Smith⁵, Peter Filzmoser²,
Alec Demetriades^{3,5}, Igor Bogatyrev⁵, Stefano Albanese^{4,5}

¹ Geological Survey of Finland, Espoo, Finland

² Institute for Statistics and Probability Theory, Vienna University of Technology, Vienna, Austria

³ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

⁴ University of Napoli Federico II, Naples, Italy

⁵ IUGS Commission on Global Geochemical Baselines

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9.1. Introduction

The Global Geochemical Reference Network project with the participation of 193 countries in the world is expected to generate a vast amount of observations and data, which should be efficiently managed. They include:

- Field observations
- Field measurements
- Digital photographs
- Coordinates of sample sites
- Analytical laboratory results
- Quality control results

If the 5-random points in each Global Terrestrial Network grid cell of 160x160 km will be used for the sampling campaigns in all countries, then the maximum number of samples per sample type that will be collected is given in Table 9.1. This estimate includes the samples from all random points in the 7356 GTN grid cells, even those falling in the sea (see Figs. 2.2 & 2.3 in Chapter 2 of this Manual). However, for planning purposes, it is better to have the maximum number of samples that could be taken if all the random points plot on land.

Table 9.1. An estimate of the maximum number of samples that will be collected in the Global Geochemical Reference Network project at a density of 5 samples per 160x160 km GTN grid cell, and field duplicates at ≈5% of sample sites (total terrestrial GTN grid cells = 7356 – see Fig. 2.2).

<i>Sample type</i>	<i>Routine sample</i>	<i>Duplicate sample</i>
Rock	36,780	1839
Topsoil	36,780	1839
Subsoil	36,780	1839
Humus (estimate)	15,000	750
Stream sediment	36,780	1839
Stream water	36,780	1839
Overbank sediment - top	36,780	1839
Overbank sediment - bottom	36,780	1839
Floodplain sediment - top	36,780	1839
Floodplain sediment - bottom	36,780	1839
Total:	346,020	17,301
Grand total:	363,321	

Apart from the safe storage of solid samples, the generated analytical results must be processed and presented. Data verification and validation of sample site information should be carried out by each participating country. However, the Data Management Committee should carry out a final validation before the permanent storage of all field observations and laboratory results.

Data management guidelines have already been given in Chapter 8 by Darnley *et al.* (1995, p.71–82). Here the practical side of data handling and map production methods will be described using the experience gained in three European multinational projects such as the FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005; Tarvainen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006a), the European Groundwater Geochemistry (Reimann and Birke, 2010) and the Geochemical Mapping of Agricultural and Grazing Land Soil – GEMAS (Reimann *et al.*, 2014a, b; Filzmoser *et al.*, 2014; Filzmoser and Reimann, 2014). However, these method descriptions are not intended to limit innovations or styles in data processing and presentation.

The data management methods described herein can be applied to any geochemical mapping programme.

As the FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006a) is the only multinational project that has been carried out according to Darnley *et al.*

(1995) specifications, different data sets will be processed and used as pictorial examples with no interpretation.

9.2. Database structure and data input

Databases and related data management systems are normally used to administer large volumes of information and to keep data consistency within the framework of geographical information systems (GIS). Specifically, GIS uses databases constructed on a relational model. In a relational database, each record in a table is uniquely associated with an identification code (ID), a key record used to establish relationships among multiple tables storing information related to the same objects or entities. Each ID is also a key component to link the informative part of the geographical information with its spatial features. Since the early 1990s, one of the most widely available database software for the management of a relational database has been Microsoft™ Access. Over time, other solutions have been developed for the same purpose, and some of them have been specifically designed and are fully integrated with GIS. In recent years, the [GeoPackage format](#), based on the [Open Geospatial Consortium](#) (OGC) standard, has been introduced for transferring geospatial information including vector features, tile matrix sets of imagery and raster maps at various scales, attributes (non-spatial data) and extensions. A GeoPackage is a database container based on [SQLite](#), and is the most widely used database engine in the world. It is the actual default file format for [QGIS](#) open source software. Hence, the Data Management Committee should develop a structure for entry of all observations and analytical results generated by the project. Input rules and constraints within the database should be used to guarantee the consistency of:

- (i) The field observations, as reported on the rock, residual soil, humus, overbank sediment, stream water, stream sediment and floodplain sediment sheets, which are presented in Appendix 1, and are based on the [FOREGS Geochemical Mapping Field Manual](#) (Salminen, Tarvainen *et al.*, 1998), and
- (ii) The analytical result fields, as given by the laboratories and subsequently verified by the Quality Control Committee. It is stressed that only data that have been validated by the Quality Control Committee should be stored in the database. However, all the original analytical reports and data files from the chemical laboratories should be stored separately.

Apart from the development of a Microsoft™ Access (or similar) database, where only validated data will be stored, individual Microsoft™ Excel Workbooks should be compiled with the analytical results of each sample type for statistical data processing and map plotting.

Important note 1: As relational databases develop over time, and stored data may not be accessed by newer versions, all analytical data and field observations should be stored in simple text format files, such as comma-delimited files (CSV). These files should be kept in each country, and the central depository. This is an important safety precaution.

9.3. Validation of database entries

The field observations and analytical data should be combined. The merged data set should be checked and validated first by the participating countries. As most mistakes are made during the transfer of sample site coordinates, a table of coordinates of each sample type and sample site number should be compiled for each country, and a sample site map of each medium plotted, and all these thoroughly checked by the participating countries. This rather cumbersome validation procedure is necessary to avoid the replotting of geochemical maps when stray samples are found later.

9.4. Handling analytical data below detection limit

In Chapters 6, 7, 8 and 10 it is pointed out that arrangements should be made with all participating laboratories to provide *uncensored* values for the estimation of the practical detection limit for each determinand (element or parameter or measurement or measurand). If this is impossible for any reason, the participating laboratories will apply a fixed detection limit (censored values).

Even in the ideal situation of all Global Geochemical Reference Network samples being analysed during the same period, the analytical data will still contain values below the estimated practical detection limit or laboratory detection limit of the particular analytical method used for their analysis. In such cases, all values reported as less than either the practical or laboratory detection limits are assigned a value of half the detection limit. For example, the detection limit of tellurium (Te) determined by ICP-MS, following a two-step digestion method, was 0.02 mg/kg in soil samples (Salminen *et al.*, 2005; Sandström *et al.*, 2005). Thus, all Te values reported as <0.02 mg/kg were converted to half the value of the detection limit, *i.e.*, 0.01 mg/kg Te. In the FOREGS Geochemical Atlas of Europe, values lower than the detection limit are shown on the plotted maps with the smallest symbol size and belong to the lowest concentration range in the colour scale (Salminen *et al.*, 2005; Tarvainen *et al.*, 2005).

Problems, however, emerge when all samples are not analysed over a short time interval, and are analysed at different periods long apart (see Chapters 7 & 8 in this Manual). In such cases, the sensitivity of analytical methods will vary throughout the project, usually because the samples are analysed using newer generation instruments (see Chapter 8). As a consequence, there will then be multiple practical or laboratory detection limits for all elements determined. This is a quality control ‘*nightmare*’ that should be avoided. However, in such a global project it is important to anticipate such problems and keep the analytical data in their original format, and retain all values below the detection limit in the original database as either text fields (<0.02) or negative values (-0.02). During statistical processing and map plotting the user extracts the data from the original database, and then decides how to handle multiple detection limits in the working copy of the data.

Important note 2: Keep in the Global Geochemical Reference Network database all the original (recorded) analytical data intact with values below the laboratory detection limit as either text fields (<0.02) or negative values (-0.02). For statistical processing and map plotting extract the data from the original database and decide how to handle multiple detection limits in the working copy of the data file.

Important note 3: Replacing determinand values below the laboratory analytical method’s detection limit (DL) by half the DL value ($\frac{1}{2} * DL$) is completely arbitrary. It is done in order to have a numerical value for the statistical calculations and map plotting. Some researchers use a value of $\frac{3}{4} * DL$. It is quite apparent that the actual minimum value below the detection limit of the laboratory’s analytical method is not known. Hence, *uncensored* determinand values are preferred whenever possible, because in these cases the practical detection limit is calculated (see Chapter 7).

Important note 4: Systematic discrepancies in analytical data produced by laboratories over time are discussed in Chapters 7 & 8.

9.5. Handling data greater than the upper limit of an analytical method

Apart from determinand values below the detection limit, there are also values ‘*greater than*’ the upper limit of an analytical method. In such a case, there should be an agreement with the laboratory that the sample solutions are diluted and reanalysed until they could give a real value

for this particular sample. However, in rare cases where the laboratory reports a value greater than the analytical method's upper limit (*i.e.*, >20,000), this value can be designated by adding a decimal number such as 0.9999 (*i.e.*, >20,000 mg/kg = 20,000.9999). Thus, determinand values above the upper limit of an analytical method can be identified in the data set.

9.6. Basic data tables

Tables should be compiled showing the statistical distribution of all determinands in all sample types determined by different analytical methods, *i.e.*, rock, residual soil (top and bottom), humus, stream water, stream sediment, overbank sediment (top and bottom) and floodplain sediment (top and bottom). The tables should provide both the practical and laboratory detection limits for each element (parameter), the percentage of samples with values below detection, the minimum and maximum values, the median absolute deviation (MAD), and a number of percentiles, *e.g.*, 2, 5, 10, 25, 50, 75, 90, 95, 98 (Table 9.2).

The arithmetic mean and standard deviation no longer have a place in geochemistry, as it is well-known that geochemical data do not follow the normal Gaussian distribution (Tennant and White, 1959; Lepeltier, 1969; Sinclair, 1976, 1983, 1986; Reimann *et al.*, 2008). Hence, for the central value and standard deviation, statistical estimators based on ranks should be used, such as the median and median absolute deviation (MAD), respectively (Table 9.2).

Table 9.2. Basic statistical parameters of Zn in sample types collected in the FOREGS Geochemical Atlas of Europe project (Salminen *et al.*, 2005). Zinc in topsoil, subsoil, stream sediment and floodplain sediment were determined by X-ray fluorescence; Zn in humus and stream water was determined by ICP-MS. Notation: MAD = Median absolute deviation; DL = Detection limit.

Parameters	Topsoil	Subsoil	Humus	Stream water	Stream sediment	Floodplain sediment
Number of samples	845	788	367	808	852	749
Order of Magnitude ¹	3.29	3.31	3.27	3.54	3.54	3.99
% samples <DL	1.78	4.82	0.0	0.0	0.0	0.267
	mg/kg			µg/l	mg/kg	
Detection limit (DL)	3.00	3.00	1.00	0.010	1.00	1.00
Minimum	<3.00	<3.00	1.00	0.090	4.00	<1.00
2 nd percentile	3.00	1.50	6.22	0.473	16.0	12.0
5 th percentile	8.20	4.00	13.0	0.597	23.0	18.0
10 th percentile	13.0	13.0	20.0	0.900	29.0	25.0
25 th percentile	27.0	26.0	30.0	1.43	45.0	42.0
50 th percentile	52.0	47.0	45.5	2.61	71.0	65.0
75 th percentile	83.0	75.3	62.6	5.28	109	102
90 th percentile	111	106	91.4	9.76	166	152
95 th percentile	139	132	110	15.4	214	252
98 th percentile	208	171	156	26.8	421	457
Maximum	2904	3062	1863	310	13,866	4911
MAD	27.0	23.0	16.4	1.42	30.0	27.0

Another parameter that is easy to grasp and provides an indication of variation is 'order of magnitude' or 'power'¹, *i.e.*, if two numbers differ by one order of magnitude, one is about 10 times larger than the other; if they differ by two orders of magnitude, they differ by a factor of about 100; if they differ by three orders of magnitude, they differ by a factor of about 1000, and if they differ by four orders of magnitude, they differ by a factor of about 10,000. In the examples shown in Table 9.2 the order of magnitude between the minimum and maximum value

¹ The Order of Magnitude is estimated by converting to logarithms (base 10) the minimum and maximum values, and subtracting the log of the minimum value from the log of the maximum value, *e.g.*, the minimum and maximum values of Zn in Topsoil samples from Table 9.2 are used as example:

$$\log_{10} 2904 - \log_{10} 1.5 = 3.463 - 0.176 = 3.287 \text{ (3.29 to two decimal places).}$$

of Zn for all sample types is approximately similar for topsoil, subsoil and humus (3.27 to 3.31); it is the same for stream water and sediment (3.54), and near to four orders of magnitude for floodplain sediment (3.99). Hence, Zn in floodplain sediment samples displays the highest variation by a factor of 4, *i.e.*, by 10,000 since the minimum value is 0.5 mg/kg Zn (half of the DL) and the maximum is 4911 mg/kg Zn.

9.7. Data distribution

Apart from tables showing the statistical distribution of determinands, it is desirable to provide a graphical display, which allows the visualisation of different statistical aspects of the data.

9.7.1. Cumulative probability plots

Cumulative probability plots (or CP-plots) were originally introduced in geochemistry by Tennant and White (1959), and subsequently by Lepeltier (1969) and Sinclair (1976, 1983, 1986). On a CP-plot, the concentration of the studied element is plotted along the X-axis (log-scale), while the probability of occurrence of a certain value is plotted along the Y-axis (Fig. 9.1). The CP-plot with log-scale allows direct visual estimation of the median (50th percentile) or any other value from the X-axis or the percentage of samples falling above or below a certain threshold from the Y-axis. Further, it allows the assigning of a percentage to any apparent break on the curve and the direct visual detection of data outliers.

Cumulative probability plots have long been used by applied geochemists to partition results into a combination of different populations (Fig. 9.1), and are even useful in establishing more realistic detection limits (see Chapters 7 & 8 in this Manual). If for a certain analytical technique, many results are below detection, then this will be directly visible on the plot, where the flattening of the graph indicates a more realistic detection limit (see Figs. 7.7 and 7.8 in Chapter 7 and Fig. 8.14 in Chapter 8). The percentage of samples below detection can again be directly read from the Y-axis of the plot. For different data sets (*e.g.*, Zn concentrations in different sample types - Fig. 9.2), or results from different analytical techniques, the statistical distribution of all data sets can be directly compared.

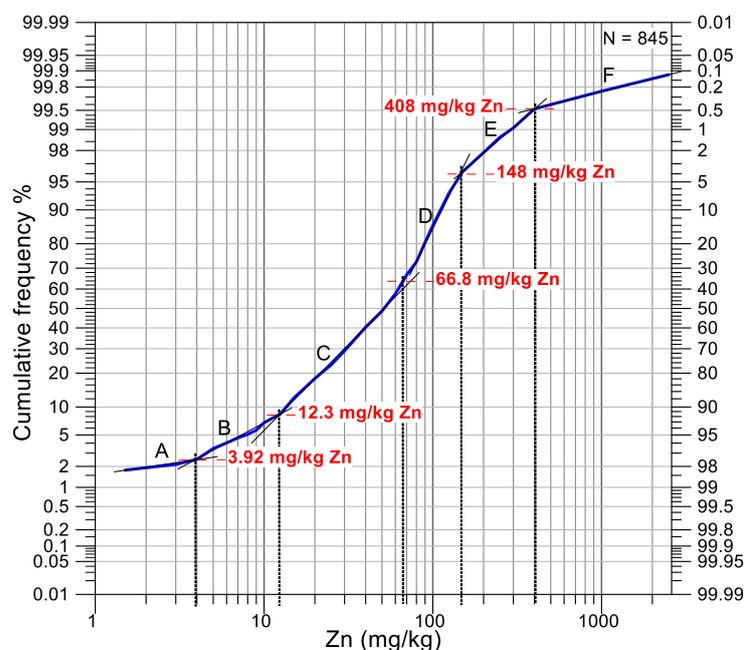


Figure 9.1. Cumulative frequency plot of Zn in floodplain sediment samples determined by X-ray fluorescence, FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005). The cumulative frequency line shows a number of breaks (inflection points), and the distribution has been divided into six log-normal populations (A to F). Plotted with Golden Software's Grapher™ v20 by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) and IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).

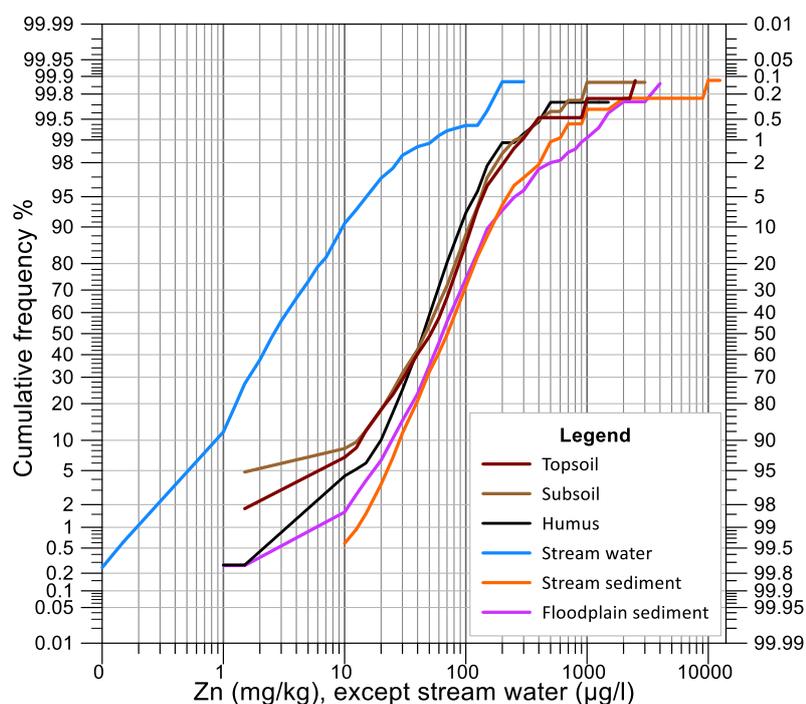


Figure 9.2. Cumulative frequency plot of total Zn concentrations in topsoil, subsoil, humus, stream water, stream and floodplain sediment samples, FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005). See Table 9.1 for basic statistics and number of samples of each medium. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

9.7.2. Boxplots

The boxplot or box-and-whisker plot is a powerful pictorial graphic of Exploratory Data Analysis (Tukey, 1977; McGill *et al.*, 1978; Hoaglin *et al.*, 1983; Kürzl, 1988; Reimann *et al.*, 2008). It is an extremely informative graphical summary of the statistical distribution of a determinand. The following parameters can be extracted from the boxplot: minimum value, 25th percentile (1st quartile), median, 75th percentile (3rd quartile) and maximum value. Further, lower and upper outliers are displayed, and these are beyond the value of 1.5 times the difference between the 75th and 25th percentiles (known as the “h-spread”).

The notched box-and-whisker plot is a modification of the standard boxplot (McGill *et al.*, 1978). The notch about the median line defines the 95% confidence level on the median. The confidence level on the notches of multiple boxplots is set to allow pairwise comparison with respect to the median to be performed at the 95% confidence level by examining whether two notches overlap (see Fig. 9.3).

A boxplot can be drawn for a single determinand, or a multiple boxplot can be plotted to compare the statistical distribution of the same determinand in different sample types (Fig. 9.3), or to compare the distribution of the same parameter determined by different analytical methods. When the notches about the median of two or more boxplots do not overlap, then there is strong evidence that the medians are significantly different at the 5% significance level. In the reverse case, where the notches about the median of two or more boxplots do overlap, then there is strong evidence that the medians are not significantly different at the 5% significance level, *i.e.*, there is only a 1 in 20 likelihood that this could have occurred by chance.

An interesting feature of the notched box-and-whisker plot is the folding-in behaviour of the 25th or 75th percentile when the value of the 95th confidence interval around the median extends beyond either the 25th or 75th percentile. In such cases, little confidence can be placed in these statistical distributions, indicating that more data are required.

Further, the boxplot can be used to define class intervals for geochemical map plotting (see below).

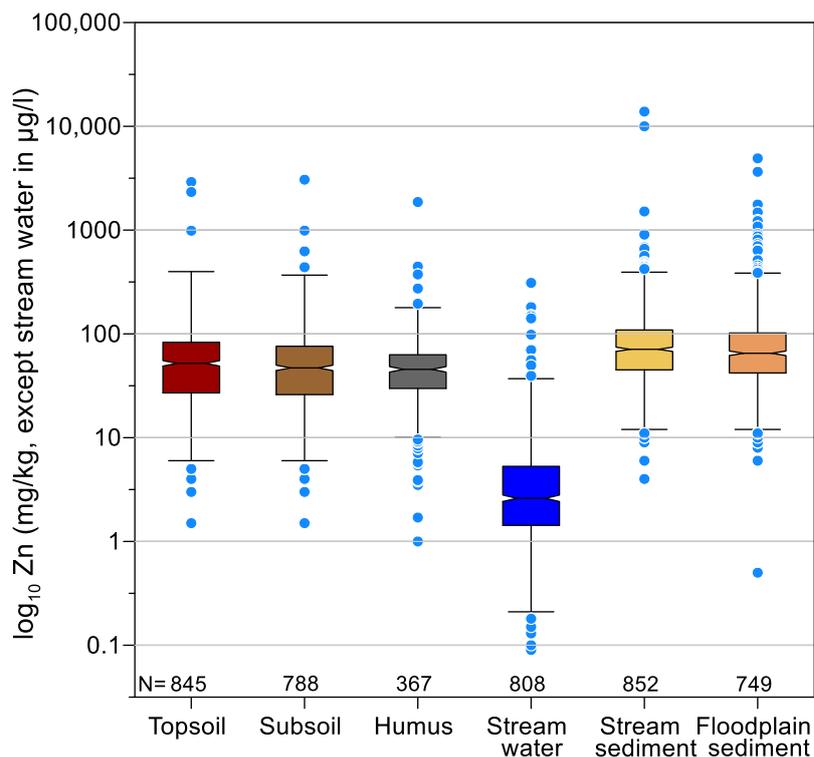


Figure 9.3. Boxplot comparison of \log_{10} -transformed total Zn concentrations in topsoil, subsoil, humus, stream water, stream and floodplain sediment samples, FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005). The advantage of using \log_{10} -transformed data is that the statistical distribution is more symmetric and lower and upper outliers are displayed. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

9.7.3. Combination of histogram, cumulative frequency, one-dimensional scattergram and boxplot

The histogram is the most widely used diagram for displaying the statistical distribution of geochemical results (Till, 1974; Koch and Link, 1970; Sinclair, 1983; Reimann *et al.*, 2008). The concentration of the studied element is plotted on the X-axis, and the frequency of occurrence (or the % frequency) on the Y-axis. The selection of class intervals is a key issue because this will show the statistical distribution of the studied determinand. The histogram is also used by some researchers for the visual estimation of populations and the threshold between background and anomalous values. Figure 9.4 shows a histogram and the difficulty of estimating populations. Hence, if the histogram is going to be used for population splitting, it is better to be combined with the cumulative frequency curve, the one-dimensional scattergram and the boxplot as displayed in Figure 9.4. This combination provides a powerful insight of the data distribution (Reimann and Caritat, 1998; Reimann *et al.*, 2003, 2008; Reimann and Birke, 2010; Filzmoser *et al.*, 2014).

9.8. Map production

The final cartographic product of all geochemical surveys, whether at the continental, regional or local scales, is a geochemical map on which the spatial distribution of a determinand is displayed. Geochemical maps may be grouped into:

- (i) Point-symbol maps showing determinand values at the sample locations.
- (ii) Colour-surface contour maps based on interpolated and smoothed data.

- (iii) Colour-surface contour maps with superimposed variable-size dots at the sample locations, and
- (iv) Multi-component maps displaying the simultaneous variation of a number of elements of interest, and these include factor analysis scores maps or colour composite RGB² maps.

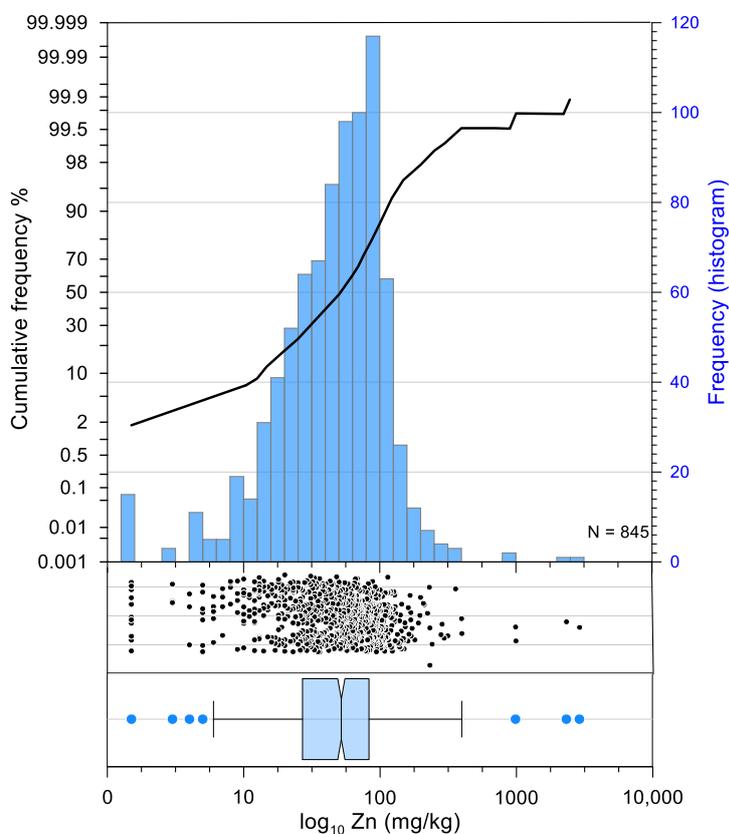


Figure 9.4. Histogram, cumulative frequency % curve (black line), one-dimensional scattergram and notched box-and-whisker plot of \log_{10} -transformed total Zn concentrations in topsoil, determined by X-ray fluorescence, FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005). The left Y-axis shows the cumulative frequency % (probability scale), the right Y-axis the histogram frequency, and the X-axis the class interval bins. The advantage of using \log_{10} -transformed data is that the statistical distribution is more symmetric and lower and upper outliers of the notched-box-and-whisker plot are displayed. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's Grapher™ v20.

Geochemical maps should show the data with as little distortion as possible, and with a minimum number of computational artefacts (Gustavsson *et al.*, 1997; Tarvainen *et al.*, 2005). Point symbol and dot maps reveal the actual sampling density, and any error in coordinates can be easily observed. Hence, these should be the first maps to be plotted. An important advantage of point symbol and dot maps is that they are easily readable, even by laypersons.

Colour-surface contour geochemical maps are favoured as they are more attractive to the eye. However, they are more difficult to construct because the point data of regional and continental-scale geochemical projects are often based on irregular sampling points, and an interpolation procedure is required to achieve a regular grid for plotting a colour-surface map. This means extrapolating values from the actual sampling points into unsampled space by using different interpolation methods (Davis, 1973, 1986, 2002; Howarth, 1983; Björklund and Gustavsson, 1987; Gustavsson *et al.*, 1994, 1997; Reimann *et al.*, 2008). There are many interpolation algorithms, and the most used are:

² RGB = Red, Green, Blue

- Inverse distance weighting (IDW – Howarth, 1983; Reimann *et al.*, 2008).
- Moving weighted median (MWM – Gustavsson *et al.*, 1994, 1997).
- Multifractal inverse distance weighting (MIDW – Cheng, 2000; Agterberg, 2001; Lima *et al.*, 2003), and
- Kriging (Matheron, 1963; Clark, 1979; Journel and Huijbreghts, 1978; Isaaks and Srivastava, 1990; Reimann *et al.*, 2008; Filzmoser *et al.*, 2014; Pereira and Soares, 2018; Maroufpoor *et al.*, 2020; Demetriades, 2021). Kriging is the general name of geostatistical interpolation methods. It is considered to be an optimal spatial interpolator or predictor because it can predict unbiased values in unsampled space with the minimum errors of estimation. However, the procedure that must be followed is cumbersome, and is not recommended for people that do not have a good command of the geostatistical procedures involved.

Whichever interpolation method is selected for plotting colour-surface maps, it is strongly recommended that many experimental maps be plotted to refine the plotting parameters used.

9.8.1. Map projection and scale

Global Geochemical Baselines maps should be compiled at the end of the project. The question is: *At what map scale should they be produced and by which projection?* Darnley *et al.* (1995, Table 9-1, p.83) suggested that based on the GTN grid size of 160x160 km and an area of 25,600 km², a map scale with a 2 mm pixel size would be 1:80,000,000. This map scale is derived from the following calculations:

- 1 sampling site/5120 km², which means a grid of 71.554 x 71.554 km, and the map scale is estimated by 71.554 km x 1000 m/km x 100 cm/m = 71,554,000 cm.

Hence, the optimum map scale, according to the sampling density of 1 sampling site/5120 km² is 1:71,554,000, and global geochemical maps at a nominal scale of 1:80,000,000 are feasible.

The following map projections for Global Geochemical Baselines are possible:

- Albers equal-area conic projection is best suited for areas extending in an east-to-west orientation at mid-latitudes rather than north-to-south (Snyder, 1987; 1993; Snyder and Voxland, 1989).
- Lambert azimuthal equal-area projection is an azimuthal projection with three aspects, *i.e.*, polar, equatorial and oblique; it is best suited for individual territories that are symmetrically proportioned, either round or square (Snyder, 1987; 1993; Snyder and Voxland, 1989).
- Van der Grinten projection is a polyconic projection, and is used for whole world maps (Snyder, 1987; 1993; Snyder and Voxland, 1989), and
- Robinson projection (compromised distortion, not equal-area) is a pseudocylindrical map projection for plotting world maps (Robinson, 1974; Snyder, 1987, 1990, 1993; Snyder and Voxland, 1989).

The Albers equal-area conic projection was used for plotting the maps of the FOREGS Geochemical Atlas of Europe project (Salminen *et al.*, 2005; Tarvainen *et al.*, 2005).

9.8.2. Exploratory Data Analysis symbol map

Figure 9.5 shows an Exploratory Data Analysis (EDA) symbol map. The objective of EDA maps is to provide an even optical weight for each symbol on a map, and to direct the researcher to focus on data structure, and not on ‘high’ or ‘low’ values (Kürzl, 1988; Reimann *et al.*, 2008). The number of symbols, or class intervals, is normally five because they are based on the main

structural components of the boxplot as indicated in Figure 9.5; they can be extended to seven classes if Tukey's near and far outliers are differentiated (*i.e.*, < or >hinge, or ± 3 * hinge width). According to psychometricians, a maximum of seven classes should be displayed on a black and white map.

A serious drawback is that there is no standard set of EDA symbols (Table 9.3). Hence, for the sake of symbol standardisation, it is here proposed that the original EDA symbol set introduced by Tukey and Tukey (1981), and subsequently popularised in applied geochemistry by Kürzl (1988) be used. The size of the EDA symbols depends on the map presentation scale. Some experimentation is, therefore, necessary to select the appropriate symbols and their size with respect to the presentation map scale. It is especially important to avoid clutter on a map.

Table 9.3. Three sets of Exploratory Data Analysis (EDA) symbols. The EDA symbol set is the original proposed by Tukey and Tukey (1981). The central symbol set uses an accentuated symbol for the highest values, and the third is an alternative set of symbols used by the Geological Survey of Canada (GSC). If necessary, these symbol sets can be easily extended to seven classes by using an additional class for the outer symbols (modified from Reimann *et al.*, 2008, Figure 5.3, p.70). The boxplot shows the relationship with the EDA symbol classes. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8.

Boxplot	Class intervals	EDA symbol set	EDA symbol set with accentuated extreme values	GSC symbol set
	Highest values	+	■	□
	Higher values	+	+	□
	Inner values	•	•	+
	Lower values	○	○	○
	Lowest values	○	○	○

9.8.3. Variable-size dot map

Figure 9.6 presents a variable-size or proportional dot map. This map type is quite simple and highly effective for displaying the spatial distribution of determinand values. For the classes either boxplot or percentile class intervals can be used. In Figure 9.6 the topsoil percentile classes tabulated in Table 9.2 were used. For plotting the proportional dot map, it is important to order the data from high to low concentrations so that the larger size dots are below the smaller ones, *i.e.*, dots are plotted in descending determinand value to avoid small dots being covered by large ones. If a white rim is added to the black dot, then the superimposed smaller dots are easily visible.

9.8.4. Colour-surface and dot map

The five random wide-spaced sampling points within each 160x160 km GTN grid cell in the FOREGS Geochemical Atlas of Europe project (Salminen *et al.*, 2005; Tarvainen *et al.*, 2005) were a challenge for the construction of colour-surface maps. Different output cell sizes were tested until the final output grid cell size was reached. Further, the selection of the colour scale was subject to experimentation (Fig. 9.7).

The map composition in Figure 9.8 of topsoil Zn data is a combination of a colour-surface and a variable-size dot map. These combined maps were used since all interpolation methods are prone to some distortion of the spatial variation, while the variable-size dots exhibit the actual class interval value at the sampling site. The proportional size open dots or circles, except the grey dot displaying the highest value class interval, do not cover the coloured surface below. Hence, this is a powerful way to present geochemical data.

The FOREGS Geochemical Atlas of Europe data of each determinand were interpolated to generate a regular grid with a 6x6 km output cell size, using the Alkemia Smooth interpolation method (Gustavsson *et al.*, 1997; Tarvainen *et al.*, 2005). For each cell, values were calculated

using a moving weighted median in a circular window with a fixed radius of 150 km. A 10-grade colour scale was selected to present the distribution. The colour scale was based on the following percentiles: 5, 15, 25, 35, 50, 65, 75, 85 and 95 (Figs. 9.7 & 9.8). If more than 5% of the data were lower than the detection limit, one or more of the lower colour classes were not applied.

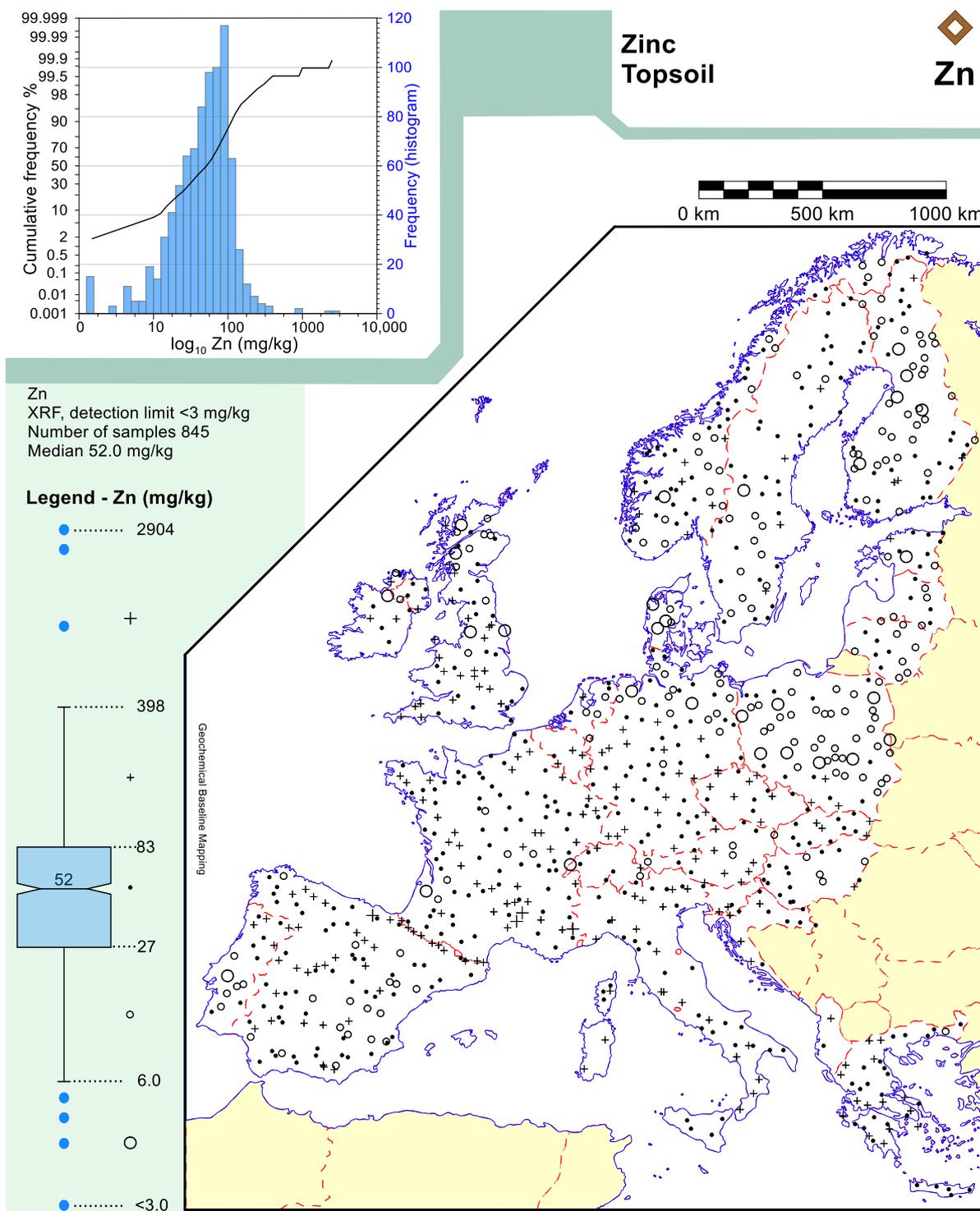


Figure 9.5. Exploratory data analysis symbol map of \log_{10} -transformed total Zn concentrations in topsoil, determined by X-ray fluorescence, FOREGS Geochemical Atlas of Europe (Salminen et al., 2005). The boxplot defines the five class intervals. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8 and Grapher™ v20.

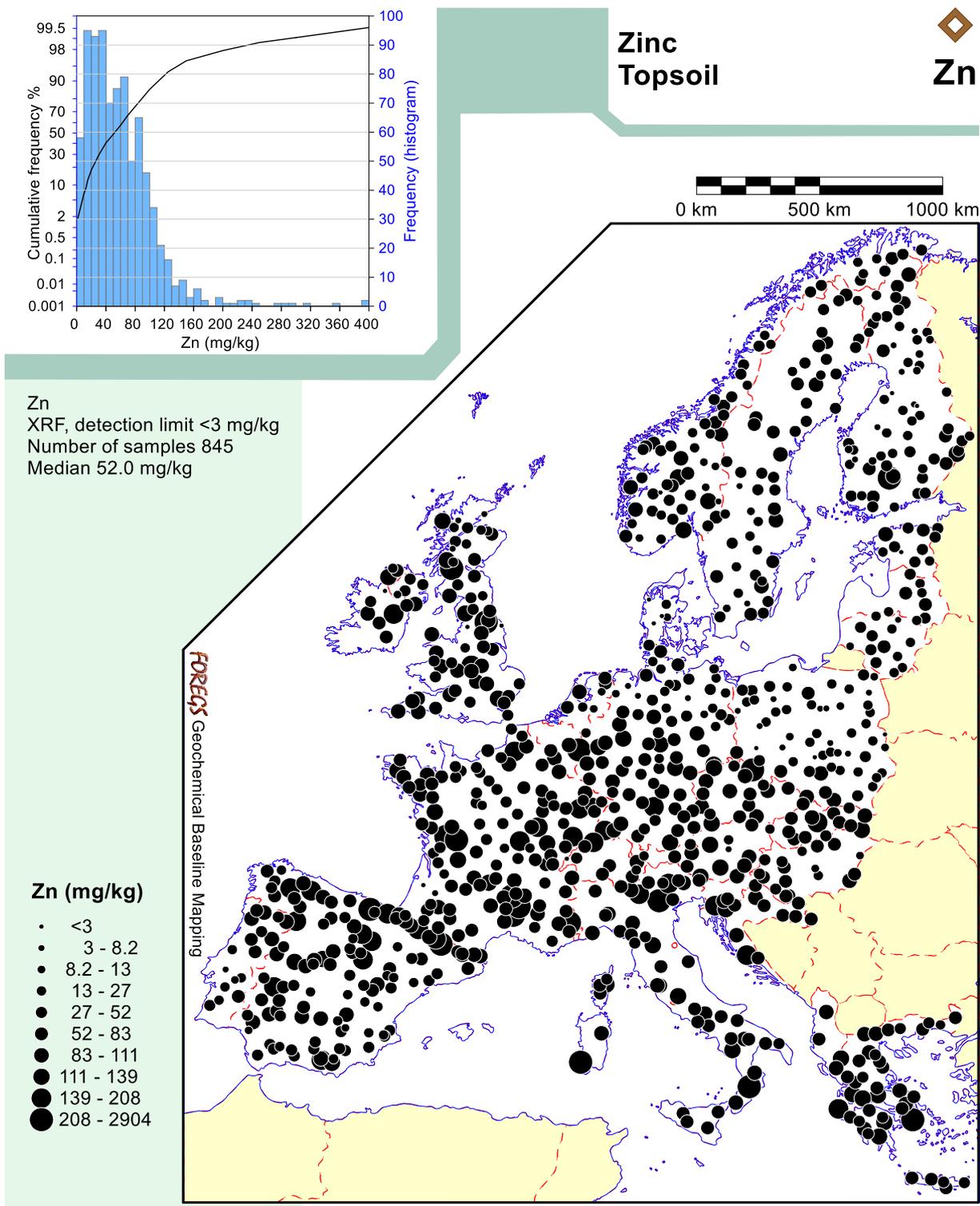


Figure 9.6. Variable-size or proportional dot map of total Zn concentrations in topsoil, determined by X-ray fluorescence, FOREGS Geochemical Atlas of Europe (Salminen et al., 2005). The dot class intervals of Zn (mg/kg) are at the minimum, the 2nd, 5th, 10th, 25th, 50th (median), 75th, 90th, 95th, 98th percentiles, and maximum. The histogram and cumulative frequency % curve show part of the statistical distribution up to 400 mg/kg Zn. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8 and Grapher™ v20.

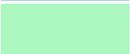
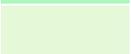
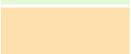
<i>Colour</i>	<i>RGB colour</i>
	48,117,158
	66,148,196
	106,176,212
	158,203,224
	172,247,191
	229,248,216
	254,224,174
	245,171,204
	243,131,189
	246,103,167

Figure 9.7. Colour scale used in the FOREGS Geochemical Atlas of Europe project (from Tarvainen *et al.*, 2005, Fig. 2, p.97; slightly modified), with the RGB colour values. The 10-grade colour scale is based on the following percentiles: 5, 15, 25, 35, 50, 65, 75, 85 and 95. Drawn by Alecos Demetriades (IGME/IUGS-CGGB) with Microsoft™ PowerPoint.

The dot maps were produced with Esri's ArcView® GIS software, using an Alkemia Circmap type dot size function to classify data (Gustavsson *et al.*, 1997). In most cases, 10% of the lowest values are presented with the smallest symbol size and 2% of the highest concentrations with the largest symbol (16 mm, grey colour dot). Between these two fixed percentiles, the rest of the distribution was divided into 14 symbol size categories using a logarithmic scale as shown in the histogram inset of Figure 9.8. If more than 10% of the samples are under the analytical detection limit, all samples with a concentration lower than the detection limit are shown with the smallest symbol size. The combination of almost continuous symbol size and logarithmic dot size function reveals anomalous patterns at both high and medium concentration levels.

The data distribution is shown as a combination of histogram and cumulative distribution function curve on the upper left corner of each map (Fig. 9.8). The histogram is based on the dot map class-interval logarithmic scale. The cumulative distribution is presented with black dots on the graph.

In addition to the distribution maps that were published in the two-volume FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006a), several working maps with different scales or combination of elements (*e.g.*, factor scores maps, topsoil/subsoil ratio maps) or combination of field data and analytical results were produced for interpretation purposes.

9.8.5. Ratio map

Ratio maps should be plotted for the determinand concentrations of top and bottom samples of residual soil, overbank sediment and floodplain sediment. These maps will show any enrichment in the top compared to the bottom sample, which could be ascribed to human-induced and/or natural causes. As there is a tendency to attribute any enrichment in topsoil to anthropogenic influences, extra care should be taken to support such an interpretation with unchallengeable evidence. Reimann and Caritat (2005) have discussed the use of so-called reference element

ratios (e.g., Al, Li, Sc, Zr or Ti) in enrichment factor calculations. An example of a topsoil/subsoil ratio map is shown in Figure 9.9.

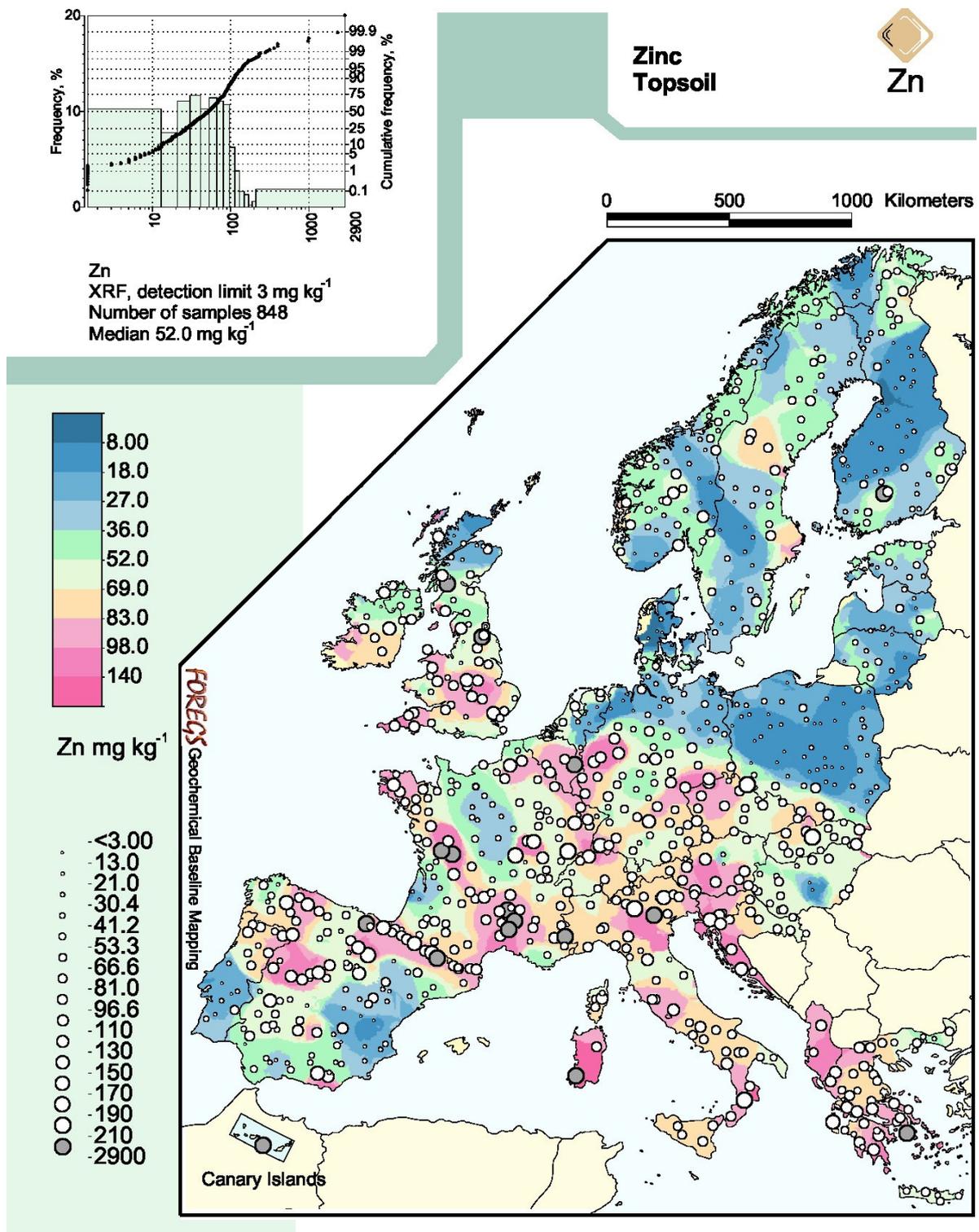


Figure 9.8. Colour-surface map with superimposed variable-size or proportional dots of total Zn concentrations in topsoil, determined by X-ray fluorescence, FOREGS Geochemical Atlas of Europe (from Salminen et al., 2005, p.513; http://weppi.gtk.fi/publ/foregsatlas/maps/Topsoil/t_xrf_zn_edit.pdf). See text for an explanation of map construction.

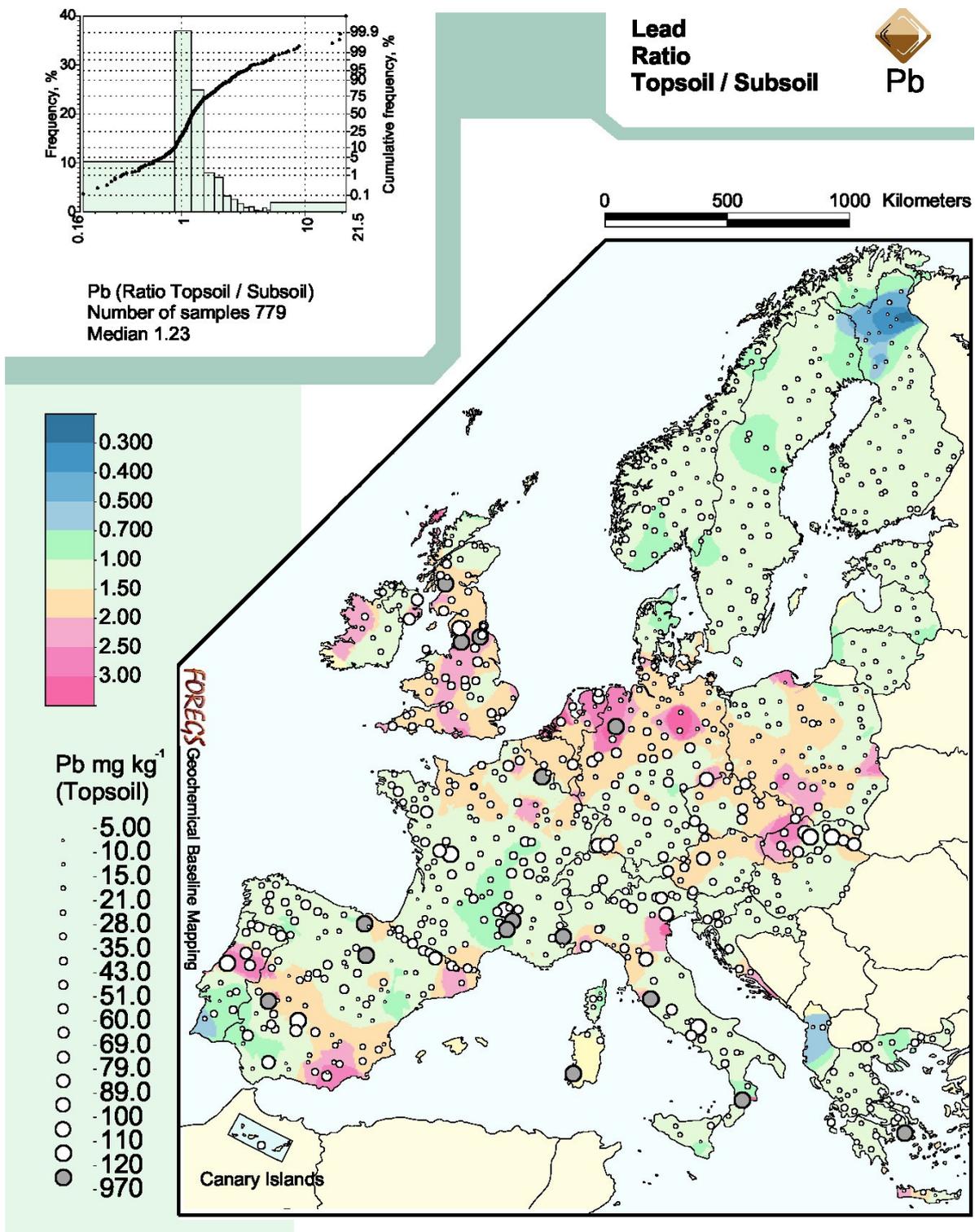


Figure 9.9. Topsoil/subsoil colour-surface map with superimposed variable-size or proportional dots of Pb topsoil concentrations, determined by X-ray fluorescence, FOREGS Geochemical Atlas of Europe (from De Vos et al., 2006b, Map 11, p.286; <http://weppi.gtk.fi/publ/foregsatlas/text/Pb.pdf>). See text for an explanation of map construction.

9.8.6. Multi-component map

Complex unobserved parameters are calculated as a combination of well-correlated measured data. Factor analysis is used for reducing algebraically a large number of variables to a much smaller number of new variables, often referred to as factors, which retain most of the information contained in the original data set. The fewer new variables allow a simple description of the multidimensional nature of the studied data set. The method investigates the complex multivariate relationships among the determinands, which are not normally exposed by simple correlation analysis. Abundant literature on multivariate statistical methods is available (Davis, 1973, 1986, 2002; Goddard and Kirby, 1976; Jöreskog *et al.*, 1976; Howarth, 1983; Morrison, 2005; Batista *et al.*, 2006; Pirc *et al.*, 2006; Reimann *et al.*, 2008). An example of a multi-component map, the Factor 1 Varimax rotated scores in topsoil, is shown in Figure 9.10.

9.8.7. Compositional data analysis map

Geochemical data are compositional in form (CODA) because they do not contain absolute but only relative information (Aitchison, 1982, 1986, 1997). The reported concentrations of all elements analysed depend on one another. The analytical results are reported as concentrations in units of mg/kg or weight per cent (wt%). If the total concentrations of all chemical elements in a sample are analysed, the analytical results must sum up to a constant, *i.e.*, 100 wt% or 1,000,000 mg/kg. Such data sets are called ‘closed data’. It was recognised quite early that such data have some special properties that can lead to erroneous results when applying the methods developed for classical statistical data analysis, especially in correlation analysis (*e.g.*, Pearson, 1897; Chayes, 1960; Miesch *et al.*, 1976; Lenahan *et al.*, 2011; Reimann *et al.*, 2012; Filzmoser *et al.*, 2014).

The inherent problem of compositional data is that if the SiO₂ or CaO concentrations are extremely high in soil samples from part of a survey area, the concentrations of all other elements must be low, because they have no space to vary freely within the composition. *For example*, if a sample contains 80 wt% SiO₂, then there are only 20 wt% left for all other elements in the periodic table. For a long time, applied geochemists considered that by not analysing the major elements, or by using partial extraction methods, which do not deliver total element concentrations, the problem of dealing with compositional data will be ‘eliminated’. However, even if all chemical elements are not analysed, the total element concentrations still depend on each other. The relevant information for every single variable in a geochemical data set lies in the ratios between all variables and not in the measured element concentrations as such. This feature was recognised by Chayes (1960), Miesch *et al.* (1976), and Russian geochemists (Beus and Grigorian, 1977).

As compositional data do not belong to the classical Euclidean space, they need to be considered in their own Euclidean geometry, namely the Aitchison geometry on the simplex (Aitchison, 1982, 1986, 1997; Aitchison and Egozcue, 2005; Filzmoser *et al.*, 2009, 2010, 2014; Egozcue and Pawlowsky-Glahn, 2011; Pawlowsky-Glahn and Buccianti, 2011; Reimann *et al.*, 2012), even for univariate data analysis and visualisations. Therefore, all classical statistical tests for comparison of the mean (median) of two geochemical data sets will deliver erroneous results because they are based on Euclidean distances. In terms of log-ratio (the logarithm of a ratio) transformation, there are three different approaches to open compositional data:

- (i) An additive log-ratio (alr)-transformation (Aitchison, 1986); this transformation has the disadvantage of sacrificing one variable, *e.g.*, TiO₂, and presenting all other results as a log-ratio with respect to TiO₂. The selection of TiO₂ could be questioned since different results would be expected when another variable is sacrificed.
- (ii) A centred log-ratio (clr)-transformation (Aitchison, 1986) where, in order to construct the log-ratios, each variable is divided by the geometric mean of all elements measured, followed by a log-transformation, and

(iii) An isometric log-ratio (ilr)-transformation (Egozcue *et al.*, 2003), which has preferable geometrical properties for multivariate data analysis but where the interpretation in terms of the original elements is more challenging.

Factor 1: Eigenvalue 15.06; Proportion of total variance explained 24.29%

Factor loadings class	Determinand associations
<0.9>0.7:	Dy*, Ho*, Tb*, Gd*, Er*, Tm*, Yb*, Sm*, Lu*, Nd*, Y, Pr, La, Ce
<0.7>0.5:	Eu, Th, MnO, Zn,
<0.5>0.4:	Co, Cu, Nb, Cd, U, As, Hf, Sc, P ₂ O ₅ , pH, In, Ni
<0.4>0.3:	Fe ₂ O ₃ *, Ta, Zr, Pb, V, TiO ₂ *, Sb, Cs, Tl, Cr, <0.06 mm*, Rb, Te, Al ₂ O ₃ *

*Normal data, and the remaining are log transformed

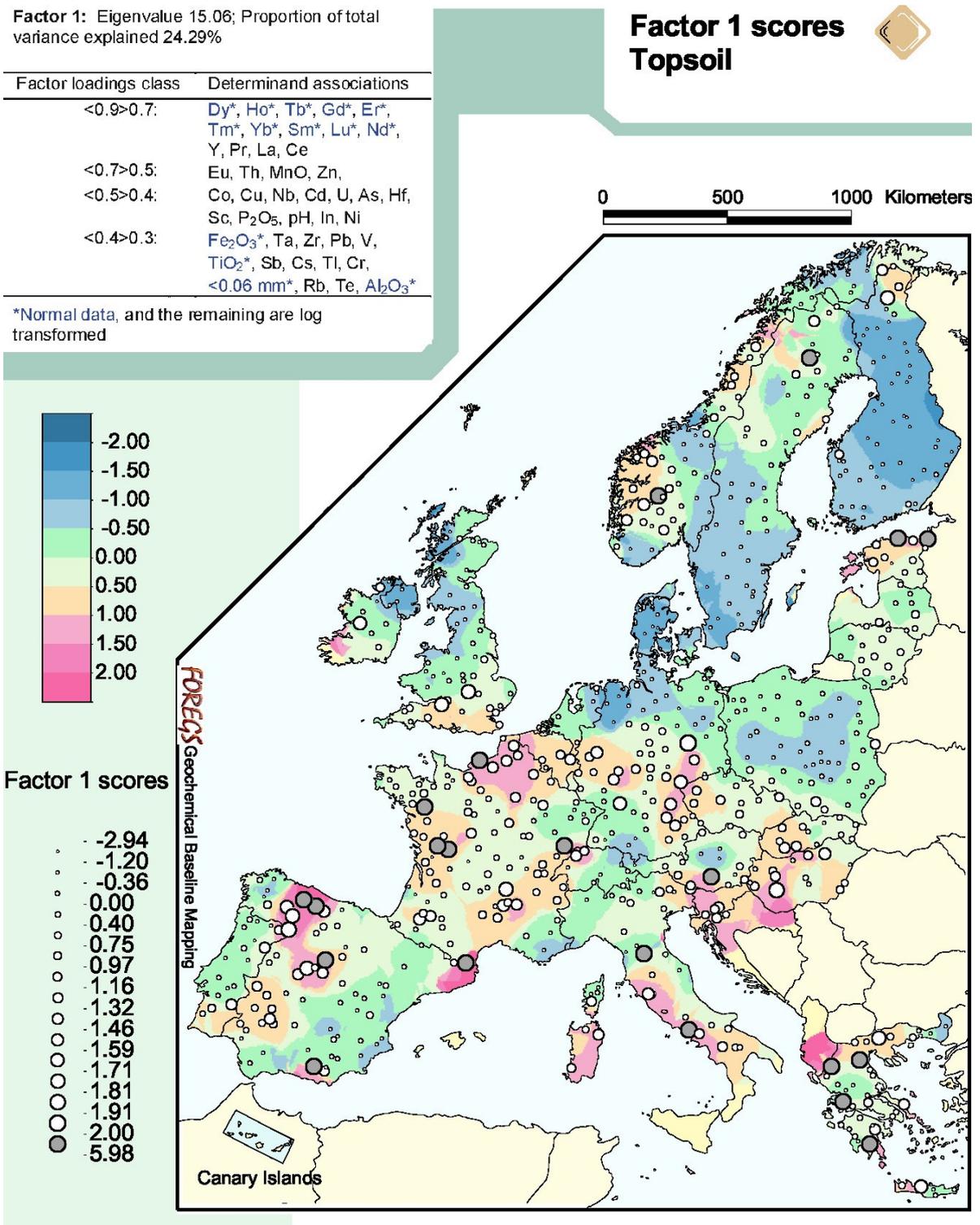


Figure 9.10. Colour-surface multicomponent map with superimposed variable-size or proportional dots of Factor 1 Varimax rotated scores in topsoil, FOREGS Geochemical Atlas of Europe (from Batista *et al.*, 2006, Fig. 6, p.582; <http://weppi.gtk.fi/publ/foregsatlas/articles/Annex5.pdf>). See text for an explanation of map construction.

An example map is given in Figure 9.11 where the clr-transformation was applied to total concentrations in topsoil samples and Zn_{clr} was selected for plotting. The compositional data

statistical analysis was performed with CoDaPack 2.03.01 (Comas-Cufí and Thió-Henestrosa, 2011). However, there exists a severe disadvantage of the clr-transformation. The resulting clr-variables have a certain information overlap because the geometric mean is used as a common divisor. Nevertheless, the clr transformation is the most used in applied geochemistry. If the Zn_{clr} (Fig. 9.11) proportional dot map is compared with the normal Zn dot map (Fig. 9.6), a few differences are detected (compare also the two histograms, and the patterns in northern Germany and Poland where Weischelian glacial retreat sand plains are dominant). It is strongly recommended that compositional data analysis maps should be plotted and compared with the normal maps.

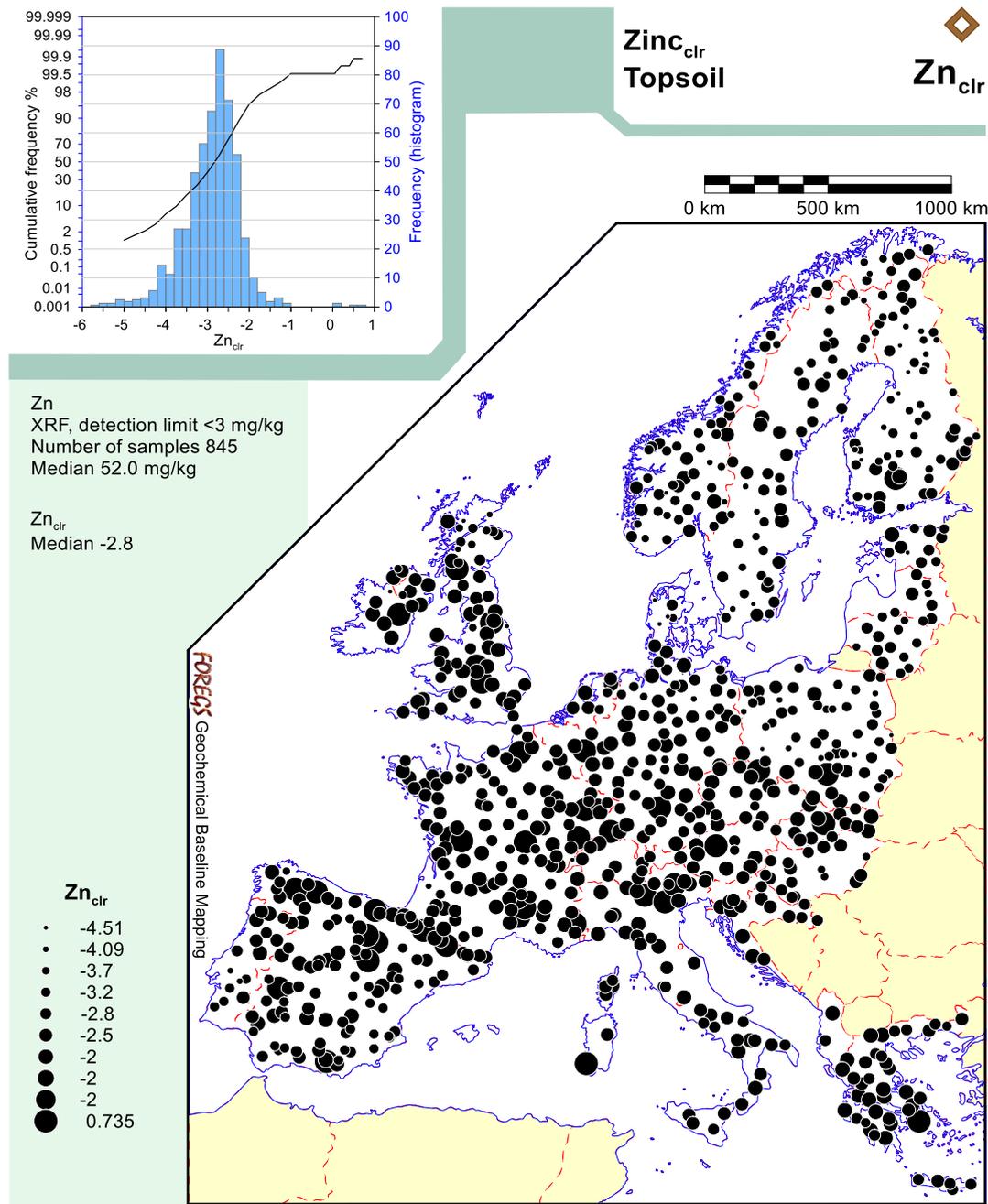


Figure 9.11. Compositional data analysis proportional dot map using the centred log-ratio (clr)-transformation (Aitchison, 1986) of total Zn concentrations in topsoil, FOREGS Geochemical Atlas of Europe (Salminen et al., 2005). Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8 and Grapher™ v20.

9.8.8. Google Earth maps

Google Earth is particularly useful for displaying data and information on a geographical and topographical background, and should also be used. Figures 9.12 and 9.13 show the stream sediment sample sites, and the distribution of Zn in topsoil samples, respectively.



Figure 9.12. Google Earth image showing the stream sediment sample sites with their identification numbers, FOREGS Geochemical Atlas of Europe (Salminen et al., 2005). The orange squares are the 160x160 km GTN grid cells. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8 and exported to a kml format file for display on Google Earth.

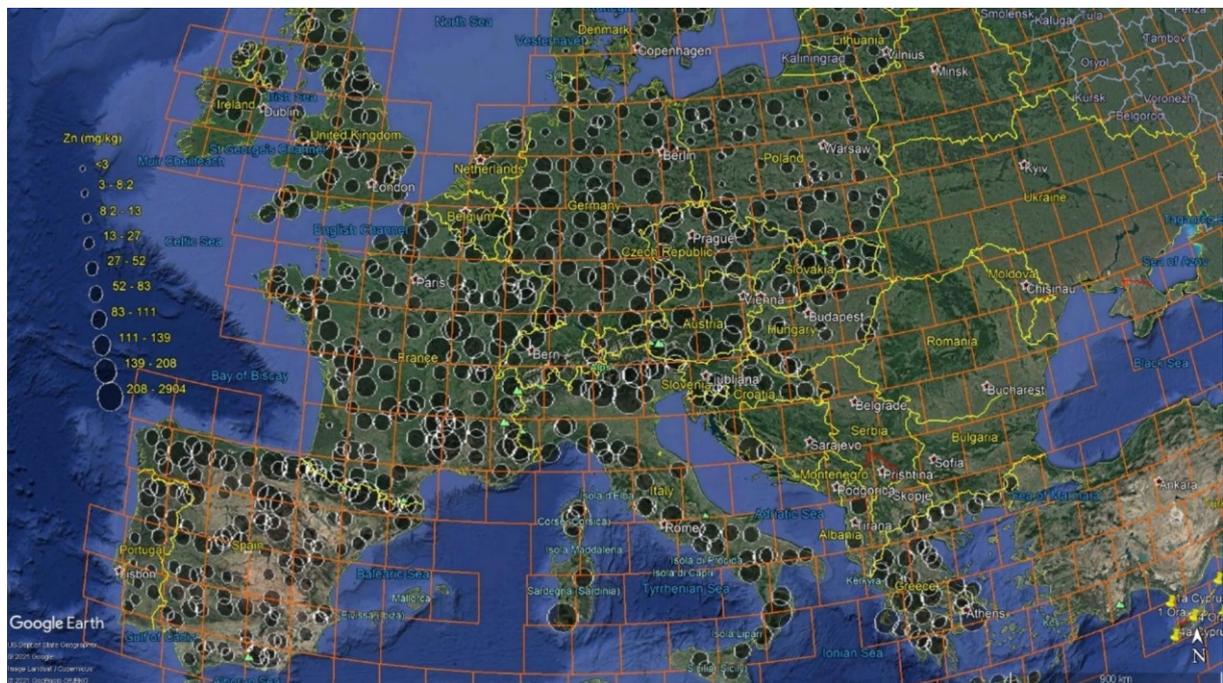


Figure 9.13. Google Earth image showing the spatial distribution of total Zn concentrations in topsoil, determined by X-ray fluorescence, FOREGS Geochemical Atlas of Europe (Salminen et al., 2005). This is the same variable-size or proportional dot map displayed in Figure 9.6. The orange squares are the 160x160 km GTN grid cells. Plotted by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8 and exported to a kml format file for display on Google Earth.

9.9. Supporting maps

The effective interpretation of the spatial distribution of determinands in samples of rock, residual soil, humus, stream water, and sediments (stream, overbank, floodplain) requires, apart from the field observations, other supporting information in map form. This could include lithology, faults, mineral deposits, mineral showings, land use, rainfall (precipitation), temperature, industries, mines (active and inactive), mining wastes, and ore beneficiation wastes. The collection of these data should start from the beginning of the project as such information is not easy to collect and compile during the interpretation stage of a project.

9.10. Field observations archive

All observations recorded on the field observation sheets should be checked and validated prior to their entry into the database. A hard copy record should be kept in the country of origin, and a second set in the Geological Survey of the Data Management Committee's Chair. This is a valuable record and should be safeguarded.

9.11. Photograph archive and presentation

The photograph archive is also extremely important and should be protected by its storage in the country of origin, and the Geological Survey of the Data Management Committee's Chair. An effective method for its access by the global community should be organised. One method is demonstrated by the handling of the photograph archive for the EuroGeoSurveys GEMAS project where two photographs at each sampling site were organised as Google Earth kml files (<http://gemas.geolba.ac.at/Photos.htm>). Figure 9.14 shows an example of such a presentation in Google Earth.



Figure 9.14. Google Earth image showing the stream sediment sampling site N27E12S5 (East: 20.527756°; North: 39.673784°), Epirus region, N.W. Hellenic Republic. The two photographs on the right hand side display the landscape of the second-order stream with stagnant water (top), and the fine-grained stream sediment (bottom), which remains as the stream bed dries out, FOREGS Geochemical Atlas of Europe project (Salminen et al., 2005). Photograph composition of Google Earth image, and two sampling site photographs compiled by Alecos Demetriades (IGME/IUGS-CGGB) with Golden Software's MapViewer™ v8.

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Note: All hyperlinks were checked on the 3rd of February of 2022.

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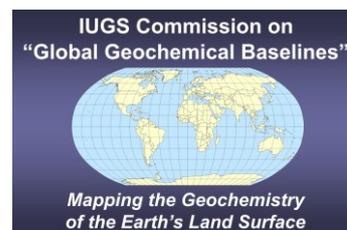
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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Chapter 10

Project Management

Alecos Demetriades^{1,9}, Christopher C. Johnson^{2,9}, David B. Smith⁹, Anna Ladenberger^{3,9},
Kate V. Knights^{4,9}, Gloria Prieto Rincón^{5,9}, Gloria Namwi Simubali^{6,9},
Paula Adánez Sanjuan^{7,9}, Christina Stouraiti^{8,9}, Ariadne Argyraki^{8,9}

¹ Institute of Geology and Mineral Exploration, Athens, Hellenic Republic

² GeoElementary, Derby, United Kingdom

³ Geological Survey of Sweden, Uppsala, Sweden

⁴ Consultant Geochemist, Dublin, Ireland

⁵ Servicio Geológico Colombiano, Bogotá, Columbia

⁶ Geological Survey of Namibia, Windhoek, Namibia

⁷ Instituto Geológico y Minero de España, Madrid, Spain

⁸ Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Hellenic Republic

⁹ IUGS Commission on Global Geochemical Baselines

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10.1. Introduction

The preceding chapters of this manual describe all the necessary components for the implementation of the Global Geochemical Reference Network project (for details see Chapters 1 and 2). Darnley *et al.* (1995, p.87) stated that a global project requires a “*single permanent agency to accept formal responsibility for securing funds, managing and coordinating these activities according to scientific guidelines determined by an external advisory committee*”. However, to successfully implement such a complex multi-national project, a robust project management structure is needed that is independent of the interest of an individual nation or organisation.

In this chapter, we propose a project management structure based on the experience of two multi-national continental-scale geochemical projects, namely the Forum of European Geological Surveys (FOREGS) Geochemical Atlas of Europe, and the Geochemical Mapping of Agricultural and Grazing land Soil (GEMAS), with 26 and 33 participating countries, respectively (Salminen *et al.*, 2005; Reimann *et al.*, 2014). Both projects relied on transparency, openness and trust among the participants. Most importantly, all the participants in these projects worked as a team with the same vision to reach a common goal. The teamwork spirit is what made both projects successful.

It is worth mentioning at this point the dedication to Professor Bjørn Bølviken¹ written on a signed card by the first multinational team working from the 21st of May 1986 to the 1st of July 1993 for the Regional Geochemical Mapping of the then Western Europe: “*Bølviken’s Regional Geochemical Mapping of Western Europe towards the Year 2000: A very important project ahead of its time. Conceived by a person with extreme foresight and supported by Europeans with different cultures, proving that European unity could be realised as long as people meet and discuss matters openly and with integrity. Thank you for bringing us together and hope that we meet again to complete the ‘dream’*” (Demetriades *et al.*, 2006, p.43). The ‘dream’ was completed thirteen years later with the publication of the two-volume FOREGS Geochemical Atlas of Europe (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006).

It is hoped that applied geochemists from all countries will share the common vision to establish the Global Geochemical Reference Network, and are willing to work as a team towards this common goal.

There is no timeframe yet for the Global Geochemical Reference Network project because there are certain steps that should be carried out before it can start:

1. The establishment of a Project Management Structure, which is discussed here.
2. Availability of necessary funds in a broad sense, *i.e.*, financial, infrastructure, personnel, etc.
3. The implementation of the Global project.

10.2. Project management structure

An international project of this magnitude and complexity is a challenge for any management scheme. The proposed management structure for the Global Geochemical Reference Network project is displayed in Figure 10.1. Ideally, the whole project should be managed by a high-power and dedicated Executive Committee consisting of one member from each of the nine continental blocks indicated in Figure 10.2. However, the multi-national nature of the project requires the active involvement of applied geochemists from all continental blocks.

The Executive Committee, depending on the needs and for the efficient running of the project, should be free to set up new Committees and to dissolve Committees, which have

¹ Chairperson of the Working Group on ‘*Regional Geochemical Mapping*’ (1986-1993) of the then Western European Geological Surveys (WEGS: 1971-1993), succeeded by the Forum of European Geological Surveys (FOREGS: 1993-2005), and presently the European Geological Surveys (EGS: 1995-present; it is noted that FOREGS and EGS coexisted for a period of ten years).

already served their purpose. Hence, the proposed management structure should be used as a guide by the Steering Committee of the IUGS Commission on Global Geochemical Baselines. According to the IUGS Statutes and Bylaws, the Steering Committee may decide to establish instead a Sub-commission for the execution of the Global Geochemical Reference Network project.

In the following sections, the role and duties of each committee of the proposed management structure are outlined. Few Committees are assigned a dual or triple role, and this is done for better management.

The membership of each committee should be five, and in exceptional cases where the Executive Committee considers it essential, a maximum of seven. The only exceptions to this recommendation are the Executive and Sampling Committees. The Executive Committee is comprised of one member from each of the other committees, for a total of seven members, including the Project Manager. The Sampling Committee consists of members from each continental block, as shown in Figure 10.2, for a total of nine members.



Figure 10.1. Organisation chart of the proposed project management structure for the Global Geochemical Reference Network project. The blue and red connection lines show the relationships between committees. The red line linkages between committees exhibit the stronger relationship as explained in the text. Drawn with Microsoft™ PowerPoint by Alecos Demetriades, Hellenic Institute of Geology and Mineral Exploration (IGME) and IUGS Commission on Global Geochemical Baselines (IUGS-CGGB).

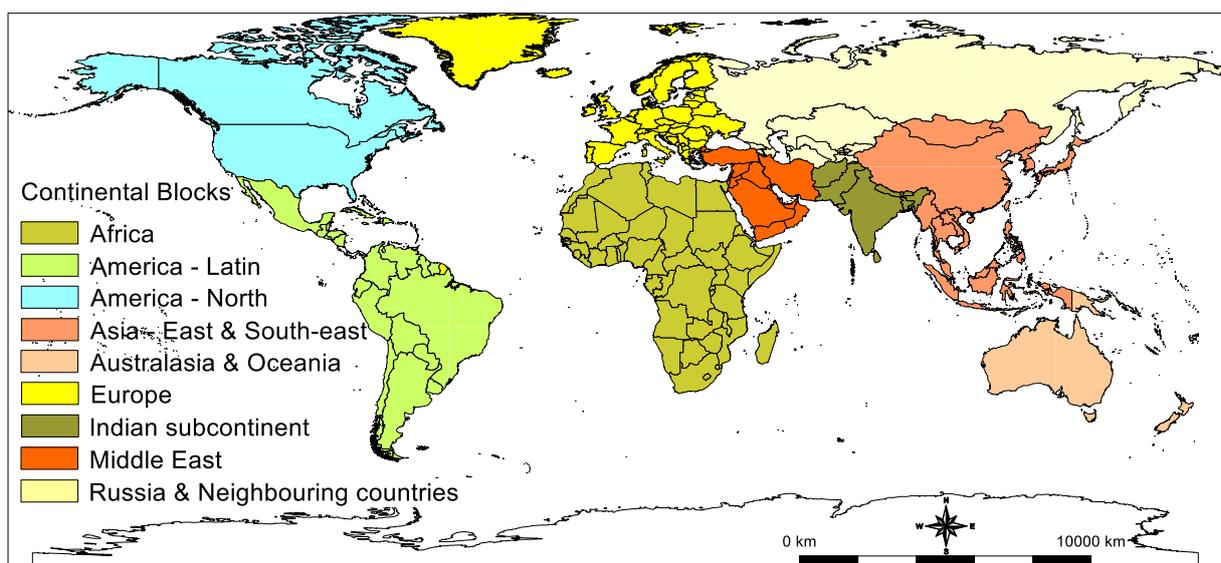


Figure 10.2. Project management continental blocks. Drawn with Golden Software's MapViewer v8 by Alecos Demetriades (IGME/IUGS-CGGB).

10.2.1. National Team members

There are presently 193 countries that are member states of the United Nations; namely 54 countries are in Africa, 33 in Latin America, 2 in North America, 15 in Asia (East & Southeast), 14 in Australasia & Oceania, 44 in Europe, 7 in the Indian subcontinent, 15 in the Middle East, and 9 in Russia & Neighbouring countries². Hence, each country should be represented by at least one member with expertise in applied geochemistry, a good command of the English language, and leadership skills such as communication, problem-solving and decision-making allowing successful project management. Another requirement is to have studied and understood the procedures described in this Manual. The National Team members will be directly in contact with the Executive Committee, and subsequently with the other Committees as the project progresses.

Each country should submit to the Chair of the Executive Committee a signed commitment for its participation in the Global Geochemical Reference Network project. It is expected that each country has priorly secured the necessary funding for its participation in the project, namely the participation of its member or members in workshops and meetings, and for collecting the samples in its territory. The source of funding could either come from the national budget or sponsorships.

The reason for this condition is to show that there is a sound national interest for participation in the project.

Funding for the purchase of the common equipment that will be used in the project, and the costs of preparation of reference materials, sample preparation and analysis will be sought from other sources, *e.g.*, Governments, European Union, Private Companies, UNESCO, geoscientific associations.

10.2.2. Executive Committee

The Steering Committee of the International Union of Geological Sciences' Commission on Global Geochemical Baselines can function as the interim Executive Committee until the Global Geochemical Reference Network project is ready to start. During this interim period, the seven

² Source: <https://www.worldometers.info/united-nations/>. In the United Nations member list, there are 2 countries that are non-member states, the Holy See and the State of Palestine, thus making a total of 195 countries. Not included in this total count of 195 countries are 39 dependencies or other territories (<https://www.worldometers.info/geography/countries-of-the-world/#example>).

members of the Executive Committee should be selected according to proven good management and communication skills. Typically, it shall consist of a chairperson, a deputy-chairperson, a secretary, a treasurer and three members. The Chairperson of the Executive Committee shall take a lead position of the Project Manager.

The duties of the Executive Committee shall be:

- To formally set up all committees as shown in Figure 10.1.
- To raise needed funds for the efficient running of the project.
- To facilitate decision making and to find viable solutions to any problems arising during project execution. The biggest problem in multinational projects is funding. Hence, the condition that each country should secure the necessary funds for sampling and participation of its representatives in meetings.
- To coordinate efficiently the whole project, which means that one Executive Committee member should serve on at least one Committee, and take direct measures to deal with any failings.
- To organise regular meetings, and the minutes to be circulated to all project members.
- To organise at least one international annual physical meeting, and virtual meetings whenever is deemed necessary.
- To compile an annual report about project progress, and to mention problems encountered and solutions given.

The motto for the Executive Committee that should be passed on to all the other committees shall be the generation of ‘*more geochemical data than meeting minutes*’.

As indicated in the organisation chart (Fig. 10.1), the Executive Committee reports to the Steering Committee of the Commission on Global Geochemical Baselines, which in turn reports to the IUGS Executive Committee. The IUGS Council is informed about the work performed by the Commission every four years on the occasion of the International Geological Congress.

10.2.3. Sampling Committee

Sampling is the most important phase of an applied geochemical mapping project (Demetriades, 2014, 2021; Demetriades *et al.*, 2018). If any mistakes are made during sampling, they are difficult to trace and correct afterwards. This means that all national sampling teams should be well-trained by experienced field applied geochemists, who are well-acquainted with the sampling methods described in Chapter 3 ‘*Sampling*’.

The duties of each Sampling Committee member shall be:

- To organise in collaboration with the Project Manager the purchase of all the sampling equipment that should be purchased centrally and distributed to all participating countries (see Chapter 3).
- To send to each country, according to the estimated total number of solid samples that will be collected, sufficient weight of the two standardised blank solid samples for inserting and packing in the field, *i.e.*, 200 grams per 50 routine samples.
- To make field training videos.
- To organise field-training workshops in their geographical region.
- To monitor the quality of sampling by being in the field with different national sampling teams. Here the Sampling Committee cooperates with the Quality Control Committee in the supervision of the sampling teams in each country.
- To collect hard copies of field observations sheets, and the corresponding digital records in Microsoft™ Excel and Comma-separated value (CSV) files. Note: The original field observations sheets to be kept in each country.

- To check the field observations sheets, and if mistakes are found to contact the national member.
- To collect digital maps of the sampling locations of each sampling medium.
- To check the sampling locations of all sample types by plotting new maps and comparing them with the submitted digital maps, and if any mistakes are found to contact the national member.
- To collect the coded digital version of all photographs taken for each sample type.
- To check the codes of all photographs, and if any mistakes are found to contact the national member.
- To submit all digital field records, including photographs, to the Quality Control Committee.

10.2.4. Quality Control Committee

The Quality Control Committee shall have a quadruple role. Apart from being responsible for the development of secondary reference materials (SRMs), and the validation of the quality of data produced, it should also facilitate the QA/QC during the two most critical stages of the project, which are sampling and sample preparation. Therefore, the Quality Control Committee must have representatives in the Sampling and Laboratory Committees.

10.2.4.1. Development of Reference Materials

In order to carry out efficiently this role, the members of the Quality Control Committee should have expertise in the procedure for standardising secondary reference materials (SRMs; refer to Chapter 5 '*Development of Reference Materials for External Quality Control*'). Five SRMs of 1 tonne each of different chemical composition of each solid sample type (rock, stream sediment, soil, and overbank/floodplain sediment) should be collected, prepared and standardised (see Section §8.5 of Chapter 8). Further, two solid blank reference materials of 1 tonne each should be prepared (refer to Chapter 5 for details).

The duties for the development of Reference Materials shall be:

- To organise the development of SRMs.
- To organise the development of two blank solid reference materials.
- To write a report for each SRM developed (see Kriete, 2012; Reimann and Kriete, 2014).
- To publish the standardisation results of all SRMs developed in the journal of '[*Geostandards and Geoanalytical Research*](#)'.

Instead of developing project reference materials, it may be possible to purchase commercial reference materials, provided, of course, suitable ones can be found in sufficient quantities for all sample types and at a reasonable price.

10.2.4.2. Quality Control

The members of the Quality Control (QC) Committee should be well-acquainted with the procedures described in Chapter 7 ('*Quality Control Procedures*'), and ideally, they should have applied most of them in their projects. Figure 10.1 shows that the QC Committee has a significant role in the project because it receives data and information from two Committees, namely Sampling and Laboratory. When any problems are found, the QC Committee should contact the aforementioned Committees for explanations and clarifications, and may even contact National Team Members if deemed necessary. As displayed in Figure 10.1, there are strong links with the Laboratory and Sampling Committees because any problems with the quality of the analytical data and field records should be cross-checked in order to deliver data of high quality and integrity to the Data Management Committee.

The duties of this Committee, with respect to the quality control of generated results, shall be:

- To organise the randomisation of project samples, their renumbering and insertion of quality control samples, according to the scheme proposed in Chapter 4 (*‘Sample Preparation and Storage’*). This procedure must be done very carefully in the sample preparation laboratory. A good record should be kept of the original project sample numbers, and their corresponding new random numbers, because upon receiving the analytical results the original sample numbers must be reassigned.
- To conduct all the data checking and computation steps described in Chapter 7.
- To ask for the repeat analysis of sample batches in which errors have been found, and in cases where many errors are identified to demand the reanalysis of the whole sample suite.
- To write a well-documented quality control report for each analytical data set, and to mention any problems encountered and solutions given (see GEMAS project QC reports by Reimann *et al.*, 2009, 2011, 2012a).
- To check all digital field records, including photographs, and after validation to pass them to the Data Management Committee.

10.2.5. Laboratory Committee

This Committee is bestowed a three-fold role, *i.e.*:

- (i) Sample preparation
- (ii) Storage of samples, and
- (iii) Data acquisition.

10.2.5.1. Sample preparation and storage

Sample preparation is the next important phase of an applied geochemical mapping project (Demetriades, 2014, 2021). Like sampling, if any mistakes are made during sample preparation, they are difficult to trace and correct afterwards. The solid blank samples that are inserted during sampling in the field, and subsequently prepared along with the routine and field duplicate samples, may provide information about contamination of samples during preparation (refer to Chapter 5). At least two solid blank samples should be inserted in each analytical batch of one hundred samples. The sample preparation laboratory should keep a written and digital record of the samples prepared each day, as this is the only way to backtrack contamination problems, if and when they arise.

Consequently, the first expertise of the Laboratory Committee should be in the procedures described in Chapter 4 *‘Sample preparation and storage’*. As sample preparation is just as important as sampling, all samples should be prepared in the same laboratory for this is the only way to ensure that the quality of sample preparation remains the same from the first to the last sample. However, an exception from this condition can be made in case each sample type is prepared in a different but dedicated sample preparation facility, *for example*,

- Rock sample preparation
- Soil sample preparation (top and bottom soil samples)
- Humus sample preparation
- Stream sediment sample preparation
- Overbank sediment sample preparation (top and bottom overbank sediment samples) and
- Floodplain sediment sample preparation (top and bottom floodplain sediment samples).

This is an acceptable sample preparation scheme because all samples of the same type shall be prepared in the same facility. The scheme that is definitely not recommended is the preparation of samples in each country as this will be exceedingly difficult to supervise and control. It is important to remember that the aim of such a multi-national project of this magnitude is the production of a harmonised and homogeneous database for each sample type regardless of country borders. Hence, any possibilities and risks for inhomogeneities in the quality of samples must be eliminated or minimised.

The duties of the Laboratory Committee with respect to Sample Preparation and Storage shall be:

- To organise, in collaboration with the Project Manager, the purchase of suitable vials for the storage of sample aliquots. Each vial for analysis should be able to hold 100 ml of material, and each vial for the archive samples should hold 200 ml (see Fig. 4.2 in Chapter 4). The same type of vial should be used for the project, solid blank and SRM samples.
- To organise, in collaboration with the Project Manager, the purchase of durable labels on which the sample number and bar or quick response (QR) code can be printed.
- To periodically check the quality of sample preparation, and to ensure that the procedures described in Chapter 4 are strictly followed by the sample preparation laboratory or laboratories.
- To receive the digital files (Microsoft™ Excel or CSV) of the daily sample preparation records, which are subsequently passed on to the Quality Control Committee.
- To organise the safe long-term storage, archiving and future access of all project samples.
- To implement, in cooperation with the Quality Control Committee, the randomisation of ten suites of project samples splits of each solid sample type (see Fig. 4.2 in Chapter 4), and the insertion of quality control samples (see Table 4.1 in Chapter 4). According to the recommendations in Chapter 8, the number of different SRMs submitted in an entire analytical batch of samples must be sufficient to produce satisfactory regression analysis plots. For example, if the active project is collecting:
 - (a) Thousands of samples, the number of SRMs inserted into a batch of 100 samples should be a minimum of two.
 - (b) Hundreds of samples, then the number of SRMs should be increased to four, and
 - (c) A small number of samples (<100) then between 1 in 20 samples and 1 in 10 samples should be an SRM.
- To ensure the safe storage of the five 200 ml archive aliquots of each sample type, and any remaining randomised 100 ml analytical aliquots of each solid sample type (see Fig. 4.2 in Chapter 4).

10.2.5.2. Data acquisition

The members of the Laboratory Committee should be experienced geoanalysts but should not be staff members of the laboratories that shall undertake to analyse the samples of the Global Geochemical Reference Network project. They should be familiar with the requirements summarised in Chapter 6 '*Geoanalytical Methods and Requirements*'. The only change in the analytical methods described that can potentially occur over time is in instrumentation.

The duties of the Laboratory Committee, with respect to the analysis of samples, shall be:

- To select the best methods for the chemical analysis of stream water and all solid samples (rock, residual soil, and sediments – stream, overbank, floodplain). It is strongly recommended that the selected analytical methods should be able to analyse 15 to 20 gram-aliquots of each solid sample type.

- To select the best methods for the determination of any additional parameters (e.g., mineralogy of rock, soil, and sediment samples; bulk density of soil samples, pH of soil and water samples, etc.).
- To select the laboratories for the analysis of each sample suite by the same analytical method and instrumentation.
- To agree with each laboratory on the number of international primary reference materials (PRMs) that should be inserted in each batch of 100 samples. According to the recommendation in Chapter 8, the analytical contract should have a requirement for the laboratory to routinely determine primary reference materials usually at a rate of four PRMs at the start and end of each analytical batch.
- To agree with each laboratory, using wet chemical extraction methods, the number of reagent blank samples that should be inserted in each batch of 100 samples.
- To agree with each laboratory the rate of sample reanalysis per batch of 100 samples (normally every 10th or 20th sample should be reanalysed free of charge).
- To agree with each laboratory the recording and submission of the daily analytical batch records in a digital format in the order analysed, and with the following information:
 - Sample number
 - Laboratory number
 - Batch number
 - Date/time stamp
 - Analytical result.
- To agree with each laboratory not to censor geochemical data below the detection limit of the analytical method used (*Note: This is an important requirement in order to estimate the practical detection limit of each analytical method and for each sample type (see Chapter 7 ‘Quality Control Procedures’)*).
- To include in the contract with the laboratory (a) the reanalysis of batches of samples in which errors have been found by the Quality Control Committee, and (b) the reanalysis of the whole sample suite in the case many errors have been identified.

Upon receipt of the analytical results, the Quality Control Committee should check the raw analytical data according to the instructions given in Section §7.3.1 of Chapter 7 in this Manual.

10.2.6. Data Management Committee

The members of this Committee should be well-acquainted with data management and map plotting techniques. In Chapter 9 (*‘Data Management and Map Production’*), the most common data management, statistical and map plotting procedures and techniques are described. However, computer data processing is continuously progressing, and new interpretative techniques are developed. Hence, the best available map plotting techniques should be utilised.

The duties of the Data Management Committee shall be:

- To compile a report about the organisation, storage and access of data and information (*i.e.*, field records, problems encountered during analysis). It is recommended to consult data management strategies used successfully by other geological surveys (e.g., Coats and Harris, 1995; Johnson, 2011; USGS, 2016a, b).

- To compile and store the raw analytical data, quality control data and field observations in two different file formats Microsoft™ Excel and CSV (comma-separated values) for access by all interested parties through a dedicated website.
- To compile and store all digital photographs for access by all interested parties through a dedicated website.
- To calculate basic statistical parameters of all data sets and make them available in a table format, *e.g.*, Microsoft™ Excel or Word or pdf.
- To plot several types of geochemical distribution maps.
- To organise the project website.
- To disseminate the data and information related to project goals and applications.
- To conduct regular inspection and maintenance of the database and ensure accessibility by all interested parties.

10.2.7. Data Interpretation and Report Writing Committee

The members of this Committee should have a satisfactory command of the English language, and good synthesis and comprehension skills of disparate data and information. They should also be good at communication as they are going to be in contact with all participants of the Global Geochemical Reference Network project.

The duties of the Data Interpretation and Report Writing Committee shall be:

- To interpret all data generated by the Global Geochemical Reference Network project.
- To compile a detailed report for the geoscientific community.
- To compile a concise popular-science report for decision-makers and the general public in collaboration with the Public Relations & Marketing Committee.
- To write a concise interpretation of the most noteworthy spatial features of each determinand map, which will be uploaded to the website together with the respective map.
- To recommend, in collaboration with the Sampling and QC Committees, the monitoring of selected sample sites after a period of twenty years.

10.2.8. Public Relations & Marketing Committee

The members of this Committee should have multilingual capabilities because they will handle all outreach activities in public relations and marketing. This is an important committee for the promotion of the Global Geochemical Reference Network project to the geoscience, public, policy and decision-making communities (Liverman *et al.*, 2008; Stewart and Lewis, 2017). Some forward-thinking Geological Surveys have public relations and marketing experts, and their assistance should be sought for developing an effective strategy (*e.g.*, Tellus surveys of the north of Ireland - Glennon *et al.*, 2016; [USGS Communications and Publishing](#); [USGS Media Contacts](#)).

The public relations side of this committee is to communicate and promote the Global Geochemical Reference Network project to the widest possible audience. Whereas the role of the marketing side is to develop strategies and tools for promoting the products and services of the Global Geochemical Reference Network project to potential sponsors.

The duties of the Public Relations & Marketing Committee shall be:

- To develop the widest possible awareness of the Global Geochemical Reference Network project and its results firstly within the applied geochemistry community and secondly the earth science society as a whole.

- To promote the Global Geochemical Reference Network project by using all available communication tools, *e.g.*, social media, radio, television, articles in newsletters, newspapers, periodicals, *etc.*
- To organise an effective promotion campaign for convincing potential sponsors from industry, scientific societies and the public sector to contribute to the execution of various parts of the project.

As there will be a need to promote and market the Global Geochemical Reference Network project in each participating country, a Public Relations and Marketing (PRM) officer should be appointed with whom the Committee should have a close collaboration throughout the project duration. The national PRM officers, apart from a good command of the local language, must be proficient in English.

10.3. Publications

All members of the Global Geochemical Reference Network project are encouraged to write articles for publication in peer-reviewed journals. Publications using data covering the whole globe will be the most difficult to handle with respect to authorship. The amicable solution found for the publication of papers on the project ‘*Geochemical Mapping of Agricultural and Grazing land Soil (GEMAS)*’ may be used in a modified format to be decided upon because of the hundreds of participant names. The published GEMAS project papers use the following format: the names of the leading authors are placed in order of contribution and at the end, the name ‘The GEMAS Project Team’ is added with a superscript, and all participant names are placed in alphabetical order usually at the bottom left-hand corner of the paper’s first page (*e.g.*, Reimann *et al.*, 2012b; Négrel *et al.*, 2021). Hence, by using this format credit is given to all project participants.

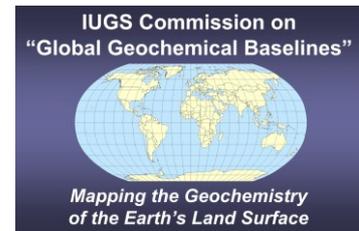
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Note: All hyperlinks were checked on the 3rd February 2022.

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**International Union of Geological Sciences
Manual of Standard Methods
for
Establishing the Global Geochemical Reference Network**

Appendix 1

Field Observation Sheets

- Rock
- Residual soil
- Humus
- Overbank sediment
- Stream water & Stream sediment
- Floodplain sediment

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Field Observations Sheet

ROCK

ROCK Sample ID: _____ Date: _____

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

SITE DESCRIPTION

Approximate average size of outcrops: From: _____ to _____ m²

Landscape / topography: _____

- Land use: Agriculture Pasture, grassland, fallow field
- Forest Wetland
- Non-cultivated, moorland, etc.; Other, specify _____

Predominant bedrock lithology within catchment basin _____

Rock type: _____

Number of sampling subsites: _____

Joints/Fractures, specify: _____

Weathering, specify: _____

Oxidation, specify: _____

Type of overburden: _____

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

Instrument type: _____

REMARKS (any unusual observations)

Photographs: _____



Field Observations Sheet

RESIDUAL SOIL

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 catchment basin _____ km²

Landscape / topography: _____

Land use: Agriculture Pasture, grassland, fallow field
 Forest Wetland
 Non-cultivated, moorland, etc.; Other, specify _____

Bedrock lithology: _____ Outcrops: Yes, specify

SITE DESCRIPTION

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; Wet

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

Abundance of organic matter in % (Top 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: _____



Field Observations Sheet

HUMUS

HUMUS Sample ID: _____ Date: _____

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

Type of forest, specify tree/shrub species in order of abundance:

1: _____ 2: _____

3: _____ 4: _____

Tree/shrub density: Typical distance between trees/bushes:

1 – 3 m 3 – 5 m 5 – 10 m >10 m

Age of forest: Young Mature

Underbrush character: Bushes _____

(Specify species, if possible) Low vegetation _____

Underbrush/low vegetation coverage: <20% 20–80% >80%

Substratum: _____

Total thickness of organic layer (cm): _____

Thickness of humus layer (cm): _____

HUMUS SAMPLE COMPOSITION

- Raw humus
- Raw humus + humus
- Humus

NUMBER OF SUBSITES: _____

PHOTOGRAPHS: Note: If the humus and residual soil samples are taken from the same area and the organic horizon is shown in the soil pit photograph, then separate photographs for humus are not required.

Photographs for humus sample were taken (see below)

No separate photographs for humus

Landscape: _____

Site: _____

REMARKS



Field Observations Sheet

STREAM WATER + STREAM SEDIMENT

STREAM WATER Sample ID: _____ Date: _____

STREAM SEDIMENT 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 catchment basin _____ km²

Landscape / topography: _____

Land use: Agriculture Pasture, grassland, fallow field
 Forest Wetland
 Non-cultivated, moorland, etc.; Other, specify _____

Bedrock lithology: _____ Outcrops: Yes, specify _____

No outcrops

Type of overburden: _____

Channel characteristics Natural; Reinforced; Human-made (ditch)

Last rainfall - before: _____ days _____ hours

Water level in stream: Low; Normal; High

Stream flow: Low; Moderate; High

Stream bed: Predominant Boulders and gravel; Gravel and sand
 Sand and silt; Mud; Vegetation

Possible sources of contamination, specify: _____

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

NUMBER OF SUBSITES (stream sediment): _____

NUMBER OF SAMPLE BAGS (stream sediment): _____

WATER CHEMISTRY Routine sample Duplicate sample Instrument

pH _____

EC (mS/m 25°C) _____

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

Instrument type: _____

DRYING (Sediment): Freeze drying; <40°C

REMARKS (any unusual observations)

Photographs: _____



Field Observations Sheet

OVERBANK SEDIMENT

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

DESCRIPTION OF CATCHMENT BASIN

Approximate size of catchment basin _____ km²
Landscape / topography: _____
Land use: [] Agriculture [] Pasture, grassland, fallow field
[] Forest [] Wetland
[] Non-cultivated, moorland, etc.; [] Other, specify _____
Predominant bedrock lithology within catchment basin _____

SITE DESCRIPTION

River width: _____ m depth: _____ m
Depth of observed ground water table (cm): _____

Grain size range of TOP sample: [] sand-silt; [] silt-clay; [] clay
Abundance of clasts >2 mm in % (Top sample): _____ %
Sediment moisture on day of sampling: [] Dry; [] Medium; [] Wet

Grain size range of BOTTOM sample: [] sand-silt; [] silt-clay; [] clay
Abundance of clasts >2 mm in % (Bottom sample): _____ %
Sediment 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: _____



Field Observations Sheet

FLOODPLAIN SEDIMENT

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

DESCRIPTION OF CATCHMENT BASIN

Approximate size of catchment basin _____ km²

Landscape / topography: _____

Land use: Agriculture Pasture, grassland, fallow field
 Forest Wetland
 Non-cultivated, moorland, etc.; Other, specify _____

Predominant bedrock lithology within catchment basin _____

SITE DESCRIPTION

River width: _____ m depth: _____ m

Depth of observed ground water table (cm): _____

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

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

Sediment moisture on day of sampling: Dry; Medium; Wet

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

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

Sediment 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: _____

“Everything in and on the Earth - mineral, animal and vegetable - is made from one, or generally some combination of, the natural chemical elements occurring in the rocks of the Earth’s crust and the surficial materials derived from them. Everything that is grown, or made, depends upon the availability of the appropriate elements. The existence, quality and survival of life depends upon the availability of elements in the correct proportions and combinations. Because natural processes and human activities are continuously modifying the chemical composition of our environment, it is important to determine the present abundance and spatial distribution of the elements across the Earth’s surface in a much more systematic manner than has been attempted hitherto” (Darnley et al., 1995, p.x). Although such a global database is urgently needed for multi-purpose use, the systematic attempt is still in its infancy because of the non-existence of a manual of comprehensive and standardised methods of sampling and other supporting procedures. The current ***‘International Union of Geological Sciences Manual of Standard Methods for Establishing the Global Geochemical Reference Network’*** fills this gap. The Manual follows the concept of 7356 Global Terrestrial Network grid cells of 160x160 km, covering the land surface of Earth, with five random sites within each grid cell for the collection of samples. This allows the establishment of the *standardised Global Geochemical Reference Network* with respect to rock, residual soil, humus, overbank sediment, stream water, stream sediment and floodplain sediment. Apart from the instructions for the collection of samples, the Manual covers sample preparation and storage, development of reference materials, geoanalytical methods, quality control procedures, geodetic and parametric levelling of existing data sets, data conditioning for the generation of time-independent geochemical data, management of data and map production, and finally project management. The methods described herein, apart from their use for *Establishing the Global Geochemical Reference Network*, can be used in other geochemical surveys at any mapping scale.

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