Geochemical Atlas of Europe: Techniques and Management

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FOREGS atlas team
(see List of Participants slide)

IUGS/IAGC Task Group on "Global Geochemical Baselines"

Mapping the Geochemistry of the Earth's Land Surface

The role of Geological Surveys in producing a state-of-the-art Global Geochemical Database

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STRUCTURE OF SEMINAR PRESENTATION

1. Introduction
2. Background of European and Global Geochemical projects
3. Objectives
4. Basic survey requirements
5. Production of high quality geochemical data sets and role of Geological Surveys
6. Organisation and management of the European Geochemical mapping project (FOREGS)
7. Hellenic fieldwork planning and execution
8. Development of the European Geochemical databases
9. Geochemical Atlas of Europe
    - Geochemical baseline concentrations of elements in soil, water and sediment
    - Use of geochemical data in mineral exploration, farming & forestry, land use policy, health issues, environmental policy
    - Robustness of geochemical patterns
    - Geochemical Atlas of Europe
10. Epilogue – Conclusions, Recommendations
11. References

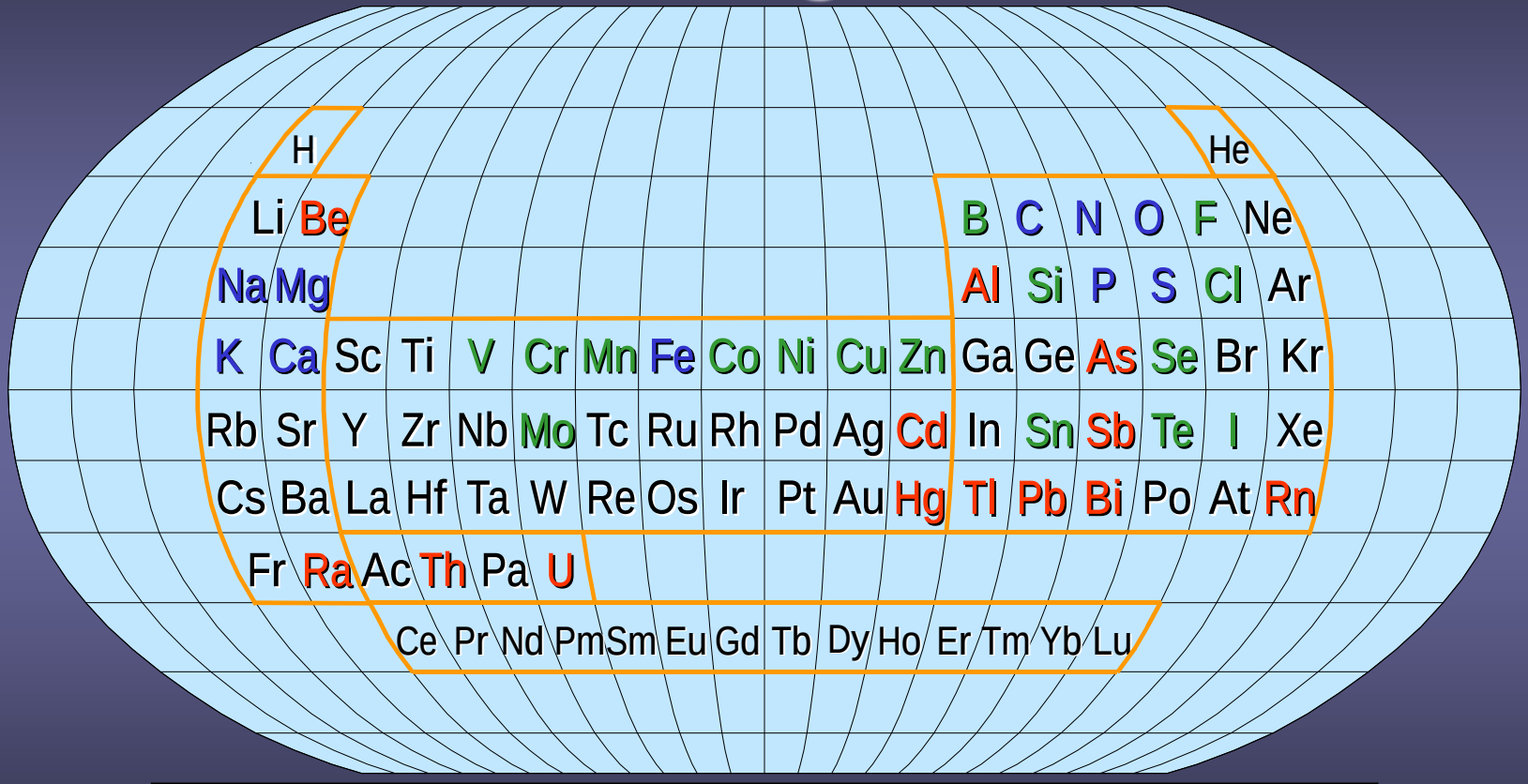
SURVIVAL OF LIFE ON EARTH

- Everything in and on earth - mineral, animal and vegetable - is made from one, or generally some combination of the 86 naturally occurring chemical elements.
- Everything that is grown, or made, depends upon the availability of the appropriate elements.
- The existence, quality and survival of life depends upon the availability of elements in the correct proportions and combinations.

Darnley et al. (1995, p. x)

http://www.globalgeochemicalbaselines.eu

Chemical elements of biological and economic significance



Harmful elements
Elements of major biological need
Elements of minor biological need

Elements of potential economic interest for the present or future

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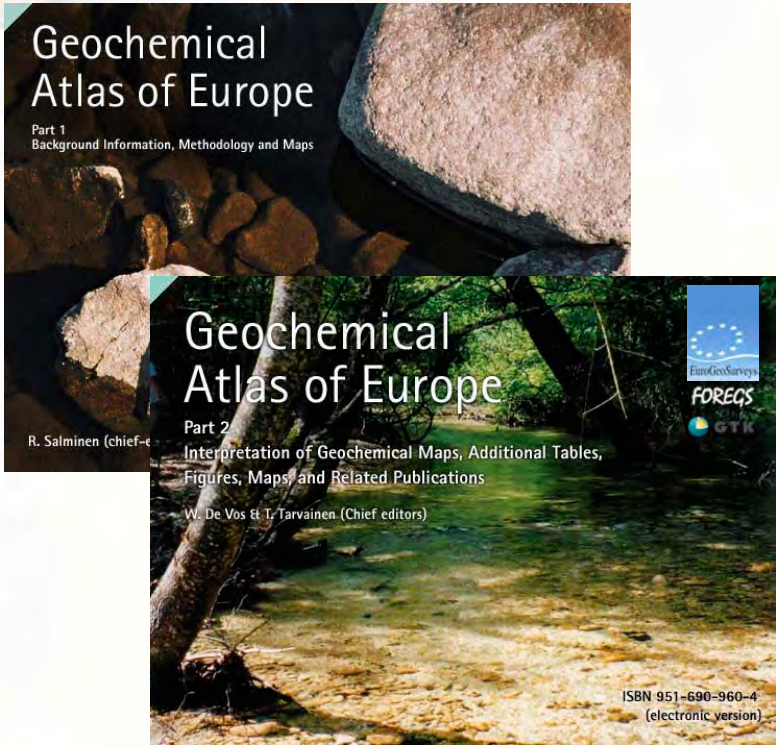
Background of European and Global Geochemical projects



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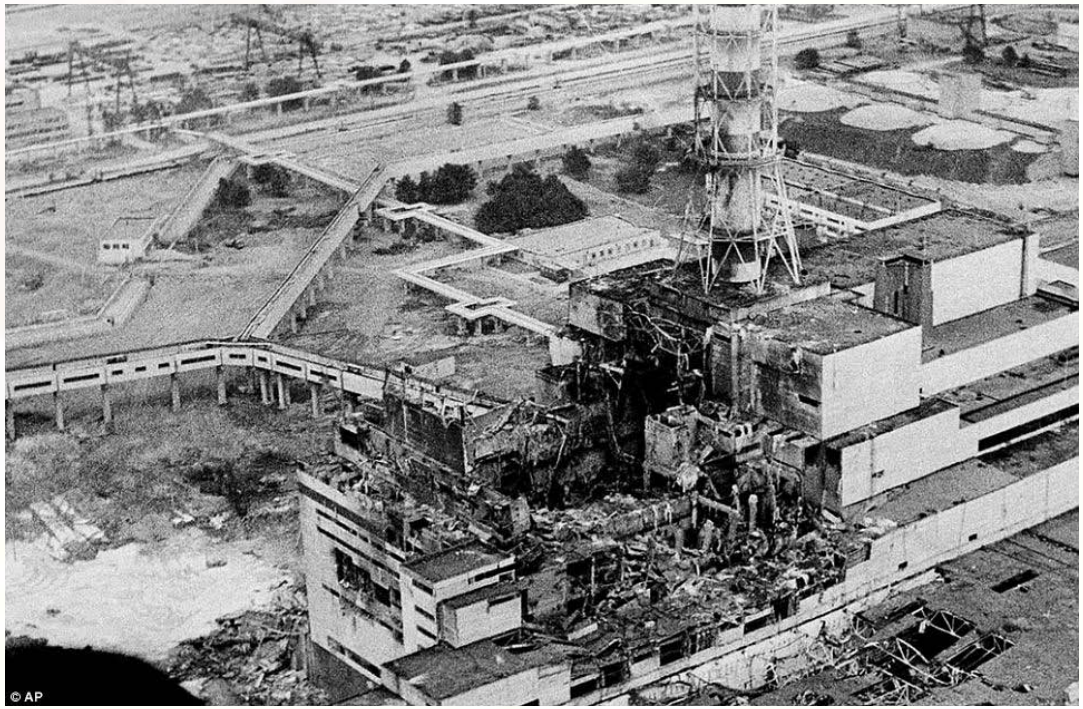
THE NEED FOR SYSTEMATIC GEOCHEMICAL & RADIOMETRIC MAPPING

Chernobyl nuclear reactor 4
26 April 1986

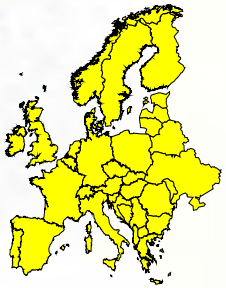


The Chernobyl accident awakened the most extreme environmental hazard, "*nuclear catastrophe*"!

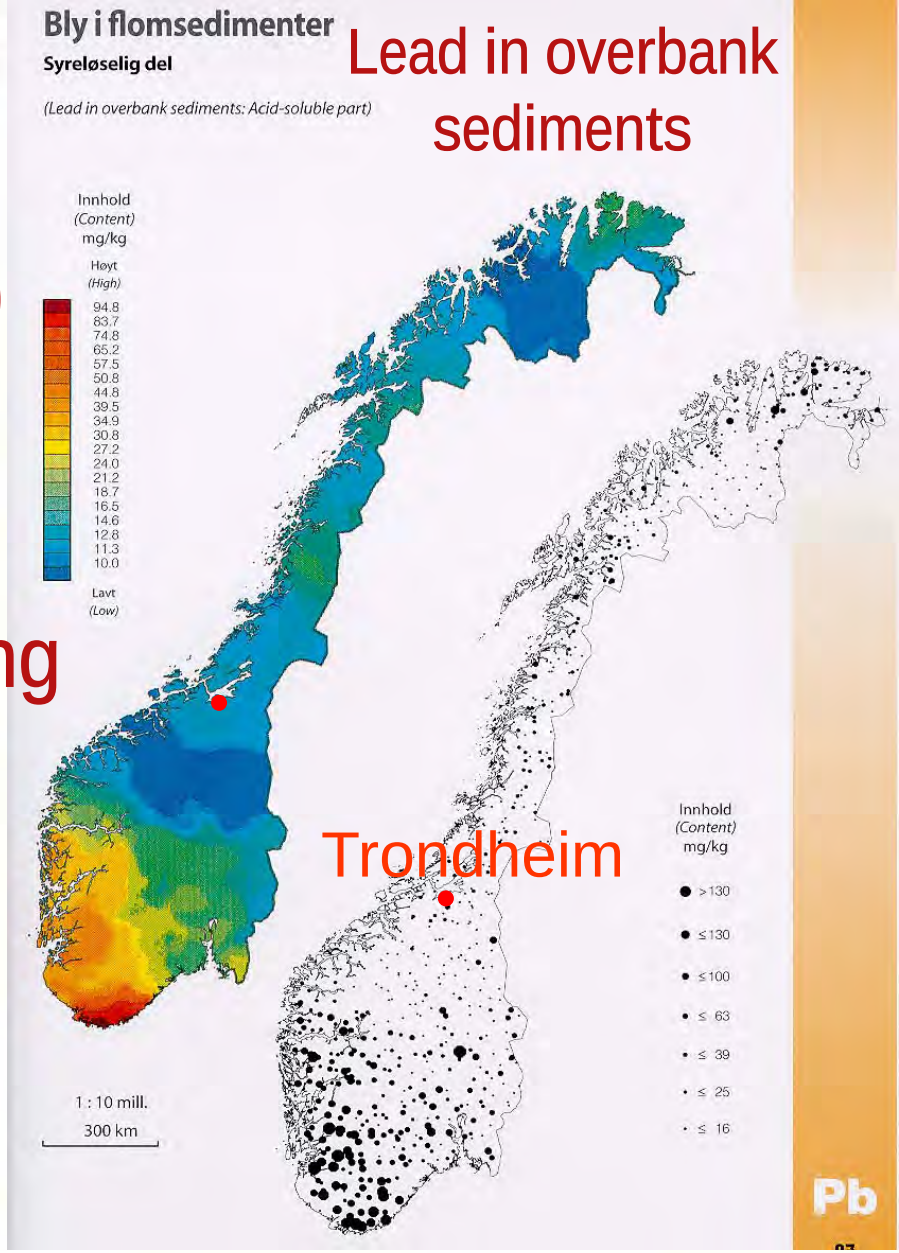
Meeting of Western European Geological Surveys' (WEGS)

Working Group on Regional Geochemical Mapping

Trondheim, Norway 21-22 May 1986



Birth of the idea of European Geochemical Mapping



Ottesen et al. (2000, p.85)

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1986 Proposal for Continental Scale Geochemical Mapping (Demetriades et al., 1990)

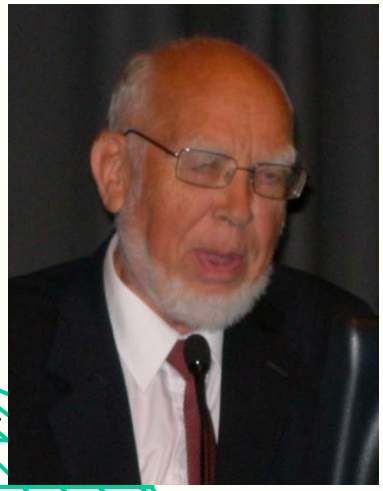
Sample density: 1 sample station/500 km^2

- Surface water
- Ground water
- Surface soil (terrestrial organic matter)
- Soil c-horizon (soil parent material) and
- Overbank sediment and
- Stream sediment (added later)

All samples were going to be analysed free of charge by the Geological Survey of Norway. The Directors of the European Geological Surveys did not accept to begin with the proposal, and the decision to go ahead with the project was taken in 1996 (ten years later), but the Norwegian offer was not there any longer.

GLOBE
Need for a Global radiometric map to define the present Baseline

EUROPE
Need for a European Geochemical Atlas to define the present Baseline



Arthur G. Darnley

Bjorn Bolviken

Ottawa

Trondheim

Birth in 1988 of IGCP 259 “International Geochemical Mapping”

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OTHER GLOBAL PROBLEMS…..

1. Most parts of the World have been settled by humans, and depending on the type of economy, the terrestrial surface has been modified accordingly. For example, Europe has a long history of mining, industrialisation, intensive agriculture/forestry and urbanisation, and it remains as one of the most densely populated and utilised land areas on earth. CCOP countries, although some of them densely populated, their economy is still mostly rural, but it is rapidly changing to an urban and an industrialised economy.
2. Human colonisation of the terrestrial surface of the Earth resulted in the development of interrelated problems of land degradation and contamination, which affect both the land and the coastal zone.

…..OTHER GLOBAL PROBLEMS

3. Deficiency conditions in crops, agricultural animals and possibly humans are increasing, partly as a result of land degradation all of over the World.
4. In industrialised countries, redevelopment of contaminated land is becoming increasingly difficult, because of legislative and financial controls. This is despite the need to reutilise “brown field” sites, rather than to extend development into “green field” areas.
5. Throughout the Globe public concern about the environment is growing. In response, national governments and the United Nations are attempting to develop policies for the protection of the environment and its sustainable development.

…..THE GLOBAL PROBLEMS

6. Attempts are also being made to establish '*Safe levels*' of Potentially Harmful Elements and Species, but these are often based on limited and/or inadequate information.
7. The available data on environmental geochemical baselines and radioactivity are not systematic in coverage or quality and, therefore, are not of the standard required to quantify the distribution of Potentially Harmful Elements and Species at the Global scale, as a basis for policy-making and monitoring future change to the environment.

CONCLUSION

- **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 that has been attempted hitherto.**
- **For a realistic assessment of pollution, it is significant to have high quality GEOCHEMICAL BASELINE DATA about the natural element variation before humans began to contaminate the environment.**

R E C O M M E N D A T I O N

TO SYSTEMATICALLY MAP THE GEOCHEMISTRY OF THE EARTH'S TERRESTRIAL SURFACE

(Darnley et al., 1995, p.x)

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Final Report of IGCP Project 259 "International Geochemical Mapping"

The report is a milestone for Global Environmental and Resource Management.

It recommends the development of a homogeneous Global Geochemical Database.

A very significant database, which is concerned with the chemistry of terrestrial life support systems.

The methodology for the development of this Global Geochemical is also given.

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Long Term Objective

Publication of the multi-element

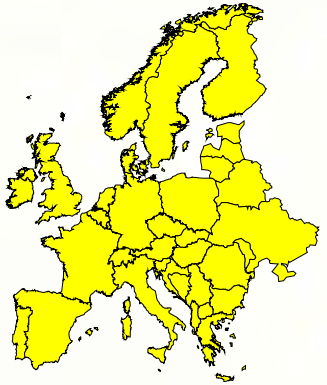
Global Geochemical Atlas & Database

with state-of-the-art technology, compatible with Geographical Information Systems.

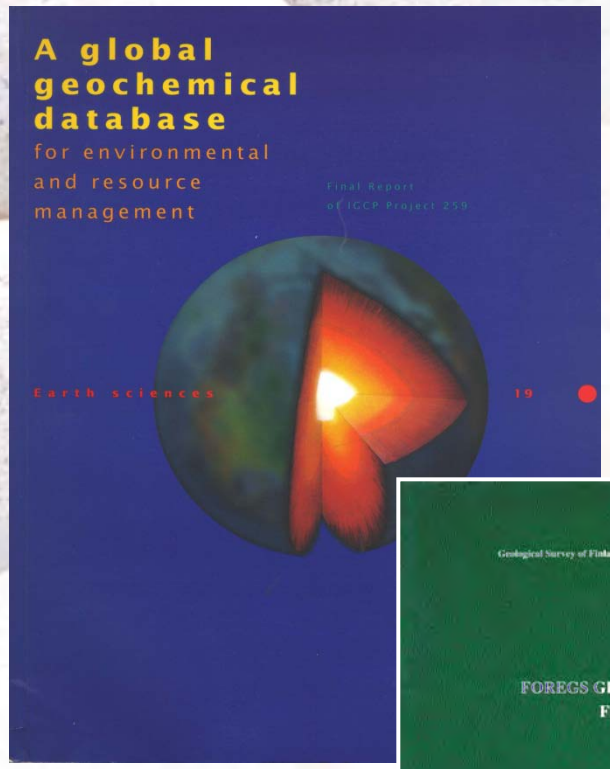
This information will constitute the environmental framework for the

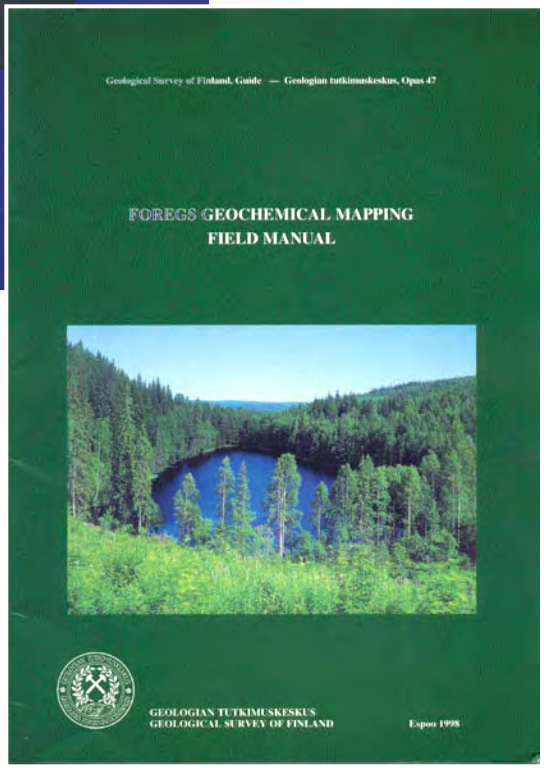
21st Century

Short term objectives for Europe



- **To complete the global Geochemical Reference Network by the year 2000 for the continent of Europe;**
- **To provide high quality digital databases, geochemical maps and interpretative publications, as a basis for environmental, land-use planning, agricultural, epidemiological, mineral exploration and geological studies, and**
- **To produce an end-20th Century review of the geochemical composition of the surface environment, based on the integration of readily available national multi-element and multi-media data sets.**





Basic survey requirements

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SURVEY REQUIREMENTS …..

Systematic baseline environmental geochemical data are necessary to inform policy-makers and to provide a sound basis for legislation. For this purpose such data are required to be:-

1. **Standardised across national boundaries;**

2. **Available in digital form for use on GIS, so that they can be viewed interactively with other data sets, such as those for land-use, and for animal and human morbidity and mortality data;**

(Plant *et al.*, 1996, p.1)

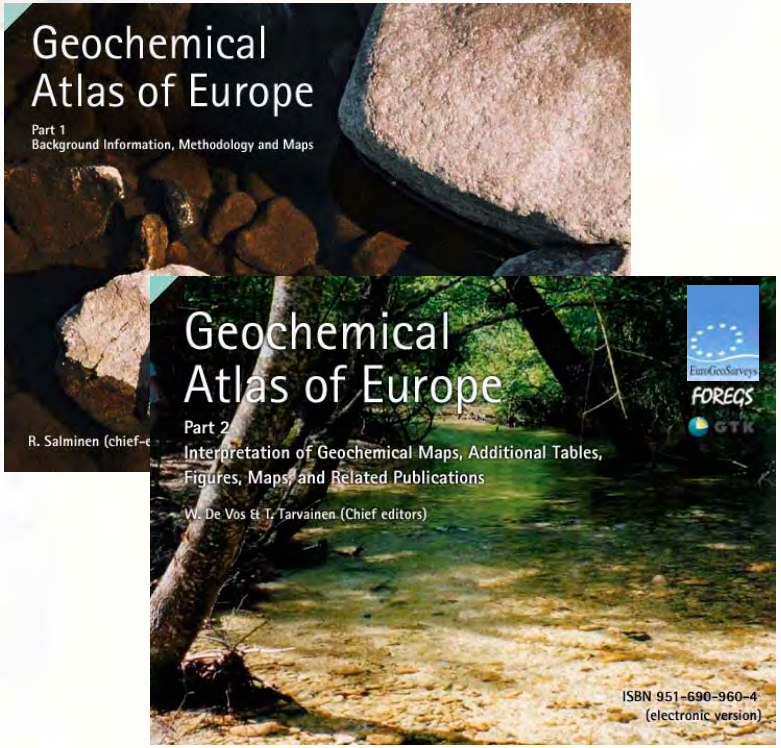
….. SURVEY REQUIREMENTS

3. **Comprehensive, to include the majority of potentially harmful elements, and ideally as many harmful chemical species as possible, including synthetic compounds, and**

4. **Based on a full suite of sample types including soil, stream sediment, surface water, ground water, and off-shore marine and estuarine sediment in the coastal zone.**

(Plant *et al.*, 1996, p.1)

Production of high quality Geochemical data sets and role Geological Surveys



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THE EUROPEAN GEOCHEMICAL ATLAS PROJECT (FOREGS)

1986 - 1993: Pilot and Research phases
1994 - 1996: Discussion and decision phase
1997 - 2006: Planning, Training and Execution

20 LONG YEARS
from inception to completion

My recommendation to the CCOP countries:
DO NOT TAKE THAT LONG
The time to act is now
Do not defer decisions to some other time. There are many reasons for Geological Surveys to go ahead with this project.

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WHY GEOLOGICAL SURVEYS SHOULD CARRY OUT THE GLOBAL GEOCHEMICAL BASELINES PROJECT?

1. The lithosphere is the fundamental base on which soils and crops develop, and through which water and fluid pollutants migrate.
2. Geological Surveys are uniquely well equipped to prepare the systematic geochemical databases for environmental concerns and mineral resource management, since:
   (a) They have the knowledge and experience of optimum methods of sampling and analysis of surface environmental materials, and are familiar with the preparation, study and interpretation of geochemical maps.
   (b) Many are already concerned with the preparation of multi-element geochemical maps of rocks, soils, surface waters, ground waters and stream sediments.

Plant et al. (1996)

.....WHY GEOLOGICAL SURVEYS SHOULD CARRY OUT THE GLOBAL GEOCHEMICAL BASELINES PROJECT?

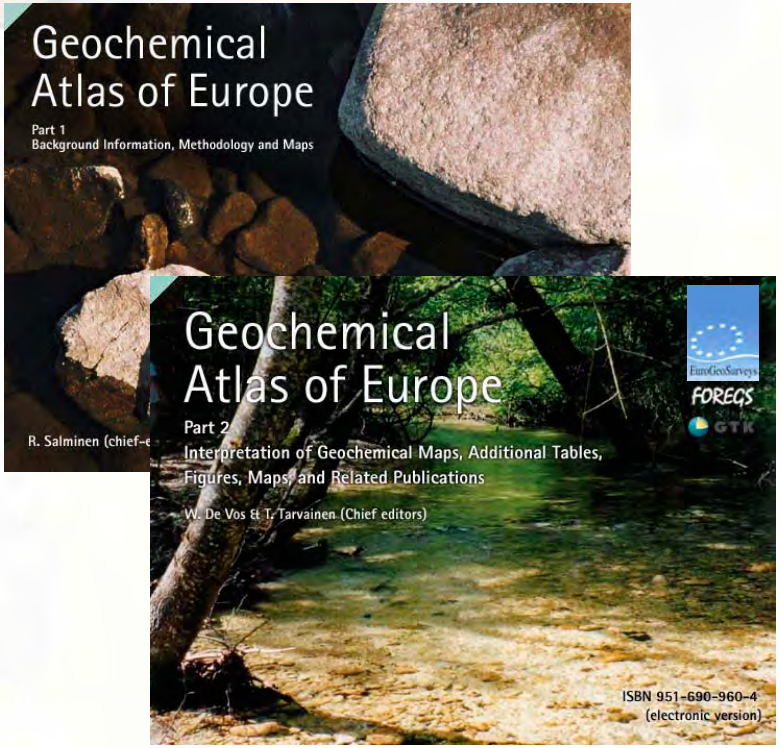
(c) Many are centres of excellence for the study of water and silicate mineral chemistry. The aim is to standardise all surveys at a high level of analytical capability.

(d) Geochemical baseline data in digital form, produced in many countries at the national scale, already enable contaminated land to be viewed in the context of naturally occurring high levels of potentially harmful elements and species, and the natural environment generally.

(e) Geological Surveys have experts on ore deposits, which provide natural analogues for understanding the distribution and migration of heavy metals, radioelements and other pollutants in different geological environments.

(g) Geological Surveys have the quality control procedures in place, and the expertise in databases and GIS, to develop and apply both environmental baseline and exploration geochemistry effectively.

Organisation and management of the European Geochemical mapping project (FOREGS)



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26 countries participated in the Geochemical Baseline Mapping of Europe

Area: 4.250.000 km²
925 sample sites
1 site/4600 km²

Each country funded its own survey

The European contribution to IUGS/IAGC "*Global Geochemical Baselines*"

Cost ~3.5 – 5+ million Euro; ~4.62 – 6.60+ US$

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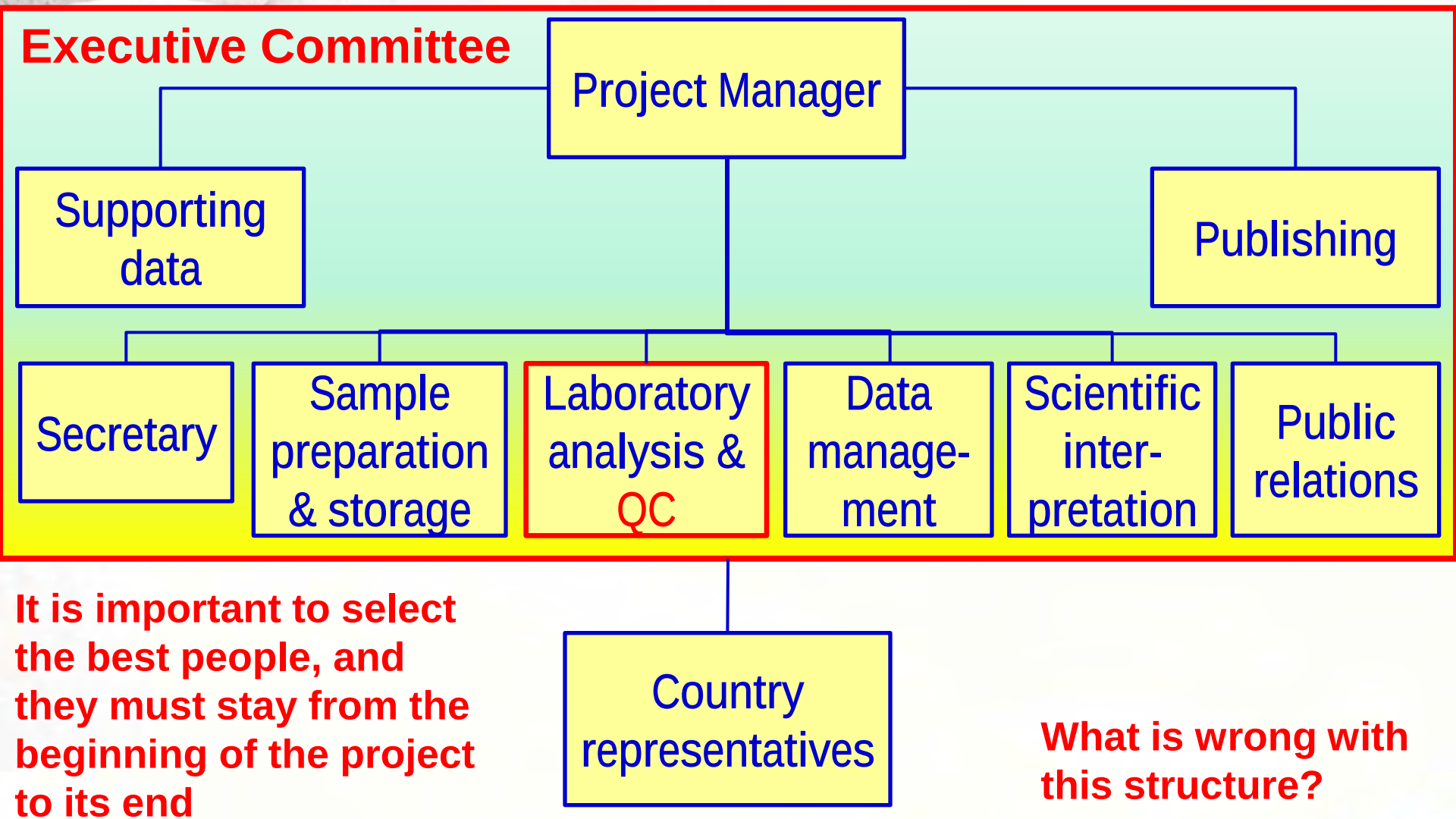
FOREGS PROJECT ORGANISATION AND MANAGEMENT



It is important to select the best people, and they must stay from the beginning of the project to its end

What is wrong with this structure?

What is wrong with this structure?

Project Manager

There is no Deputy Project Manager.
What happens if something goes wrong with the Project Manager?
Hence, a Deputy Project Manager is required.

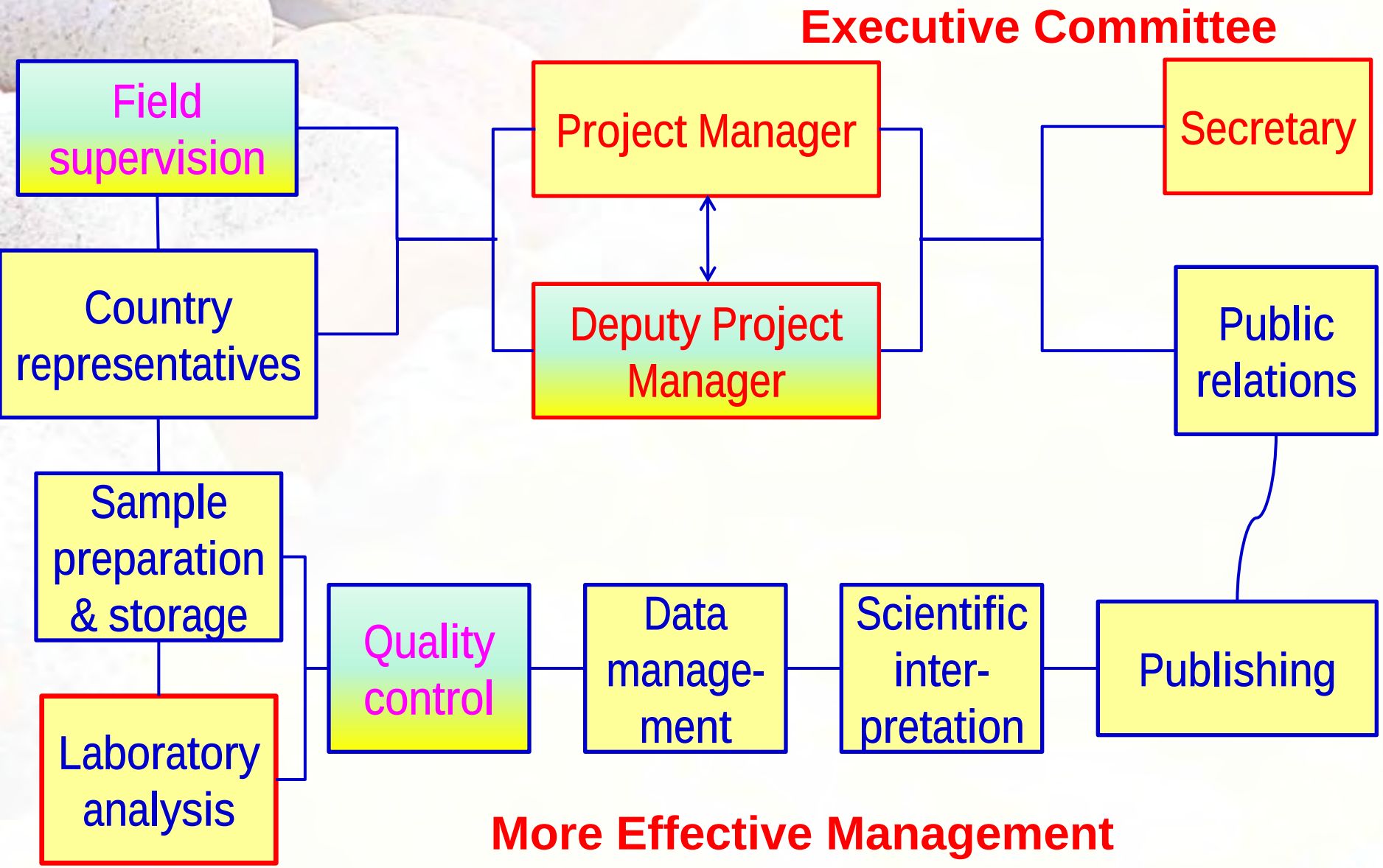
Executive Committee

There are Nine people in the Executive Committee. Too many!

Laboratory analysis & QC

The Laboratories, apart from their internal laboratory control, they are responsible for the Independent Quality Control. This is definitely wrong.

PROJECT ORGANISATION AND MANAGEMENT



More Effective Management

OTHER IMPORTANT MANAGEMENT ACTIONS…..

Project Management

Purchase of all equipment centrally and distribution to all participating countries

Written confirmation from all countries that they will carry out the project and bear the costs

Field supervising team

Field training of all country representatives

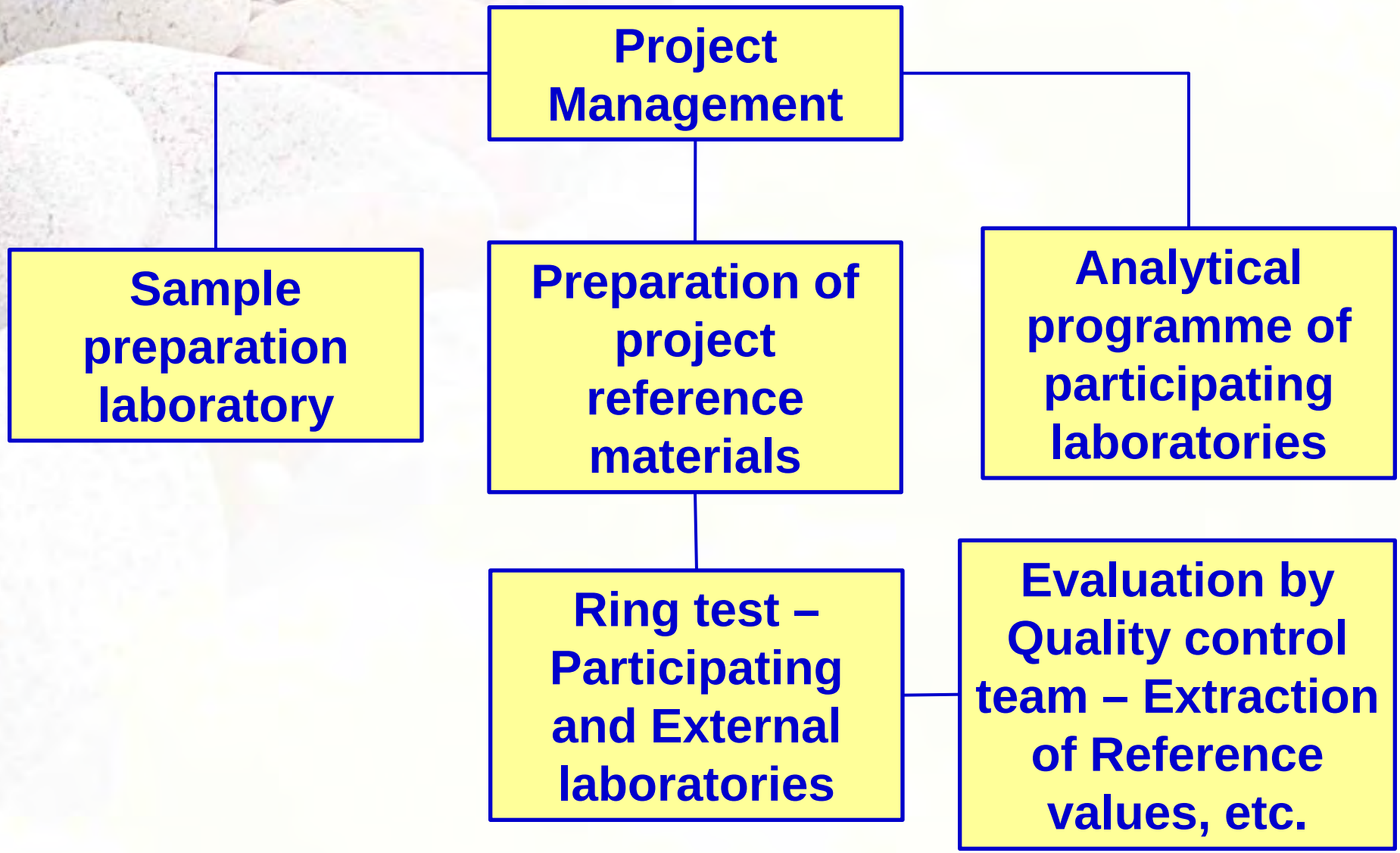
All stream water containers to be trace element free

Field supervising team

- To provide random sampling sites within GTN cells;
- To check all sampling plans;
- To give further information whenever needed, and
- Upon completion of all sampling the team must check all sample site coordinates, field sheets, and photographs

The field supervising team was missing from the FOREGS project

…..OTHER IMPORTANT MANAGEMENT ACTIONS…..



…..OTHER IMPORTANT MANAGEMENT ACTIONS

Intellectual Property Rights

This is a very important issue in a multi-national and a multi-person project.

- **The data are generated by the collective efforts of all participants.**
- **The national data sets belong to each participating country.**
- **But, the whole data set belongs to everybody; it belongs to the Project.**

…..OTHER IMPORTANT MANAGEMENT ACTIONS

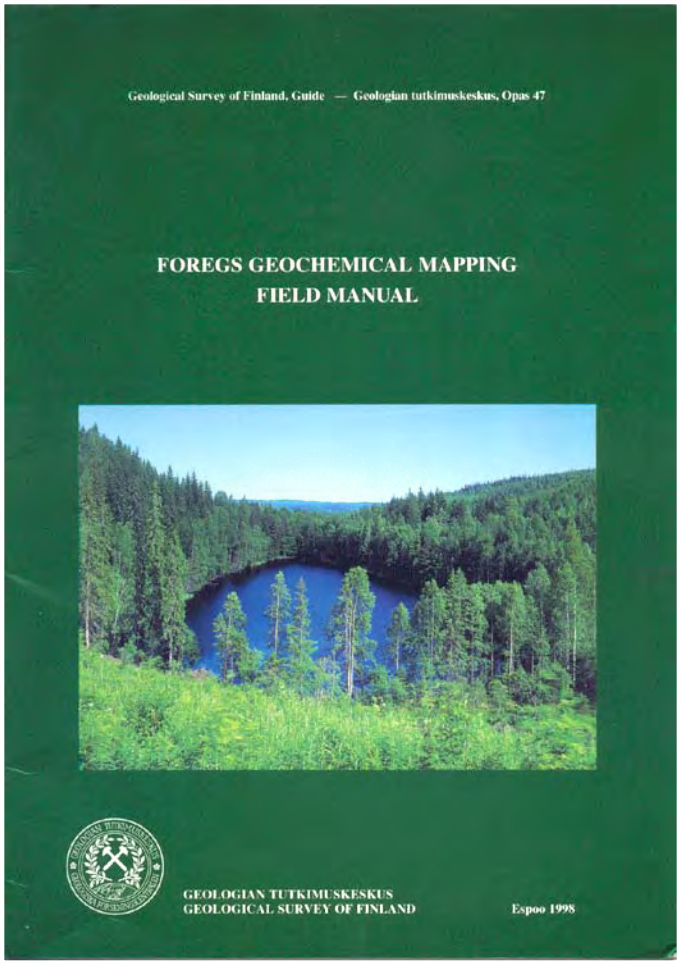
Intellectual Property Rights

Hence, authorship of the CCOP geochemical atlas must be discussed at the beginning of the project.

The Directors of the European Geological Surveys decided that all names should be cited in all European publications.

The Project Team, after some problems, decided that all publications should be circulated to all participants, and only the contributing persons will be co-authors, and all the other names mentioned in the acknowledgements.

FOREGS GEOCHEMICAL MAPPING FIELD MANUAL



Includes field sampling instructions for Temperate and Mediterranean type terrains, and it is being updated to include instructions for Karst, Desert, Tropical, Tundra and Arctic terrains

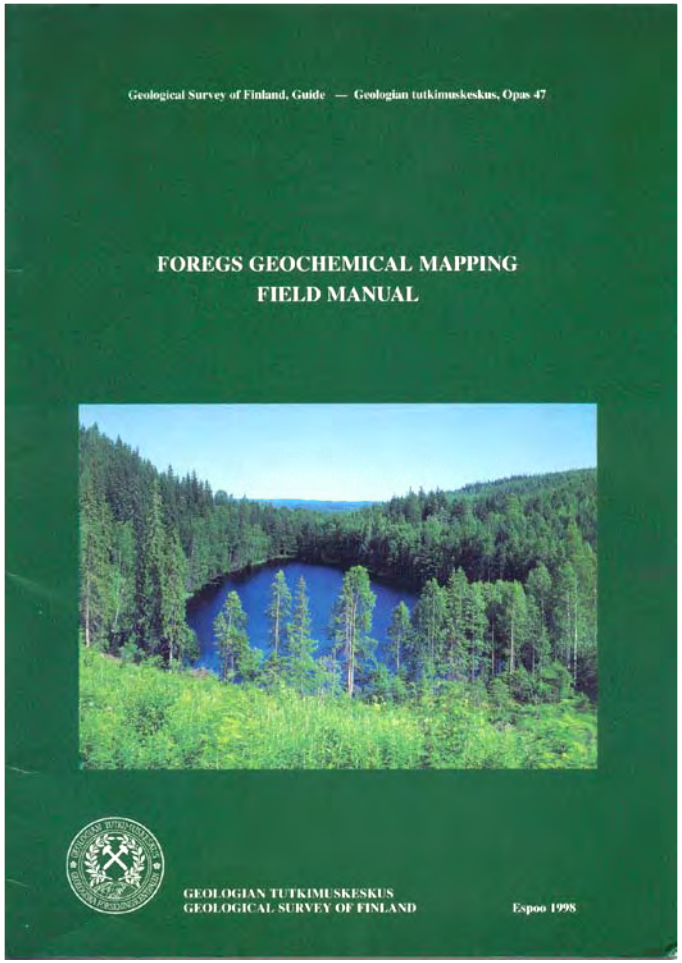
The first version was written at the end of 1996 and beginning of 1997, and was finalised in June 1997 during a field meeting in Slovakia

http://www.gsf.fi/foregs/geochem/fieldman.pdf

FIELD WORK PLANNING

Blue book

Green book



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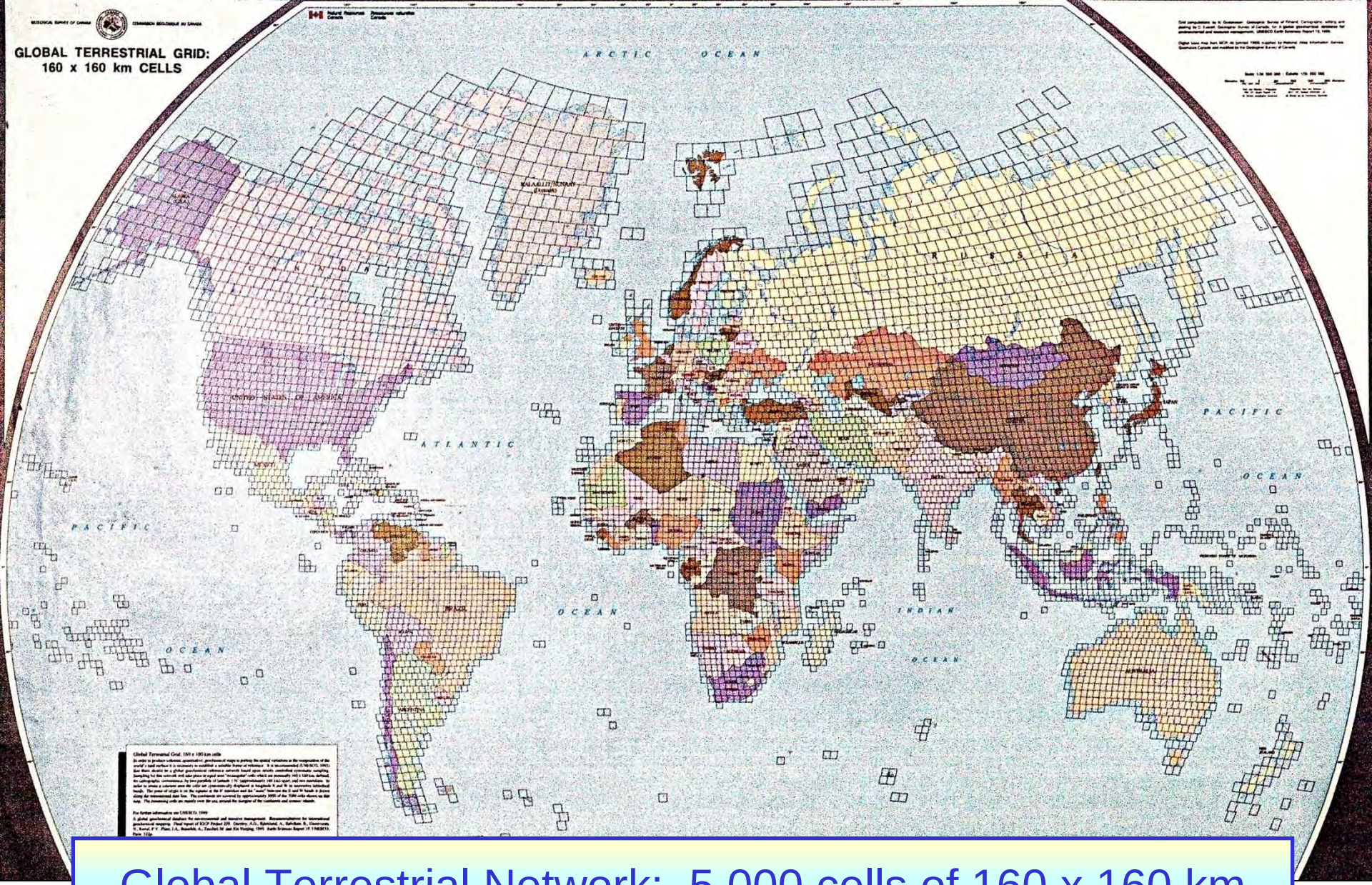

Global Terrestrial Network: 5,000 cells of 160 x 160 km

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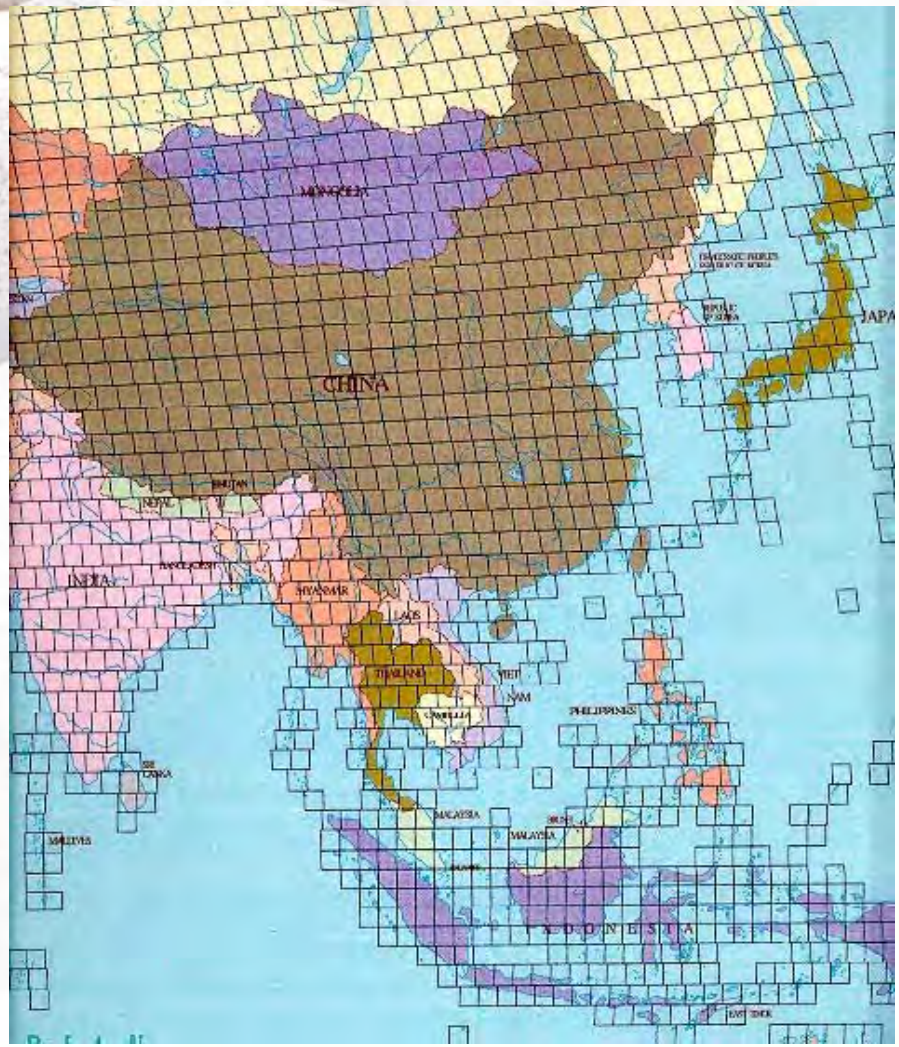
Part of Asia showing C.C.O.P. countries

GTN or GRN cells
160 x 160 km

Global Terrestrial Network (GTN) or Geochemical Reference Network (GRN)



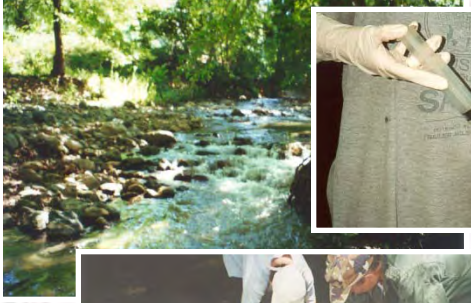
In some cases there are no GTN or GRN cells in coastal areas. The reason is that at least three basins should be sampled in a 160 x 160 km cell.

In the FOREGS project it was decided, somewhat late, to sample coastal cells, with even one drainage basin, in order to have a complete coverage.

Sample types to be collected

- Stream water (filtered and unfiltered)
- Stream sediment (mineral sediment, <0.150 mm)
- Residual soil, upper horizon (topsoil) 0 - 25 cm with out the top organic layer (<2 mm)
- Residual soil, lower (C) horizon (subsoil); a 25 cm layer within a depth range of 50 to 200 cm (<2 mm)
- Humus where present
- Overbank sediment, upper horizon 0-25 cm (<0.150 mm, optional)
- Overbank sediment, bottom layer (<0.150 mm, optional)
- Floodplain sediment, upper horizon 0 - 25 cm (<2 mm)
- Floodplain sediment, bottom layer (<2 mm, optional)

Recommendation: Collect all sample types

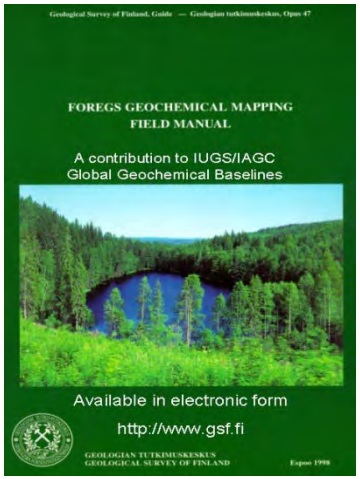


➢ River water (filtered & unfiltered)

➢ Stream sediment

- Wet sieving

- Dry sieving



A practical guide for field sampling

➢ Residual soil (top & bottom)

➢ Humus

➢ Floodplain and/or overbank sediment

TRAINING

All European field sampling teams were trained in Slovakia in June 1997

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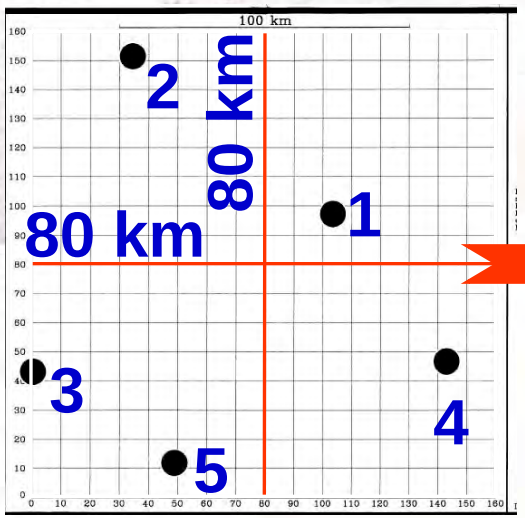
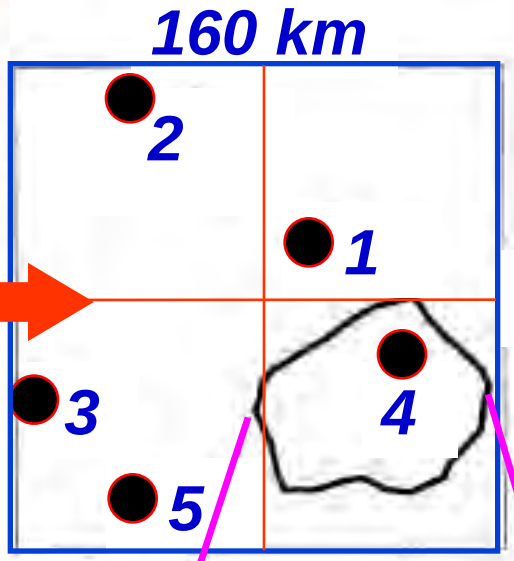
SAMPLING SCHEME

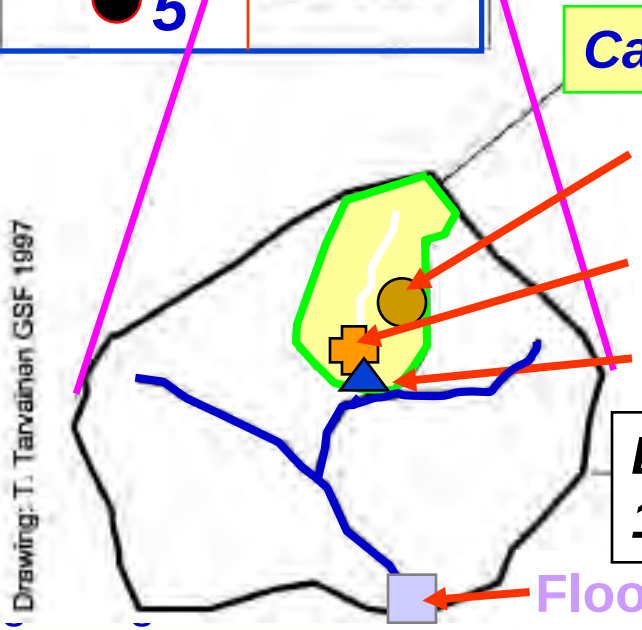
According to the specifications of IGCP 259 "*International Geochemical Mapping*" report





Randomly selected points in GTN cell N43E09

Random selection of drainage basins in each 160 x 160 km cell. At least one basin falls in each 80 x 80 km sub-cell.



Catchment <100 sq.km

Humus & Soil

Overbank sediment

Stream water & stream sediment

Large drainage basin 1000-6000 sq.km

Floodplain sediment

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PRODUCTION OF HIGH QUALITY GEOCHEMICAL DATABASES.....

REQUIRES GOOD PLANNING AT ALL STAGES OF:

Sampling

Sample preparation

Laboratory analysis

Geochemical database management

Map production

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..... PRODUCTION OF HIGH QUALITY GEOCHEMICAL DATABASES .....

REQUIRES THE INSTALLATION OF STRICT QUALITY CONTROL PROCEDURES AT ALL STAGES OF:

Sampling

Sample preparation

Laboratory analysis

Geochemical database & maps

….. PRODUCTION OF HIGH QUALITY GEOCHEMICAL DATABASES

Sampling

Sample preparation

- **These are the two most crucial stages of any geochemical survey.**
- **Any errors during these two stages is carried forward, and can result in the failure of a whole survey.**

Laboratory analysis

- **Errors can be corrected by re-analysis of samples, provided there is available enough sampling material.**

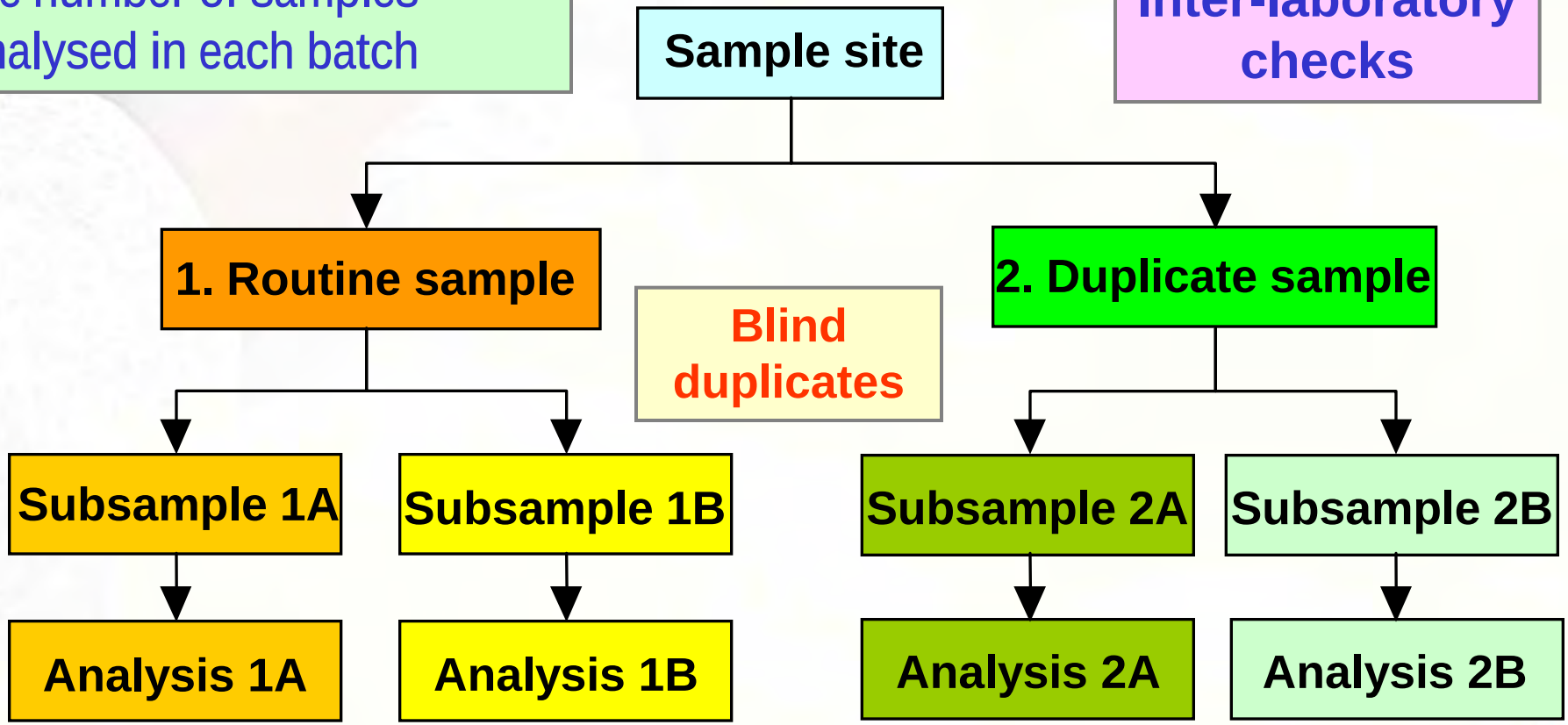
QUALITY CONTROL SCHEME

Analysis of *International and Project reference Samples*, which must be inserted at regular intervals according to the number of samples analysed in each batch

Duplicate field samples

Randomisation of ALL samples prior to analysis

Inter-laboratory checks



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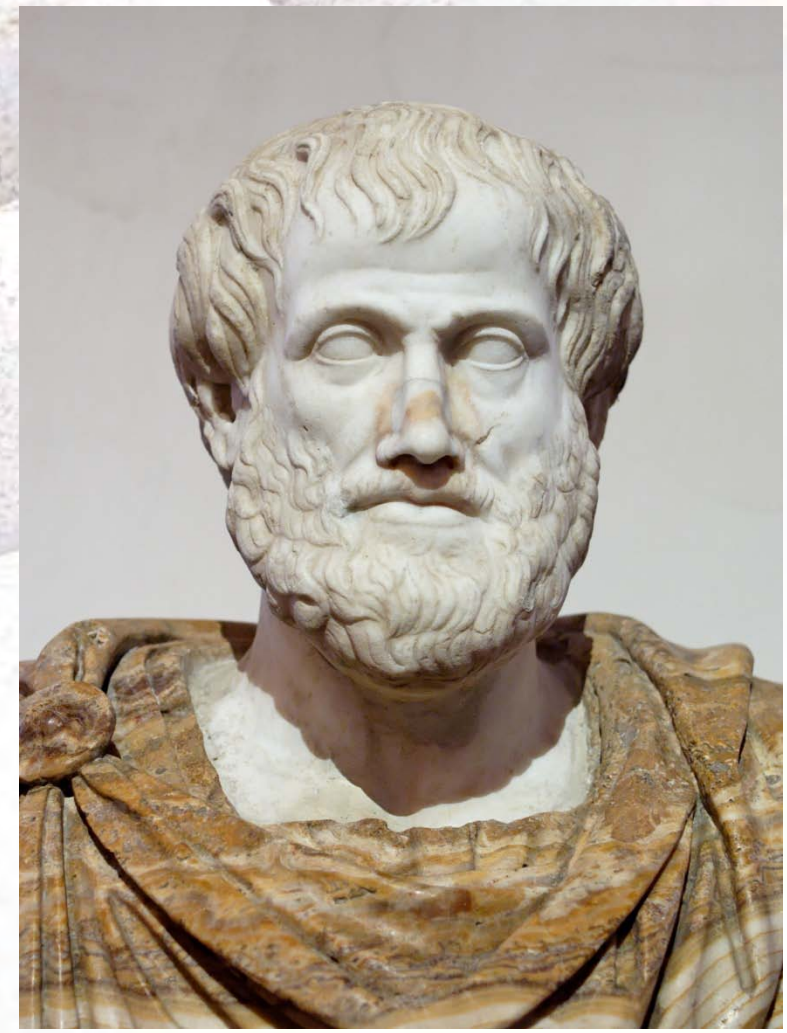
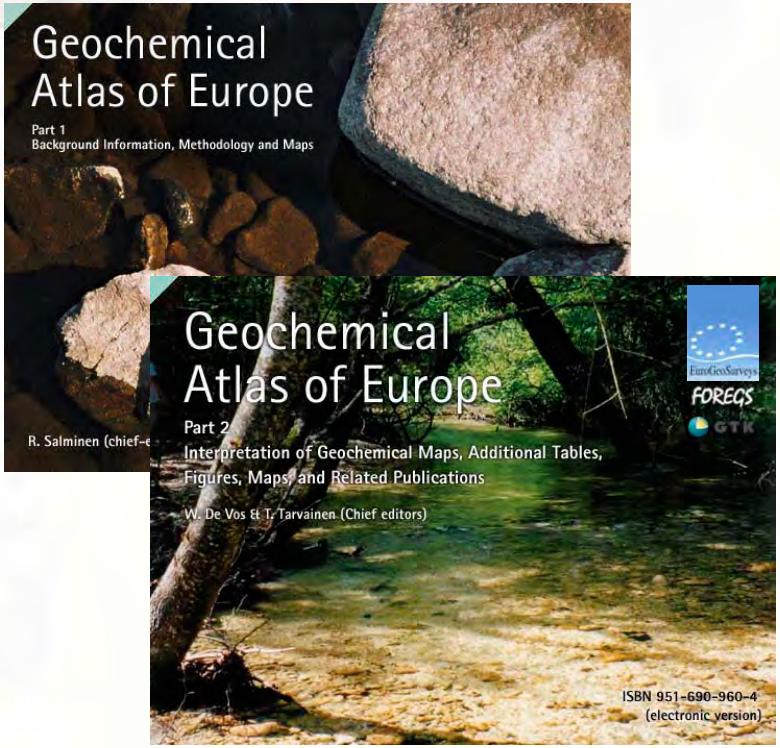


"*We are what we repeatedly do; excellence, then, is not an act but a habit*" Aristotle (384-322 B.C.)

'*Quality*' it is something that is being discussed from ancient to recent times. Already Aristoteles, the renown ancient Hellene philosopher considered '*quality*' in his famous work '*Categories*'. The Aristotelian philosophical approach demands a rational assessment of quality. Therefore, one can assume with good reason that it is not an easy topic to grasp and apply. The problem with the attribute of '*quality*' is that it is somewhat subjective and may thus be understood differently by different people. In modern times, it is most often defined as '*fitness-for-purpose*'.

Hellenic fieldwork planning and execution



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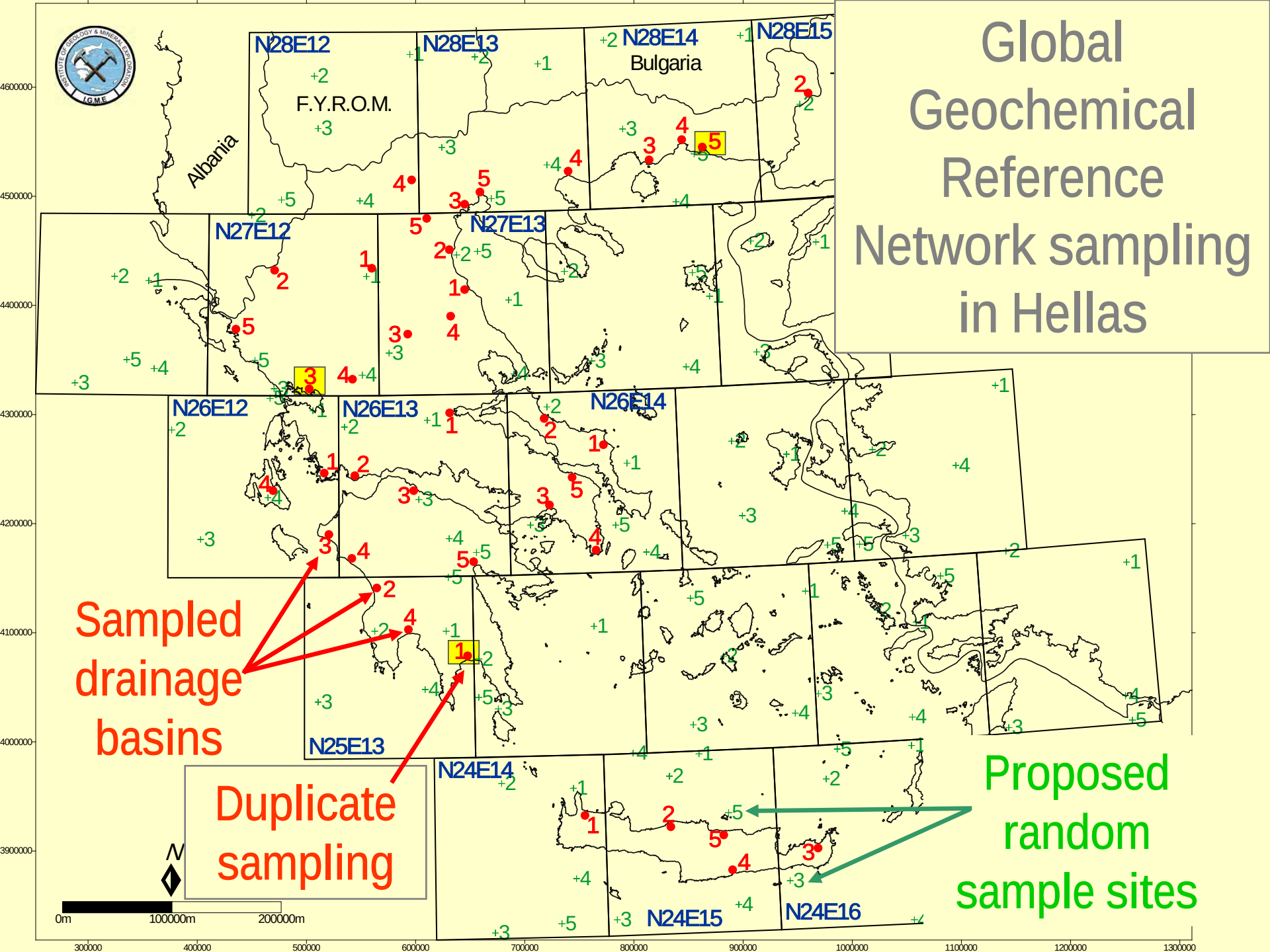
Global Geochemical Reference Network sampling in Hellas
N28E12
N28E13
N28E14
N28E15
N27E12
N27E13
N26E12
N26E13
N26E14
N25E13
N24E14
N24E15
N24E16
F.Y.R.O.M.
Albania
Bulgaria
Sampled drainage basins
Duplicate sampling
Proposed random sample sites
0m
100000m
200000m

STREAM SEDIMENT SAMPLING EQUIPMENT

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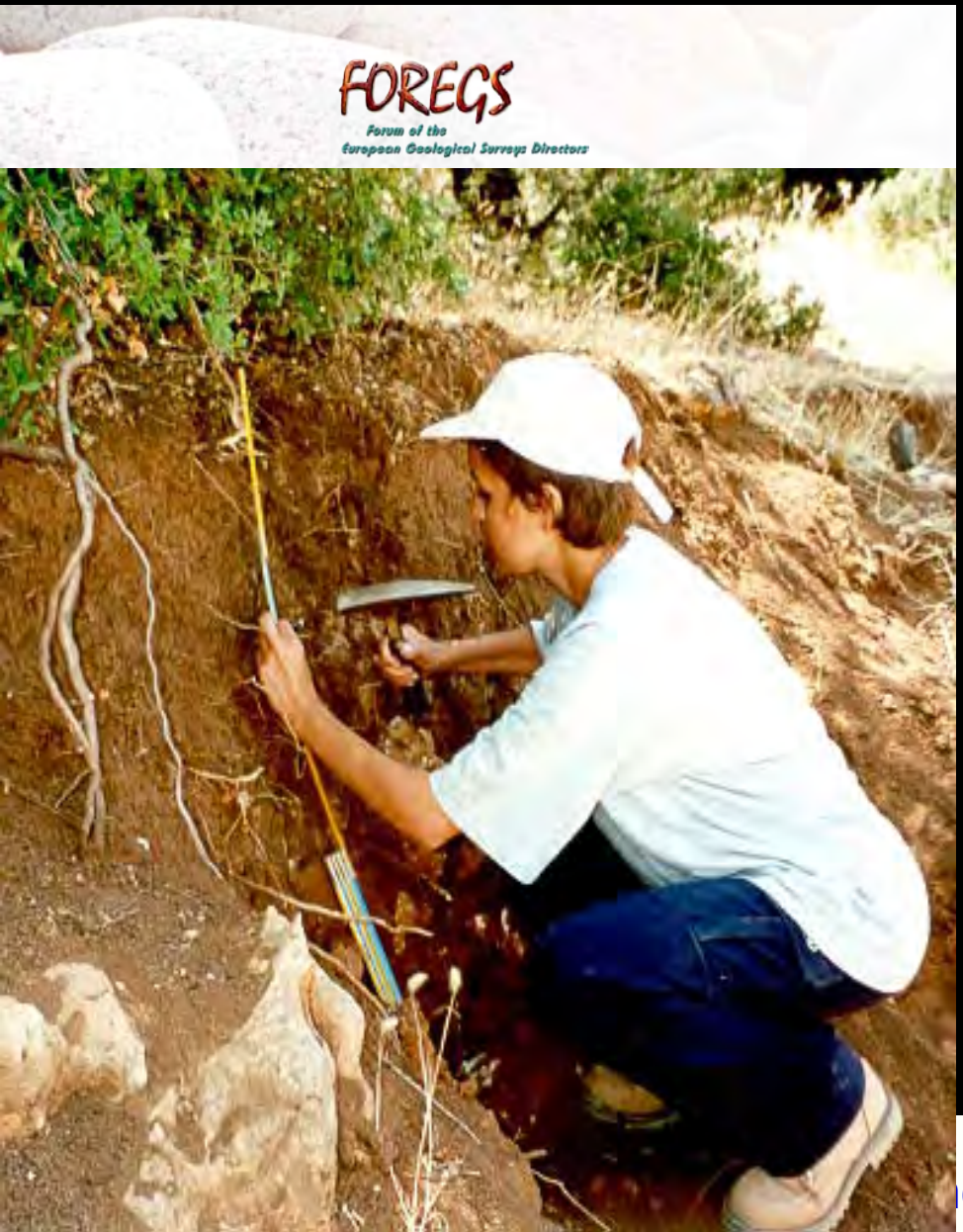
STREAM WATER SAMPLING EQUIPMENT

SOIL, OVERBANK & FLOODPLAIN SEDIMENT SAMPLING EQUIPMENT

Sampling of Residual Soil



***Soil* samples reflect variations in geogenic composition of the uppermost layers of the Earth's crust.**

Comparison between *topsoil* and *subsoil* samples provide information about enrichment or depletion processes (such as anthropogenic contamination) between the layers.

The <2 mm fraction is analysed according to environmental standards.

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Humus sampling (not in Hellas)

***Humus* samples can be used to determine atmospheric (anthropogenic) input of elements to the ecosystem.**

Extra precautions must be taken, not to contaminate humus samples.

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Stream Water

***Stream water* reflects the interplay between geosphere / hydrosphere and human activities, which in most cases result in its pollution.**

At the same time it is the main source of drinking water and irrigation.

Therefore, it is significant to know its quality.

lbaselines.eu

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Stream Water Sampling

Stream Water can easily be contaminated during sampling. *Therefore, it is important to take extra precautions*:

- **by removing all hand jewellery,**
- **by wearing powder free gloves, and**
- **all tools and contaminants must be free of contaminants.**

Sediment Sampling

Stream sediment, Floodplain sediment and Overbank sediment **samples reflect the average geogenic composition of a drainage basin.**

Stream sediment **is susceptible to contamination by human activities.**

Floodplain **or** ***Overbank sediment*** **layers provide a record of the geochemical history of a drainage basin.**

Sampling of floodplain or alluvial sediment from large drainage basins (1000-6000 km^2)

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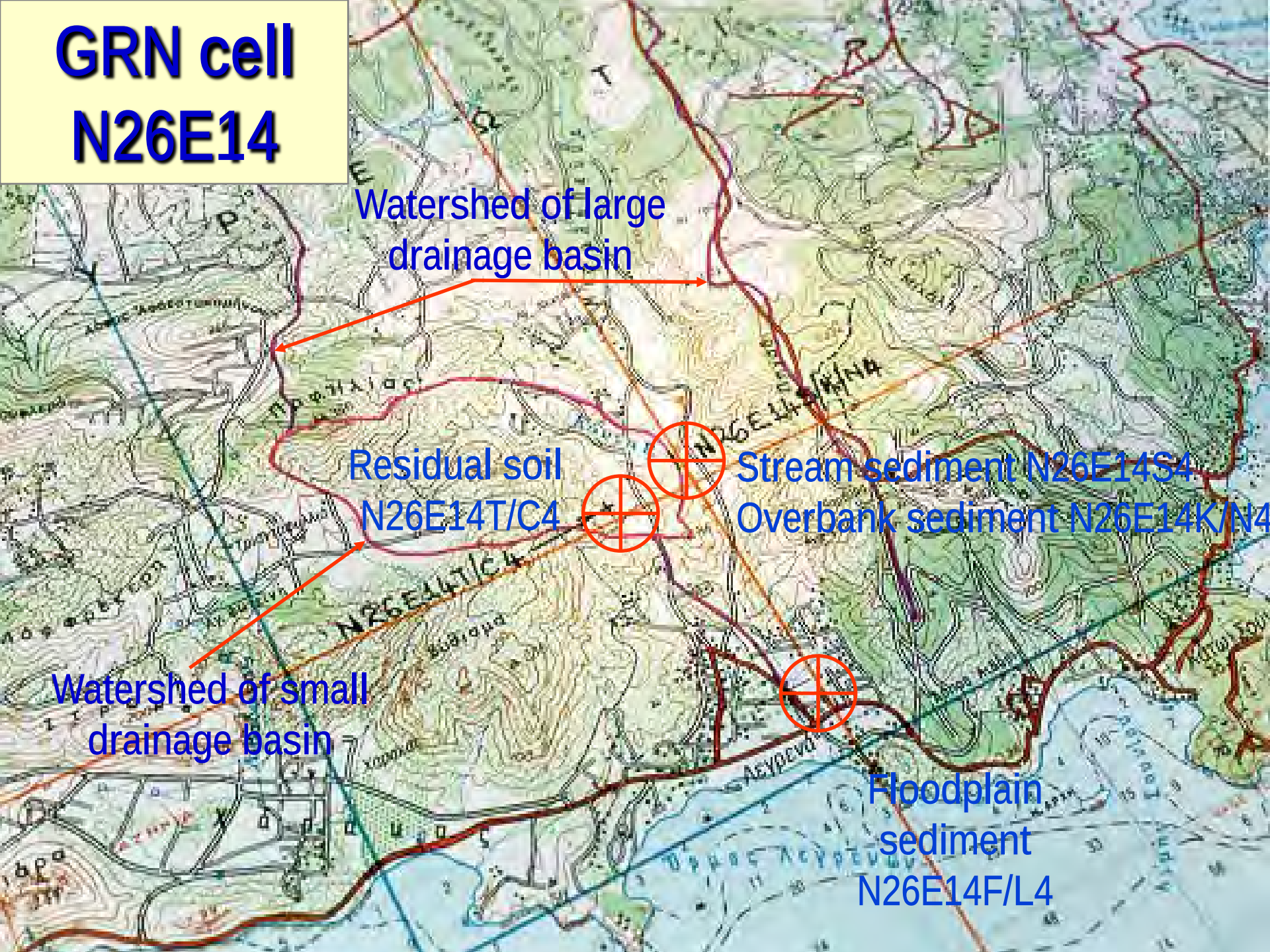
Sampling of overbank or alluvial sediment from small drainage basins (<100 km^2)


GRN cell
N26E14
Watershed of large
drainage basin
Residual soil
N26E14T/C4
Stream sediment N26E14S4
Overbank sediment N26E14K/N4
Watershed of small
drainage basin
Floodplain
sediment
N26E14F/L4

It is important before leaving the sampling site to mark on the topographical map the exact location of the sample

Sampling Sites Photo Archive

N26E09T1 (IT)

N42E10C2 (FI)

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Geochemical Atlas of Europe

The European sample archive has been moved from the Geological Survey of the Slovak Republic to their permanent storage place at the British Geological Survey

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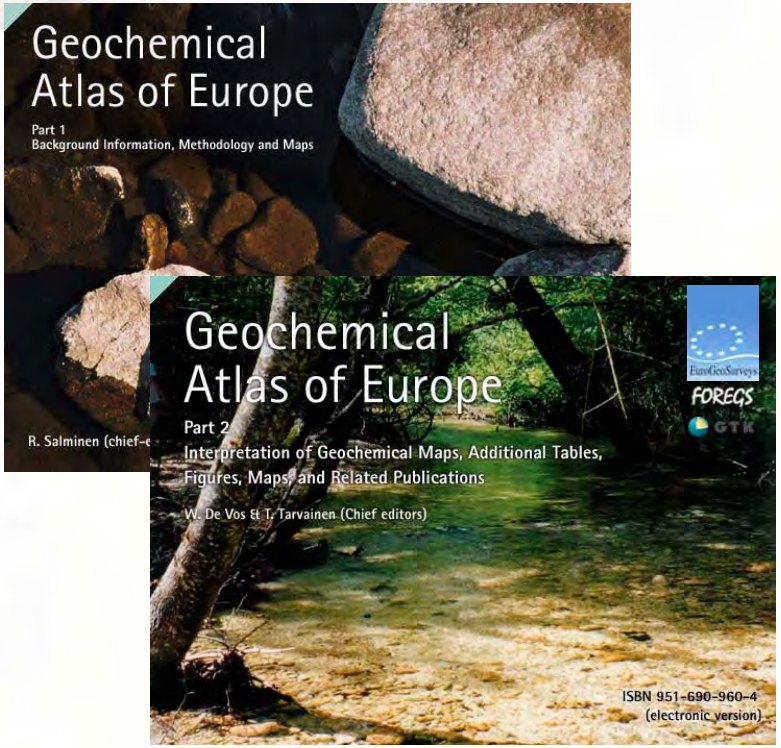
Development of the European Geochemical databases



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DEVELOPMENT OF A UNIFORM AND HOMOGENEOUS GEOCHEMICAL ANALYTICAL DATABASE

Laboratory analysis of samples

The samples were analysed in Eight laboratories of the European Geological Surveys

For the development of a uniform and homogeneous geochemical analytical database, ALL samples of the same type were analysed at the SAME laboratory by exactly the SAME analytical method and for the SAME suite of chemical elements.

In addition, a strict quality control (QC) procedure was applied to ensure the generation of analytical data of high quality and integrity.

This is the only way to produce uniform and compatible geochemical databases across political boundaries, and to satisfy the conditions of the IUGS/IAGC Global Geochemical Baselines project, and not only.

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Stream water	ICP-QMS / ICP-AES	BGR - Germany
	IC & DOC analyser	BGS - UK
Humus	ICP-MS	TNO - Netherlands
	Hg - analyser	MAFI - Hungary
Residual topsoil Residual subsoil	WD-XRF	BGR - Germany
	ICP-MS	GTK - Finland
	ICP-AES / AR	PGI - Poland
	Granulometry / TOC	TNO - Netherlands

Stream sediment Floodplain sediment	TOC	GSSR - Slovakia
	XRF	BGS - UK
	ICP-MS	BRGM - France
	ICP-AES / AR	GTK - Finland
		PGI - Poland
	Hg - analyser	MAFI - Hungary

Analytical methods & laboratories

Stream water (n=808)

66 determinands: Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, I, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Se, SiO_2, Sm, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, pH, EC, HCO_3^-, Br^-, Cl^-, F^-, NO_3^-, SO_4^{2-}, DOC

Humus (n=377)

12 determinands (total extraction): Ba, Cd, Co, Cu, Ga, Hg, La, Ni, Pb, Rb, Sr, Zn

Residual topsoil (n=845)

Residual subsoil (n=790)

12 determinands (aqua regia extractable): As, Ba, Co, Cr, Cu, Fe, Mn, Ni, Pb, S, V, Zn

64 determinands (total extraction): Ag, Al_2O_3, As, Ba, Be, Bi, CaO, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe_2O_3, Ga, Gd, Hf, Hg, Ho, I, In, K_2O, La, Lu, MgO, MnO, Mo, Na_2O, Nb, Nd, Ni, P_2O_5, Pb, Pr, Rb, Sb, Sc, SiO_2, Sm, Sn, Sr, Ta, Tb, Te, Th, TiO_2, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, TOC, pH, 4 grain-sizes

Stream sediment (n=852)

Floodplain sediment (n=749)

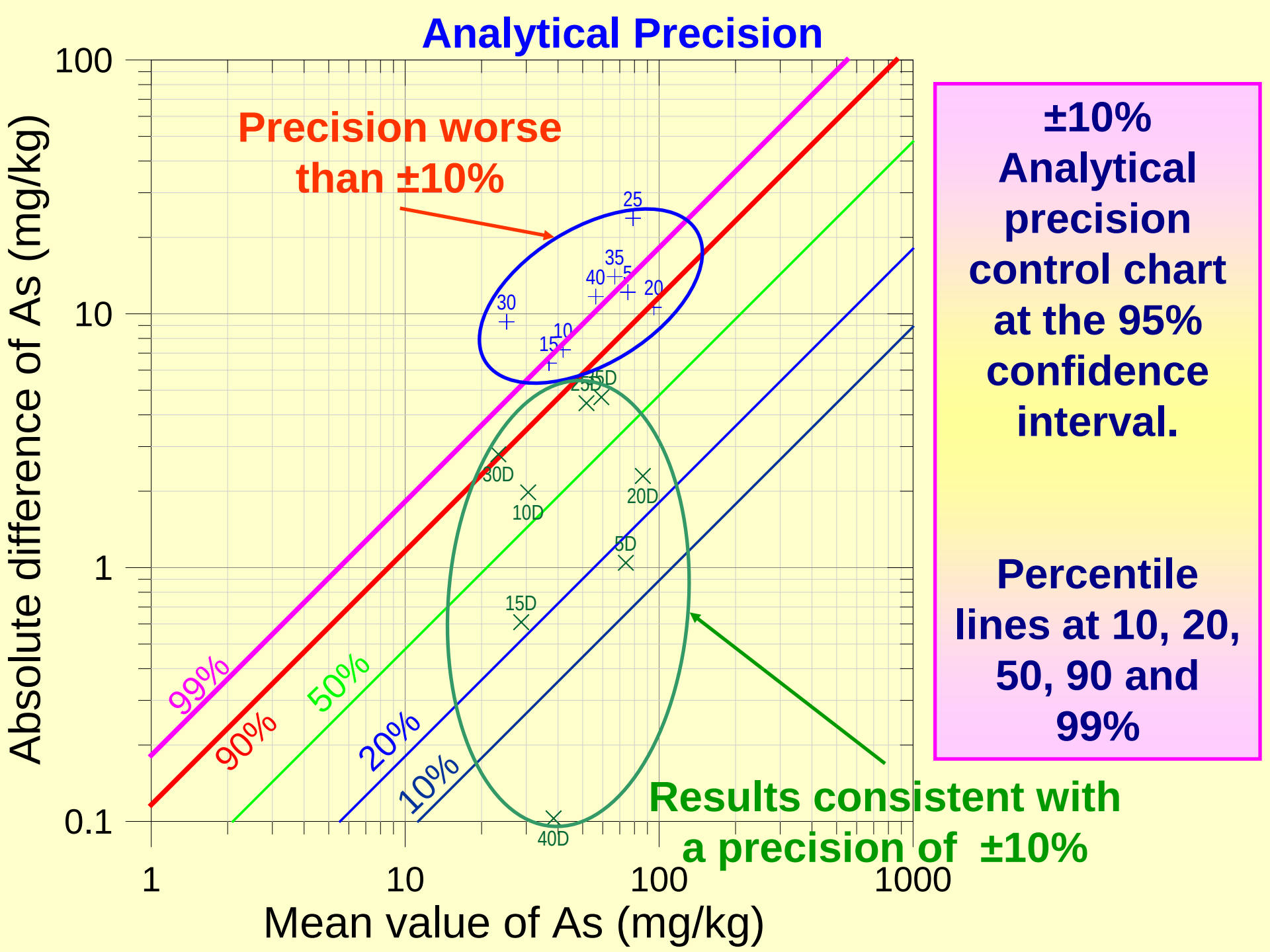
12 determinands (aqua regia extractable): As, Ba, Co, Cr, Cu, Fe, Mn, Ni, Pb, S, V, Zn

54 determinands (total extraction): Al_2O_3, As, Ba, Be, CaO, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe_2O_3, Ga, Gd, Hf, Hg, Ho, K_2O, La, Li, Lu, MgO, MnO, Mo, Na_2O, Nb, Nd, Ni, P_2O_5, Pb, Pr, Rb, Sb, SiO_2, Sm, Sn, Sr, Ta, Tb, Th, TiO_2, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, TOC

Determinands analysed

Prior to data treatment the analytical results MUST be carefully examined

- **Study of results of Quality Control samples – ANOVA.**
- **Study of dot distribution maps, basic statistical tables and scattergrams of elements.**
- **Correction of sample characteristics and site coordinates.**
- **Laboratory checks by reanalysing samples to verify analytical results.**
- **Correction of results below detection limit to half the detection limit, *e.g.*, Te <0.2 mg kg^{-1} → 0.1 mg kg^{-1}.**
- **Compilation of final analytical database for the estimation of statistical parameters and the production of geochemical distribution maps.**


Analytical Precision
Precision worse than ±10%
±10% Analytical precision control chart at the 95% confidence interval.
Percentile lines at 10, 20, 50, 90 and 99%
Results consistent with a precision of ±10%
99%
90%
50%
20%
10%
25
35
40
5
20
30
10
15
25D
30D
10D
20D
5D
15D
40D
100
10
1
0.1
1
10
100
1000
Absolute difference of As (mg/kg)
Mean value of As (mg/kg)

Quantification of sources of variation …..

In a Geochemical Survey, it is important to quantify all inherent errors due to different sources of variability:

ANOVA →

- **Sampling**
- **Analytical (or Laboratory)**
- **Spatial (or Geochemical)**

Question: **What property are we mapping in a geochemical survey?**

Answer: **We are mapping the *spatial variability* of an element in a specific geological sample, of certain grain-size, which is determined by a particular analytical method.**

Conclusion: **Since in a geochemical survey we are mapping the *spatial variability* of an element, the largest variation must be the *Spatial or Geochemical variability*.**

….. Quantification of sources of variation …..

Applied geochemists, since the 1950's have developed different methods for the quantification of errors (A.T. Miesch R.G. Garrett, R.J. Howarth, M. Thompson).

The most recent is by M.H. Ramsey, M. Thompson, M. Hale and A. Argyraki, who have also included the estimation of measurement uncertainty.

ISO and Eurochem have also developed methods of estimation of measurement uncertainty.

Errors can also be estimated by Geostatistics, provided that a sufficient number of samples have been collected (>50).

….. Quantification of sources of variation …..

According to Ramsey, Thompson and Hale (1992) the maximum proportions of the Sampling and Analytical variance must not exceed 20% of the Total Variance. They even stipulate the minimum conditions to be satisfied, *i.e.*,

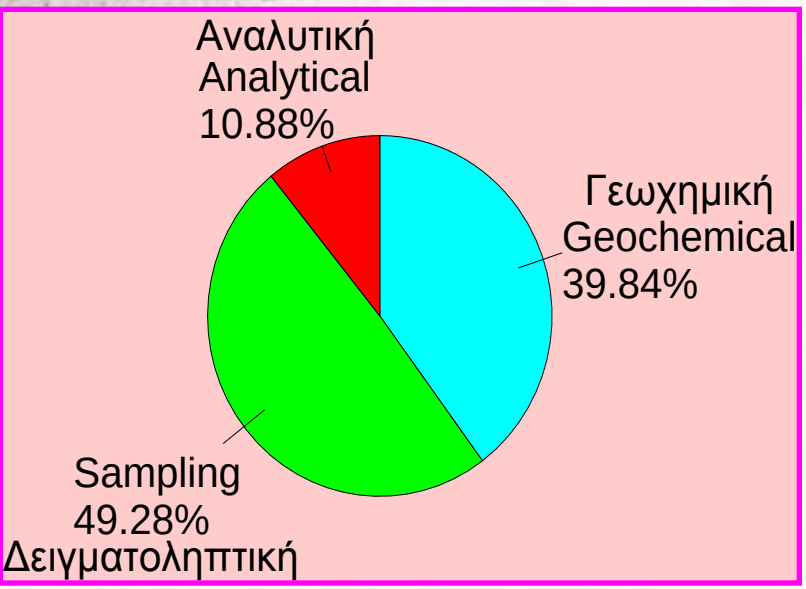
- ***Maximum Analytical variance*** **should not exceed 4% of Total variance, and**
- ***Maximum Sampling variance*** **should not exceed 16% of Total Variance.**

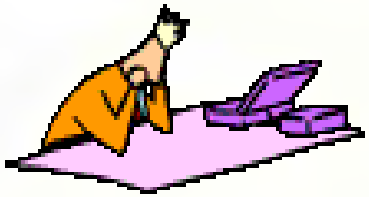
Therefore, the minimum *Spatial or Geochemical variance should be 80% of Total Variance*.

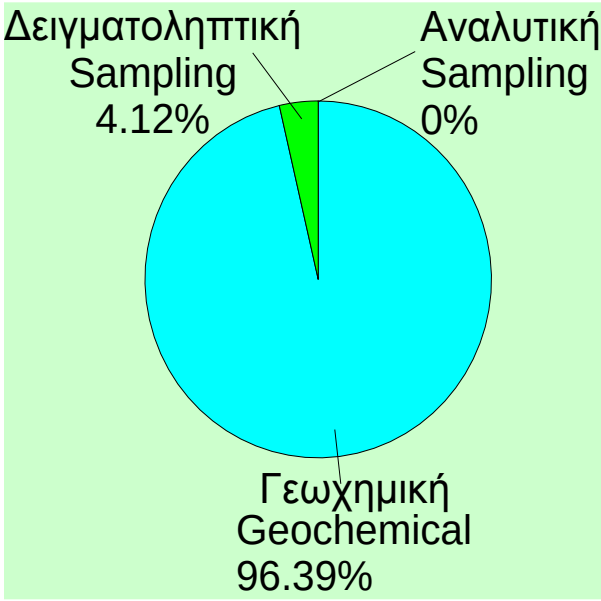
Unacceptable results

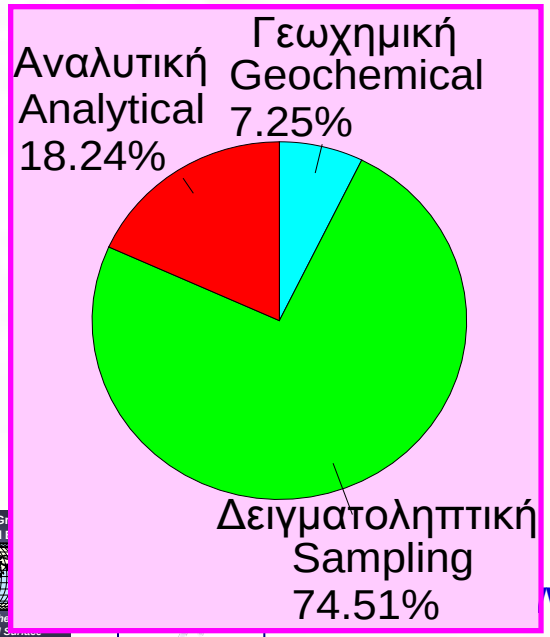
… Quantification of sources of variation …

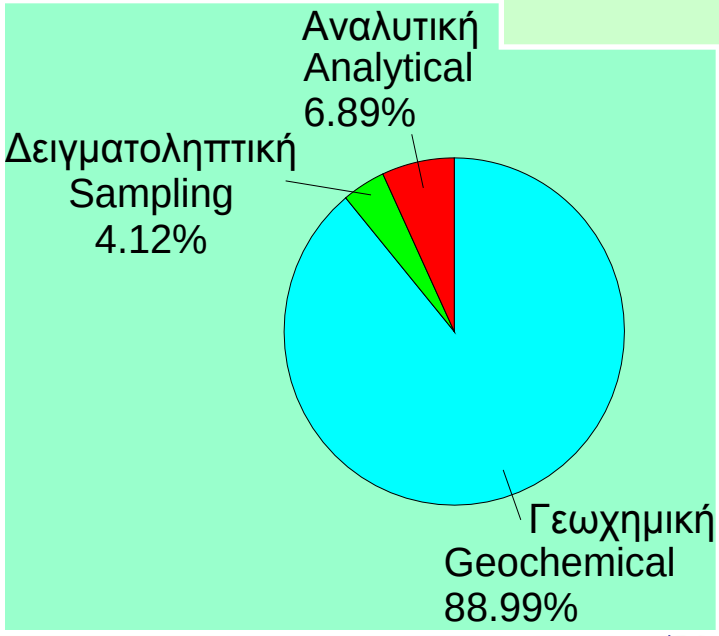
Acceptable results







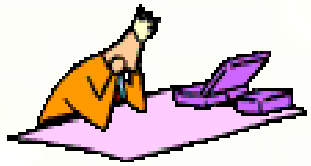


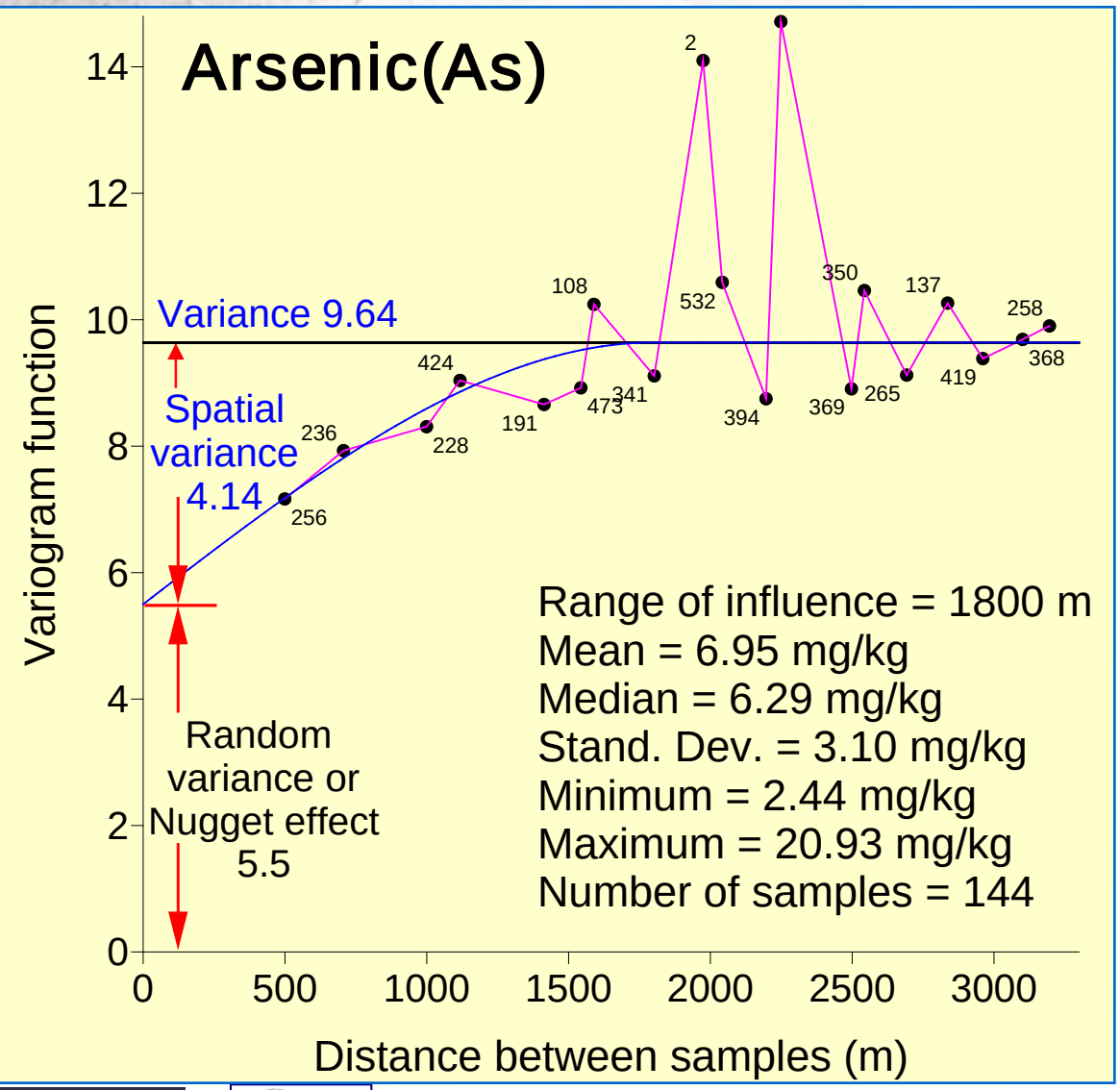


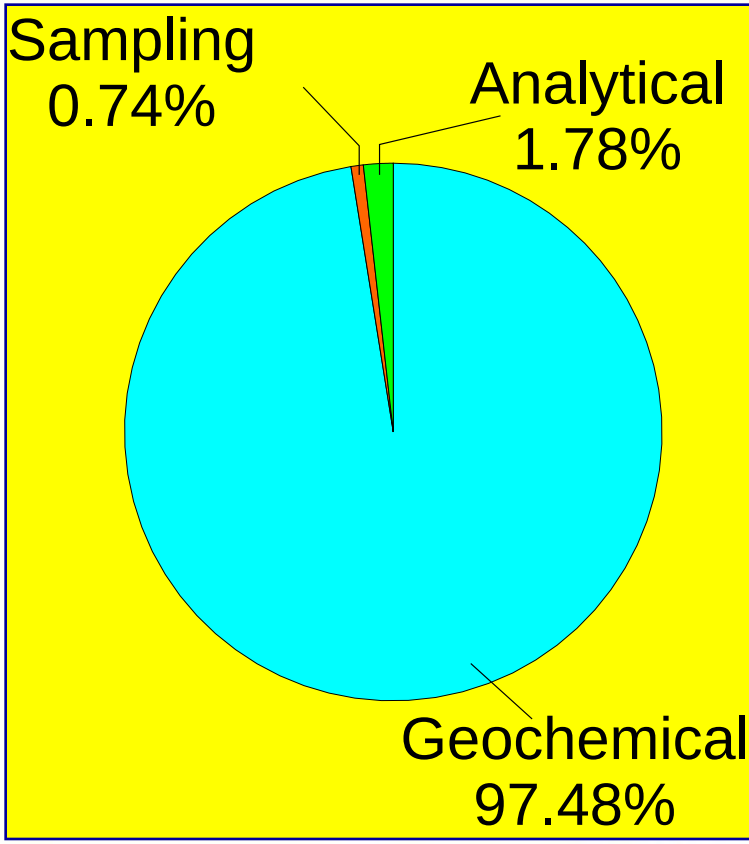
…Quantification of sources of variation

Geostatistics

Analysis of Variance







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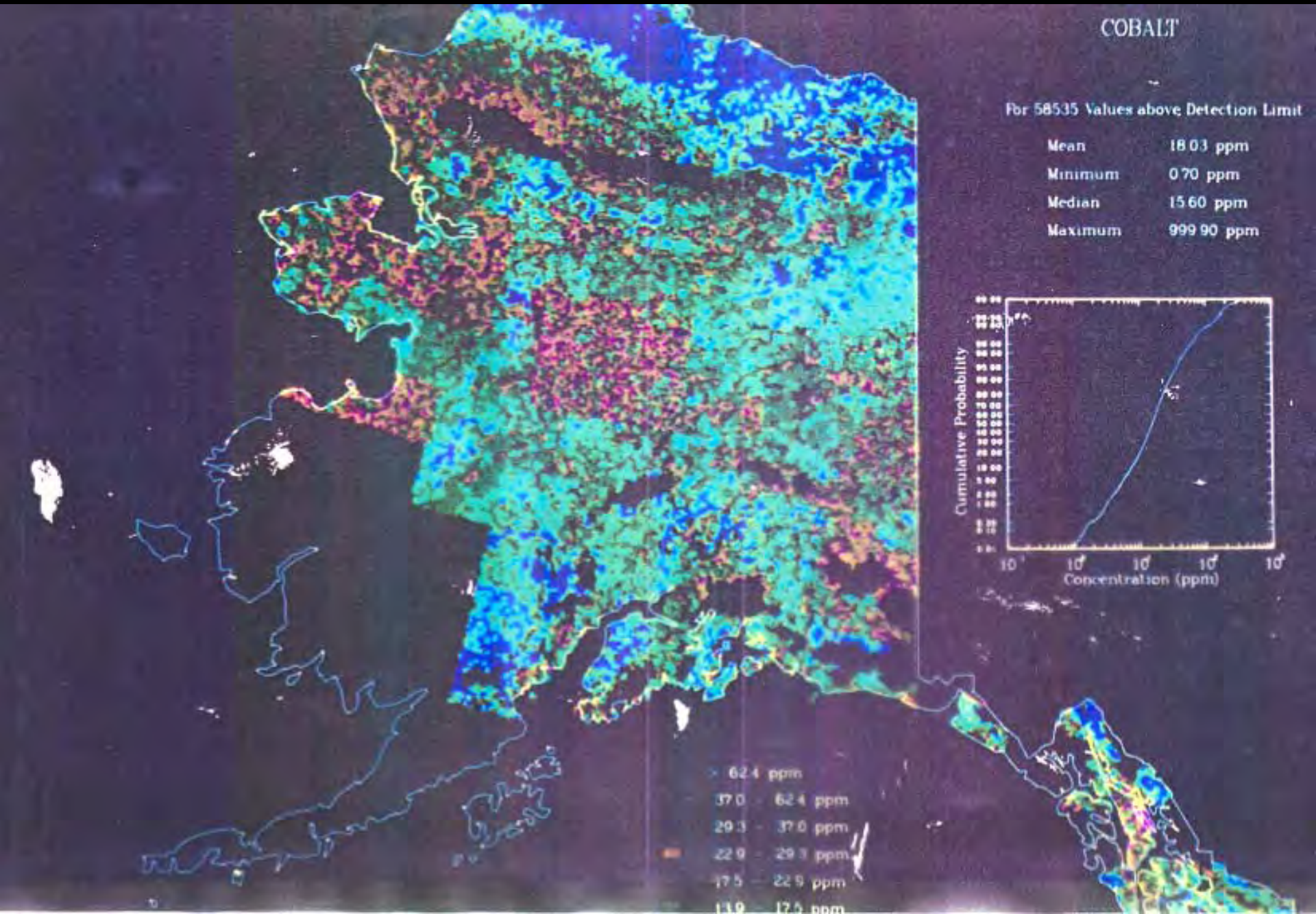
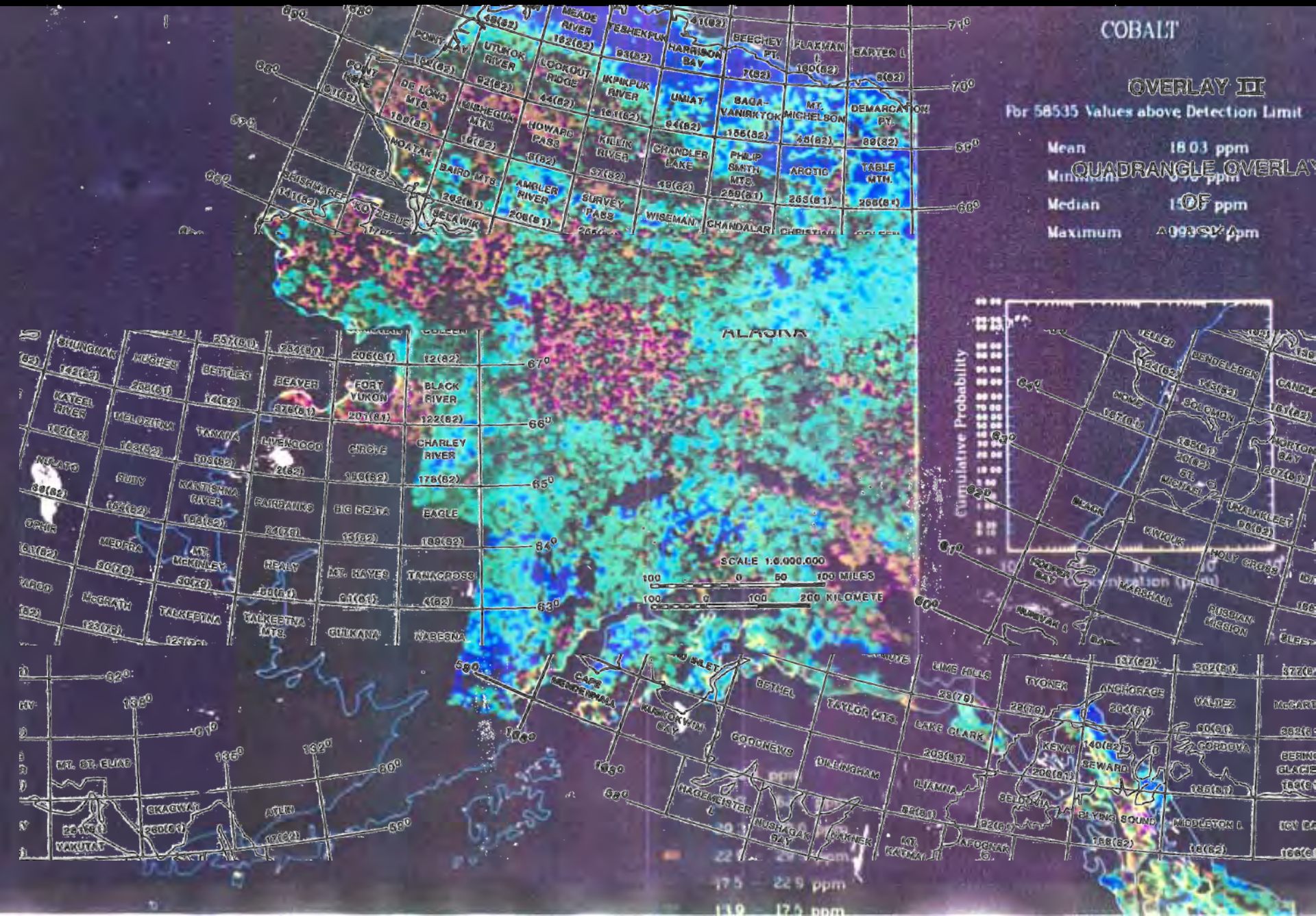
FOREGS SERIOUS MISTAKES.....

- **Management structure was not effective.**
- **Sampling started in some countries in 1997 directly after the field meeting in Slovakia, and it continued until 2001, with one country sampling stream sediment in 2005.**
- **Due to pressure from the FOREGS Directors, samples were analysed in randomised batches, starting from the end of 1998 until 2003, and for the stream sediment in 2005. Hence, the whole of each sample set was not randomised – Serious quality control problems were developed, and the consequence was a "quality control nightmare".**

Geochemical Survey of Alaska – Cobalt (Co)



Geochemical Survey of Alaska – Cobalt (Co)



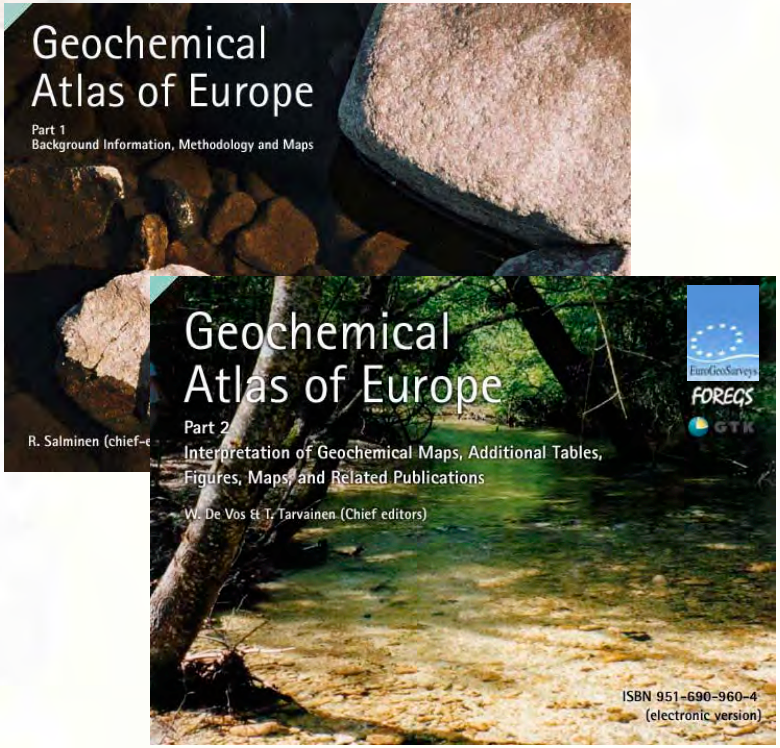
.....FOREGS SERIOUS MISTAKES

- **Further, some laboratories changed analytical instruments, which were more sensitive and the result was different lower detection limits. Another serious quality control problem.**

- **The quantity of the prepared reference materials was just enough to complete the FOREGS work. Another serious quality control problem.**

- **Incomplete coverage by not sampling GTN cells near coastal areas. This was realised two years after the start of the project. So, countries that had already completed their sampling, they were not willing to carry out fill-in sampling.**

Geochemical Atlas of Europe



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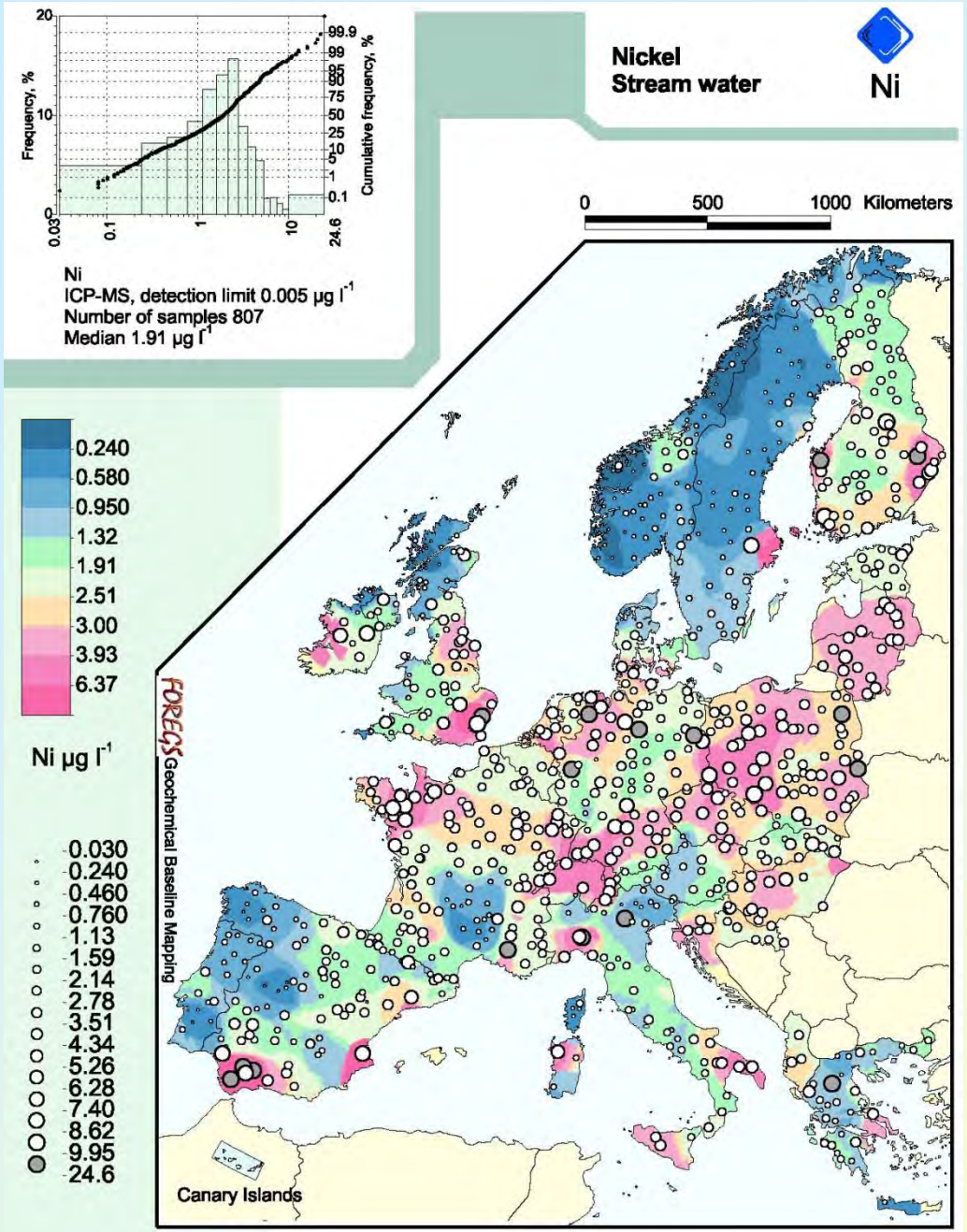


Geochemical baseline concentrations of elements in soil, water and sediment

EXISTENCE OF TWO SOURCES OF ABOVE NORMAL CONCENTRATIONS OF ELEMENTS

Baseline

Natural geogenic variation of element

≡

Natural variation of element

Lithology

«Background»

+

Abnormal concentration of element

Mineralisation & Lithology

ANTHROPOGENIC CONTAMINATION

≡

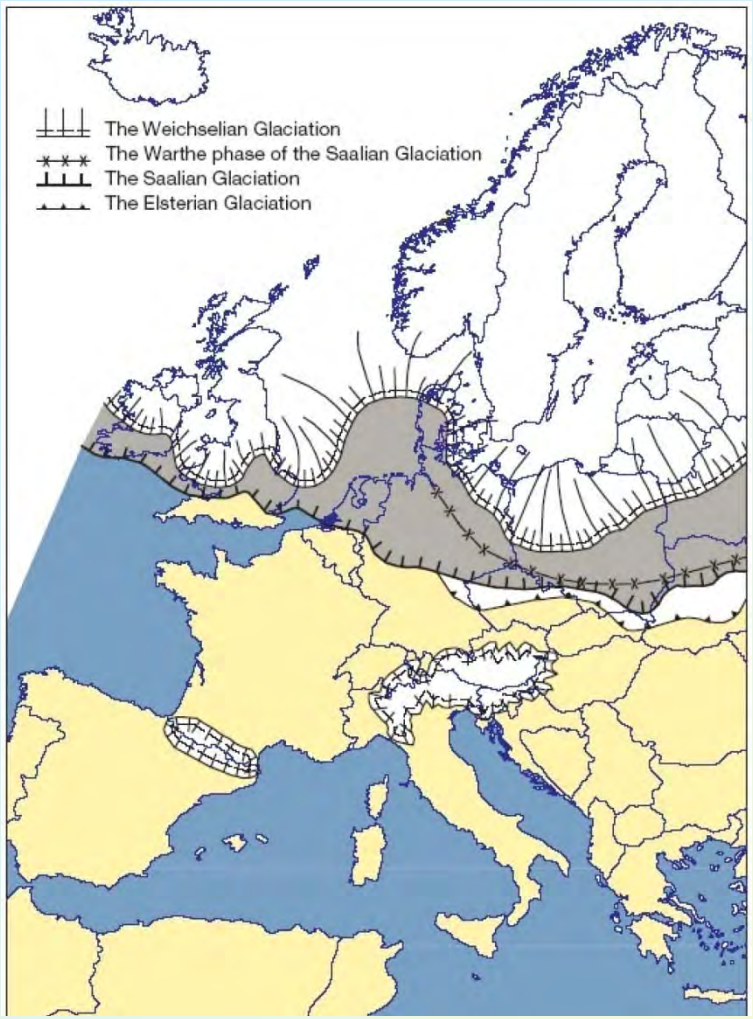
Natural geogenic variation of element

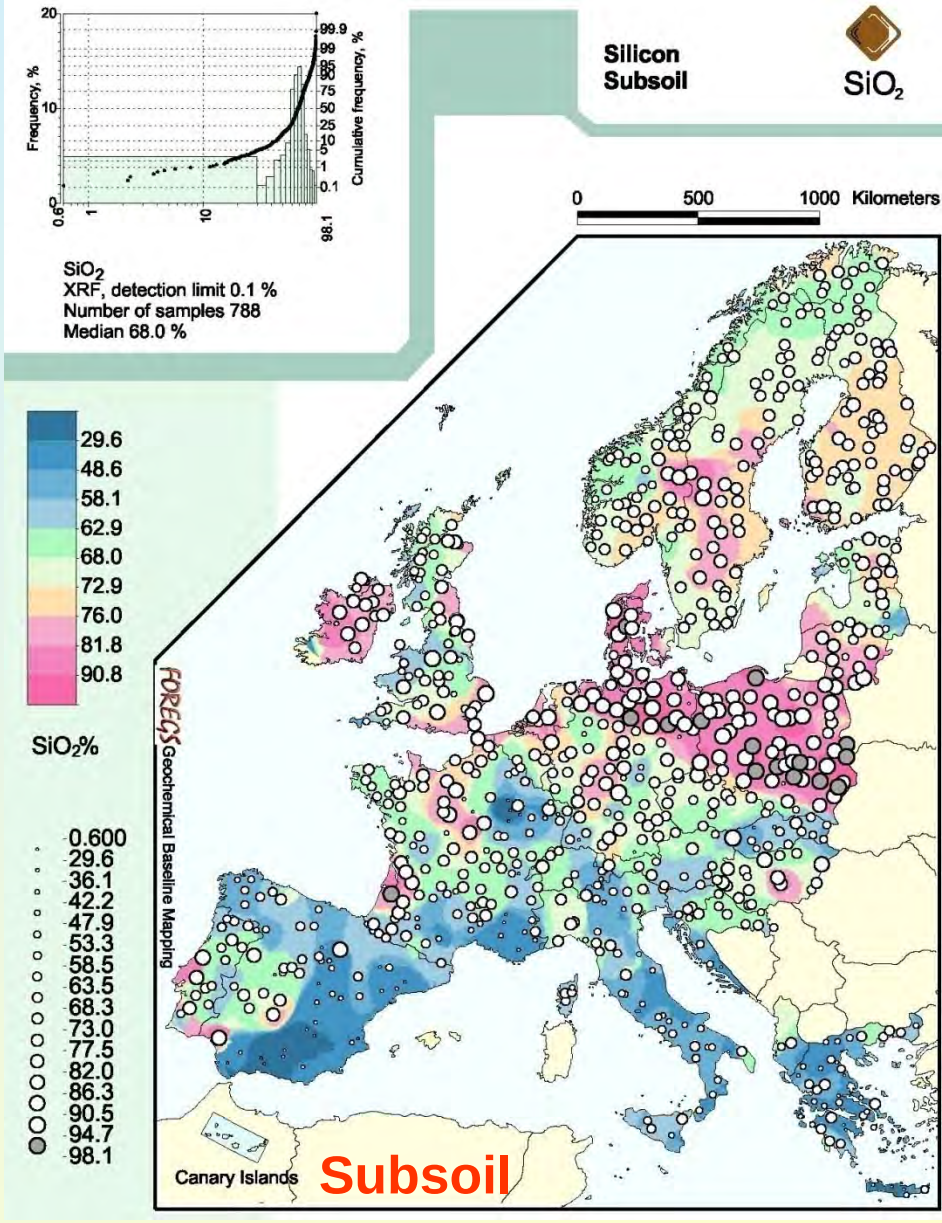
+

Concentration of element from anthropogenic activities

This concept is not understood or unknown to decision makers and the general public

Geochemical Atlas of Europe





Mapping of the limit of the last glaciation

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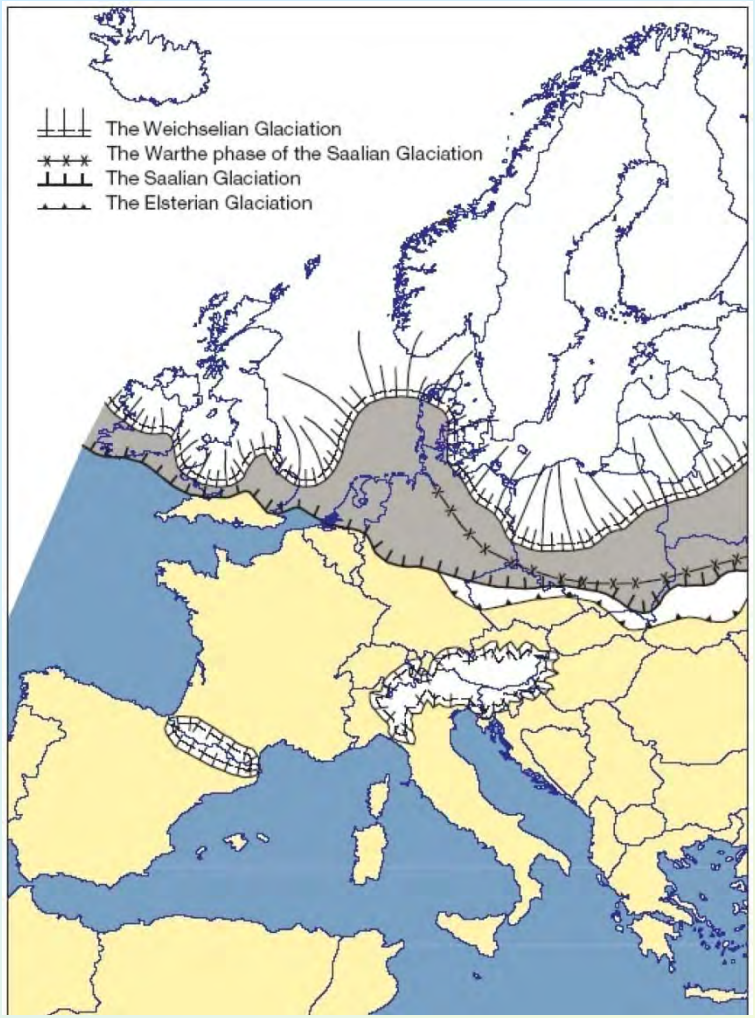

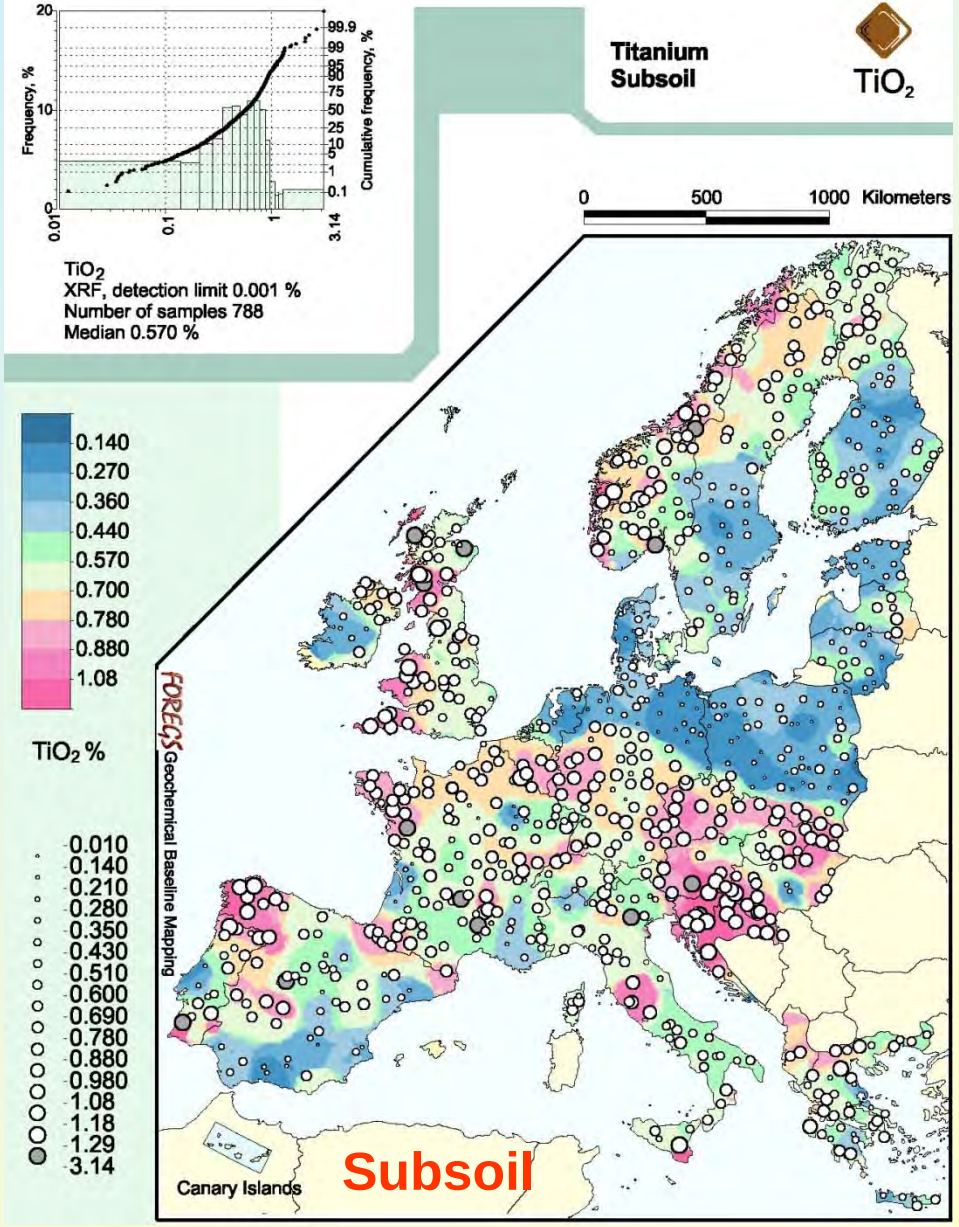

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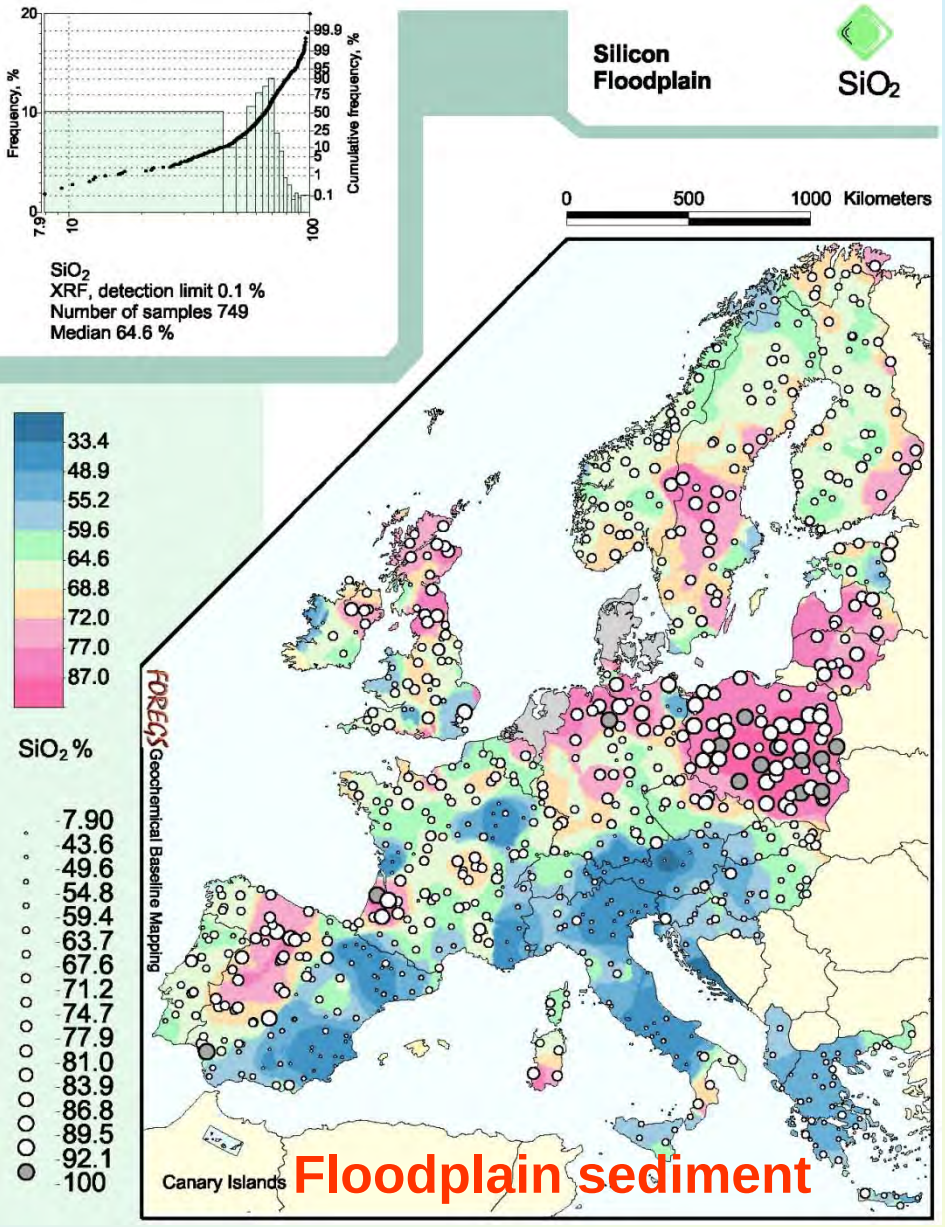

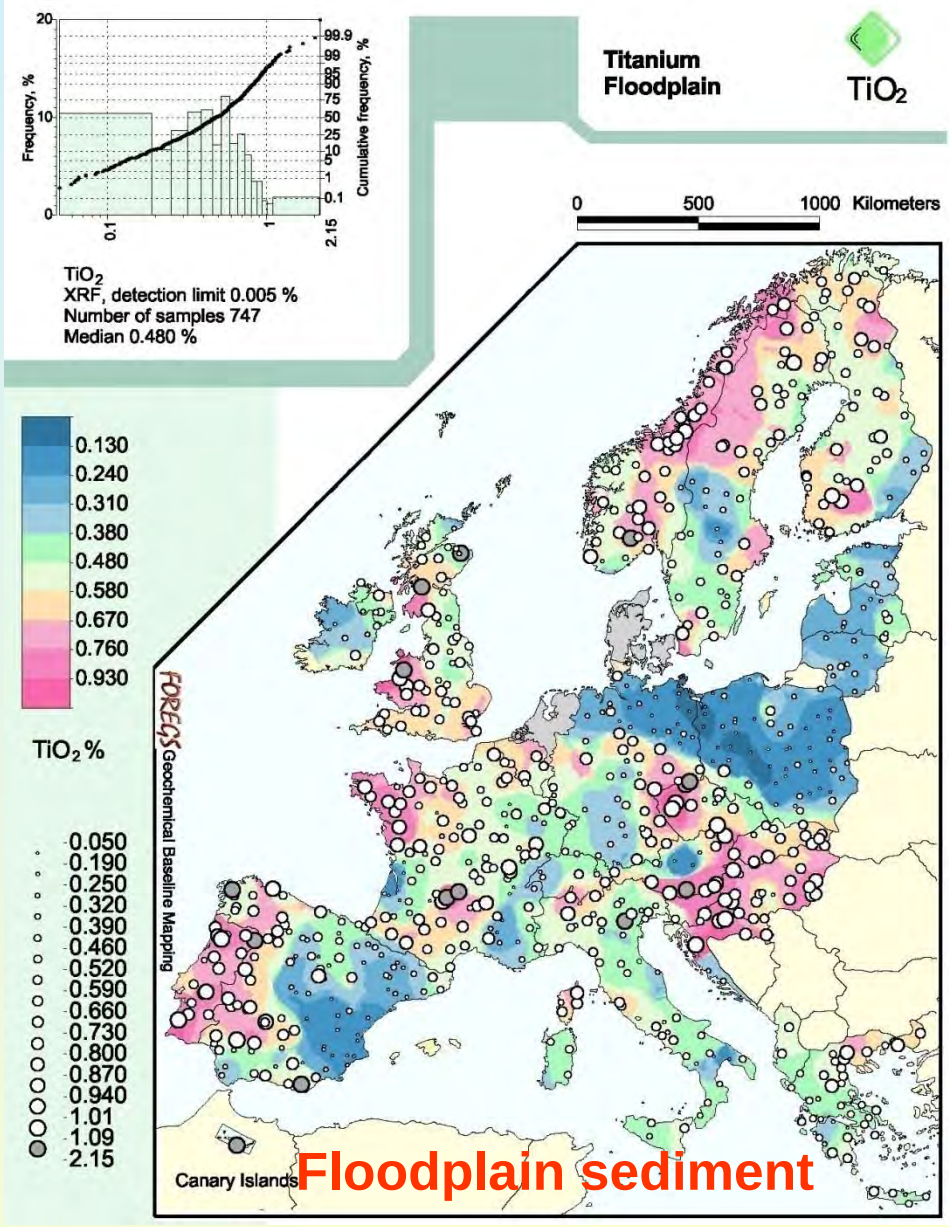

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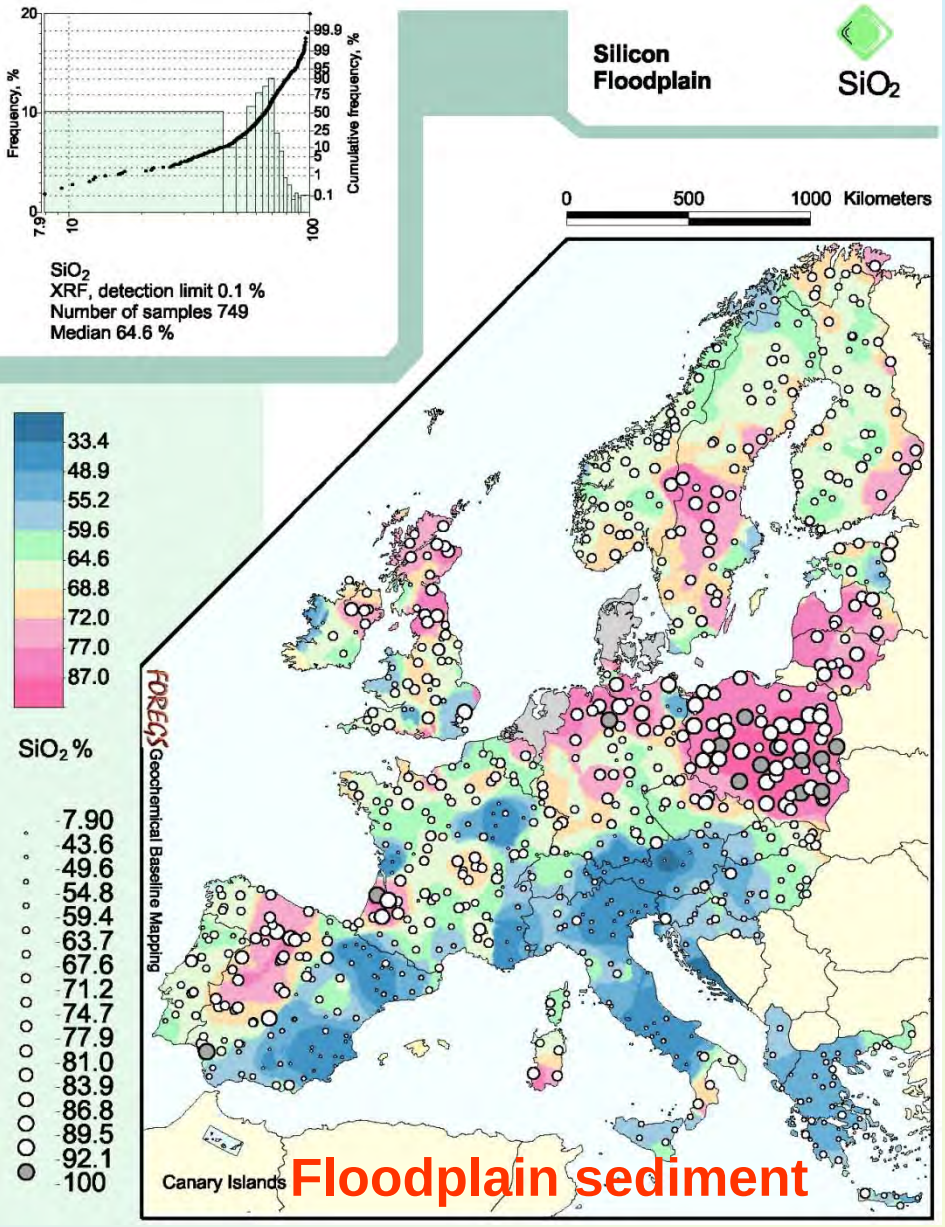

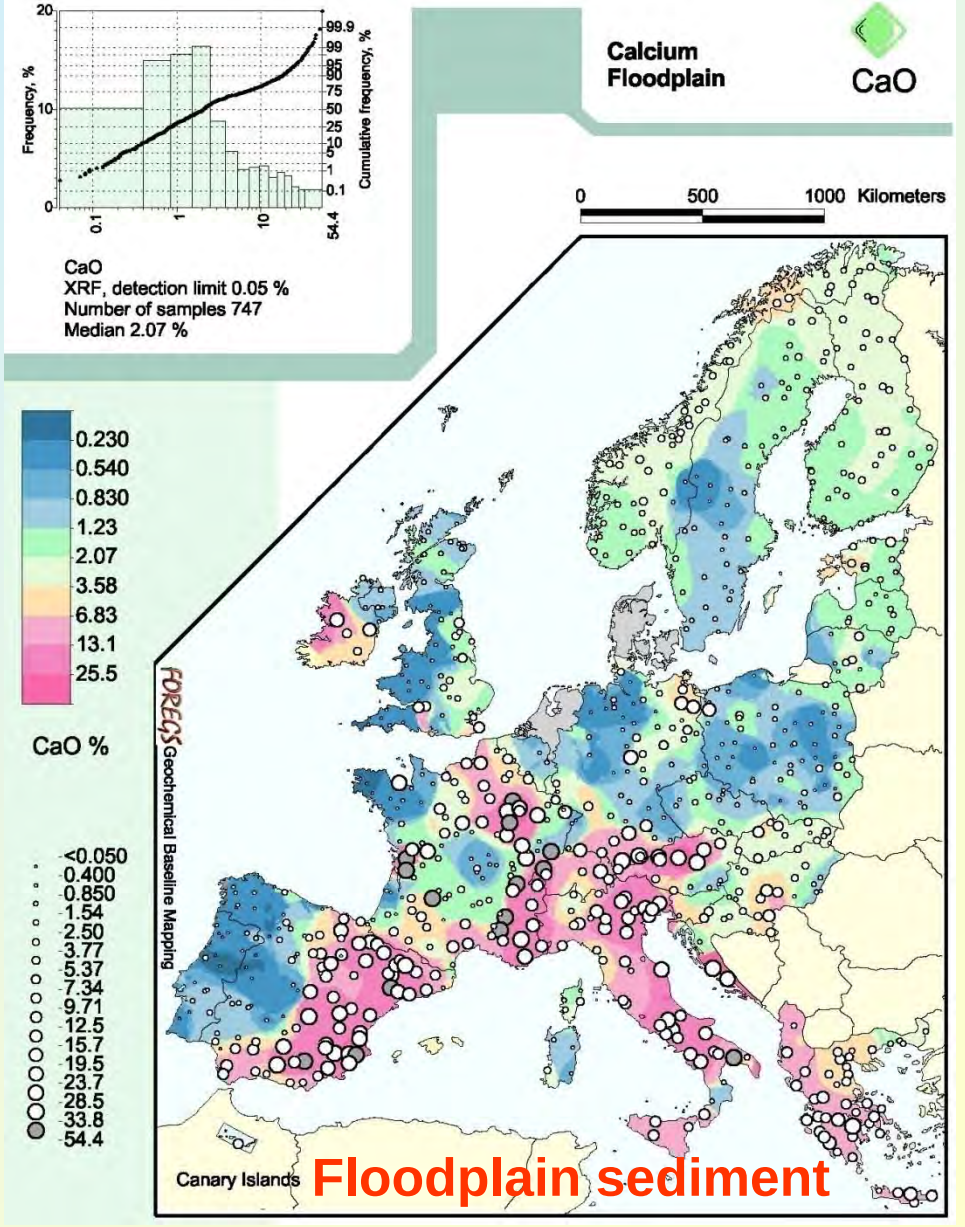

Mapping Felsic and Carbonate rocks

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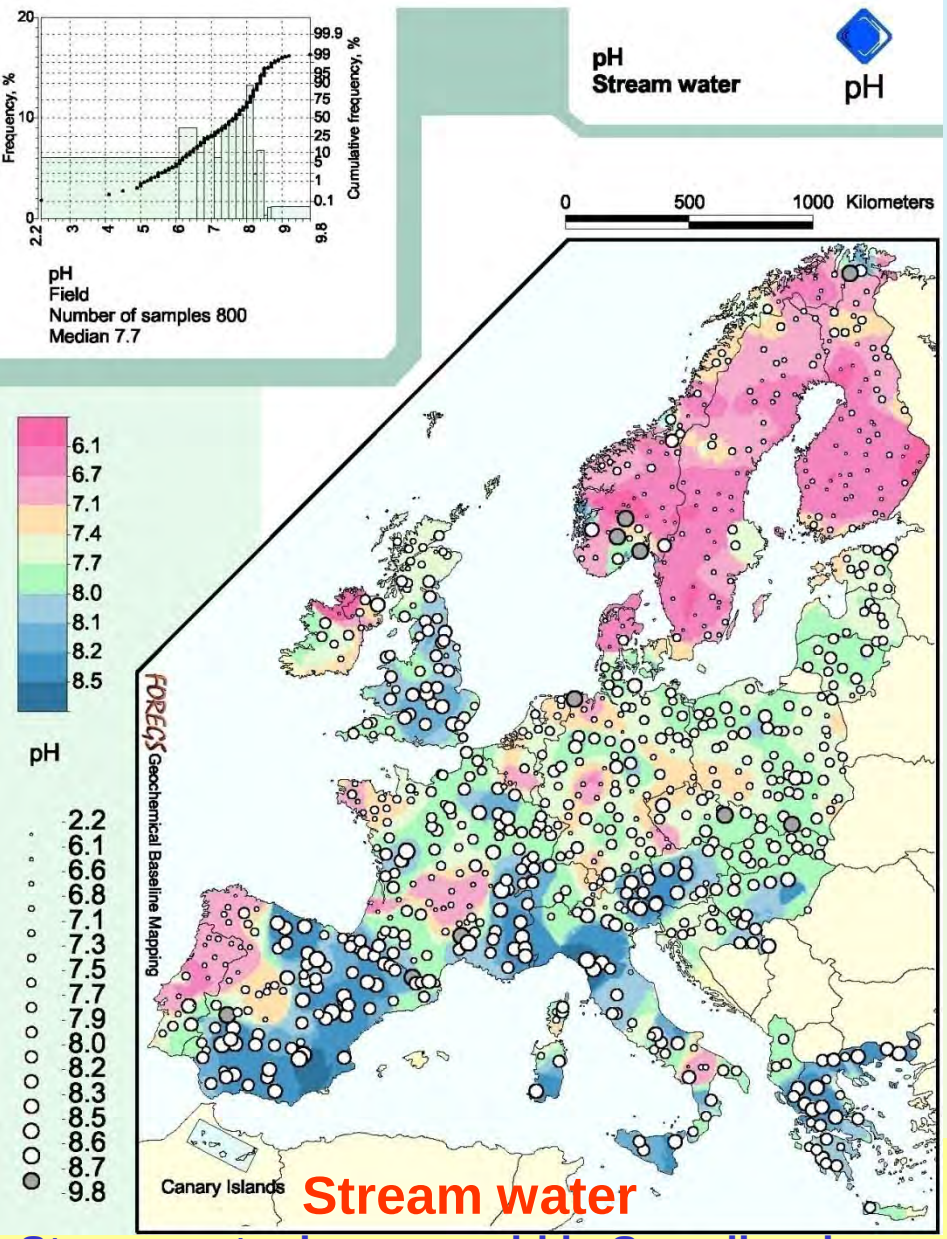
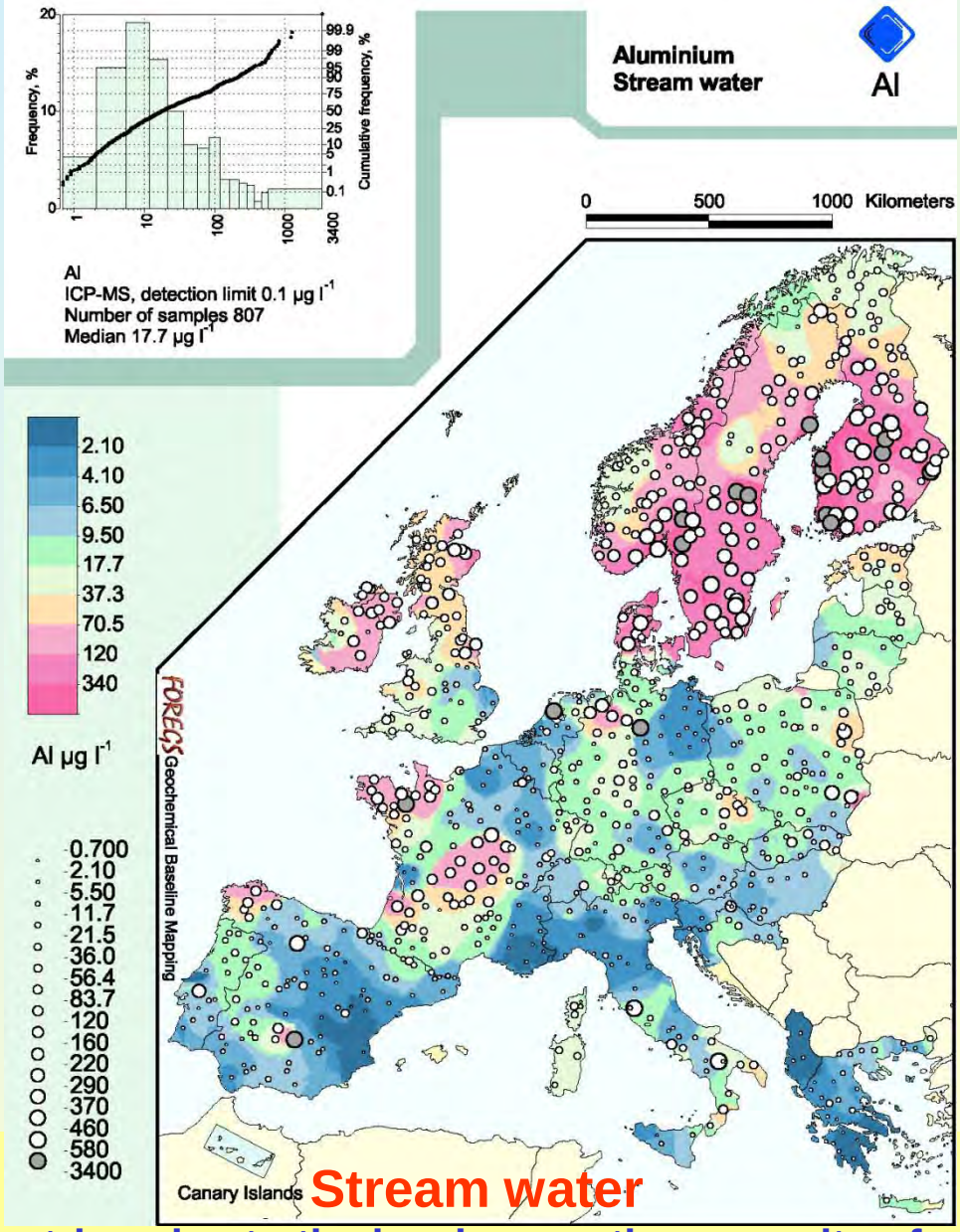
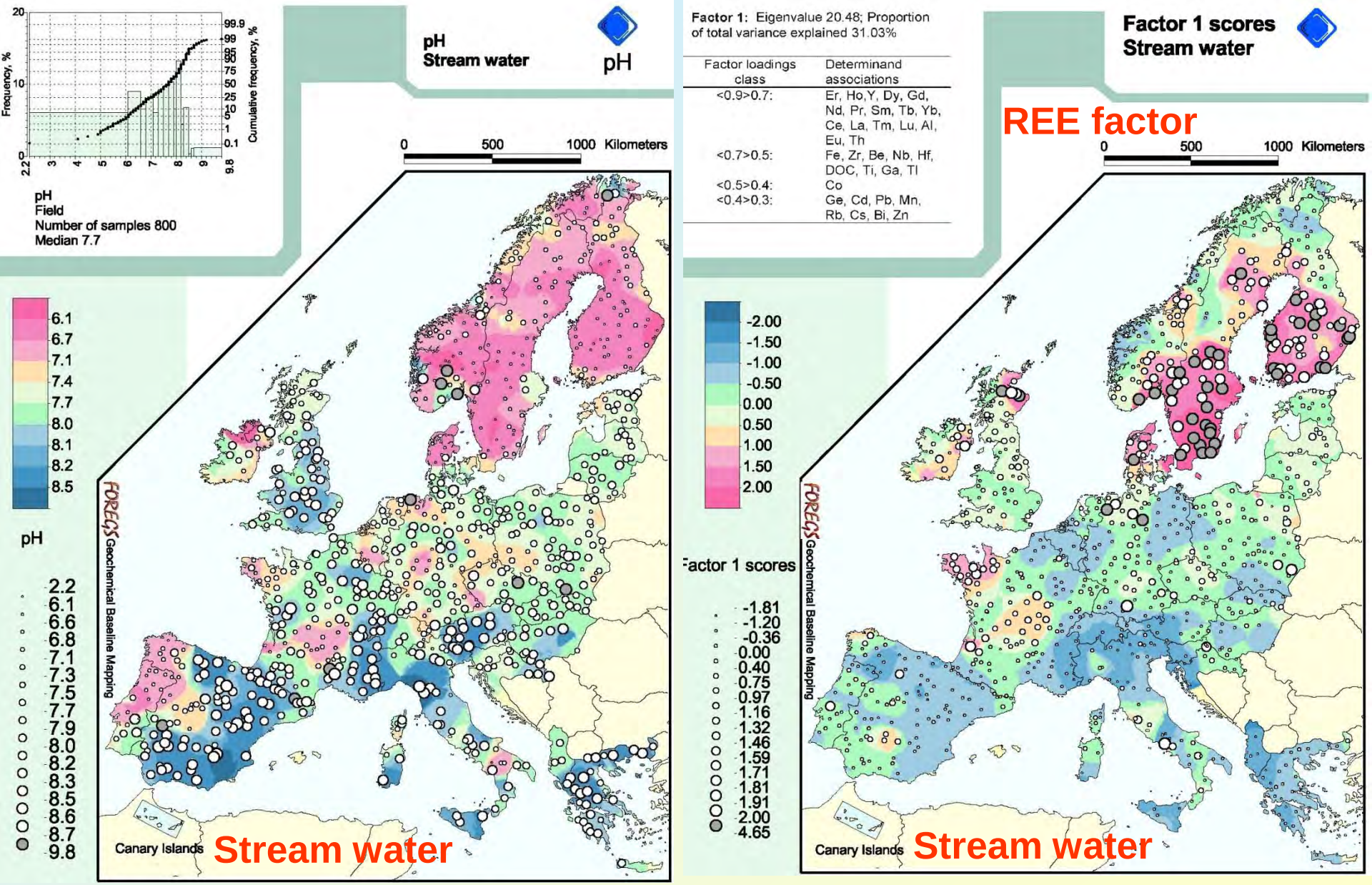




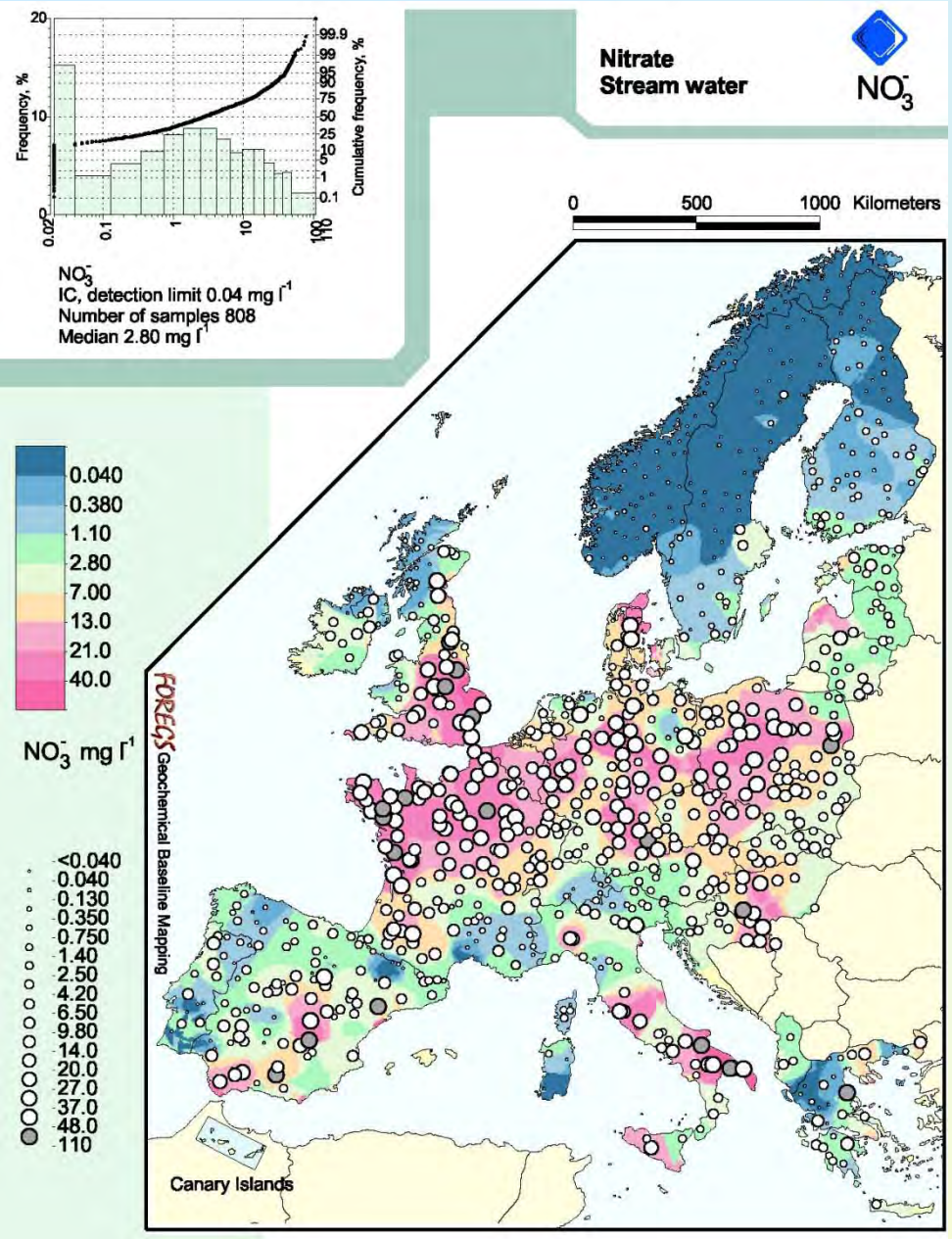
Stream water is more acid in Scandinavian countries, due to the low base cation capacity of metamorphic basement rocks and high concentration of humic and fulvic acids, typical of boreal climate.

Low pH values result in higher solubility of aluminum and some heavy metals.



Factor 1: Rare earth elements. REEs anomalies in southern Fennoscandia are related to acid pH and high levels of dissolved organic carbon.

Geochemical Atlas of Europe



Nitrate concentrations in stream water are elevated in central Europe, due to intensive agriculture

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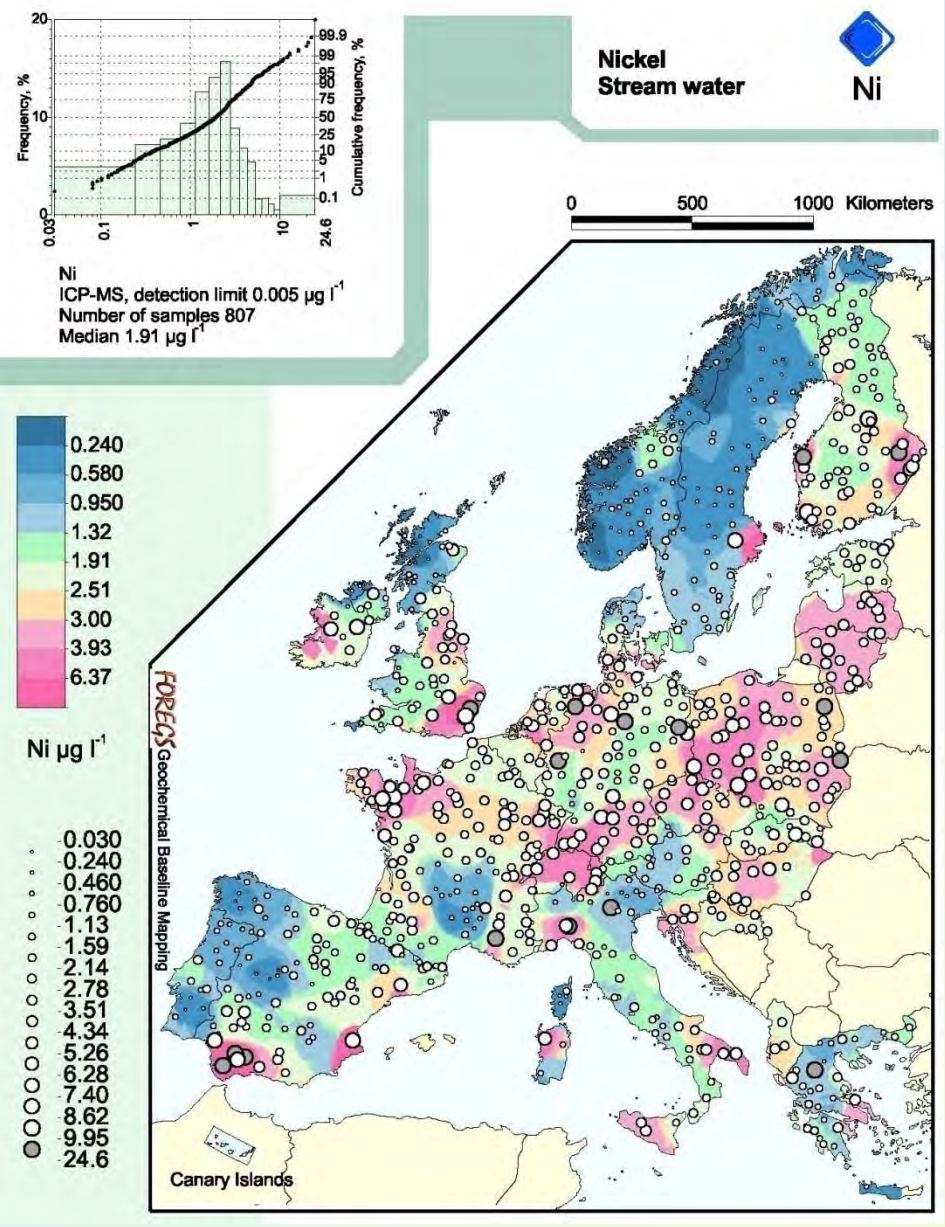

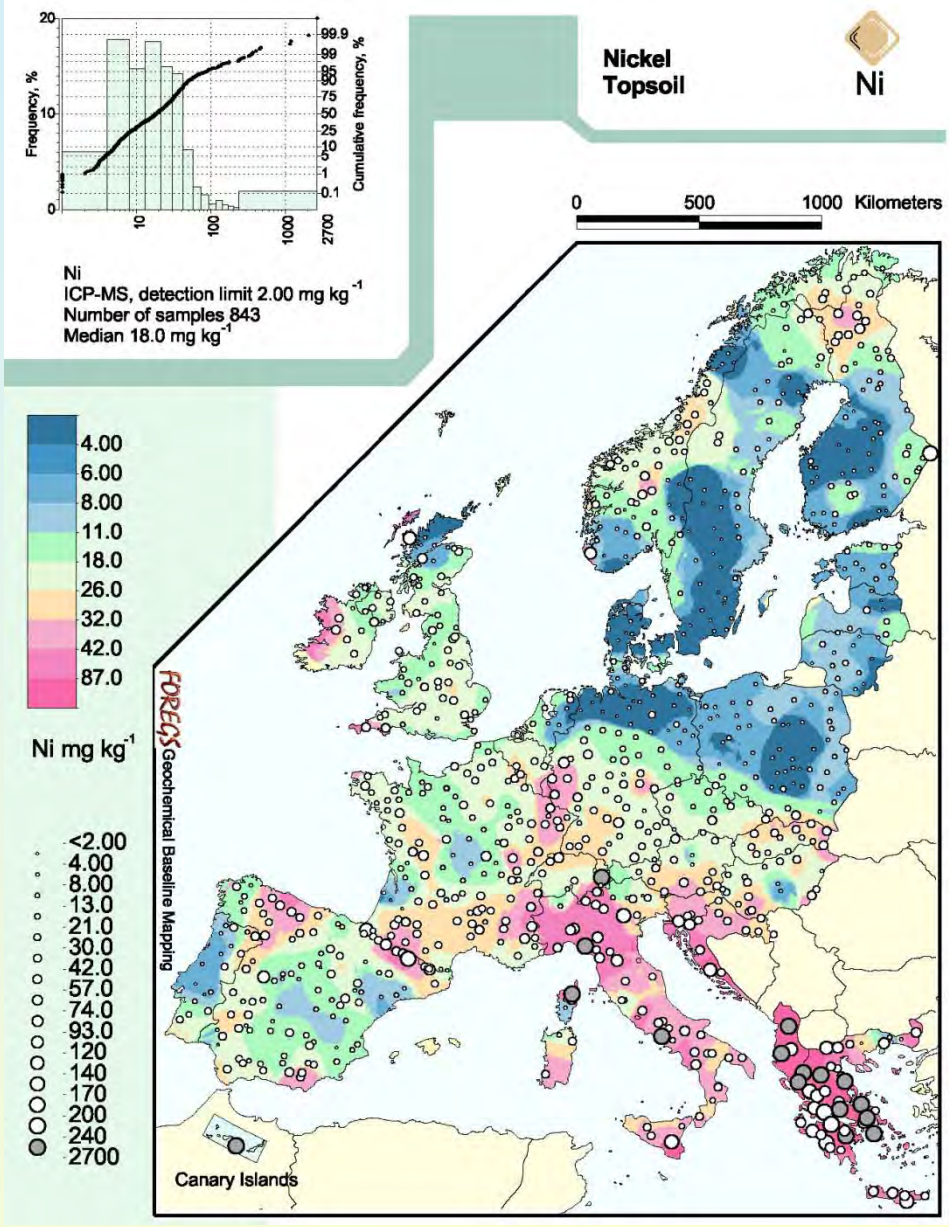

Stream water **Topsoil (0-25 cm)**

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Factor 2: Eigenvalue 7.25; Proportion of total variance explained 13.42%

Factor loadings class	Determinand associations
<0.9>0.7:	Ni, Cr, Co, V, Fe_2O_3
<0.7>0.5:	Cu, MnO, TiO_2, Zn Ga, Al_2O_3*
<0.5>0.4:	Eu, MgO,
<0.4>0.3:	Ba, Nb, Na_2O, Li, P_2O_5

*Normal data, and the remaining are log transformed

Factor 2 scores
Stream sediment

Mafic/Umafic elem. factor

0 500 1000 Kilometers

-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
1.50
2.00

Factor 2 scores

-3.51
-1.20
-0.36
0.00
0.40
0.75
0.97
1.16
1.32
1.46
1.59
1.71
1.81
1.91
2.00
3.75

FOREGS Geochemical Baseline Mapping

Canary Islands

Stream sediment

Factor 5: Eigenvalue 7.30; Proportion of total variance explained 13.52%

Factor loadings class	Determinand associations
<0.9>0.7:	Ni, Cr, Co, Fe_2O_3*, V*
<0.7>0.5:	MnO, TiO_2*, Cu, Ga*
<0.5>0.4:	Al_2O_3*, Zn, MgO, Nb
<0.4>0.3:	Li, Eu, Y*, Be, Mo, Na_2O, Ce, La, Pr, As, Sm, Nd
<-0.18>-0.2:	-SiO_2*

*Normal data, and the remaining are log transformed

Factor 5 scores
Floodplain

Mafic/Umafic elem. factor

0 500 1000 Kilometers

-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
1.50
2.00

Factor 5 scores

-2.79
-1.20
-0.36
0.00
0.40
0.75
0.97
1.16
1.32
1.46
1.59
1.71
1.81
1.91
2.00
3.72

FOREGS Geochemical Baseline Mapping

Canary Islands

Floodplain sediment

Factor analysis: Association of elements in mafic and ultramafic rocks

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Factor 2 scores
Stream sediment

Mafic/Umafic elem. factor

0 500 1000 Kilometers

-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
1.50
2.00

Factor 2 scores

-3.51
-1.20
-0.36
0.00
0.40
0.75
0.97
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*Normal data, and the remaining are log transformed

Factor 5 scores
Floodplain

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-0.50
0.00
0.50
1.00
1.50
2.00

Factor 5 scores

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-1.20
-0.36
0.00
0.40
0.75
0.97
1.16
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Floodplain sediment

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Factor 2: Eigenvalue 10.13; Proportion of total variance explained 16.34%

Factor loadings class	Determinand associations
<0.9>0.7:	Cr, Ni, Sc, Co, V, Fe_2O_3*, Cu
<0.7>0.5:	MgO, TiO_2, Al_2O_3*, In, Zn, Ga*, MnO, Eu
<0.5>0.4:	Te
<0.4>0.25:	<0.06 mm*, Y, Ce, Pr, Mo, Ta, P_2O_5, La, Hg, Ho*, Ba, Dy*, Tb*, Er*, Gd*, As, Tm*, Yb*, Sm*
<-0.4>-0.5:	-d50

*Normal data, and the remaining are log transformed

Factor 2 scores Subsoil

Mafic/Umafic elem. factor

0 500 1000 Kilometers

-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
1.50
2.00

Factor 2 scores

-3.74
-1.20
-0.36
0.00
0.40
0.75
0.97
1.16
1.32
1.46
1.59
1.71
1.81
1.91
2.00
4.46

FOREGS Geochemical Baseline Mapping

Canary Islands

Subsoil

Factor 2: Eigenvalue 9.52; Proportion of total variance explained 15.35%

Factor loadings class	Determinand associations
<0.9>0.7:	Fe_2O_3*, V, Sc, Cr, Co, TiO_2*
<0.7>0.5:	Ni, MgO, Al_2O_3*, Ga*, In, Cu
<0.5>0.4:	MnO, Te, Zn, Eu, <0.06 mm*, Nb
<0.4>0.25:	Mo, Ho*, Ta, Y, Er*, Dy*, Tm*, Na_2O, Tb*, Yb*, Lu*, Gd*, Ce, Pr, I, Sm*, As, La, Sr, Nd*
<-0.4>-0.5:	-d50

*Normal data, and the remaining are log transformed

Factor 2 scores Topsoil

Mafic/Umafic elem. factor

0 500 1000 Kilometers

-2.00
-1.50
-1.00
-0.50
0.00
0.50
1.00
1.50
2.00

Factor 2 scores

-2.17
-1.20
-0.36
0.00
0.40
0.75
0.97
1.16
1.32
1.46
1.59
1.71
1.81
1.91
2.00
5.12

FOREGS Geochemical Baseline Mapping

Canary Islands

Topsoil (0-25 cm)

Factor analysis: Association of elements in mafic and ultramafic rocks

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Use of geochemical data in

- mineral exploration
- farming & forestry
- land use policy
- health issues
- environmental policy

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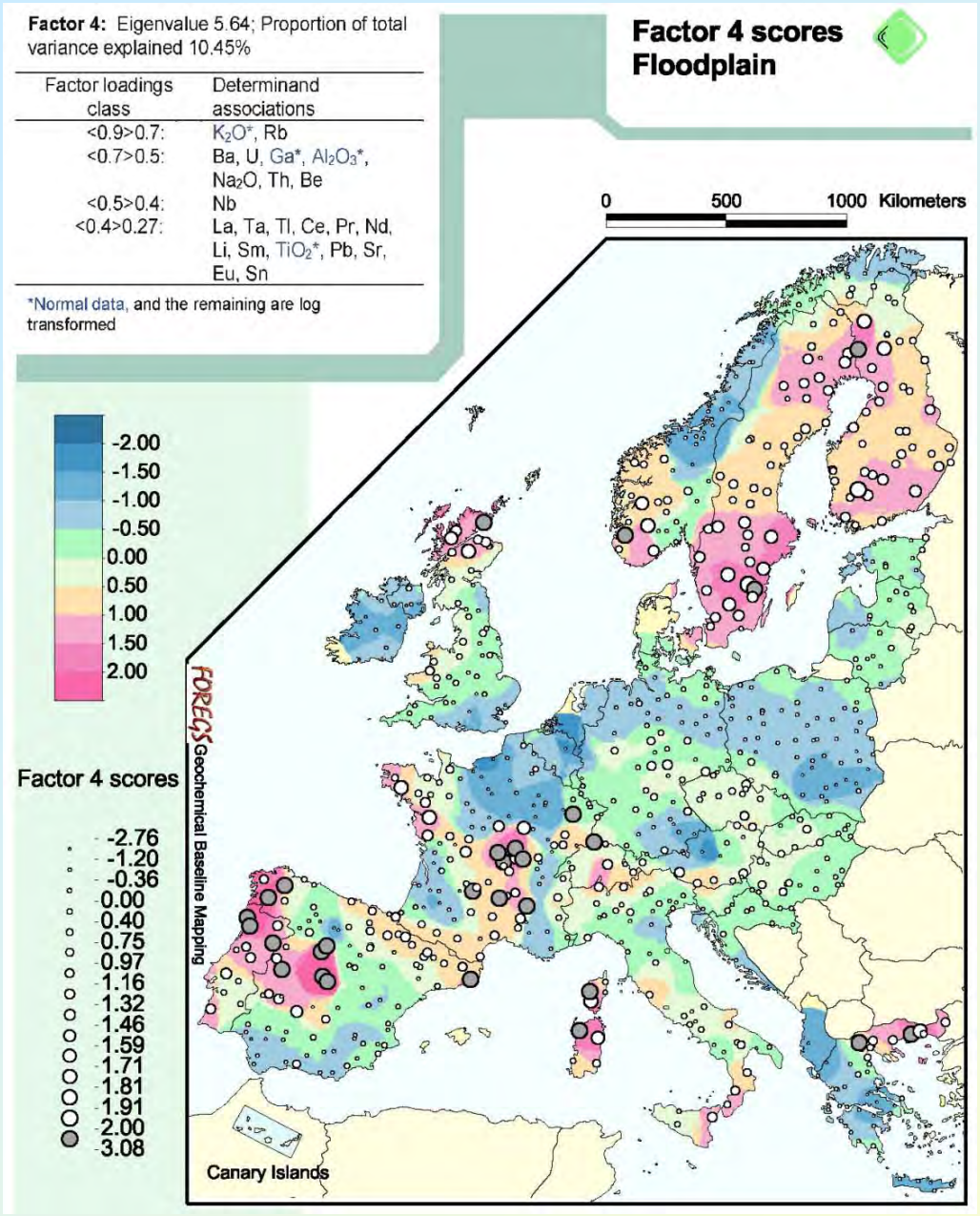

Use of geochemical data in mineral exploration

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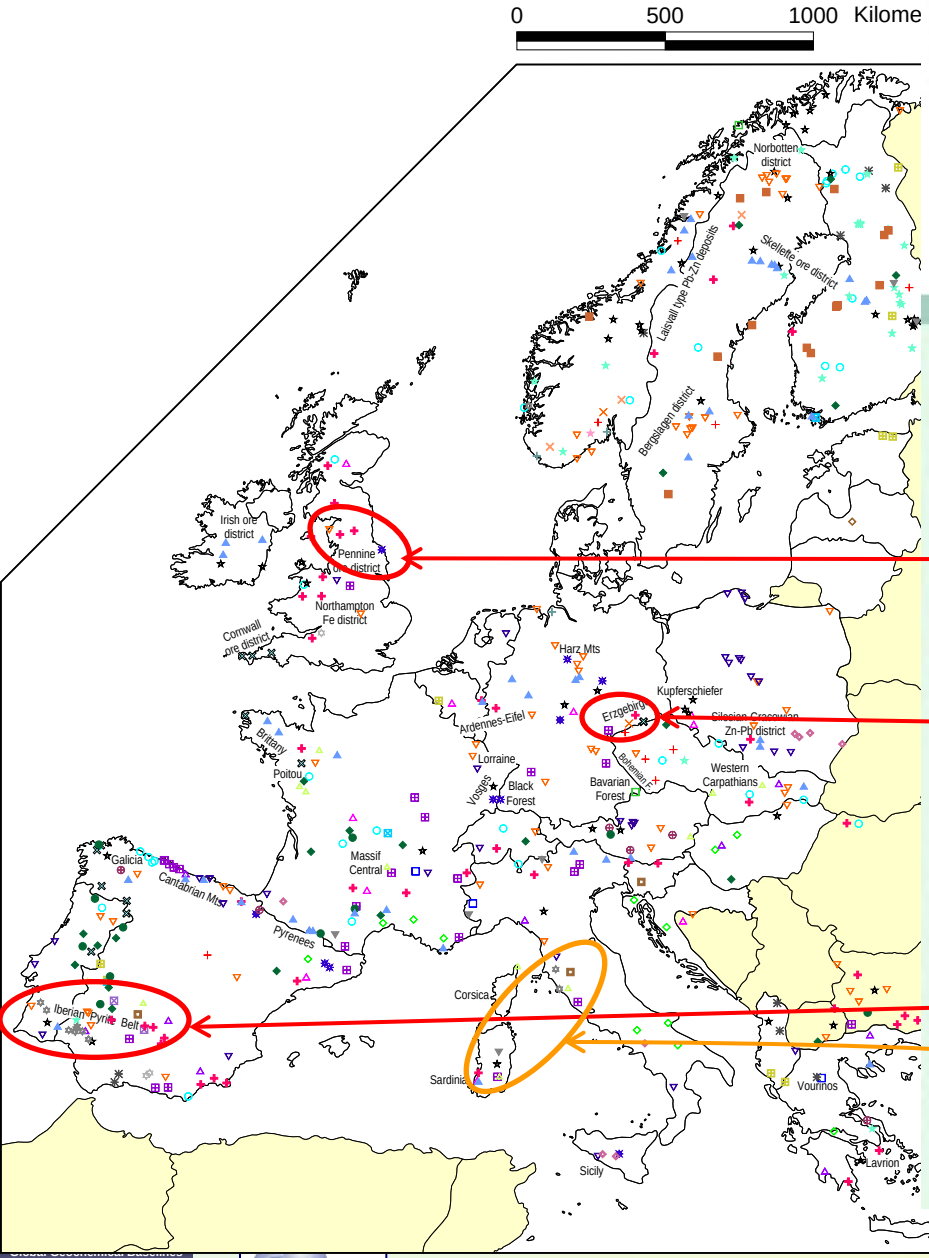
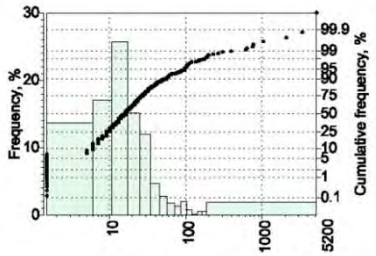
Major mineral deposits of Euro

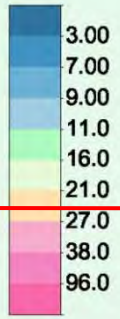




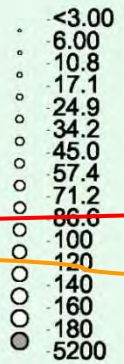
Pb - Aqua regia
ICP-AES, detection limit 3 mg kg^{-1}
Number of samples 747
Median 16.0 mg kg^{-1}

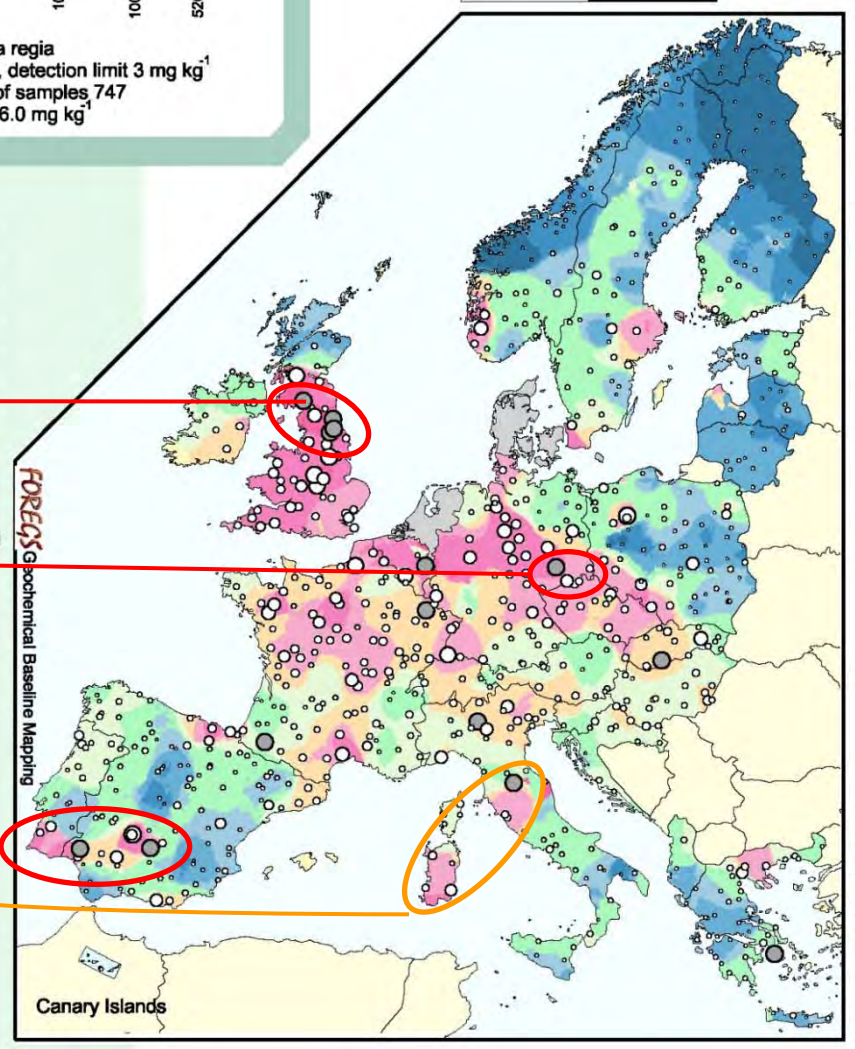
Lead Floodplain

Pb



Pb mg kg^{-1}





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Use of geochemical data in farming & forestry

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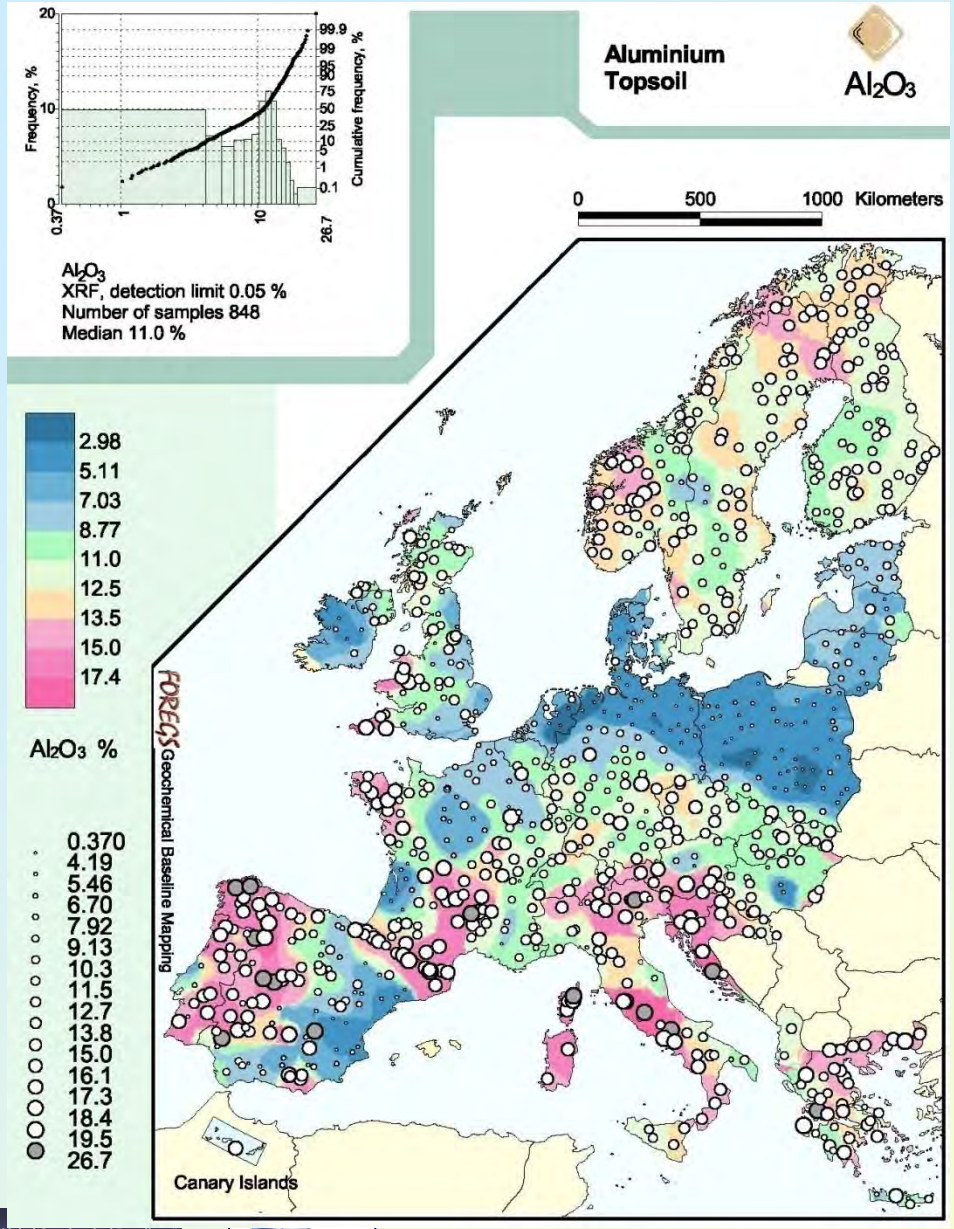
Essential chemical elements for plants and animals



- **Seventeen trace elements are considered essential for all plants: Al, B, Br, Cl, Co, Cu, F, Fe, I, Mn, Mo, Ni, Rb, Si, Ti, V and Zn.**
- **Essential elements for animals are: Ca, Cl, Co, Cr, Cu, F, Fe, I, K, Mg, Mn, N, P, S, Se and Zn**

The Geochemical Atlas of Europe can pin point problem areas for follow-up work.

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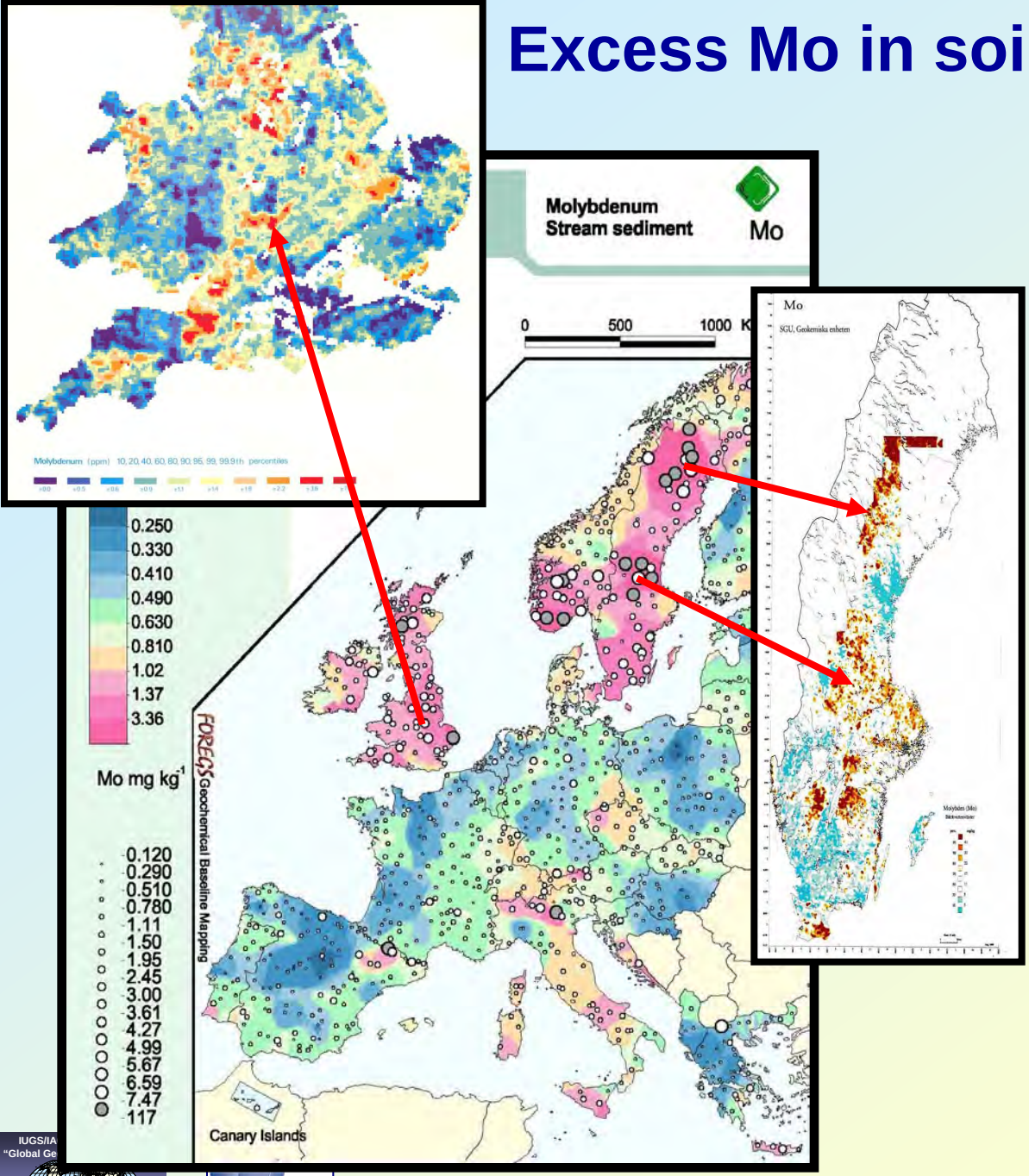
Synergism: Increased availability of a nutrient to the plant due to the increase level of another nutrient

Antagonism: Decreased availability to the plant of a nutrient, due to the action of another nutrient

Mulder's chart Interaction between the various nutrients

- Zn absorption by a plant is dependent upon the levels of P, Fe & Ca in soil.
- High P levels in soil antagonise the uptake of Zn, Cu & K, but stimulate the uptake of Mg.

Excess Mo in soil



In England, excess Mo in soil, and thence in pastures and fodder, caused a similar Mo excess in grazing cattle; due to the excess of this element, these cattle acquired a deficiency in another element, Cu. Copper deficiency in these cattle was exhibited as stunted growth, late maturity and decreased production. Supplementing the Mo rich pastures with Cu corrected the problem.

Use of geochemical data in land use policy

The Geochemical Atlas of Europe can be used for effective land use planning, *i.e.*, to decide if the particular land is fit for:

- **agriculture,**
- **animal husbandry,**
- **parks,**
- **new towns, etc.**

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Use of geochemical data in health issues

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http://www.gl[illegible]geochemica[illegible]

planetearth Earth Sciences for Society

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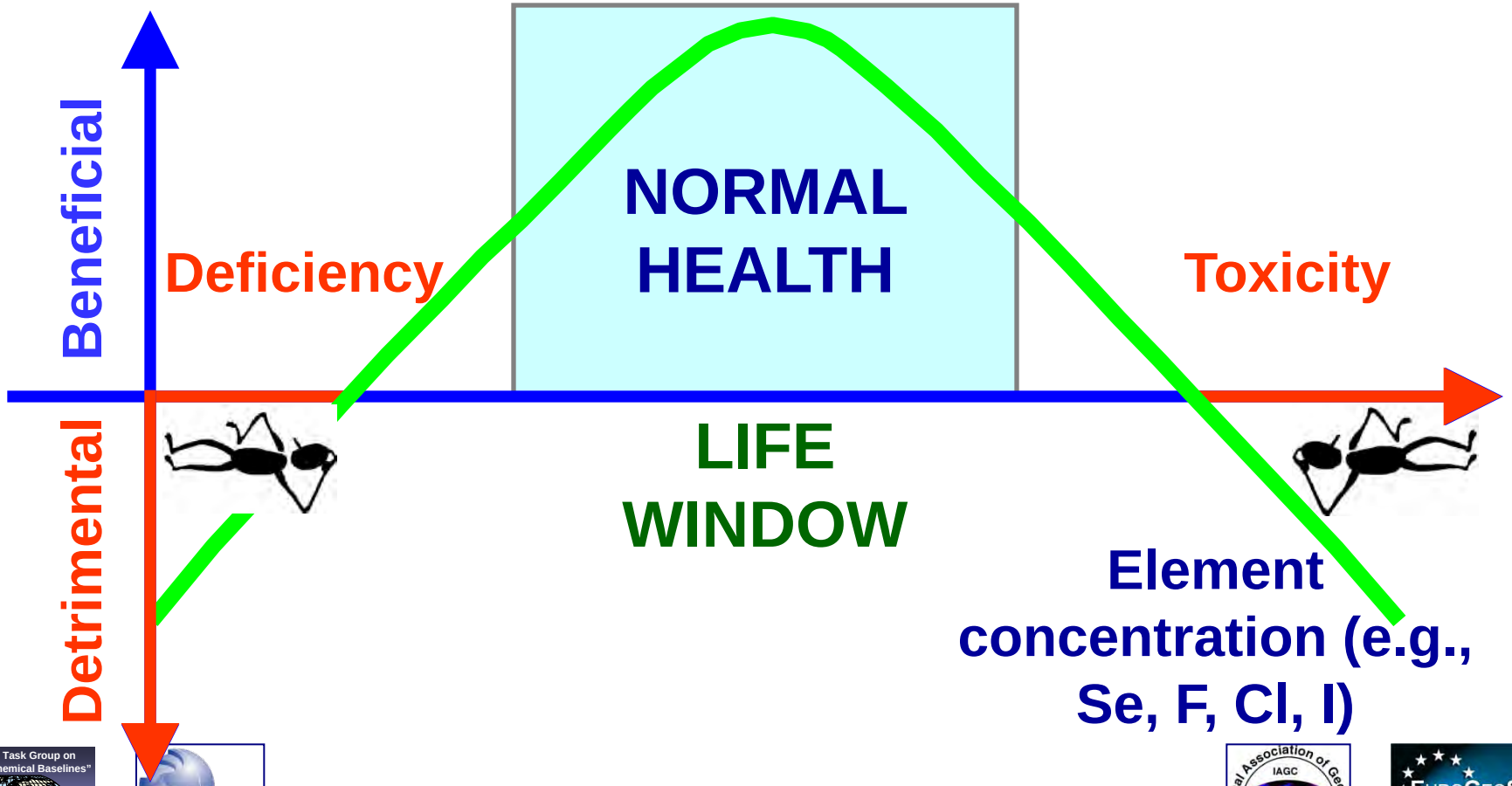
DOSE – RESPONSE CURVE



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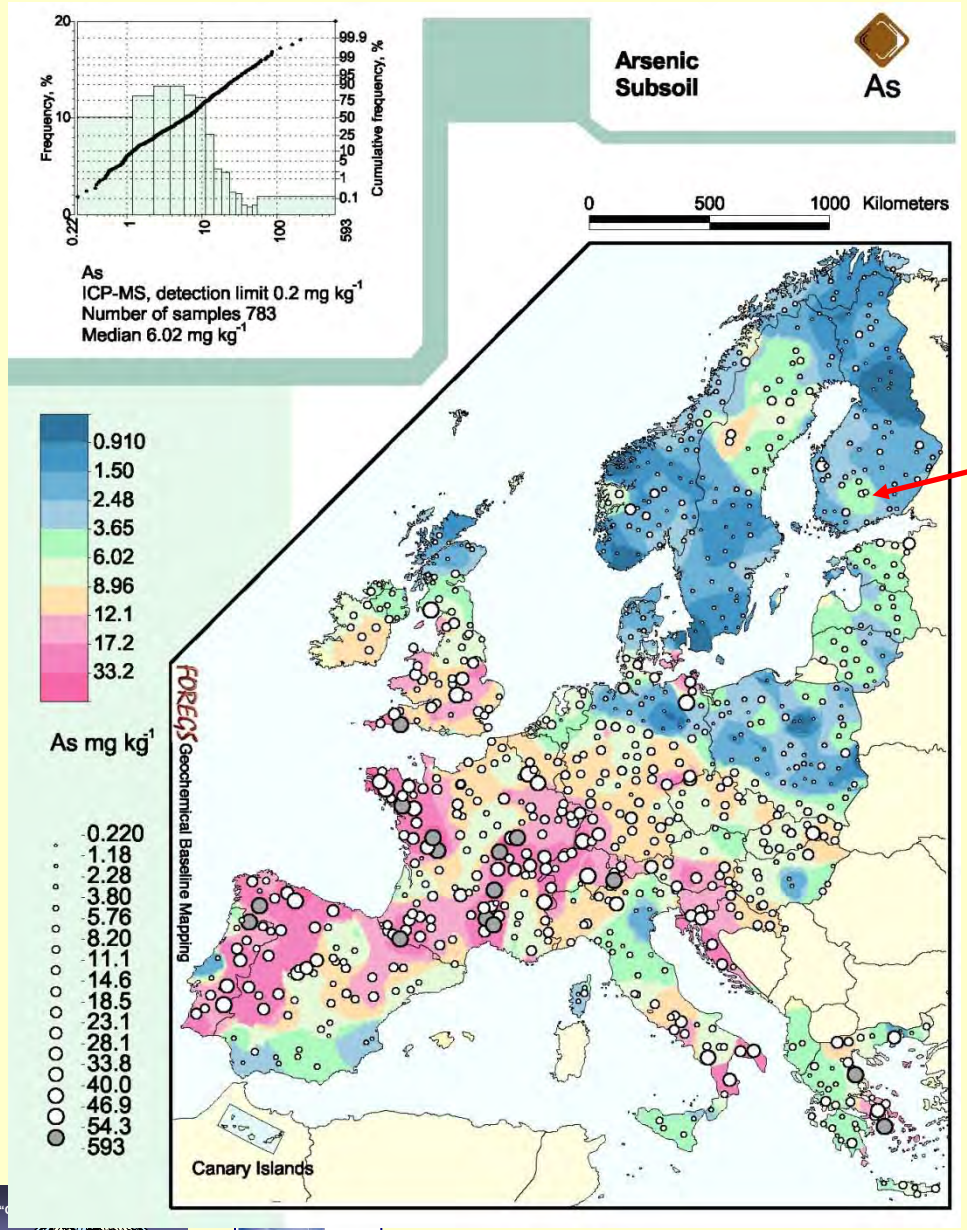
Arsenic distribution and health …..

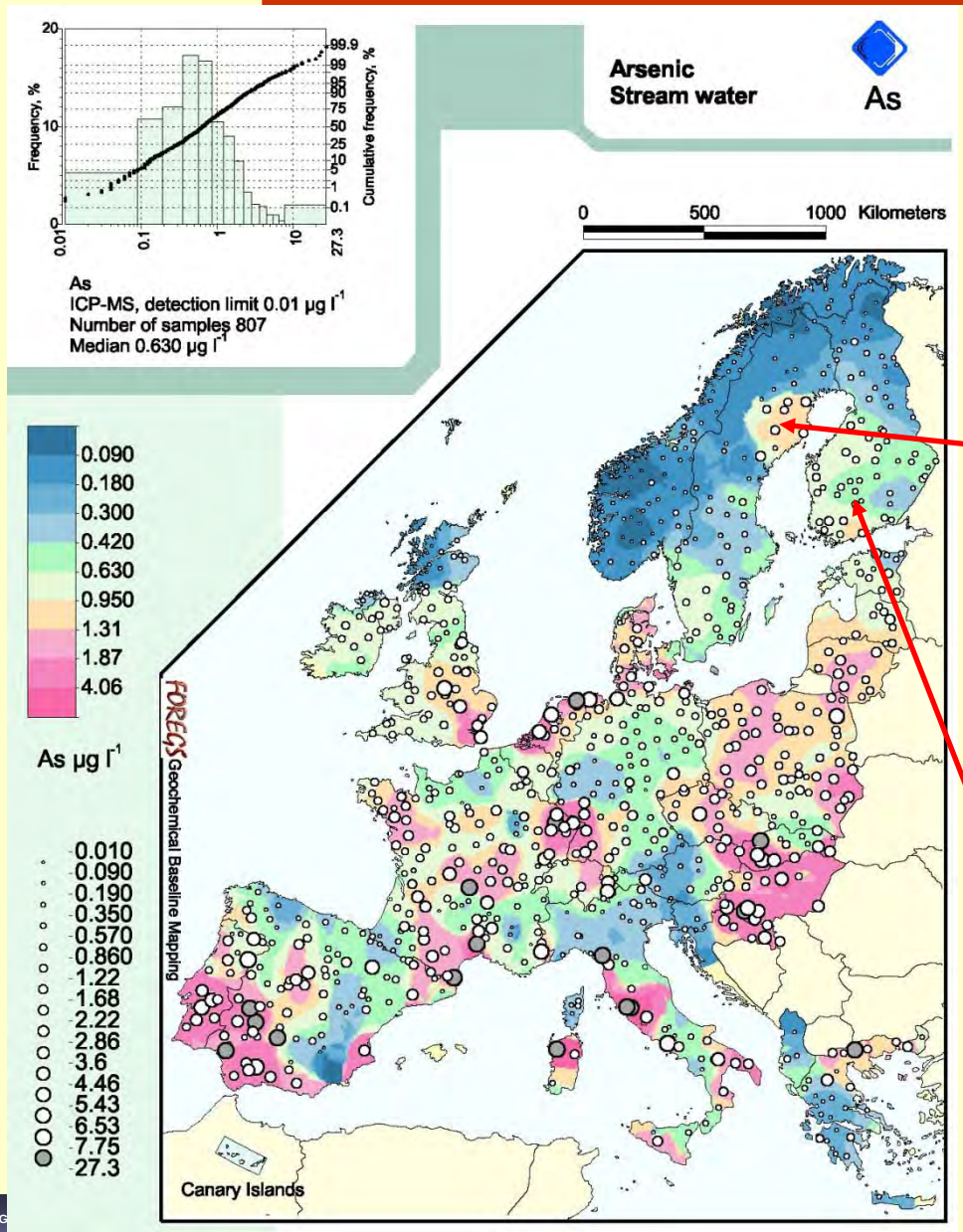


Pirkanmaa, Finland

Subsoil reflects bedrock chemistry.

What is the As-concentration in bedrock hosted ground water?

Arsenic distribution and health



<10 µg/L Arsenic is the maximum admissible concentration in drinking water (WHO/EU)

Values up to 800 µg/L As have been found so far in the area of the As-anomaly in Sweden.

Pirkanmaa Finland: Maximum As-value is 2230 µg/L in a bedrock drinking water well.

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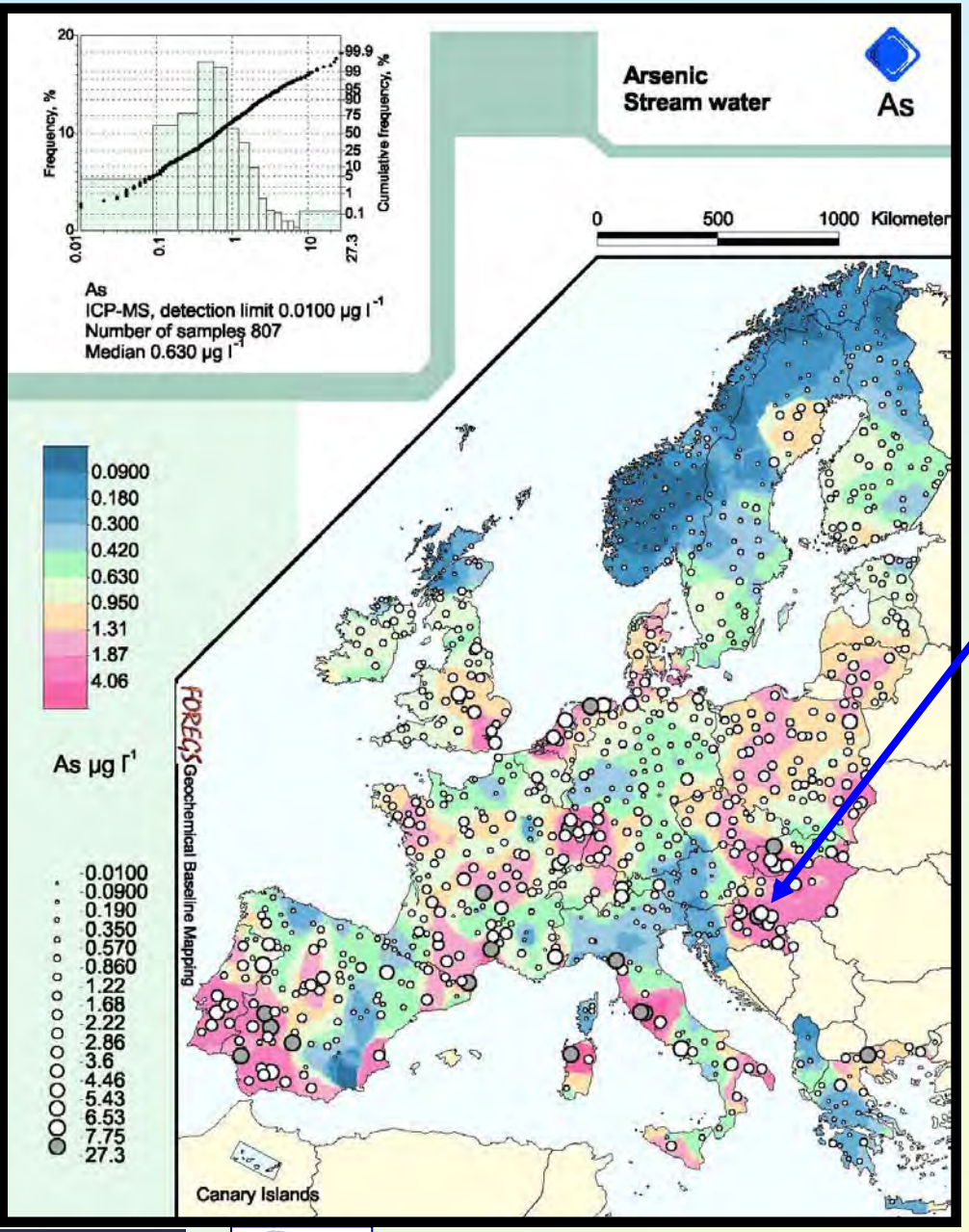

Balkan endemic nephropathy (BEN) is a severe, potentially fatal kidney disease leading to end-stage renal failure requiring blood dialysis, and is often associated with a particular kidney cancer. The disease only occurs amongst rural villagers in Croatia, Bosnia, Bulgaria and Serbia without access to municipal (treated) water supplies. The principal aquifers in the BEN regions are extremely low-rank (geologically young) Pliocene lignite (coal), containing many relatively chemically reactive hydrocarbons. Scientists believe that the water leaches the hydrocarbons from the lignite. Drinking this naturally contaminated water can result in BEN.

Balkan Endemic Nephropathy (BEN)

BEN patient in a dialysis clinic (Romania)

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(Provided by Olle Selinus, SGU, Sweden)

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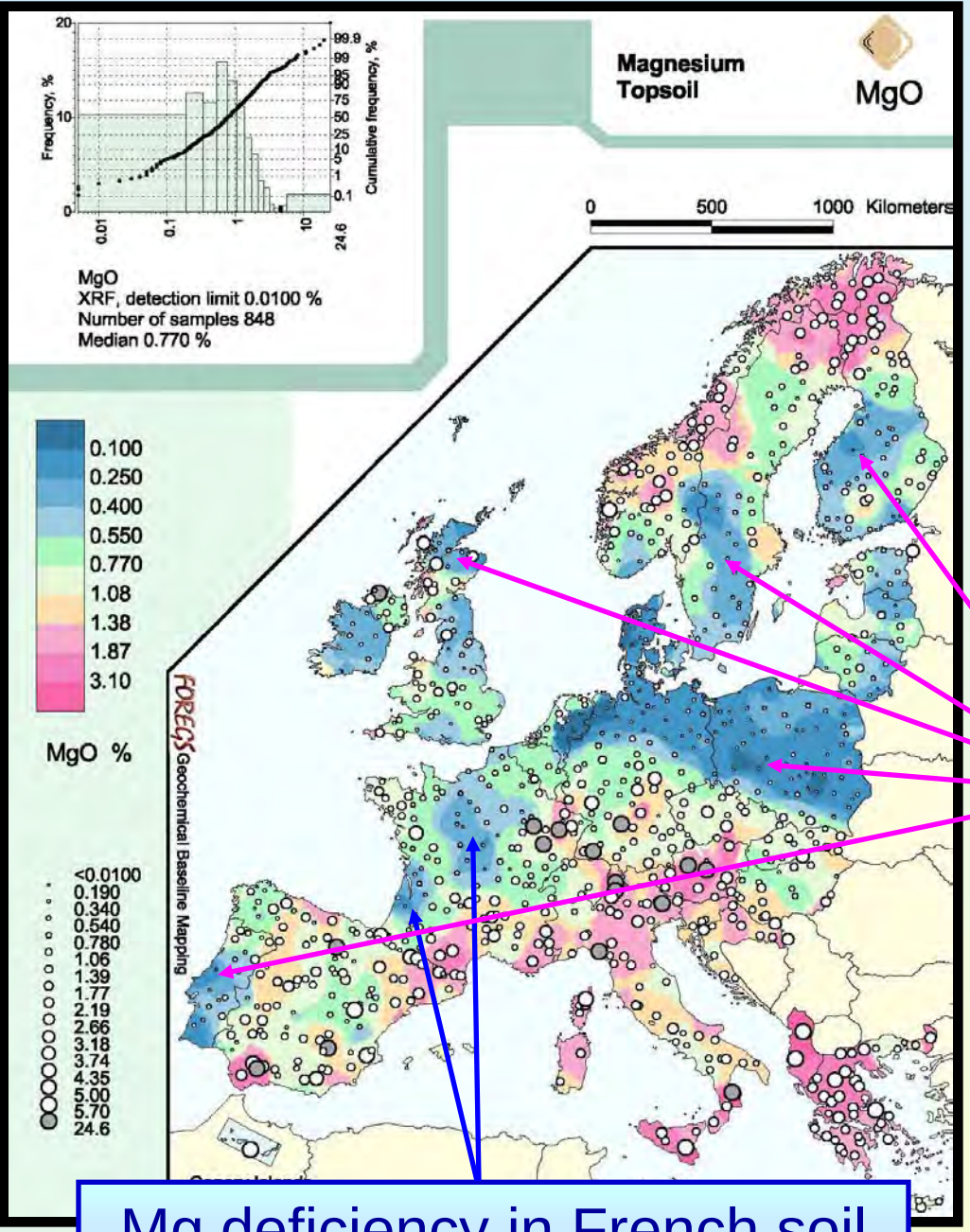
France

Magnesium deficiency in certain types of soil has been associated with specific kinds of cancer.



High risk areas with magnesium deficiency in soil should be investigated

Mg deficiency in French soil

Use of geochemical data in environmental policy

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National guideline values:

1. to protect human health
2. to protect ecosystems
3. to protect ground water

Geochemical *baselines*

Future land use

Potentially contaminated soil
Levels of pollutants (total)
Chemical species

Levels >> Guideline values and ***Baseline*** → **Remediation**

Levels < Guideline values, ***Baseline*** →**Consider clean**

Pathway to ground water

Pathway to surface water, air, direct contact

Levels ~= Guideline values
→Study chemical species, binding
→Potentially mobile form
→Study pathways
→3D modelling

(Provided by Timo Tarvainen, GTK, Finland)

icalbaselines.eu

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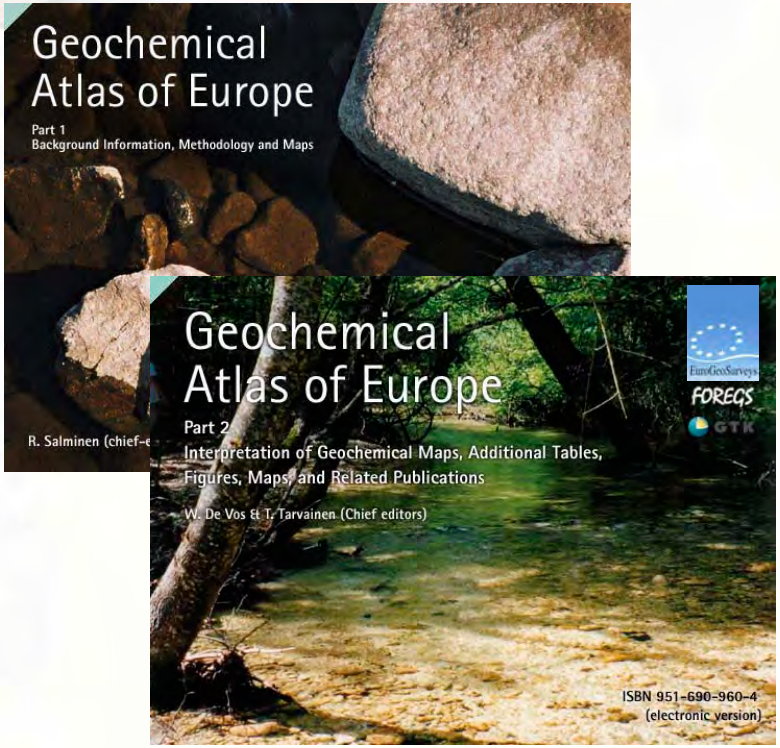
Robustness of Geochemical patterns



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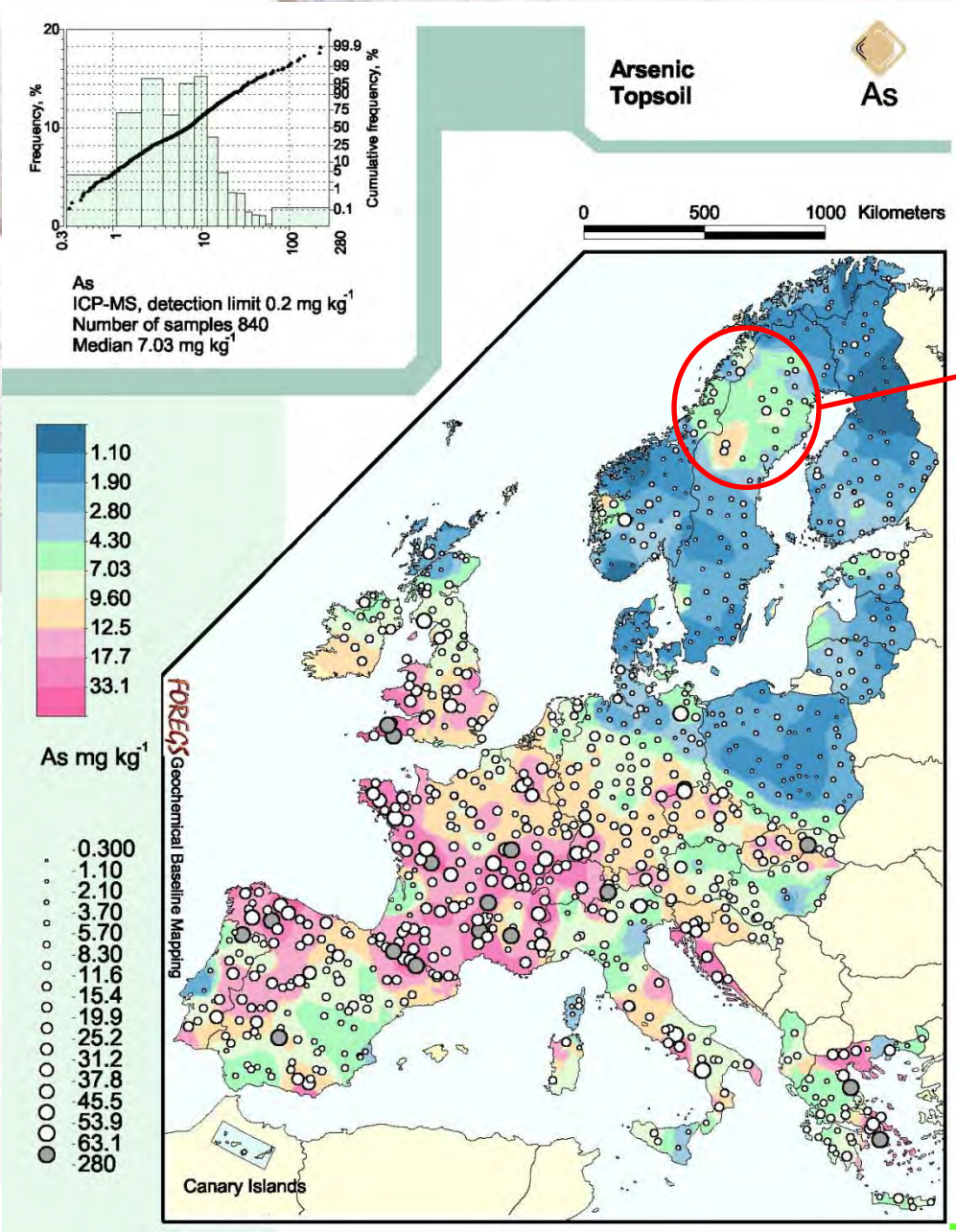

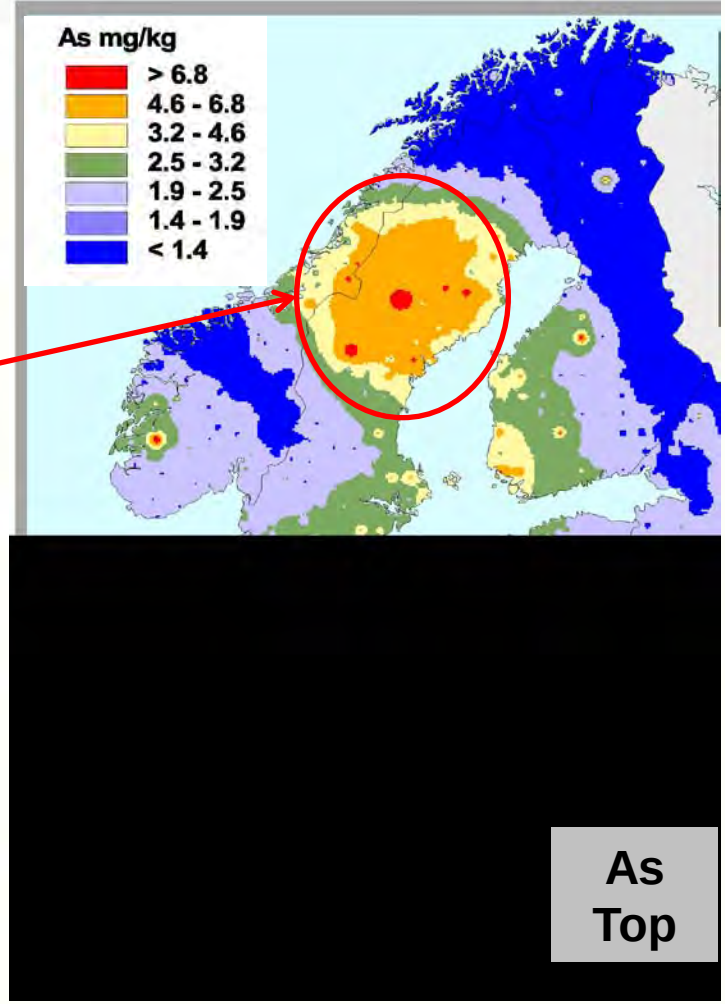

Baltic Soil Survey: As-concentrations in agricultural soil.
Sample density: 1 site / 2500 km²
Topsoil: 0-25 cm (Reimann et al., 2003)

Sample density: 1 site / 4,600 km²

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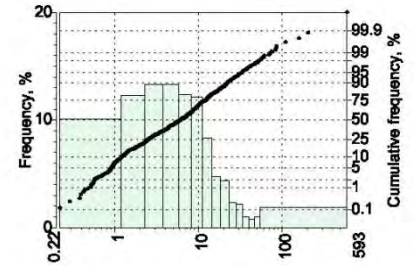

Arsenic Subsoil

As

0 500 1000 Kilometers

0.910
1.50
2.48
3.65
6.02
8.96
12.1
17.2
33.2

As mg kg^{-1}

0.220
1.18
2.28
3.80
5.76
8.20
11.1
14.6
18.5
23.1
28.1
33.8
40.0
46.9
54.3
593

FOREGS Geochemical Baseline Mapping

Canary Islands

Sample density:
1 site / 4,600 km^2

Arsenic concentrations in the fine fraction of till soil, Finland

As mg/kg

6.8
6.0
5.4
4.8
4.3
3.8
3.4
3.0
2.7
2.4
2.2
1.9
1.7
1.5
1.4
1.2
1.1
1.0
0.9

Kittilä

Pirkanmaa

Helsinki

0 100 km

Sample density: 1 site / 300 km^2
(Koljonen, 1992)

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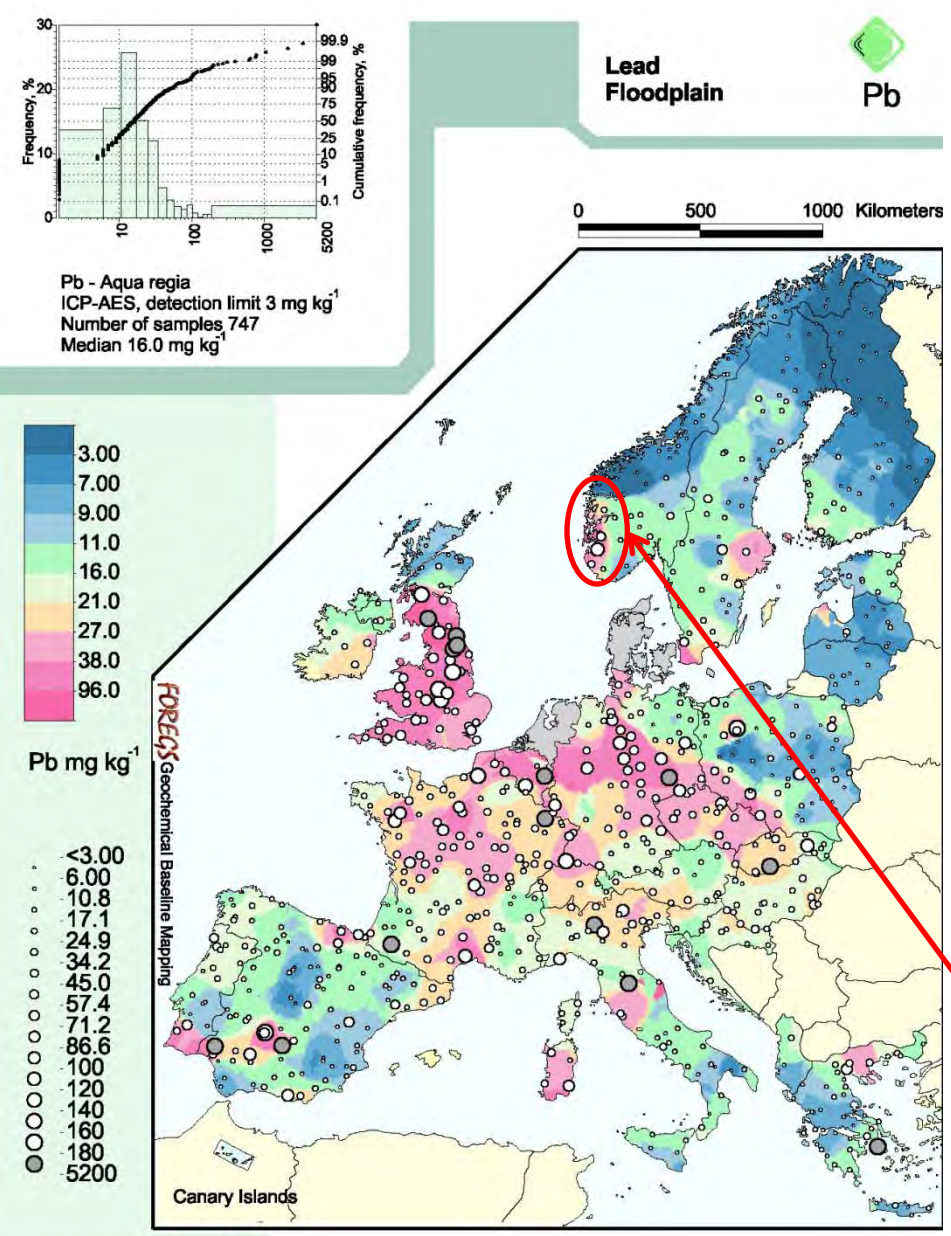
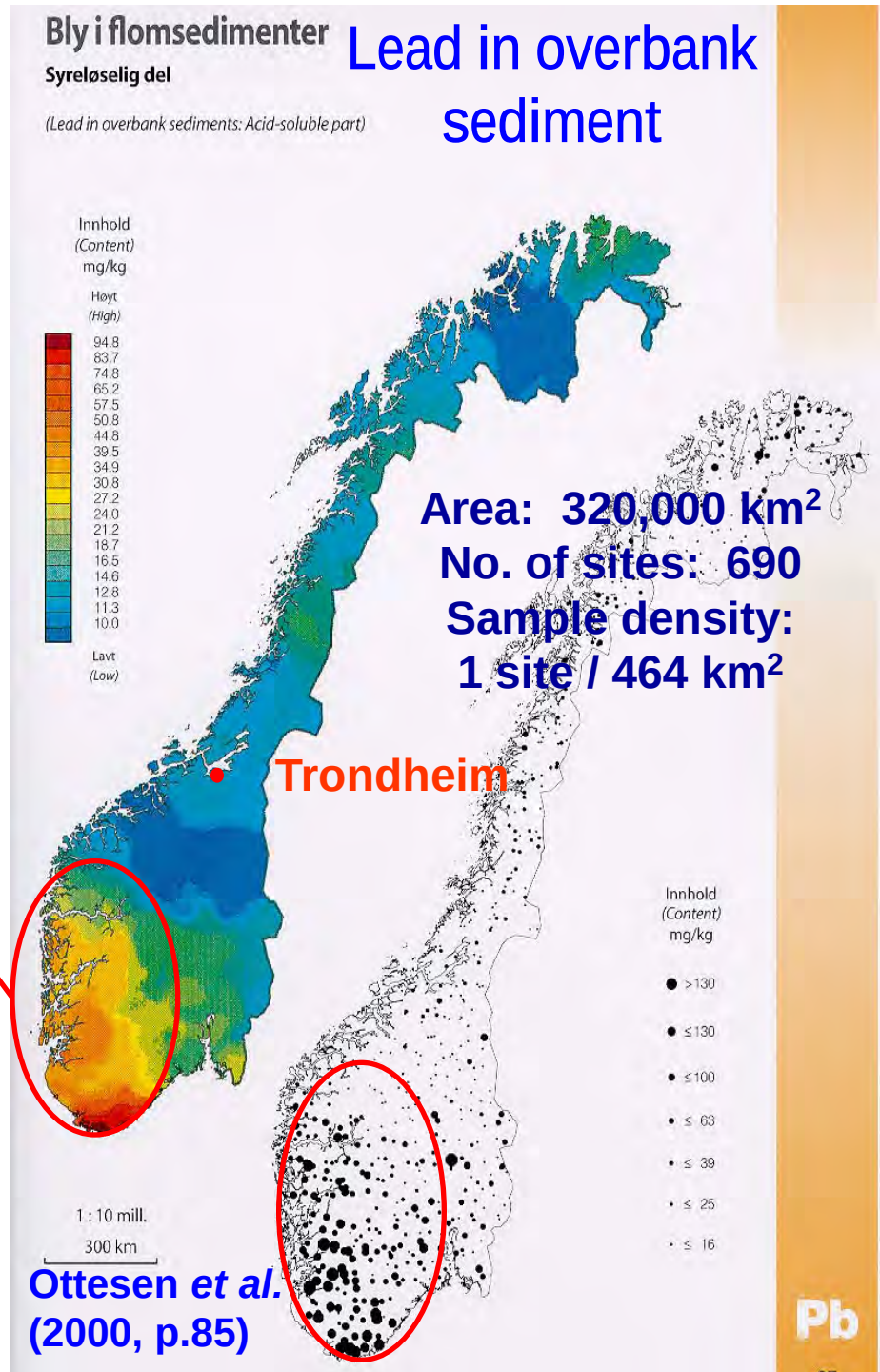


Sample density: 1 site / 4,600 km²



Epilogue

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EPILOGUE

High quality geochemical databases are necessary for ALL Continents:

- **for mineral exploration, environmental purposes, health related issues and legislation,**
- **for the documentation of natural spatial distribution of chemical elements, and impacts caused by human activities, and**
- **for the location and delineation of potentially hazardous areas in order to carry out follow-up surveys.**

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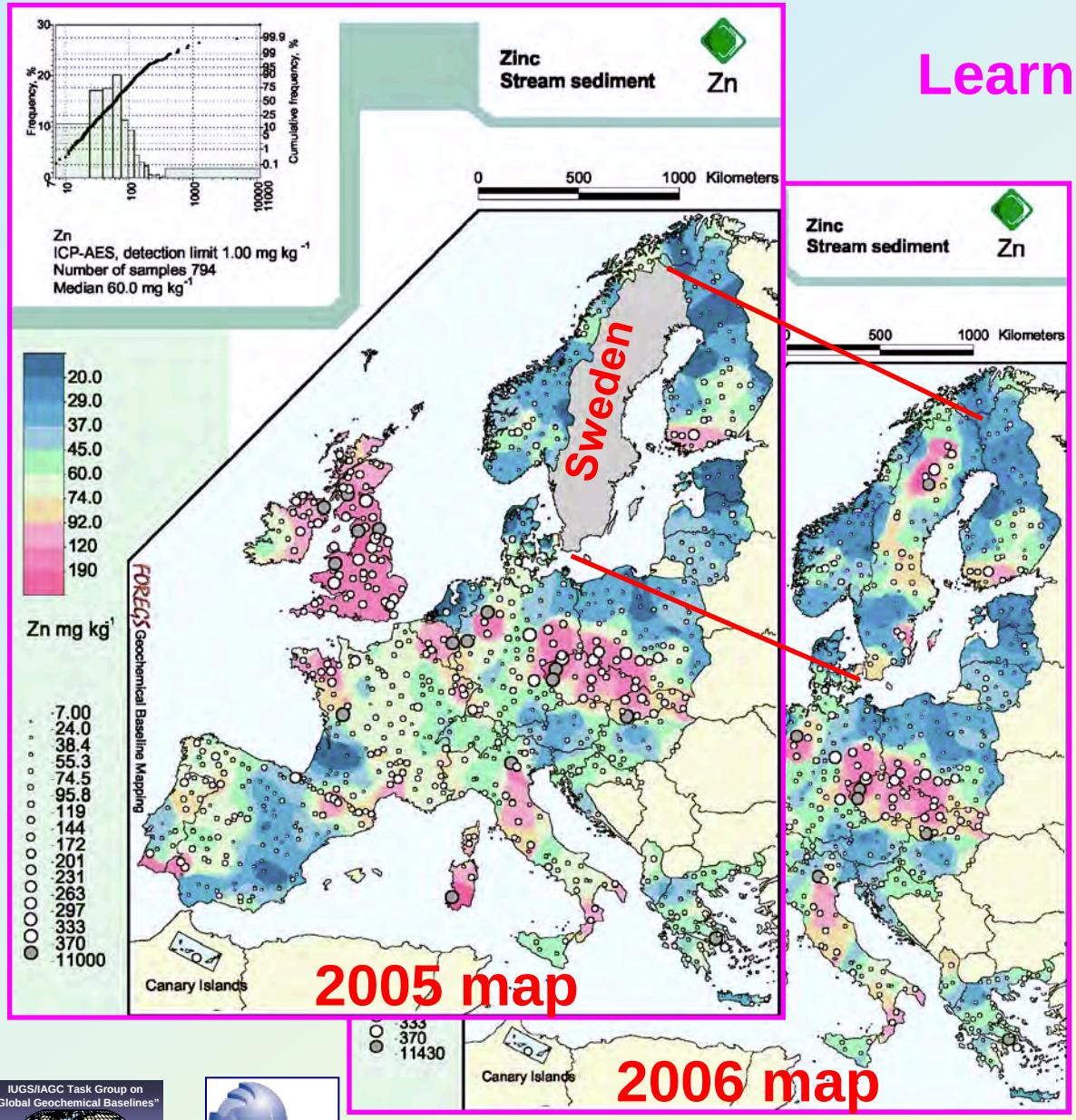
Some conclusions

- **After overcoming the different quality control problems, the Geochemical Atlas of Europe documents very clearly that natural element concentrations in soil, stream sediment, floodplain sediment and stream water vary by up to 4 orders of magnitude on the European scale.**
- **Large scale geochemical patterns emerge, which are mainly caused by a combination of geology and climate.**
- **At the European scale, the geochemical distribution of elements in the surface environment is clearly governed by natural processes; *anthropogenic contamination plays a minor role for most elements, and is of local concern*.**
- **Because of large spatial variation of elements, it is impossible to define one common "*good quality*" value to be applied over the whole of Europe.**

Recommendations



Learn from our mistakes.

All 14 CCOP countries should participate in the Geochemical Mapping project, because it will be of benefit to the people of each country.
Do not make the mistake Sweden did.

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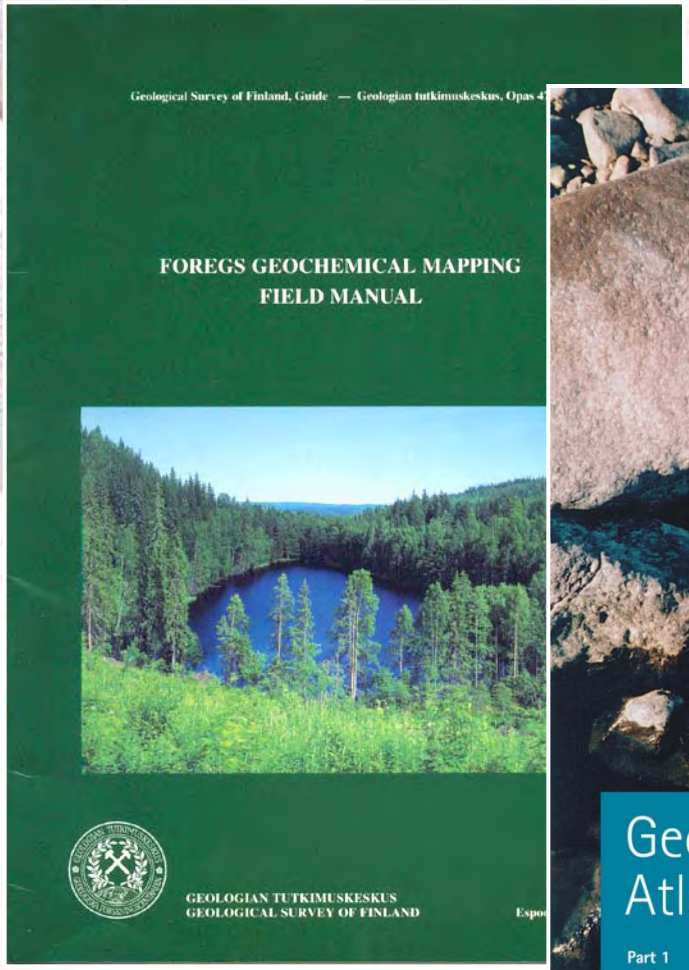
Key Recommendations…..

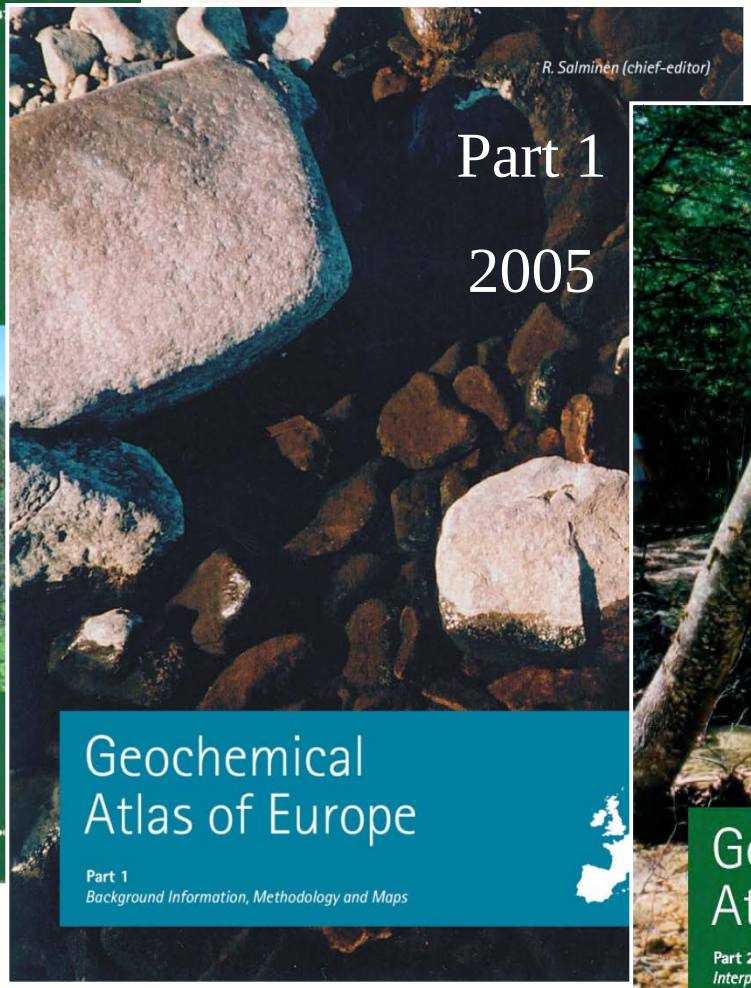
1. Collect samples in all countries during the same period;
2. Collect duplicate field samples at 1 to 20 sample sites (or 1 in 10);
3. At the same time collect large samples from all media in order to make the internal project standards; the samples must be large enough for future uses;
4. All samples ideally should be prepared in the same laboratory; homogenised and split into sub-samples for analysis and storage for future use;
5. Randomise all samples, insert field duplicate splits, internal reference (standard) samples, and international reference samples;

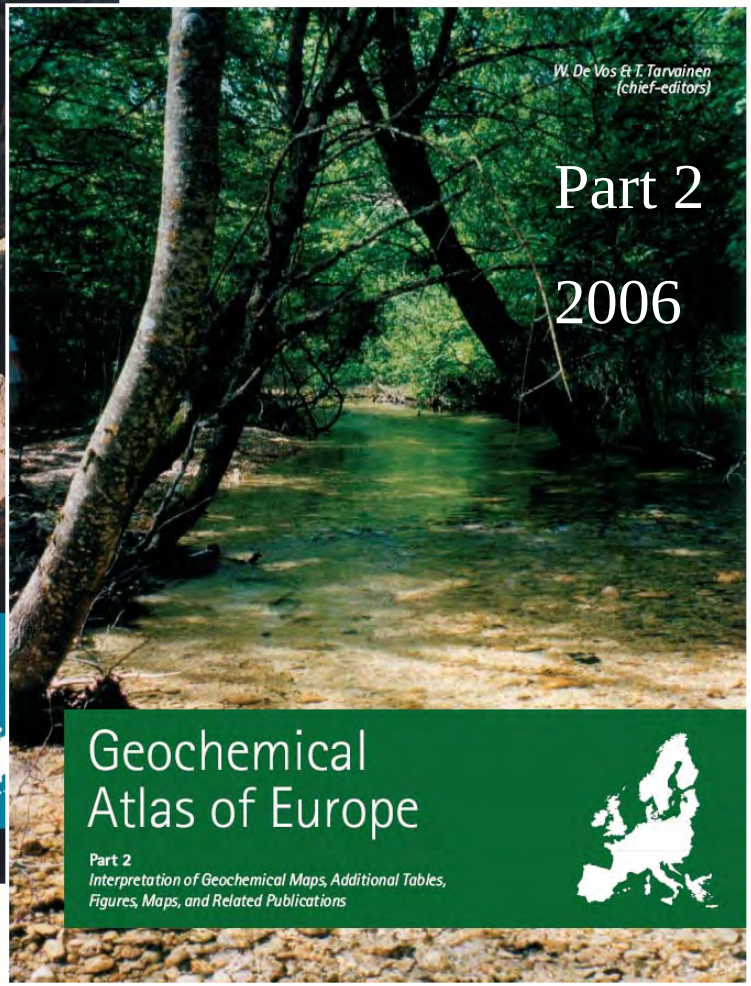
…..Key Recommendations

6. All samples MUST be analysed at the same laboratory for the same suite of determinands (elements/parameters);
7. Ask the laboratory not to cut-off values at the detection limit of the method used, but to report all values, even sub-zero (negative) values;
8. Check all sample site coordinates;
9. All countries must submit the field observation sheets, and high definition digital photographs to the Manager;
10. Upon receipt of analytical results, their quality must first be checked; if problems are found, these must be checked by re-analysis of batches. A Quality control report must be written on the results of each participating laboratory.
11. Compile database files for processing.

Geochemical Atlas of Europe







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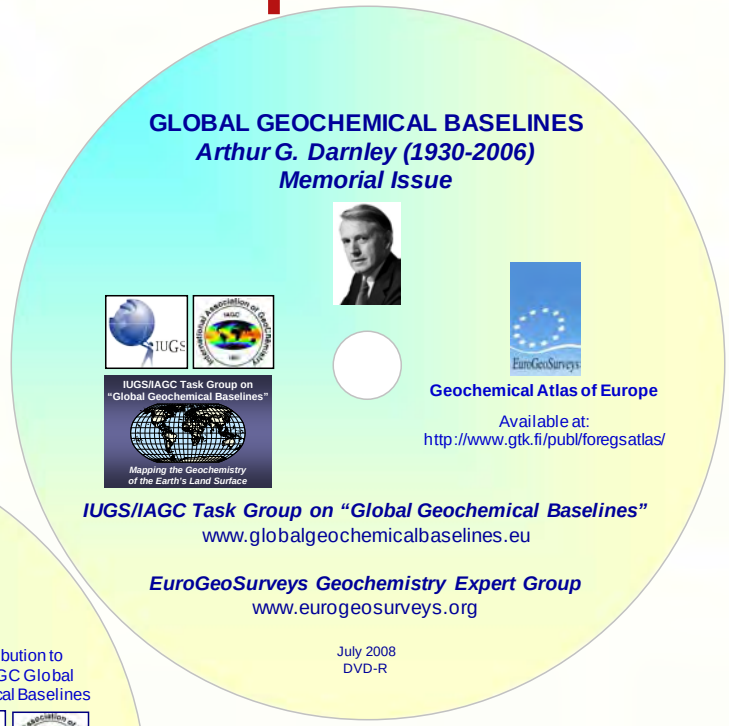

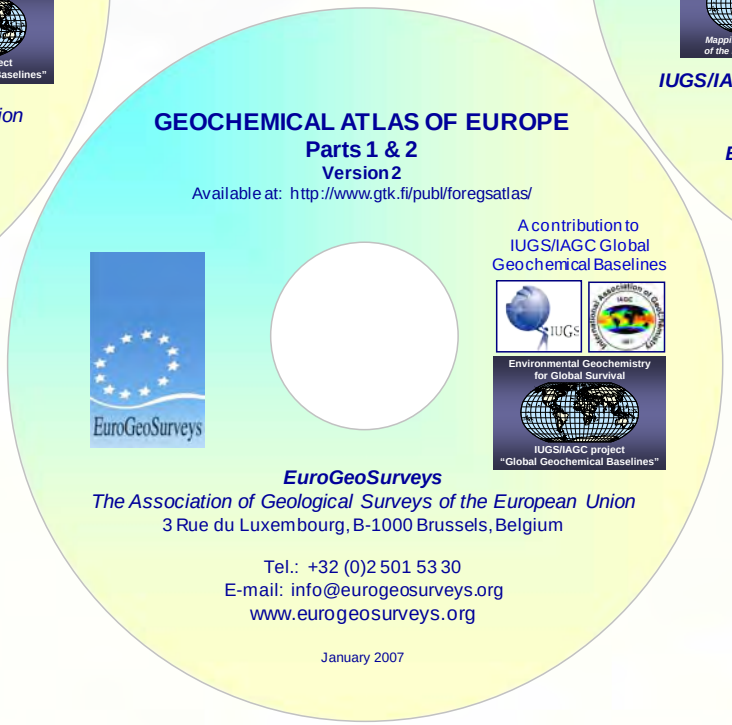

CD includes all the material of the 2 printed volumes and the Field Manual

DVD includes also all publications from 1989 to 2008

CD & DVD available from alecos.demetriades@gmail.com

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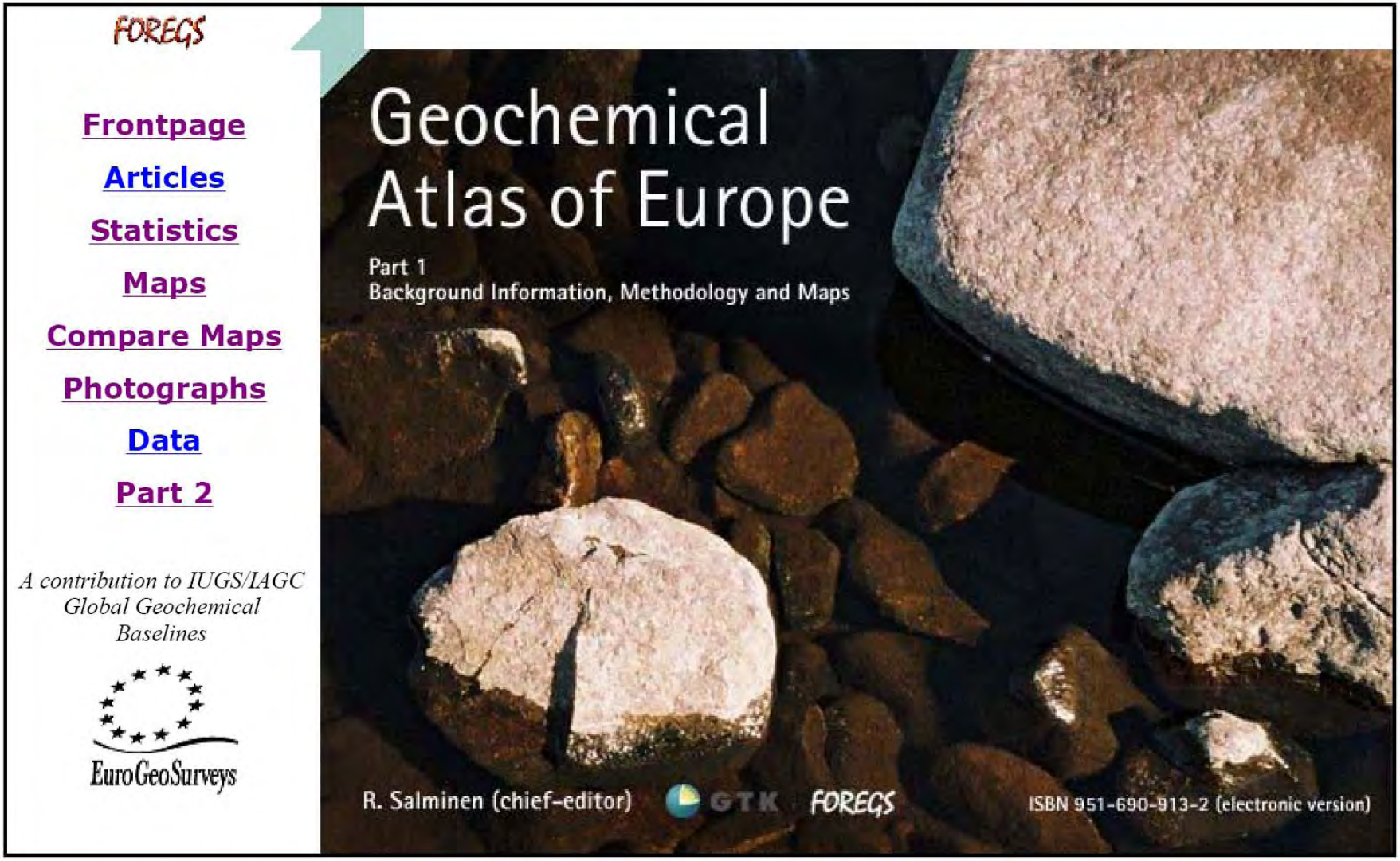

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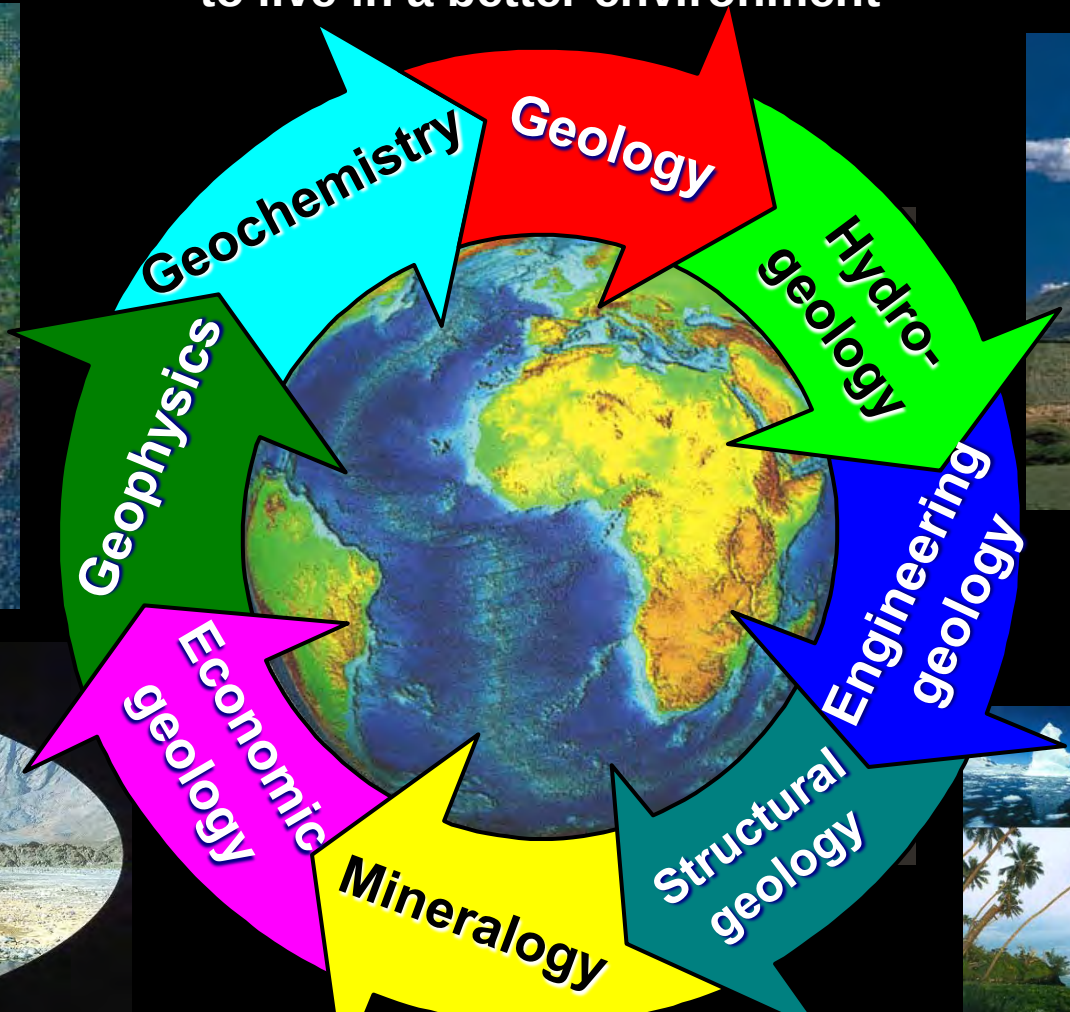
The Geological Sciences by definition are concerned with the Earth's environment

It is, therefore, the Geological Surveys' obligation to provide geochemical databases of high integrity and quality to help the present and future generations to live in a better environment



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