ASSESSMENT OF DRAINAGE BASIN CONTAMINATION BY STREAM AND FLOODPLAIN SEDIMENT GEOCHEMICAL SURVEYS

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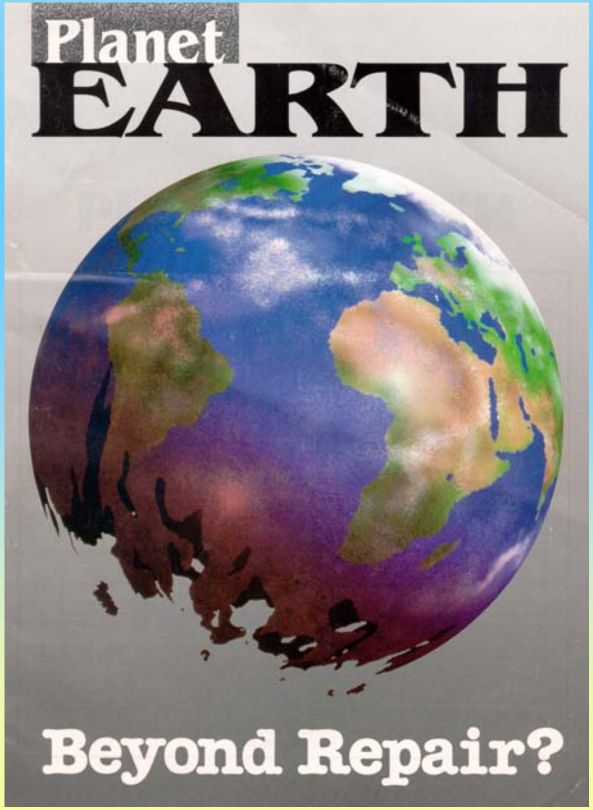
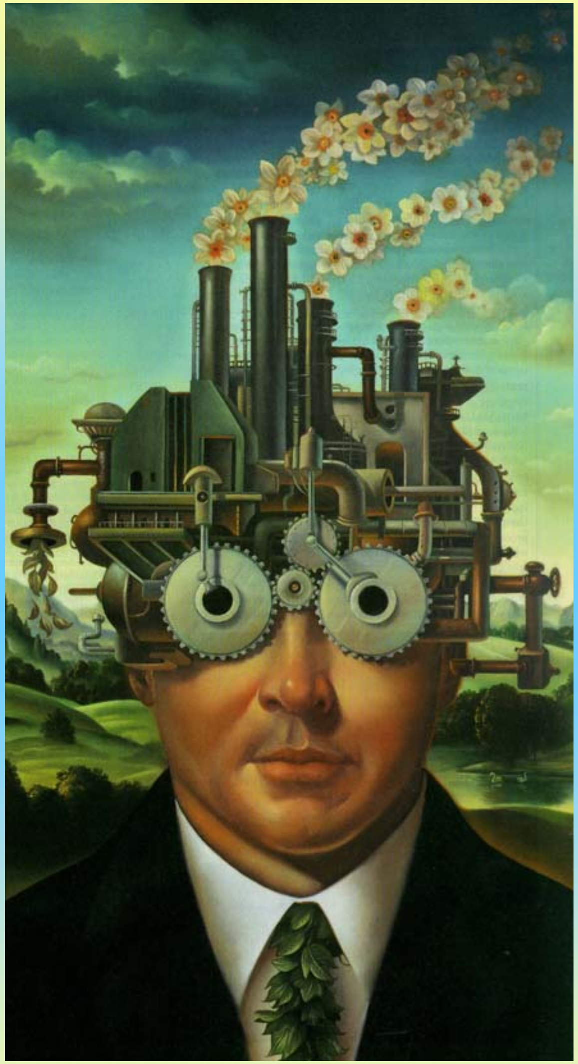
PRESENTATION PARTS

1. General Introduction
2. Sampling
3. Stream and floodplain sediment surveys
4. Quality control procedures
5. Geochemical baseline concentrations of elements in sediments
6. Epilogue

General introduction

<u>The Global Problem</u>: Humans, since their appearance on Earth, have been altering the chemistry of the natural environment by their activities to such an extent that *life support systems are now in danger.*





CONCLUSION

It is necessary to develop a cost-effective method to assess contamination with a high degree of confidence, depending on the mapping scale, and also to be able to monitor future changes.

This information is necessary for establishing the baseline conditions, and any abnormal situations in order to plan the restoration of the environment, wherever is considered necessary.

Geochemical Baseline Data

For a realistic assessment of contamination it is significant to have high quality

GEOCHEMICAL BASELINE DATA

about the natural element variation before humans began to contaminate the environment

Contamination

Natural or Anthropogenic induced abnormal element concentrations are superimposed on a variable natural background

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

Sample media for regional and follow-up geochemical surveys

- Active stream sediment
- Floodplain or Overbank sediment

PRODUCTION OF HIGH QUALITY GEOCHEMICAL DATABASES …..

REQUIRES GOOD PLANNING AT ALL STAGES OF:

Sampling

Sample preparation

Laboratory analysis

Geochemical database management

Map production

….. 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

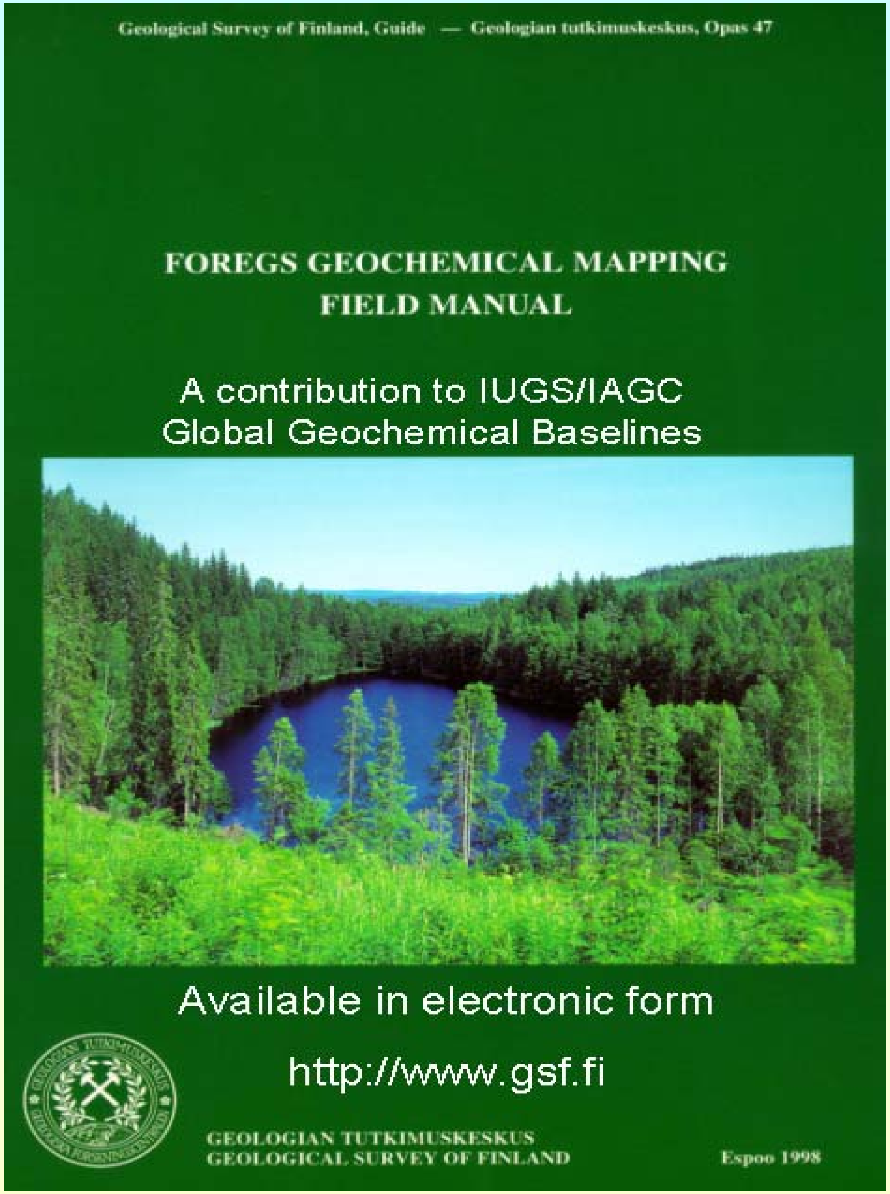
Sample preparation

- 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 enough sampling material is available.

Sampling



SAMPLING

Field Manual

was published in 1998

Salminen, Tarvainen *et al*. (1998). *FOREGS Geochemical Mapping, Field Manual*. Geological Survey of Finland. Guide Number 47

Field sampling manual was compiled by experienced applied geochemists in sampling in different morpho-climatic environments, and then tested in the field before finalisation

URL: http://www.gtk.fi/foregs/geochem/fieldman.pdf

➢ Stream sediment

- **Wet sieving**

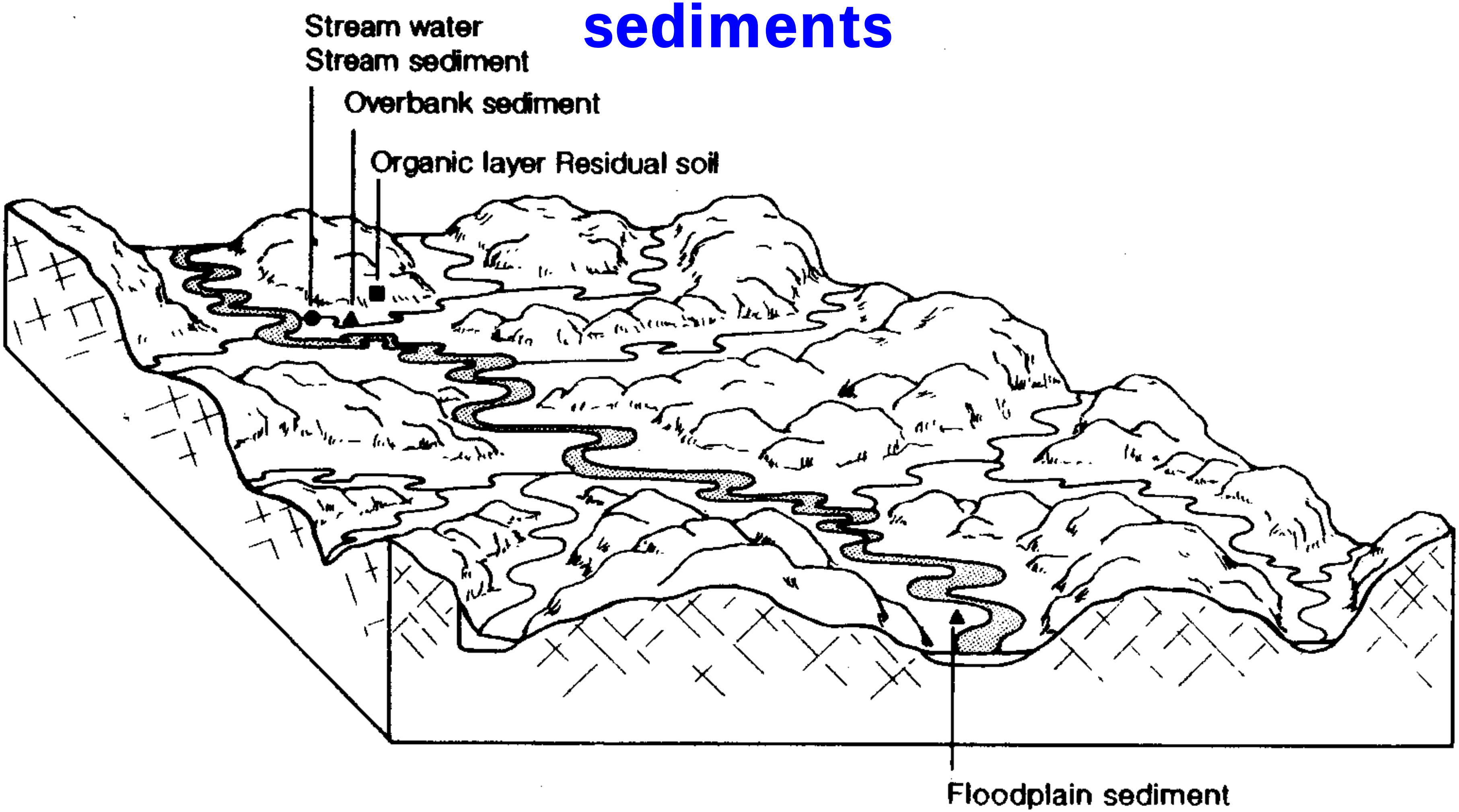
- **Dry sieving**

➢ Floodplain and/or overbank sediment

TRAINING

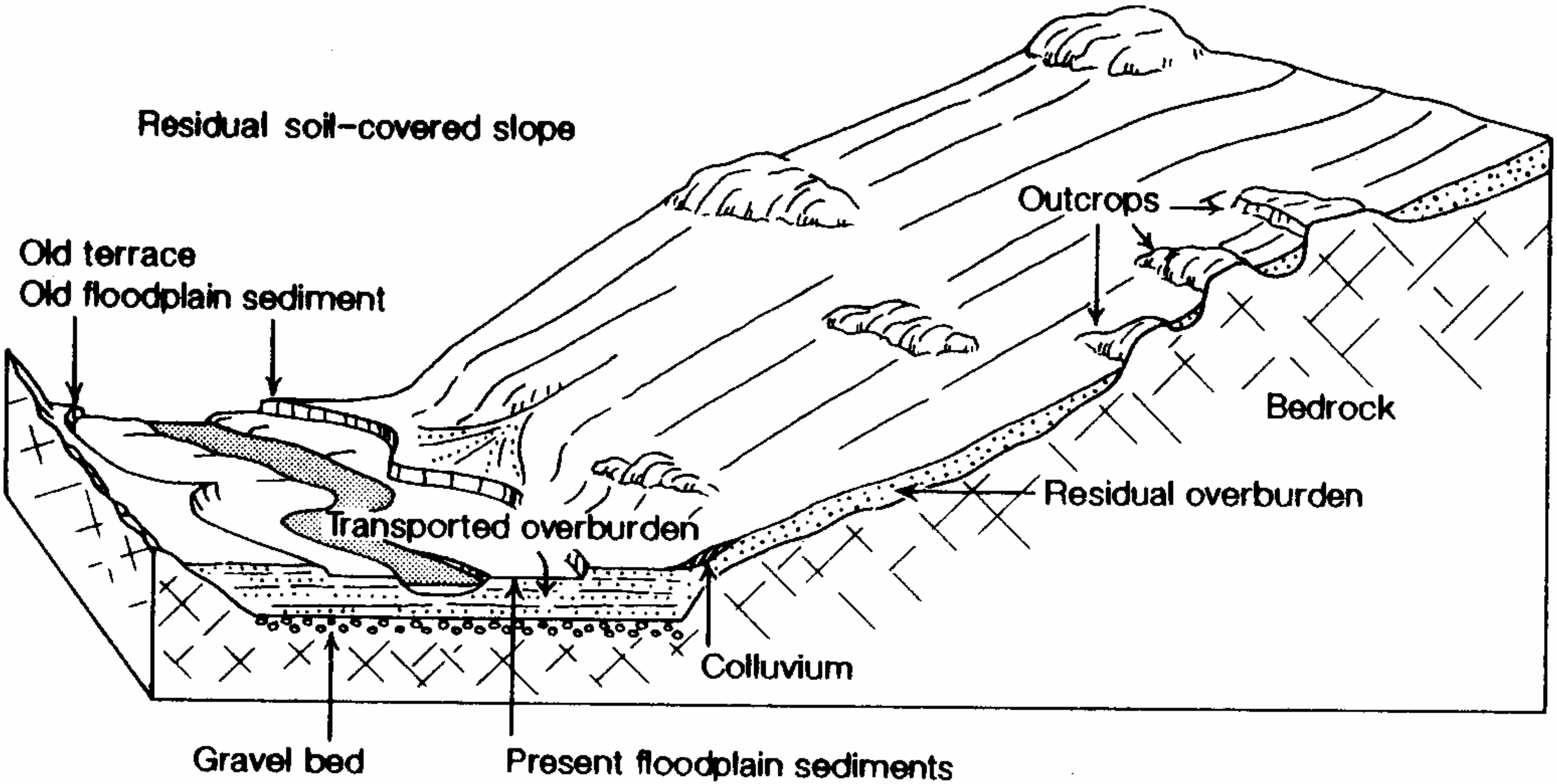
Sampling teams must be well trained

Block diagram showing drainage basin with sites for sampling overbank / floodplain sediments

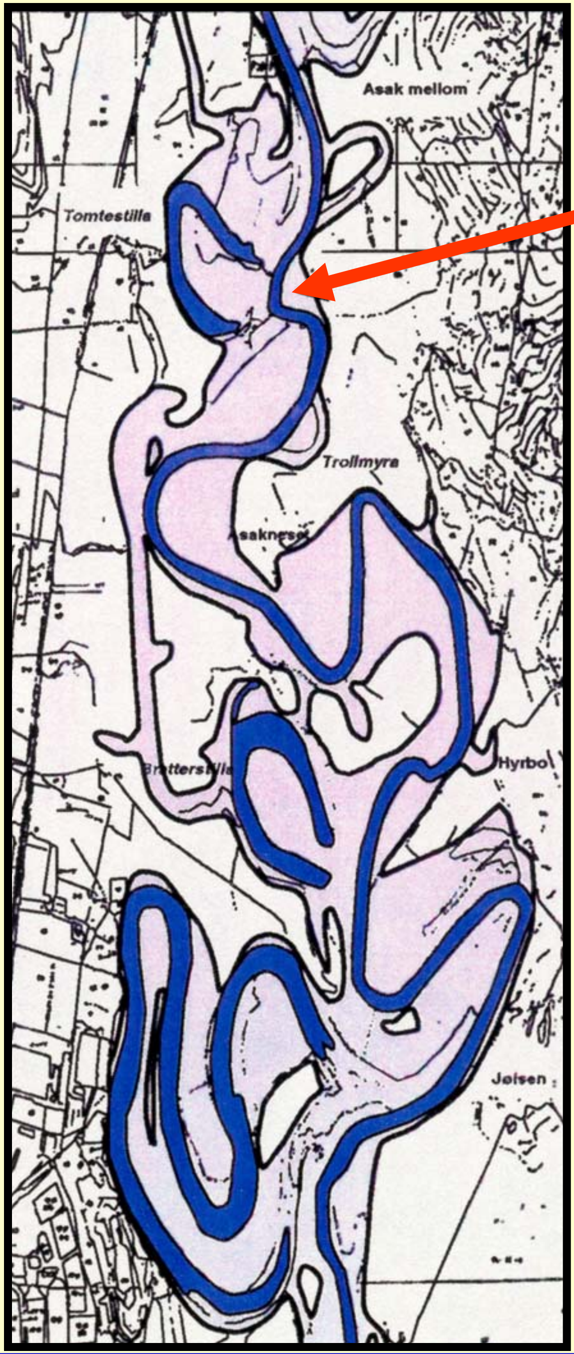


(Salminen, Tarvainen et al., 1998, Fig. 4, p.14)

Block diagram showing drainage basin with old and present day floodplain sediments



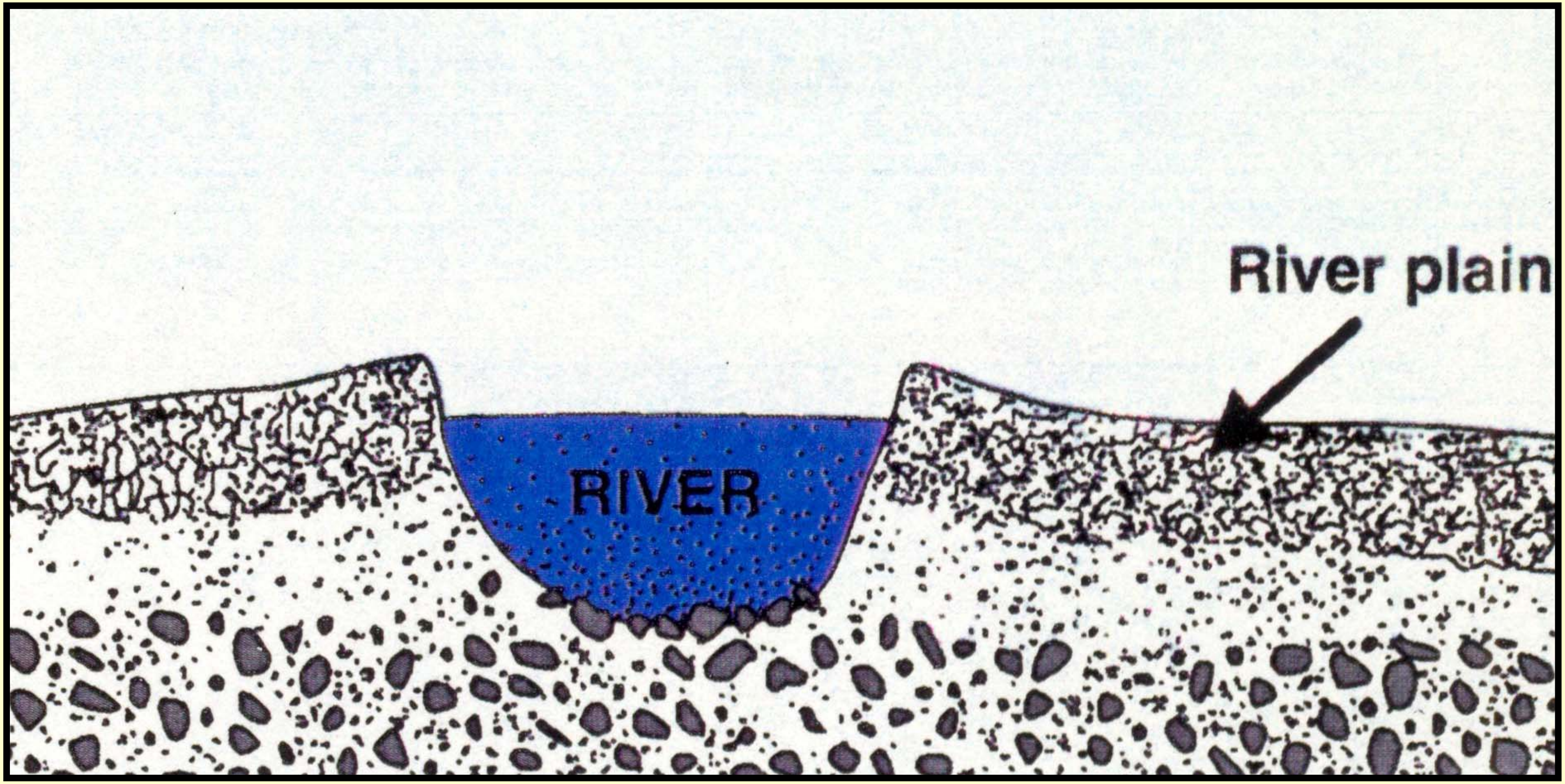
(Salminen, Tarvainen et al., 1998, Fig. 5, p.14)



River plain inundated during flood

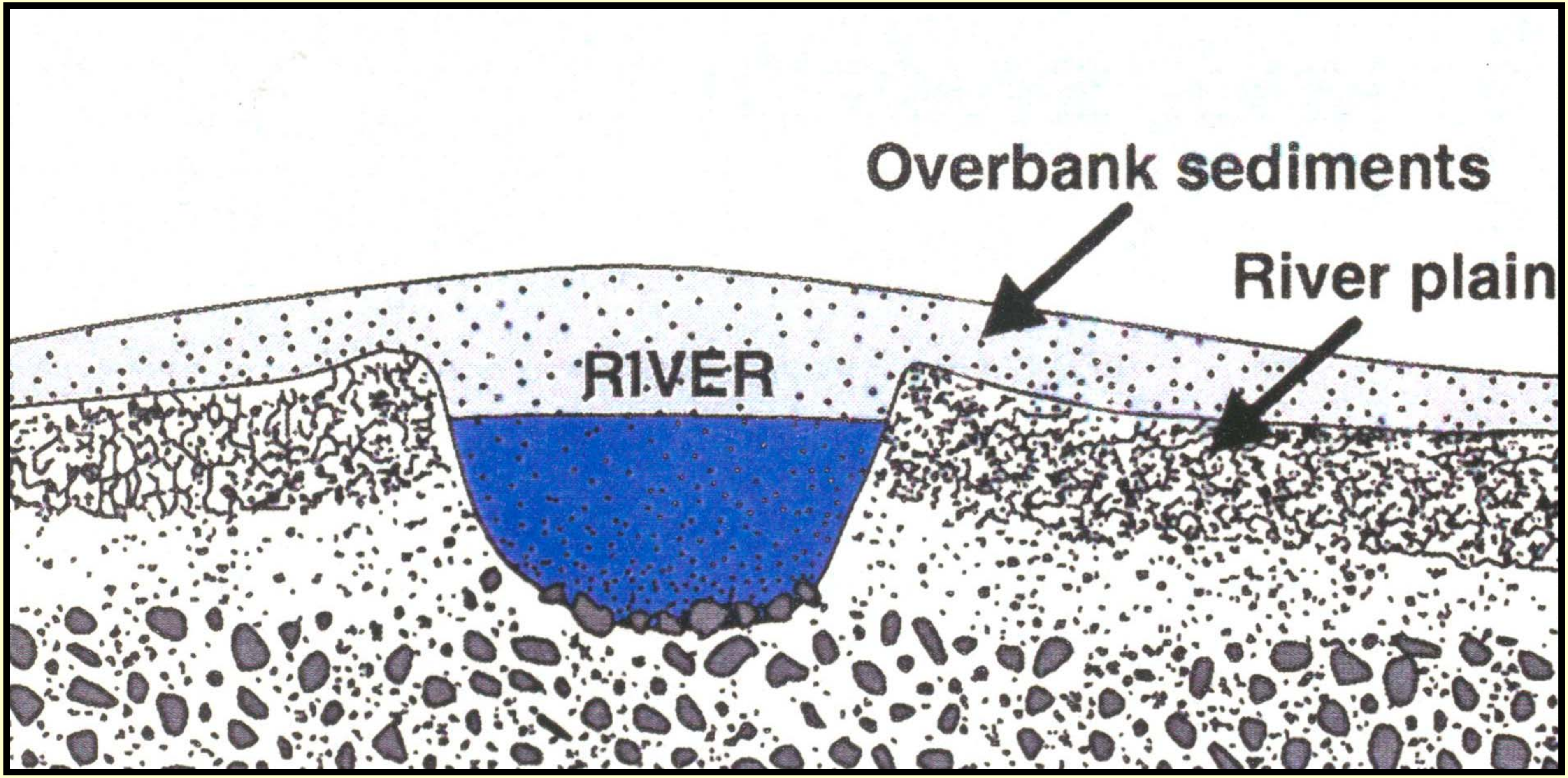
Map showing flooded parts of a river

(Bolviken et al., 1993, Fig. 4.2, Appendix 4, p.4)



Vertical section during Normal water discharge

(Bolviken et al., 1993, Fig. 4.2, Appendix 4, p.4)



Vertical section during flood stage conditions and deposition of overbank or floodplain sediments

(Bolviken et al., 1993, Fig. 4.2, Appendix 4, p.4)

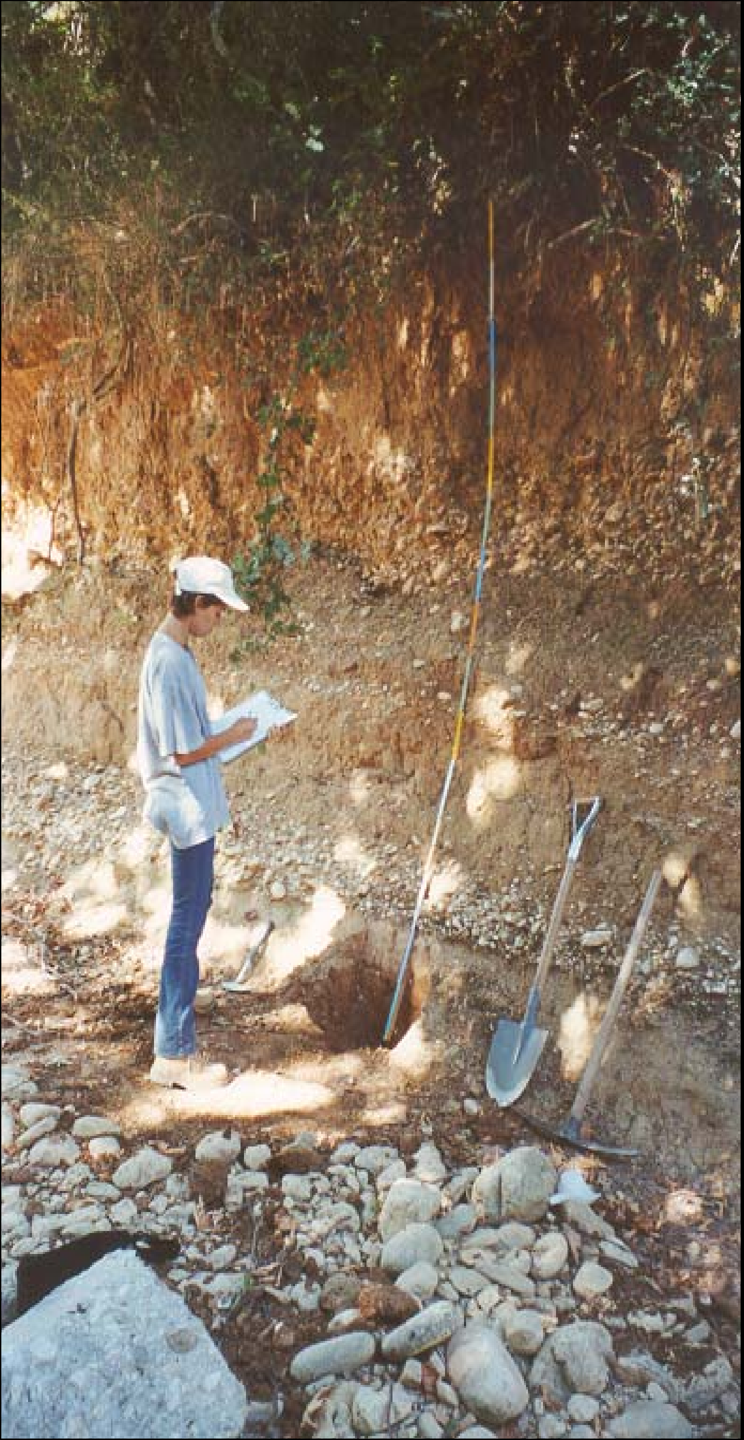
Sediment Sampling

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.**

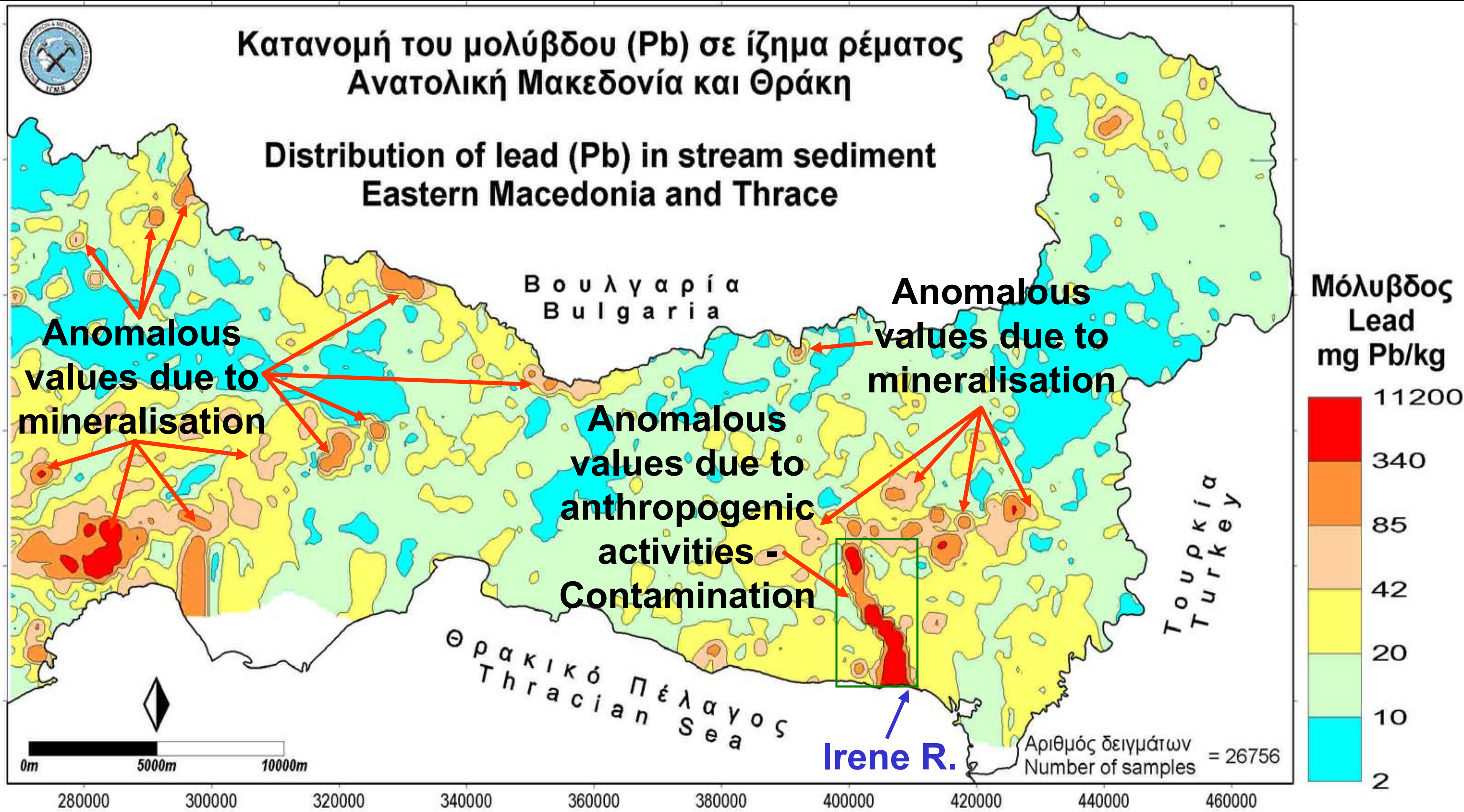
Sampling of floodplain or alluvial sediment from large drainage basins (1000-6000 km^2)

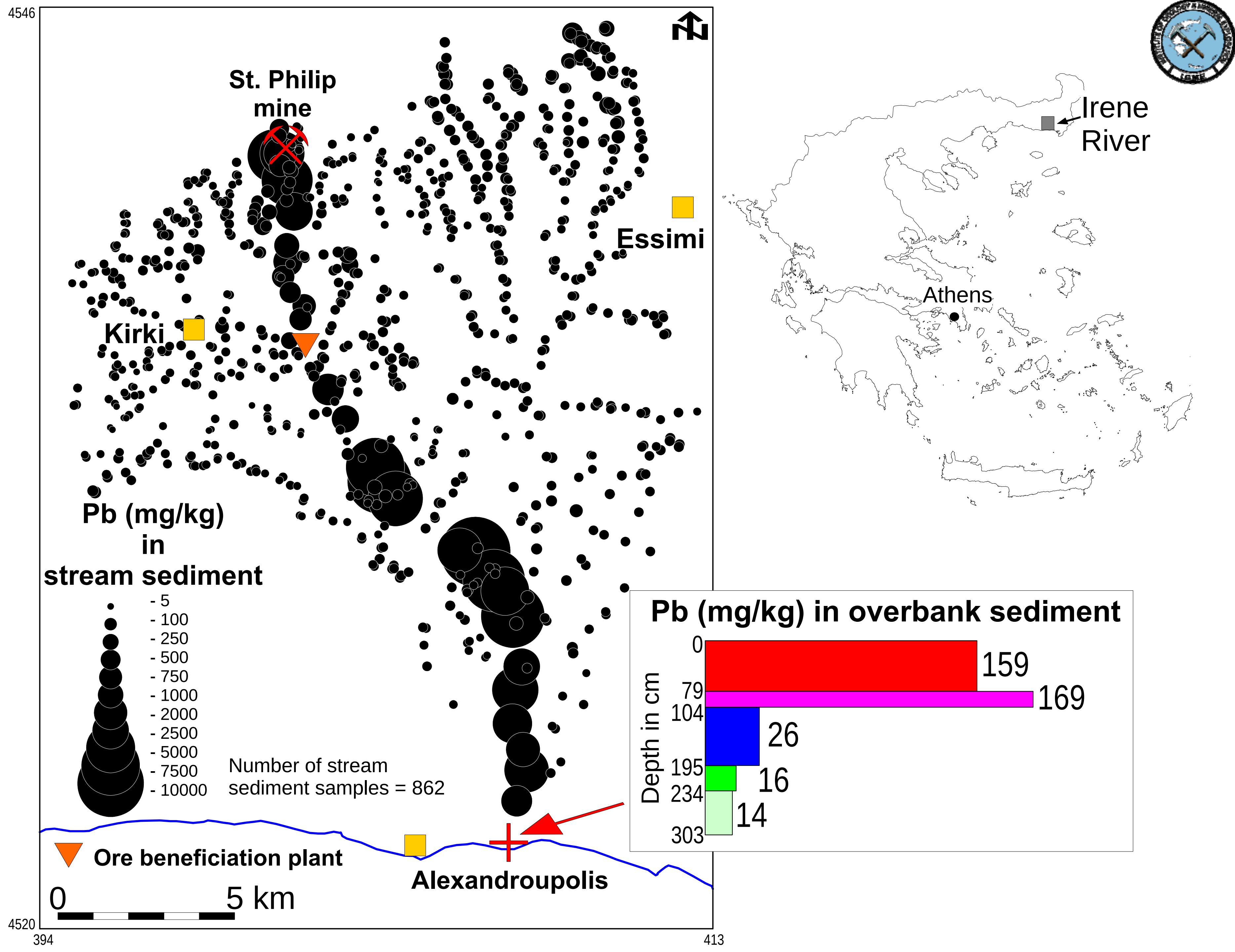


Sampling of overbank or alluvial sediment from small drainage basins ($<100\ km^2$)

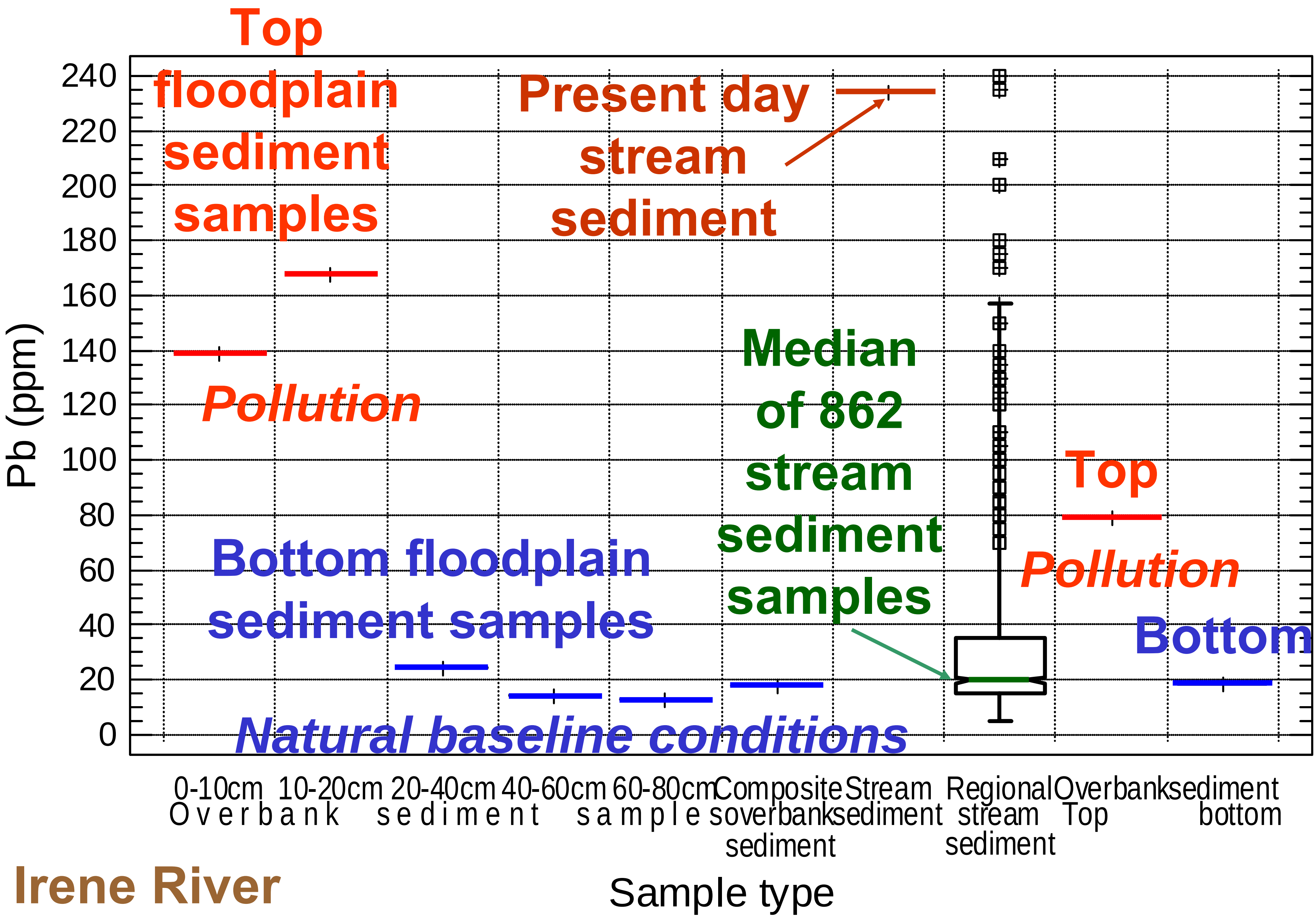
Stream and floodplain sediment surveys

Regional geochemical mapping
Sample density: 2-3 samples/km^2,
Eastern Macedonia and Thrace, Hellas





4546
St. Philip mine
Essimi
Kirki
Pb (mg/kg) in stream sediment
- 5
- 100
- 250
- 500
- 750
- 1000
- 2000
- 2500
- 5000
- 7500
- 10000
Number of stream sediment samples = 862
Ore beneficiation plant
0
5 km
Alexandroupolis
4520
394
413
Irene River
Athens
Pb (mg/kg) in overbank sediment
Depth in cm
0
79
104
195
234
303
159
169
26
16
14

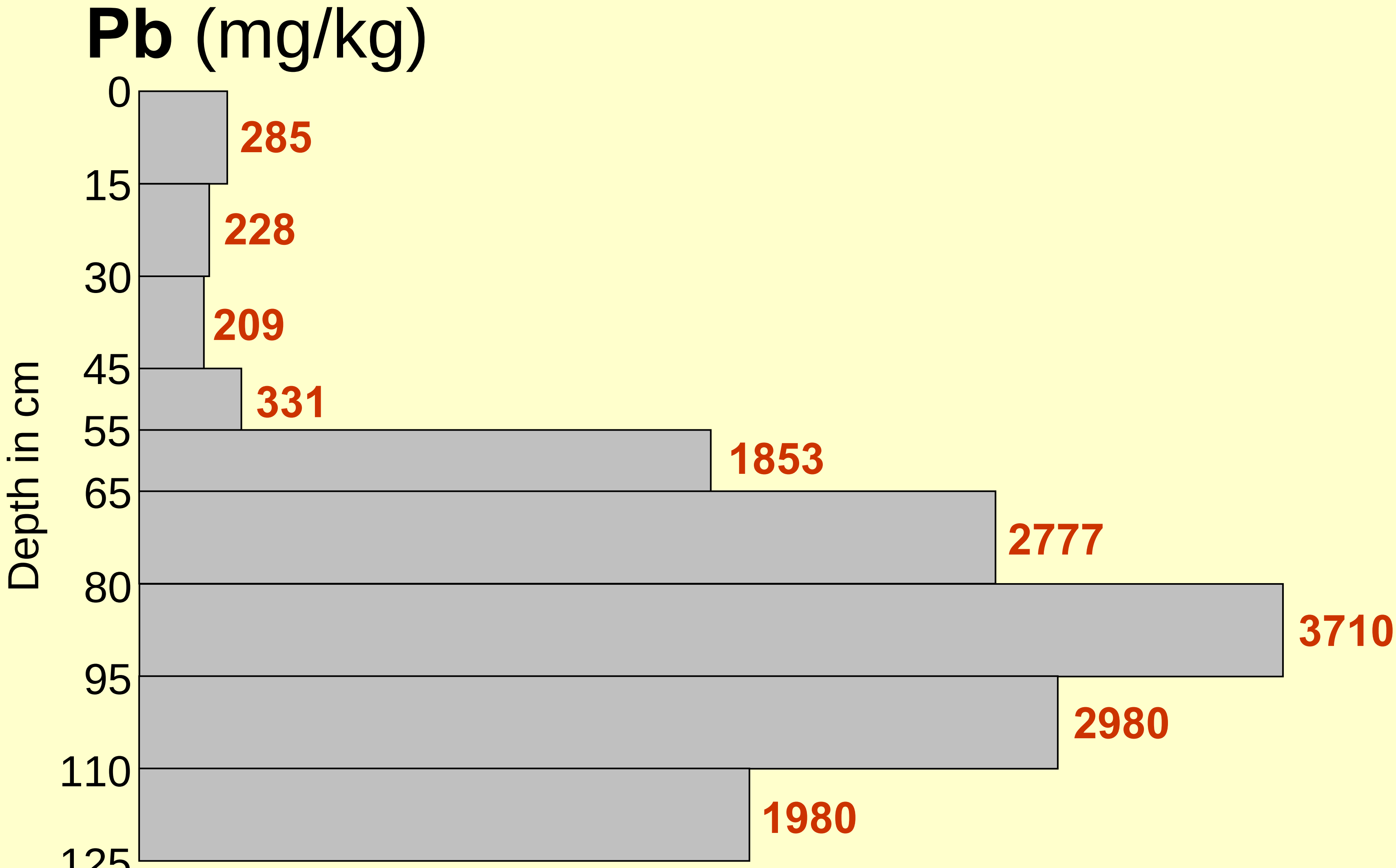


Irene River

Lead (Pb) in stream & floodplain sediment samples

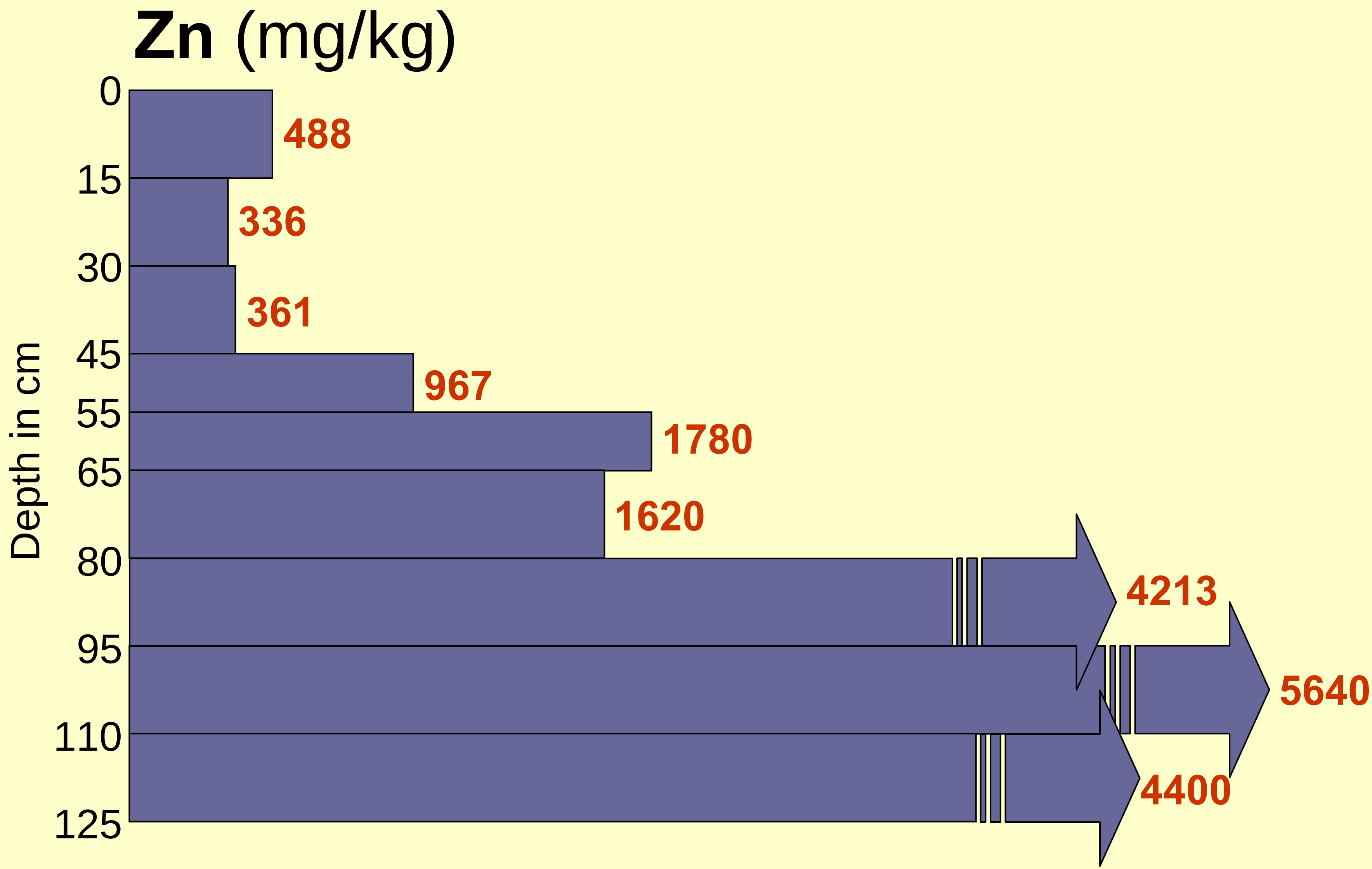
Distribution of Pb in overbank sediment layers, Bieber, Germany

(about 50 km to the east of Frankfurt)



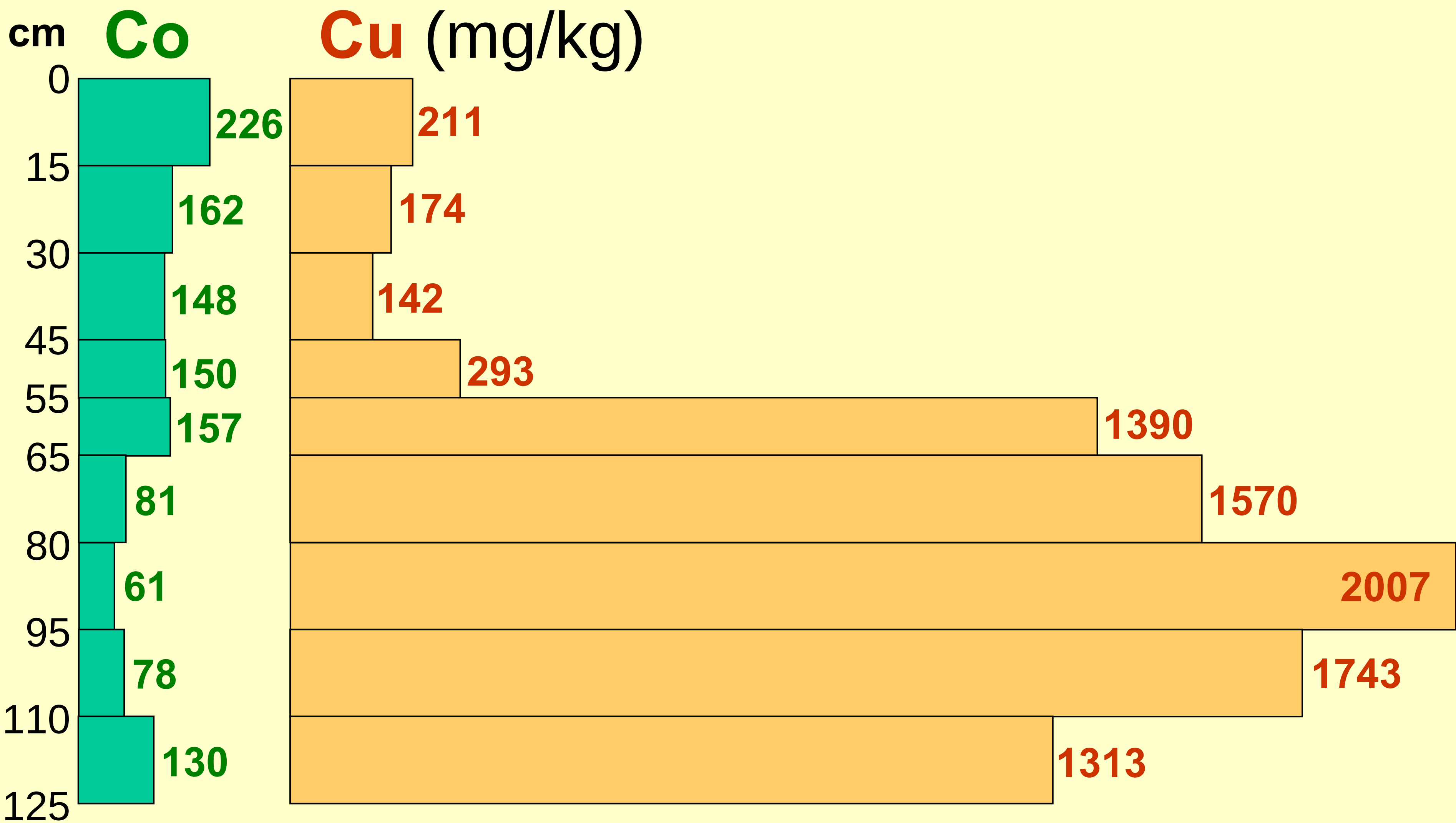
(Bolviken et al., 1996, Fig. 6, p.154)

Distribution of Zn in overbank sediment layers, Bieber, Germany



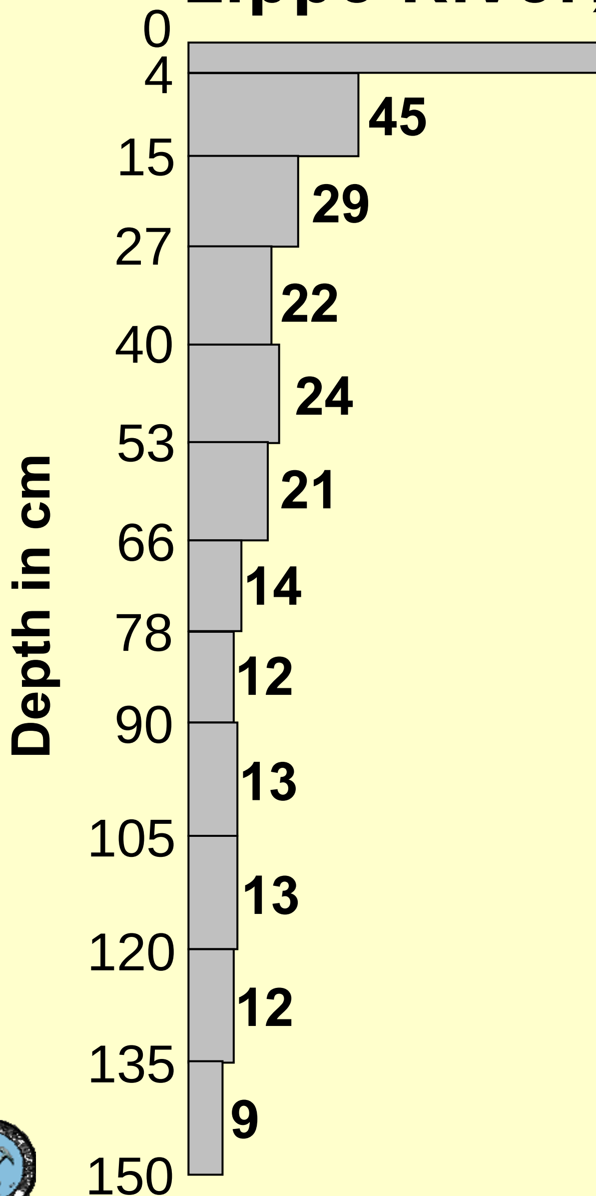
(Bolviken et al., 1996, Fig. 6, p.154)

Distribution of Co and Cu in overbank sediment layers, Bieber, Germany

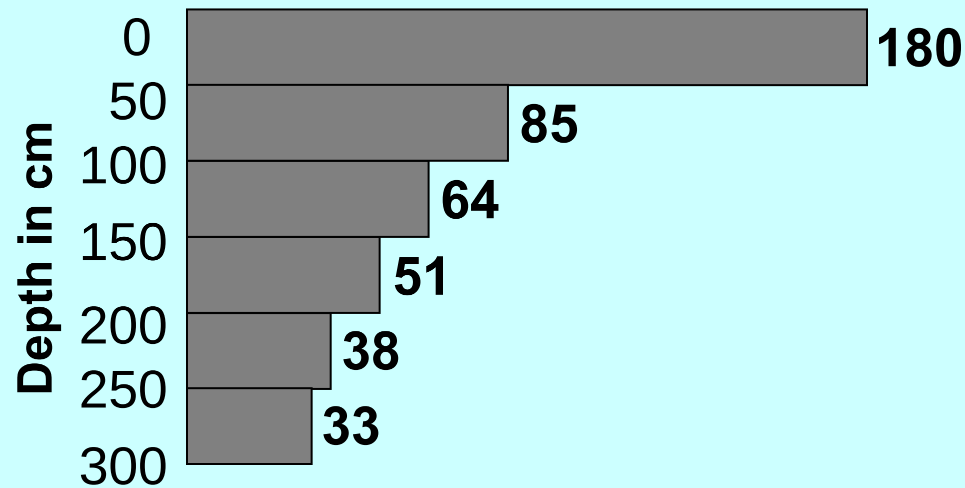


(Bolviken et al., 1996, Fig. 5, p.153)

Distribution of Pb (mg/kg) in overbank sediment layers, Lippe River, Dorsten, Germany

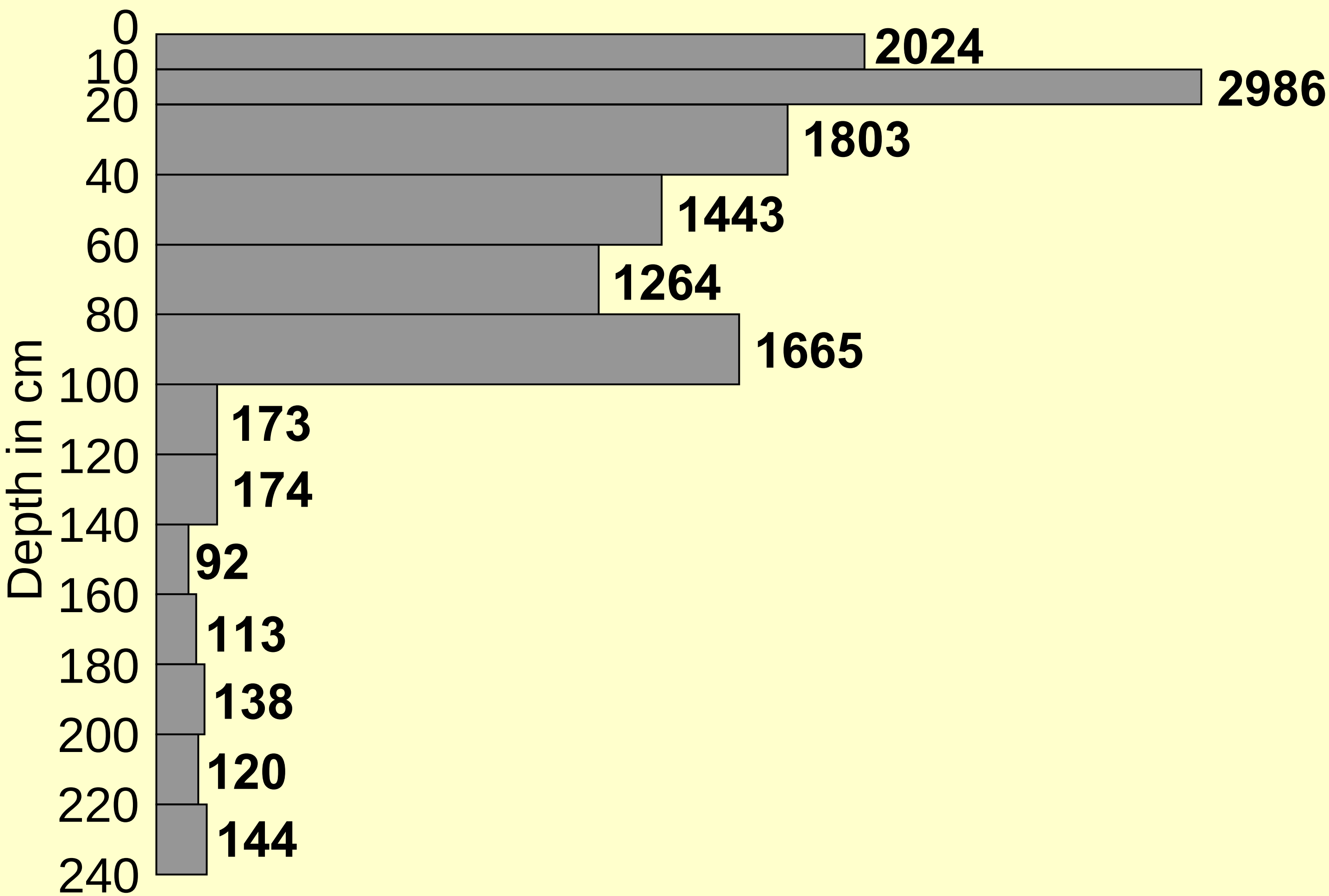


Distribution of Pb (mg/kg) in overbank sediment layers, Enna River, near Hieflau, Austria



(Bolviken et al., 1996, Fig. 5, p.153)

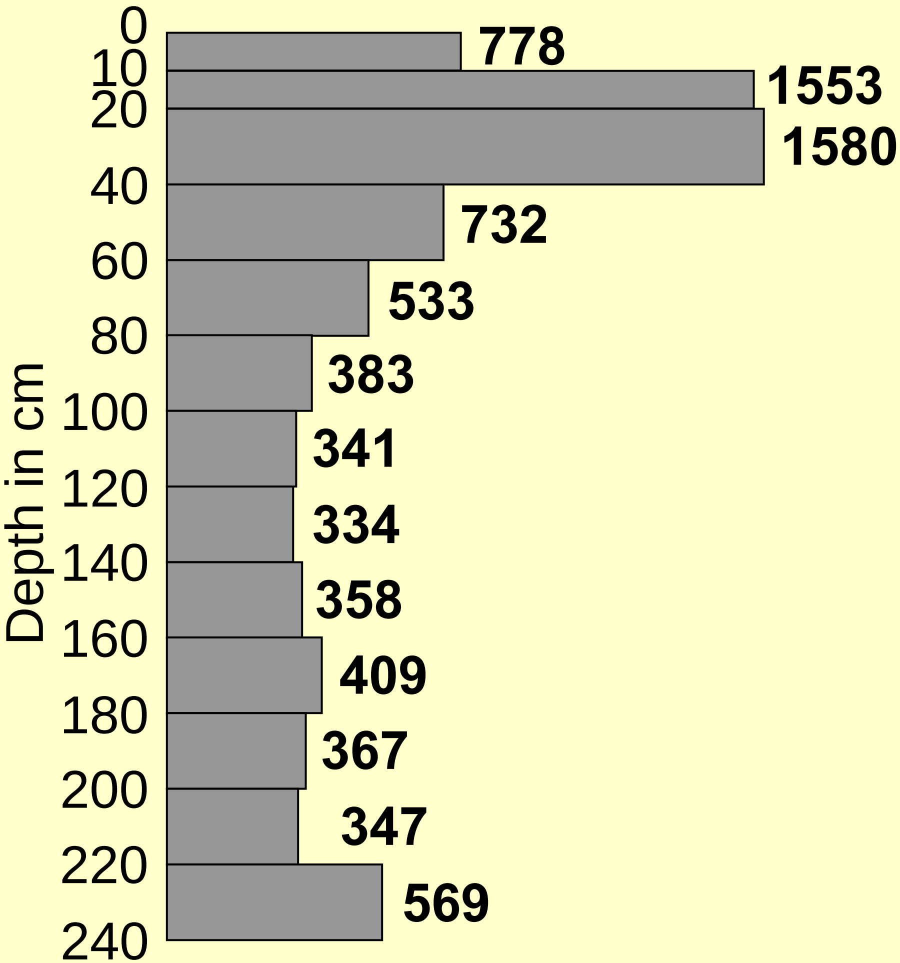
Distribution of Pb (mg/kg) in overbank sediment layers, Glenmalure, Avoca River, Ireland



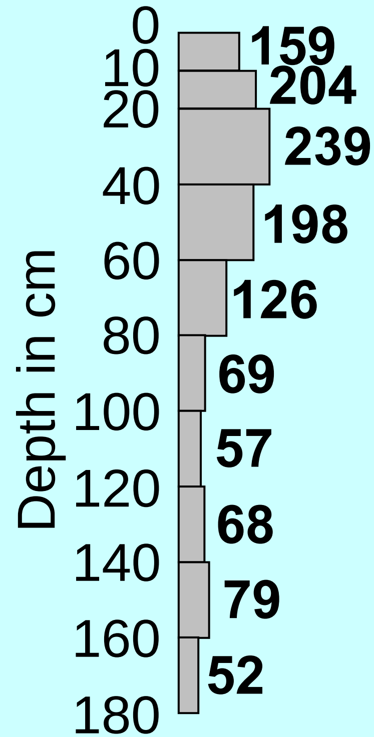
(Bolviken et al., 1996, Fig. 5, p.153)

Distribution of Pb (mg / kg) in overbank sediment layers

Low Prudhoe, Tyne River, United Kingdom

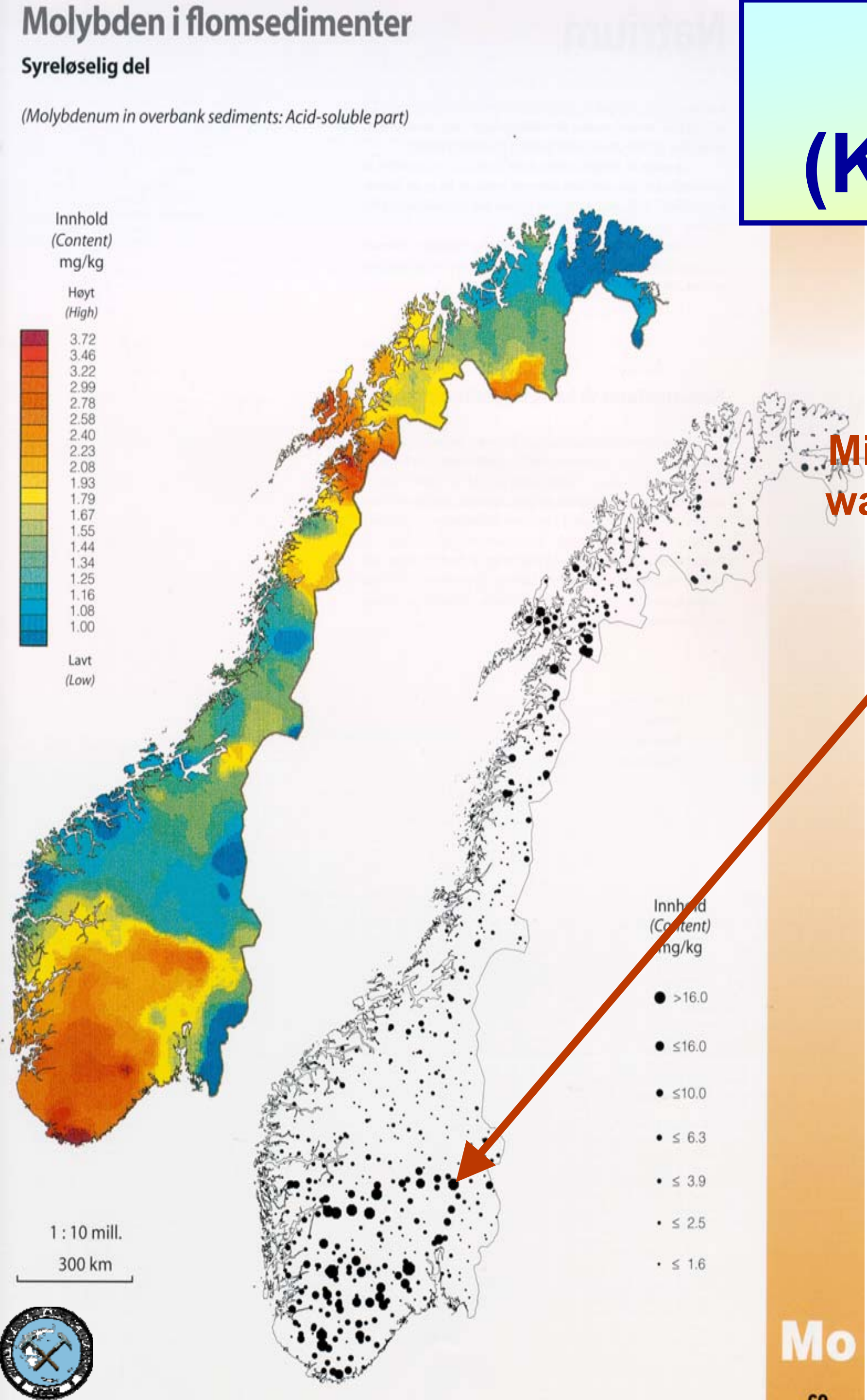


Manzanares River, Spain

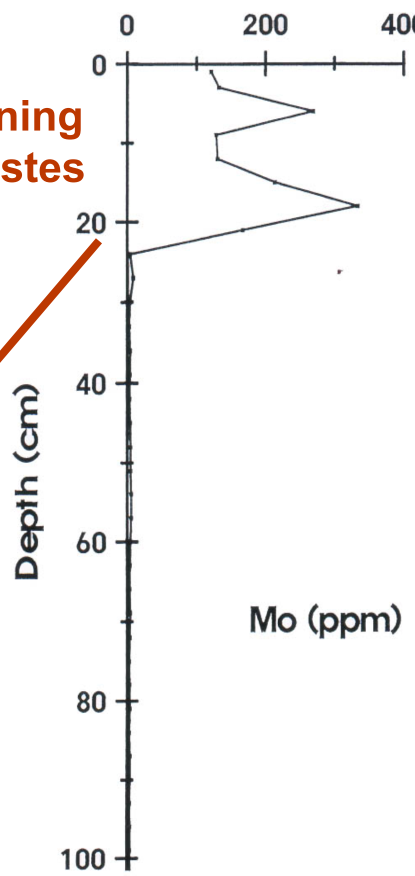


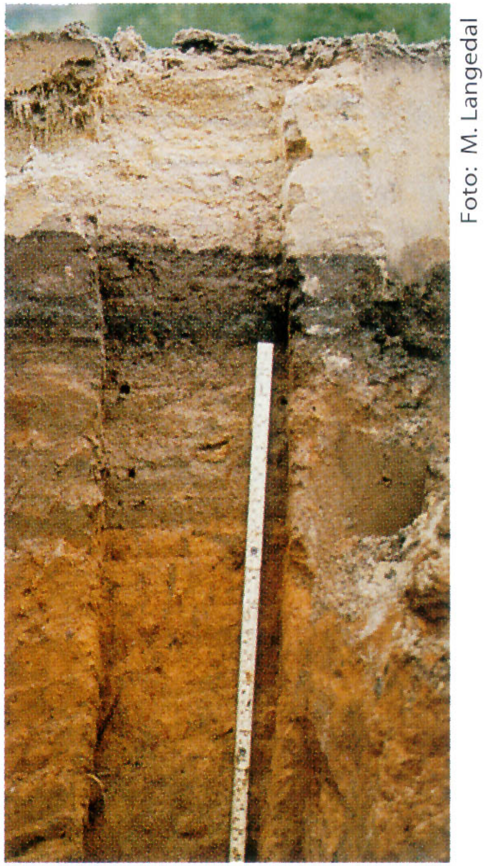
(Bolviken et al., 1996, Fig. 5, p.153)

Distribution of Mo (Knabeani River, Norway)



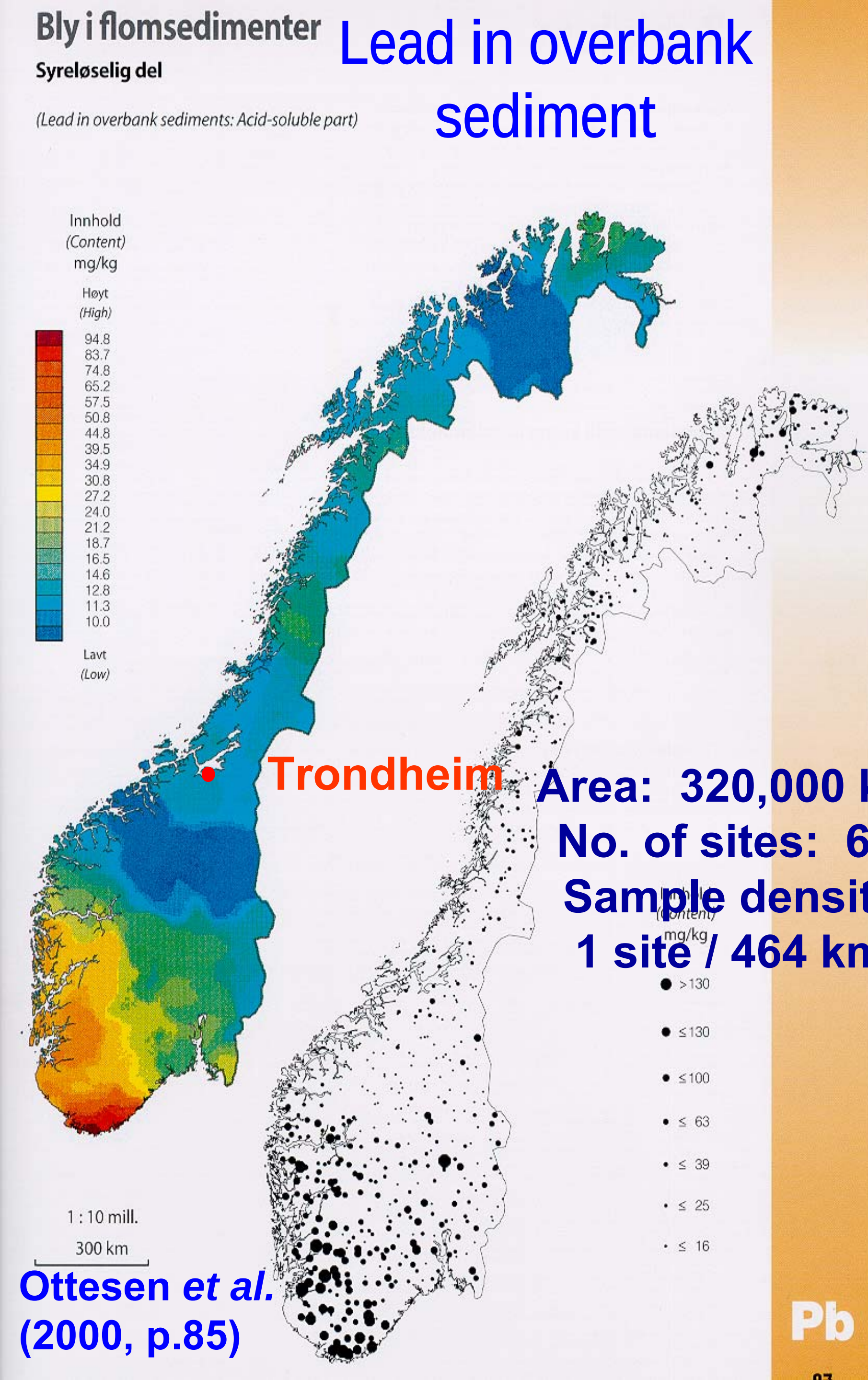
Mining wastes





(From Ottesen et al., 2000, Fig. 2, p.9)

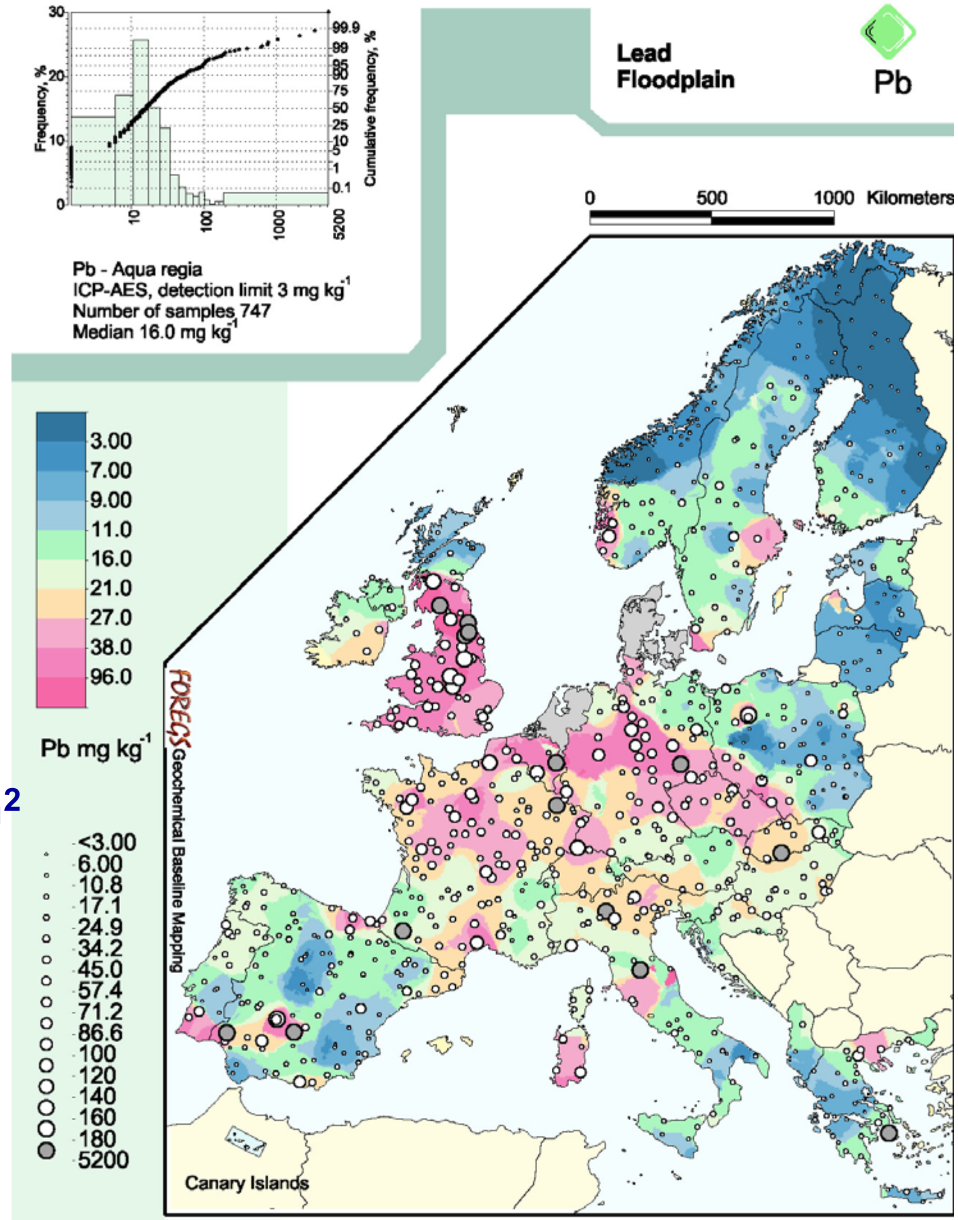
Lead in overbank sediment



Trondheim

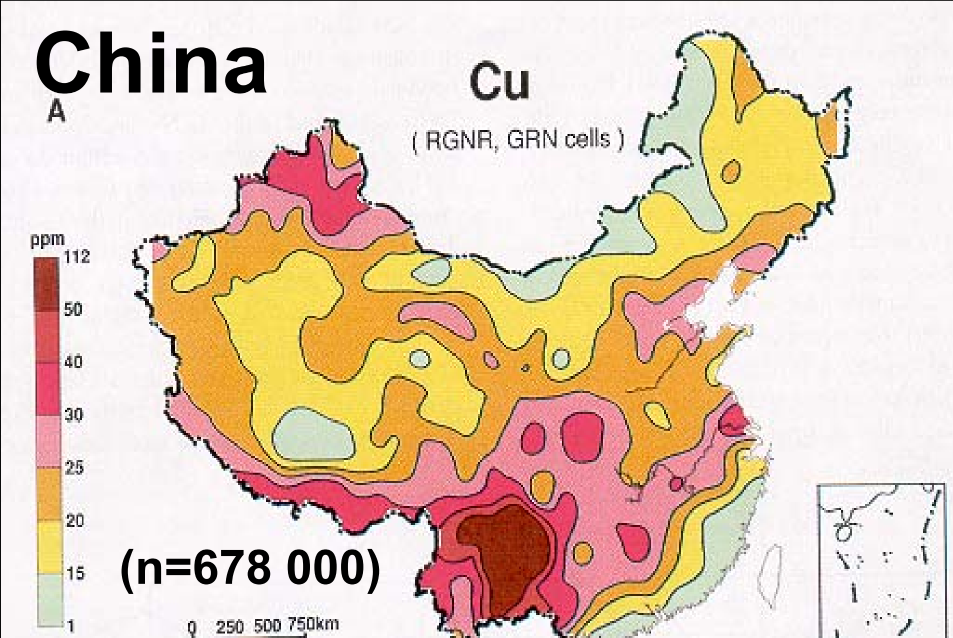
Area: 320,000 km^2
No. of sites: 690
Sample density: 1 site / 464 km^2

Ottesen *et al.* (2000, p.85)



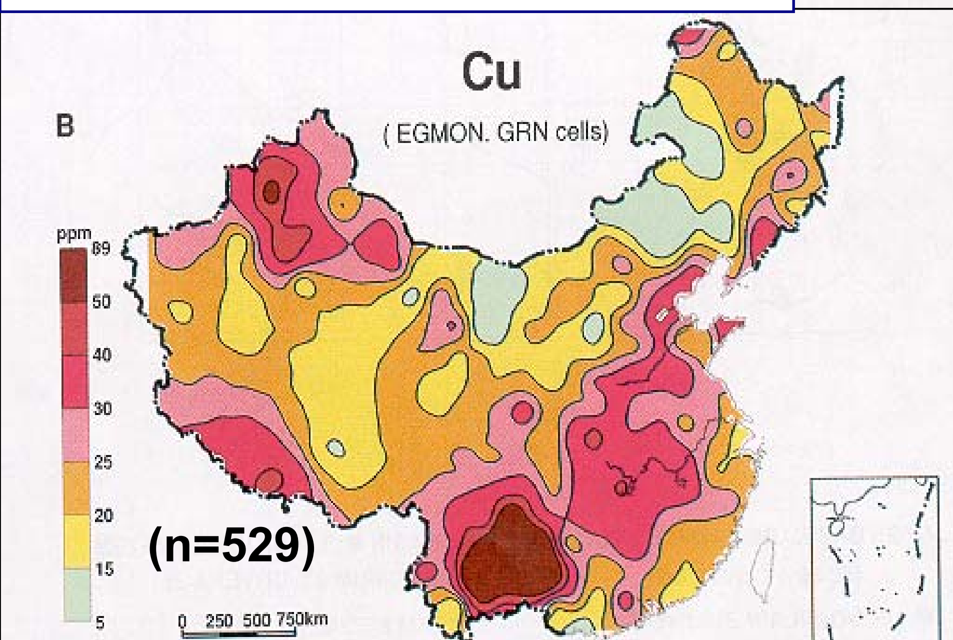
Sample density: 1 site / 4,600 km^2

China



(n=678 000)

Average density: 1 site/14 km^2



(n=529)

Average density: 1 site/18,100 km^2

Maps of moving mean values:

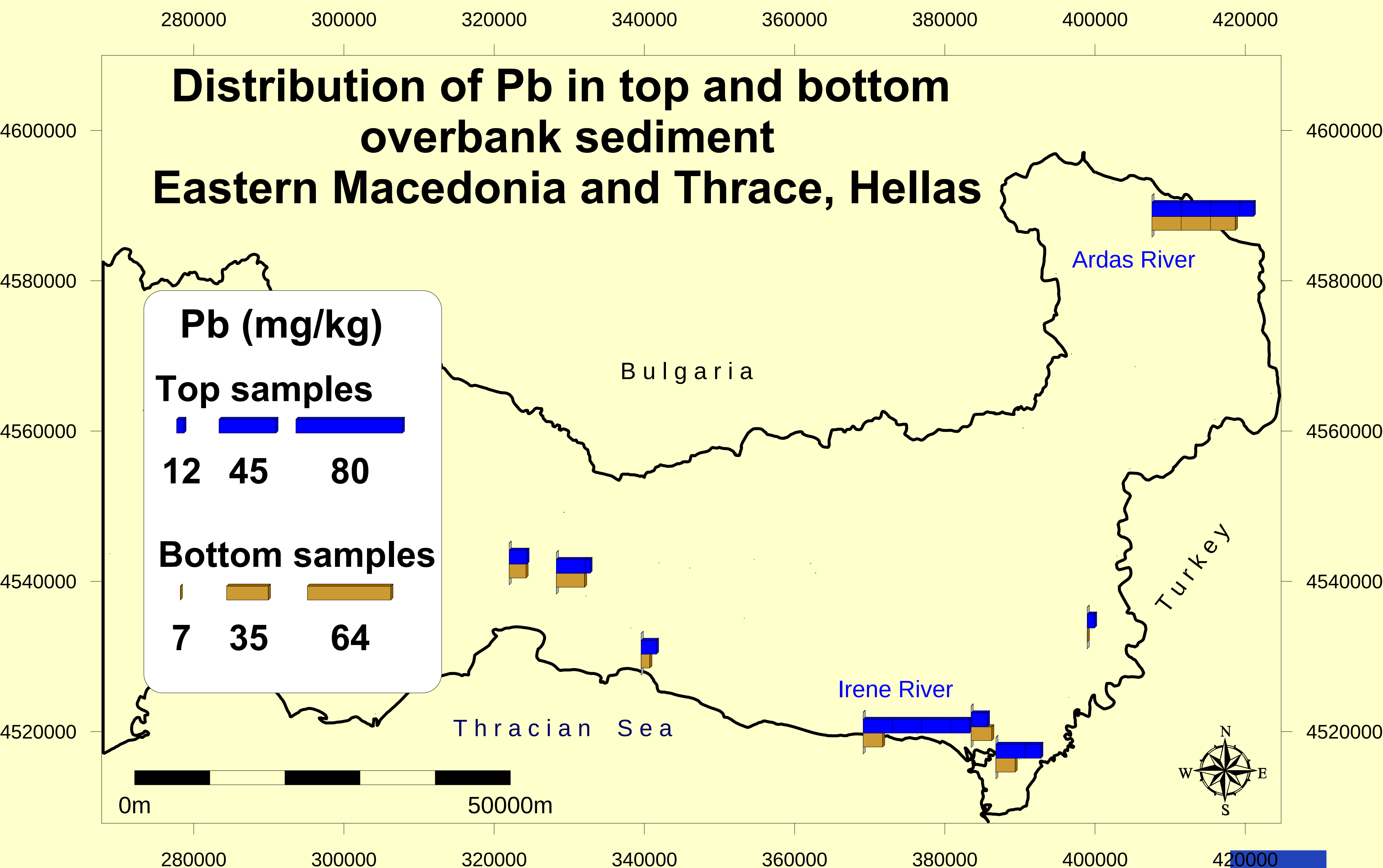
(A) Mean value of about 6400 stream sediment samples in each GRN cell

&

(B) Mean value of 5 floodplain sediment samples in each GRN cell

(From Xuejing *et al*. 2001, Fig. 3, p.1312)

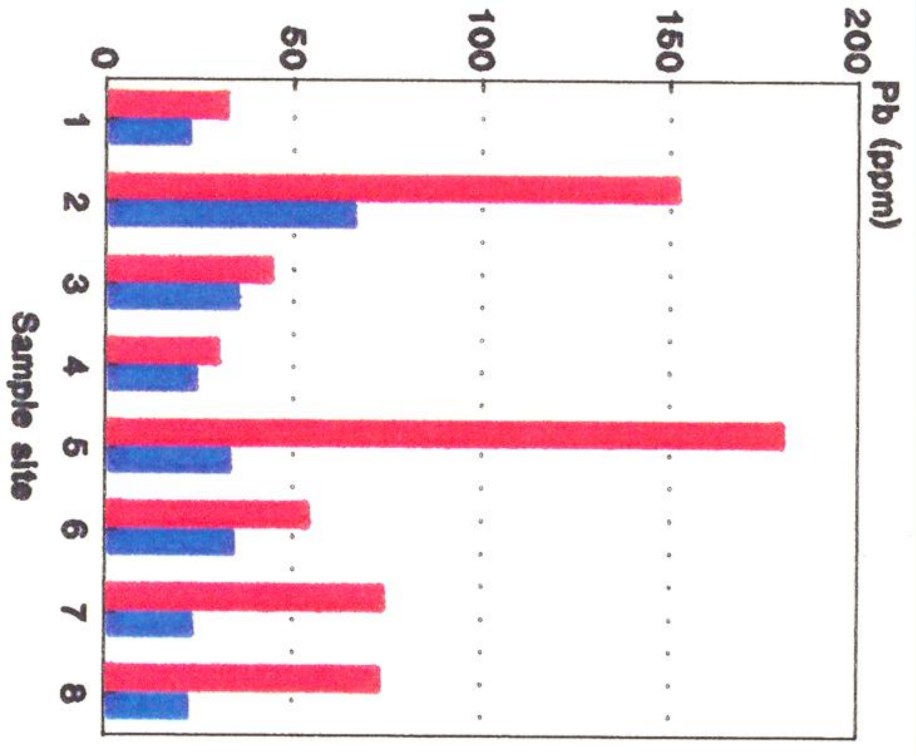
中国地质调查局
CHINA.GEOLOGICAL.SURVEY



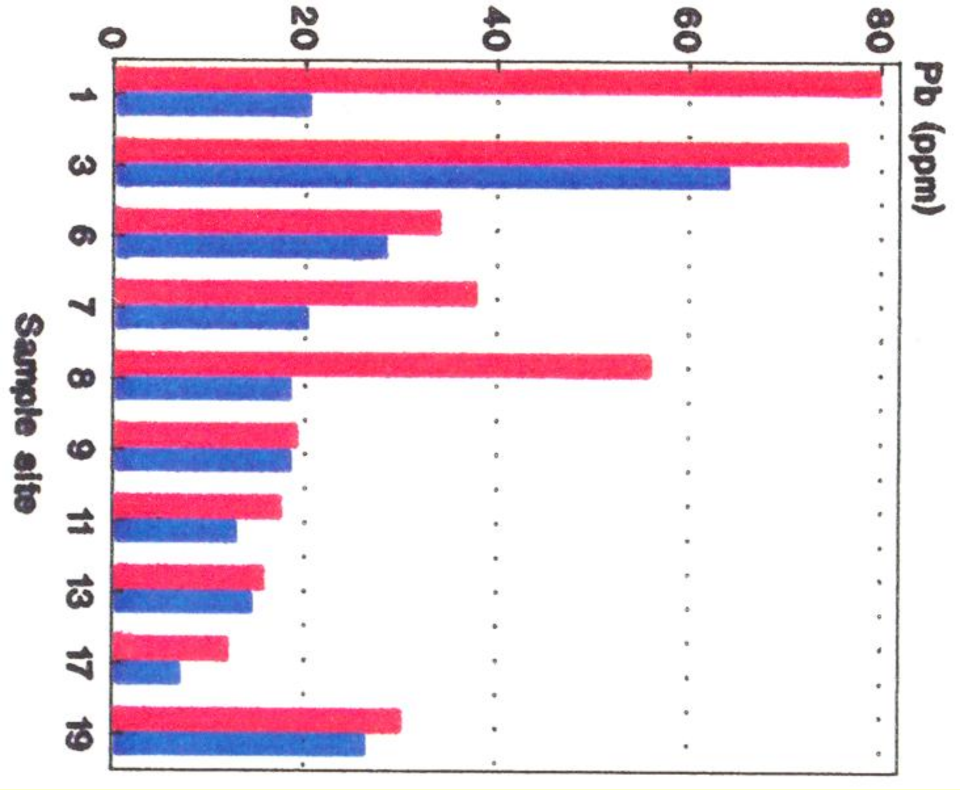
Distribution of Pb in top and bottom overbank sediment
Eastern Macedonia and Thrace, Hellas
Pb (mg/kg)
Top samples
12 45 80
Bottom samples
7 35 64
Bulgaria
Turkey
Thracian Sea
Ardas River
Irene River
0m
50000m
N
S
E
W
280000
300000
320000
340000
360000
380000
400000
420000
4600000
4580000
4560000
4540000
4520000

Pb contents in samples of post- and pre-industrial overbank sediments …..

Austria



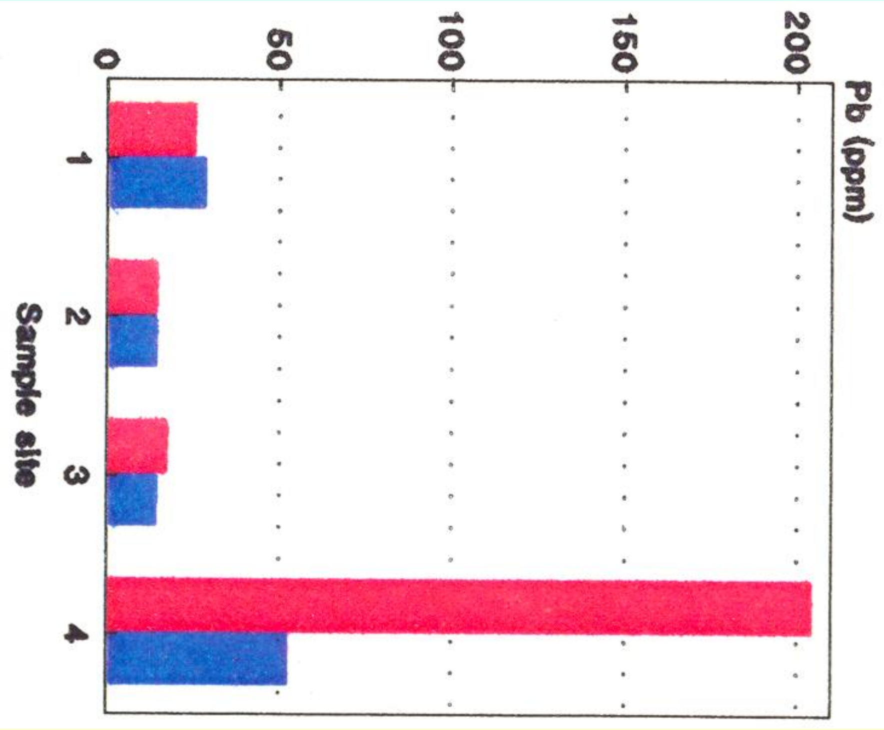
Greece



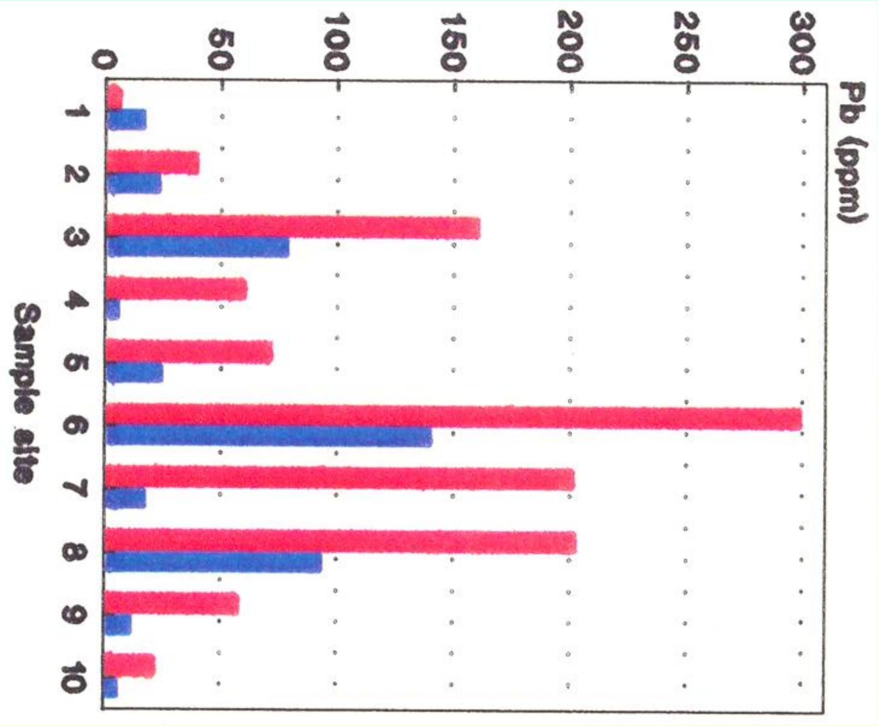
(From Bolviken et al., 1996, Fig. 7, p.155)

….. Pb contents in samples of post- and pre-industrial overbank sediments

Spain



Netherlands



(From Bolviken et al., 1996, Fig. 7, p.155)

CHINA.GEOLOGICAL.SURVEY

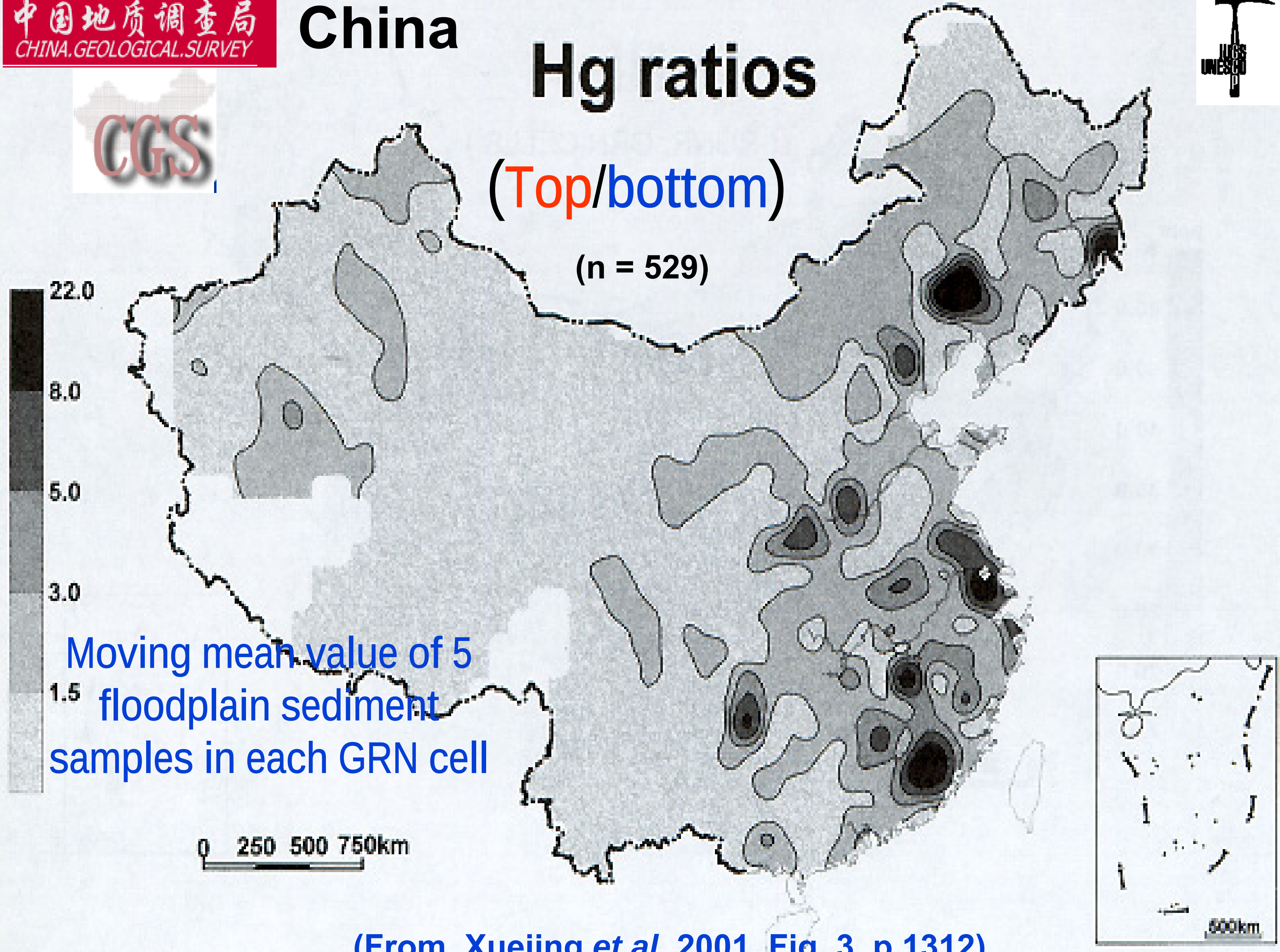
CGS

China

Hg ratios

(Top/bottom)

(n = 529)



Moving mean value of 5 floodplain sediment samples in each GRN cell

(From Xuejing *et al*. 2001, Fig. 3, p.1312)

Assessment of drainage basin contamination by stream and floodplain sediments

- **Stream sediment is susceptible to anthropogenic contamination and, therefore, maps the present day situation of the upstream drainage basin.**
- **Sampling of pre- and post-industrial overbank or floodplain sediments is the only method that can assess drainage basin contamination:**
  - **Surface samples, map the current situation, and**
  - **Bottom samples, the past or pristine conditions, if a deep enough sample is taken.** ***Deep overbank sediment samples are able to map the natural geochemical patterns, even in strongly contaminated areas.***

Quality control procedures

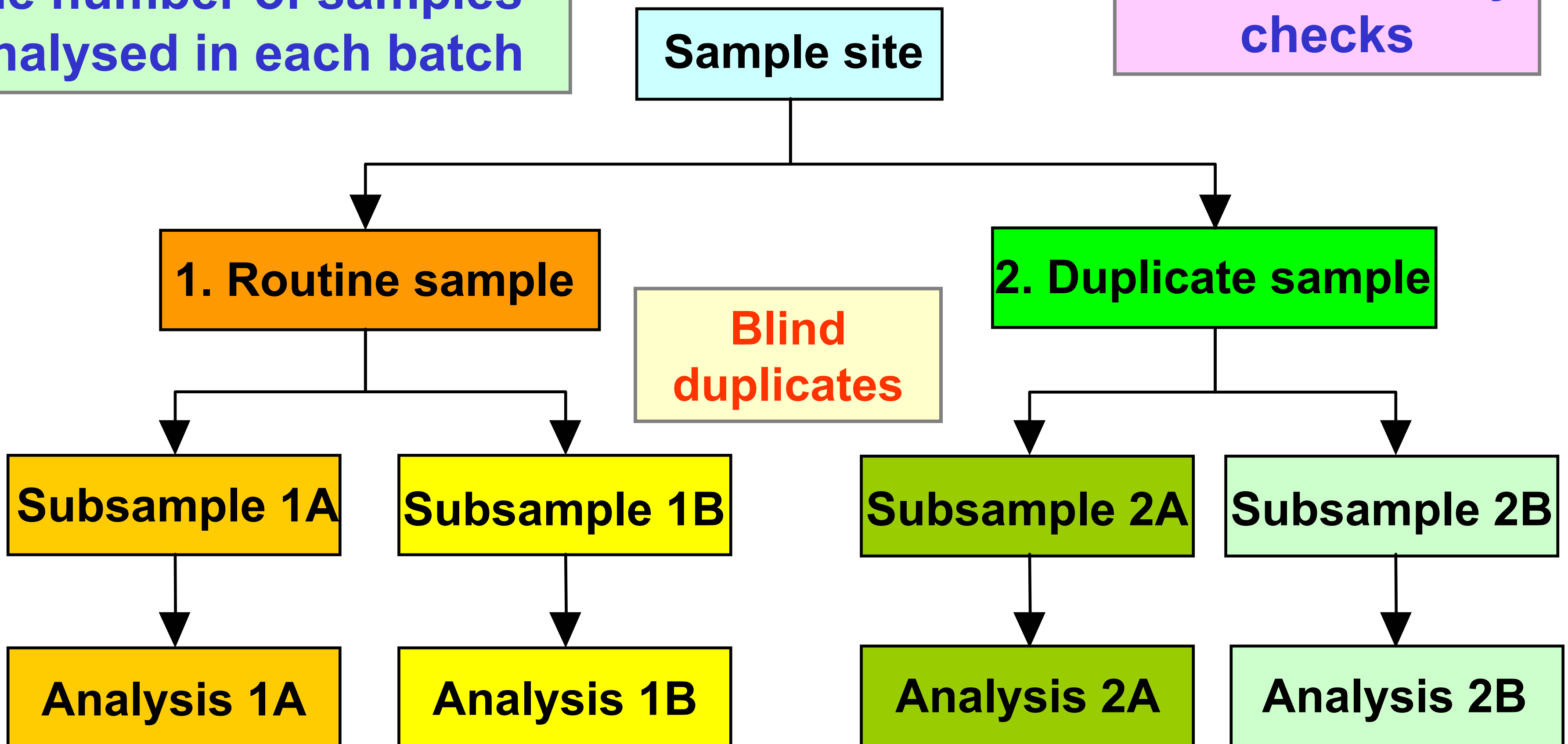
QUALITY CONTROL SCHEME

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

Duplicate field samples

Randomisation of samples

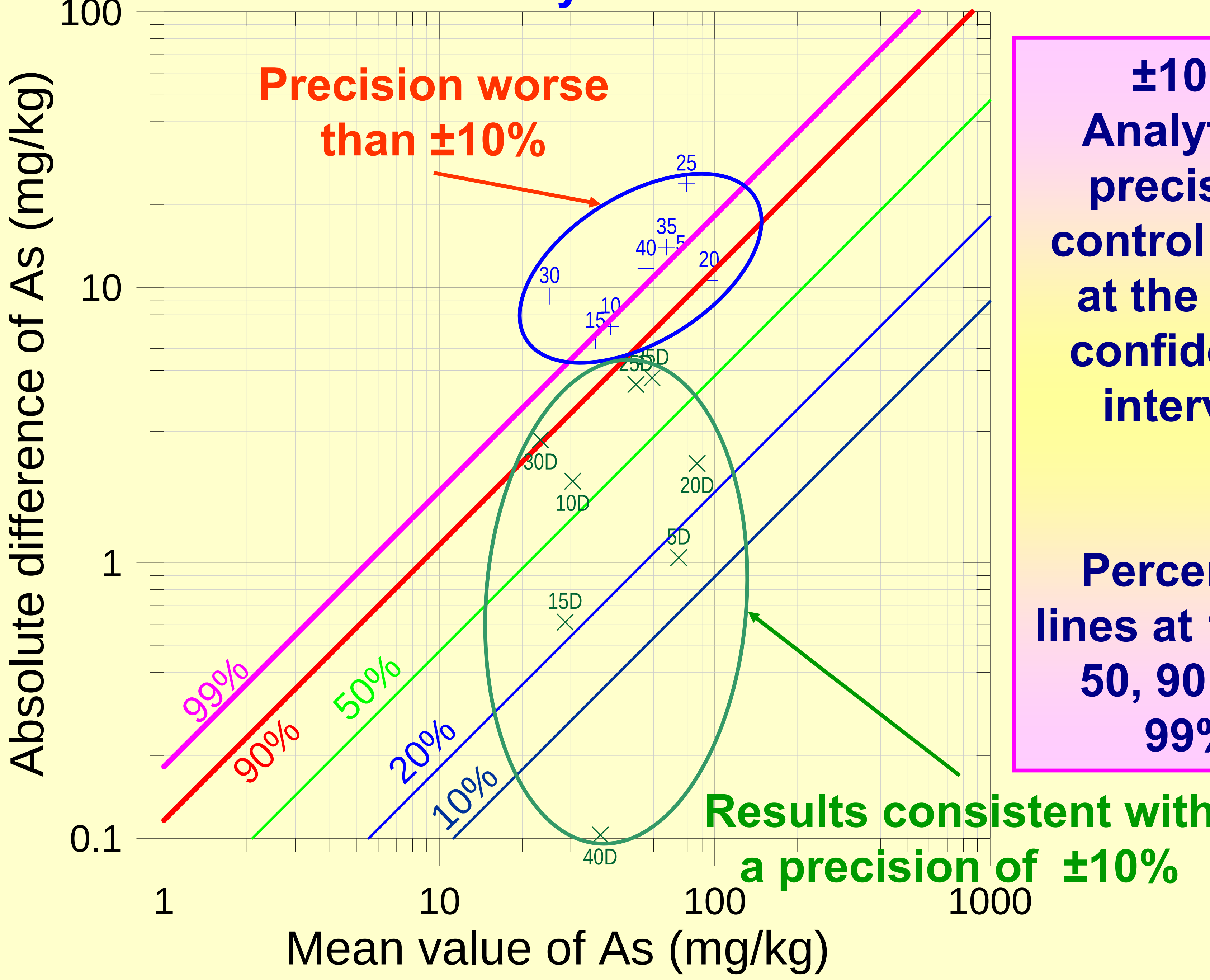
Inter-laboratory checks



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



±10% Analytical precision control chart at the 95% confidence interval.

Percentile lines at 10, 20, 50, 90 and 99%

Quantification of sources of variation …..

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

- **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.*,

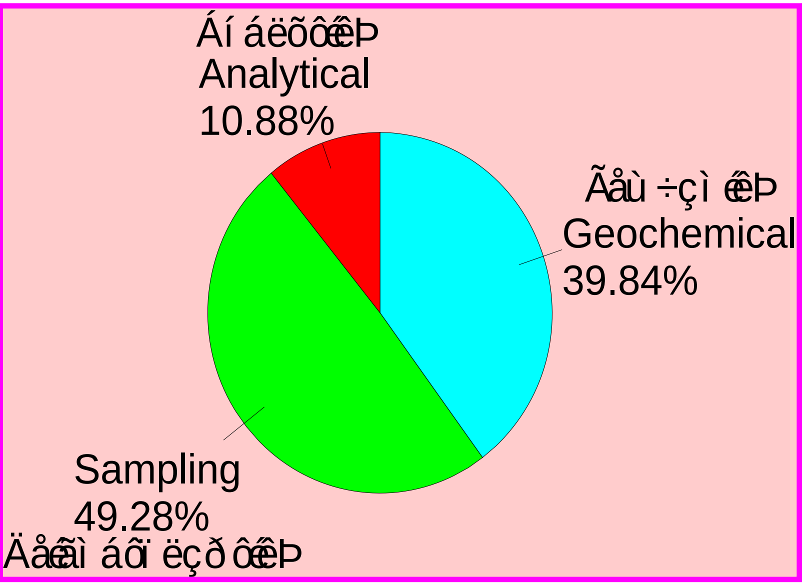
- ***Maximum Analytical variance*** **should not exceed 4% of the Total variance, and**
- ***Maximum Sampling variance*** **should not exceed 16% of the Total Variance.**

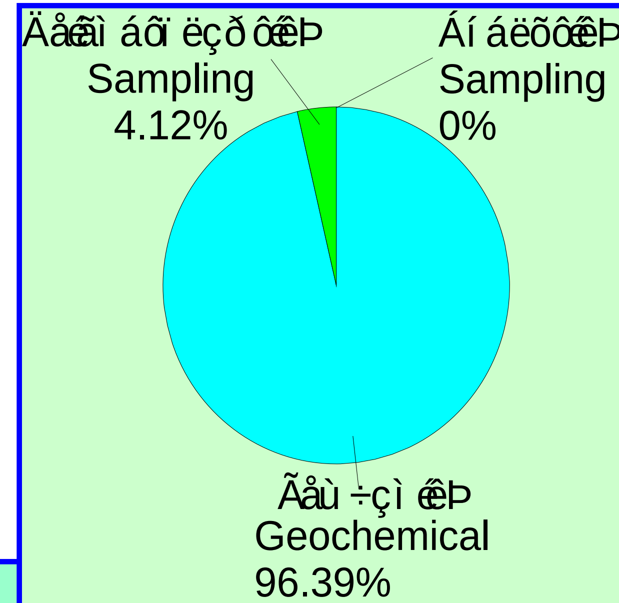
Therefore, the minimum *Spatial or Geochemical variance should be 80% of the Total Variance*.

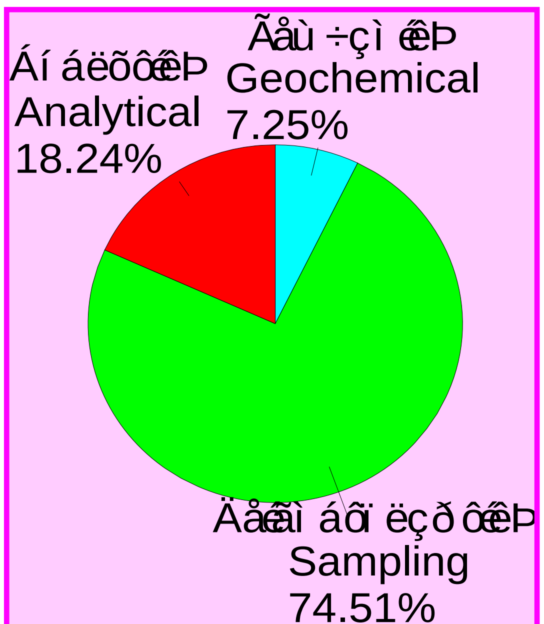
Unacceptable results

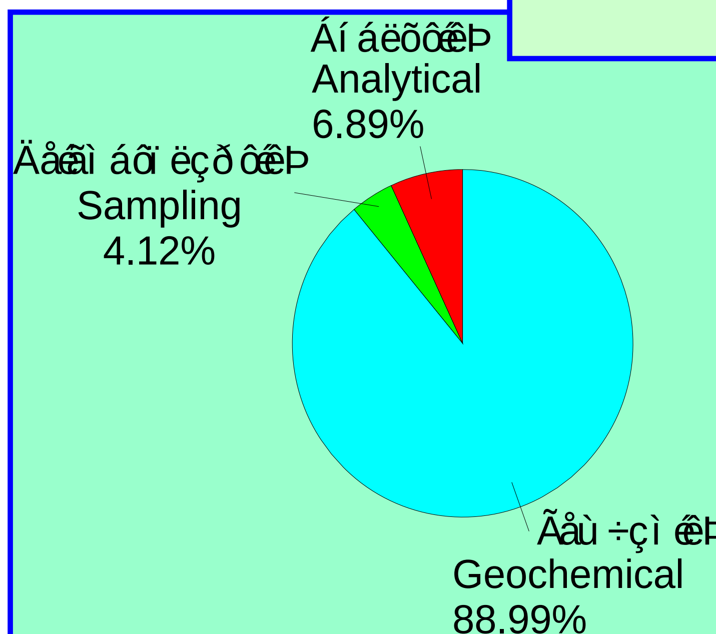
… Quantification of sources of variation …

Acceptable results









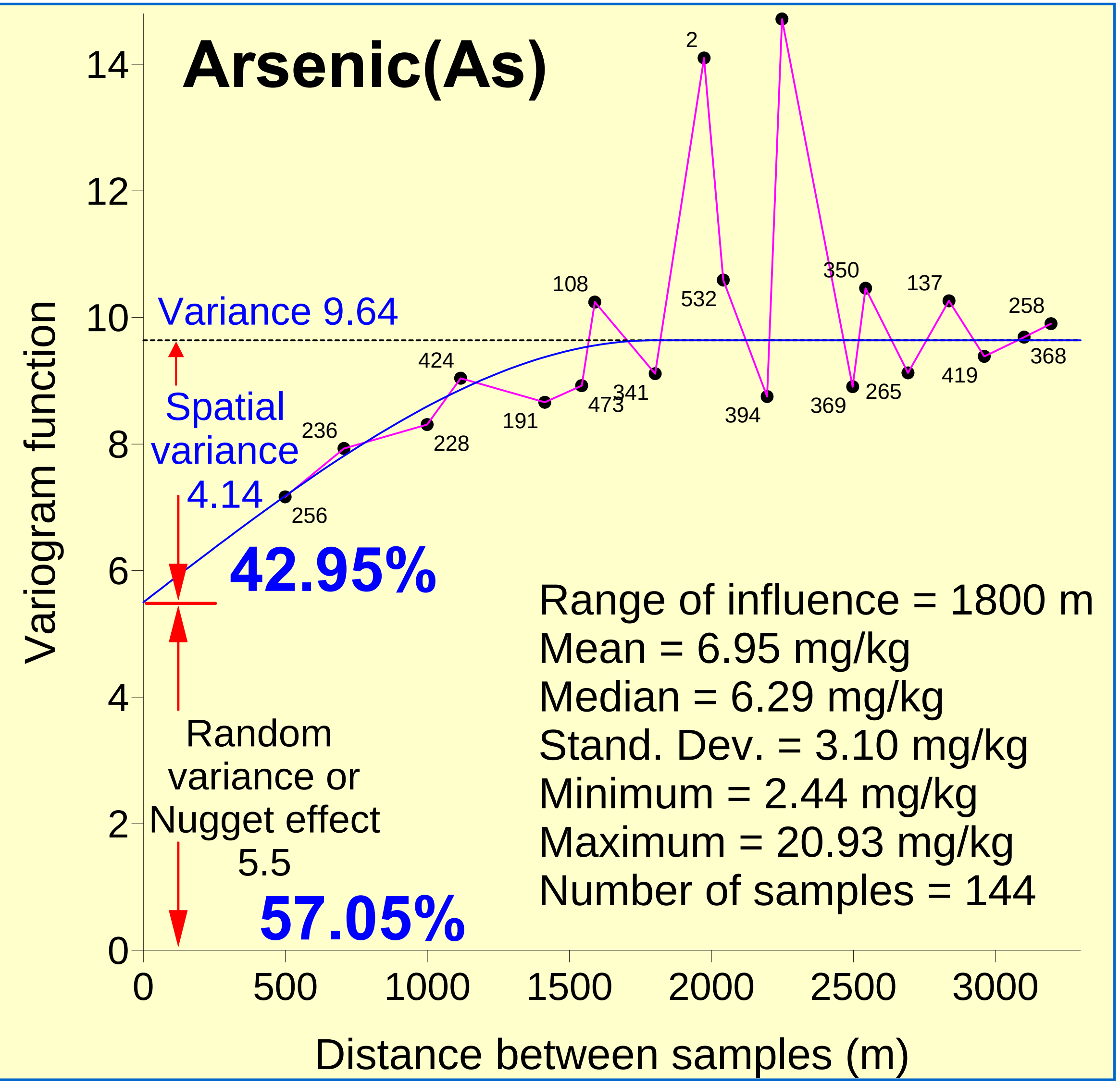
FOREGS

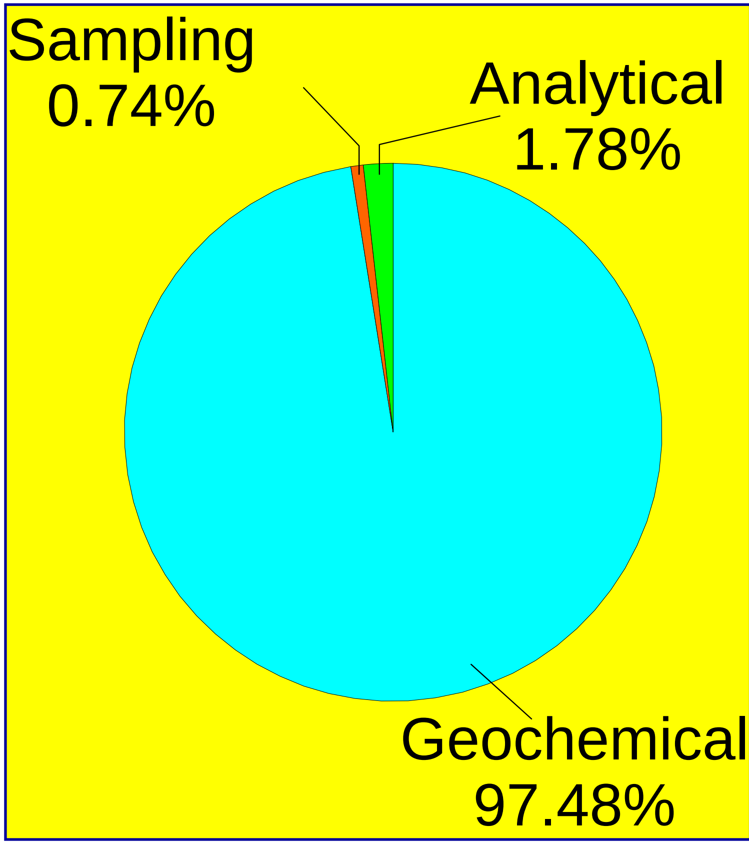
EuroGeoSurveys

Geostatistics

…Quantification of sources of variation

Analysis of Variance





FOREGS Forum of the European Geological Surveys Directors

IUGS

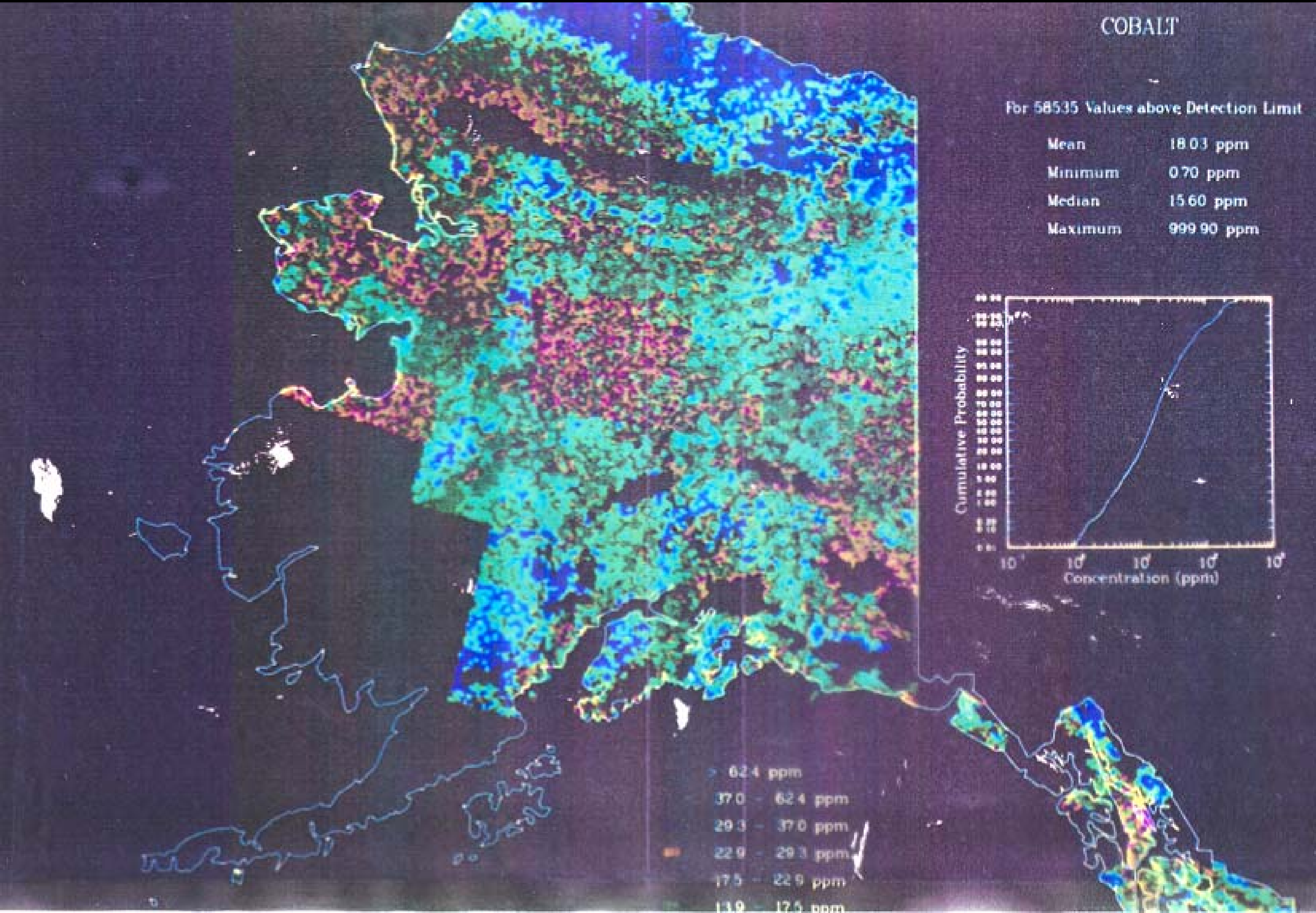
International Association of Geochemistry

Environmental Geochemistry for Global Survival IUGS/IAGC project "Global Geochemical Baselines"

planetearth Earth Sciences for Society

EuroGeoSurveys

Geochemical Survey of Alaska – Cobalt (Co)



Geochemical Survey of Alaska – Cobalt (Co)

Geochemical baseline concentrations of elements in sediments

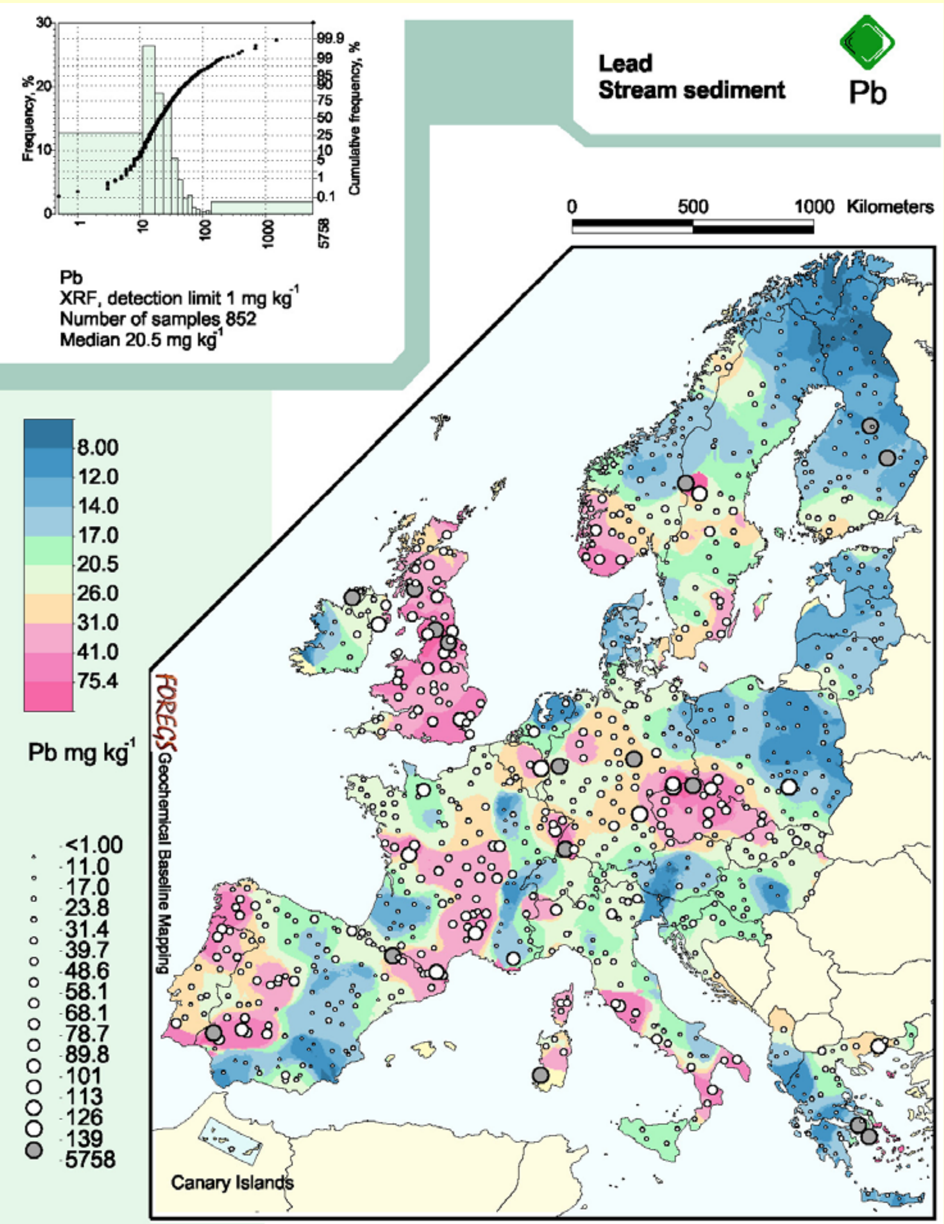
26 countries participated in the Geochemical Baseline Mapping of Europe

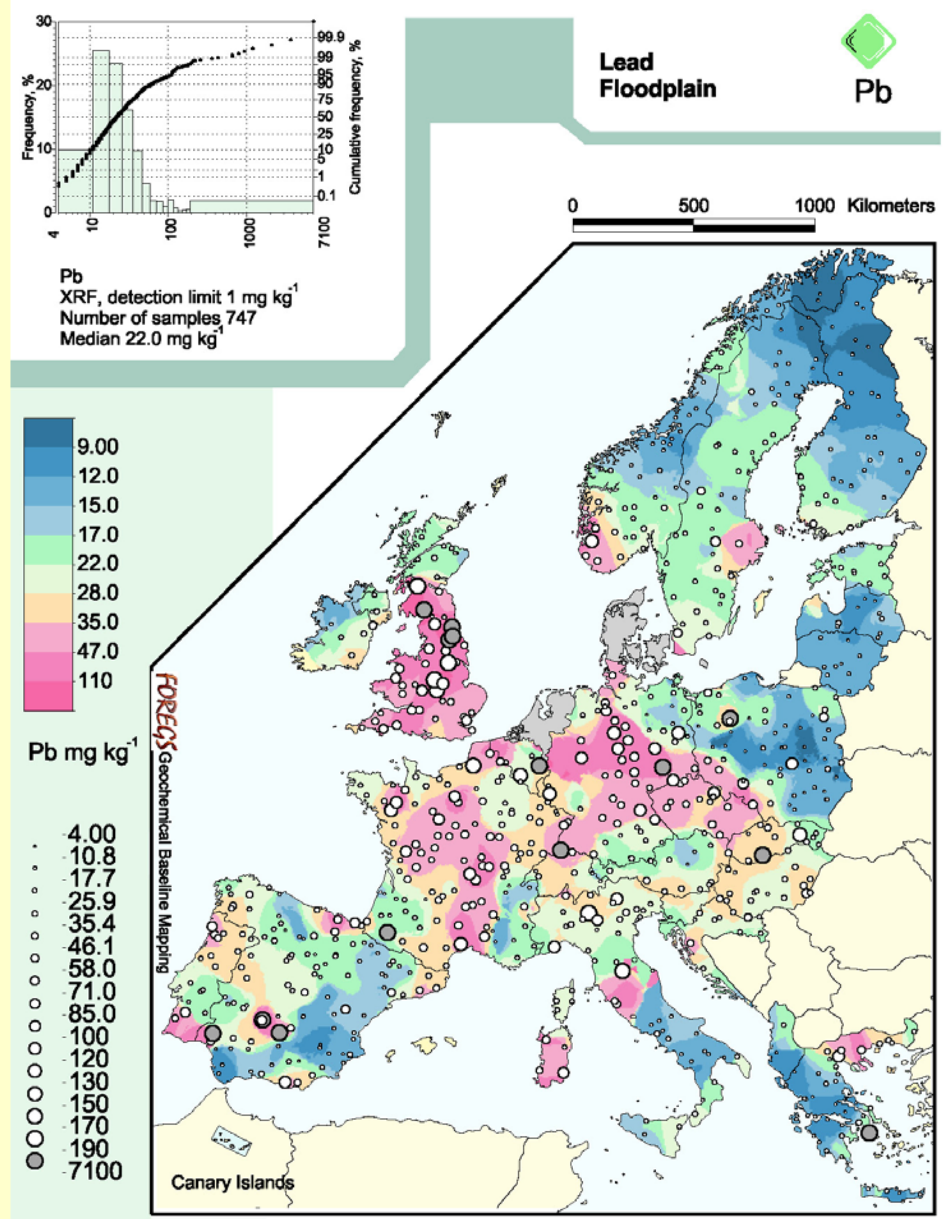
Area: 4.250.000 km^2
925 sample sites
1 site/4600 km^2

Environmental Geochemistry for Global Survival
IUGS/IAGC project "Global Geochemical Baselines"

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

http://www.gtk.fi/publ/foregsatlas/





From Salminen et al., 2005 & http://www.gtk.fi/publ/foregsatlas/

Epilogue

National guideline values:

1. to protect human health
2. to protect ecosystems
3. to protect groundwater

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 groundwater

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

Pathway to surface water, air, direct contact

Samples should be stored carefully for future use

The European sample archive is kept in storerooms of the Geological Survey of the Slovak Republic

EPILOGUE …..

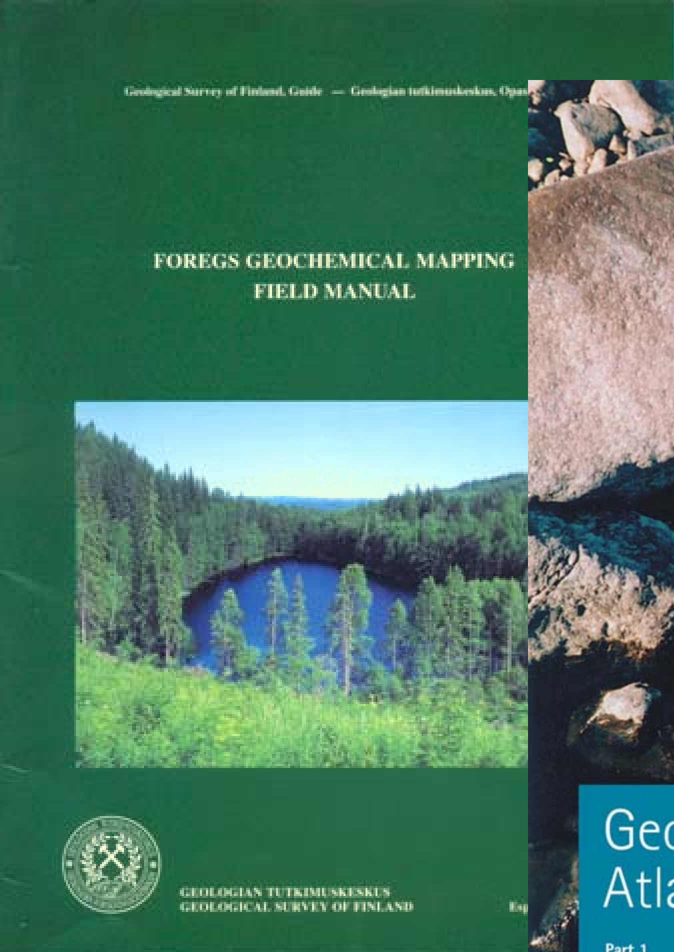
High quality geochemical databases are necessary for Europe, but also for the other Continents:

- for 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.

….. EPILOGUE

- ❖ Combined Stream and Floodplain/Overbank sediment surveys can be used for the assessment of contamination in drainage basins.
- ❖ Stream sediment is generally susceptible to contamination by anthropogenic activities. The same applies to top floodplain sediment.
- ❖ Bottom floodplain sediment gives pristine conditions.
- ❖ Collection of top and bottom floodplain sediment enables the assessment of contamination of a drainage basin.

Printed publications

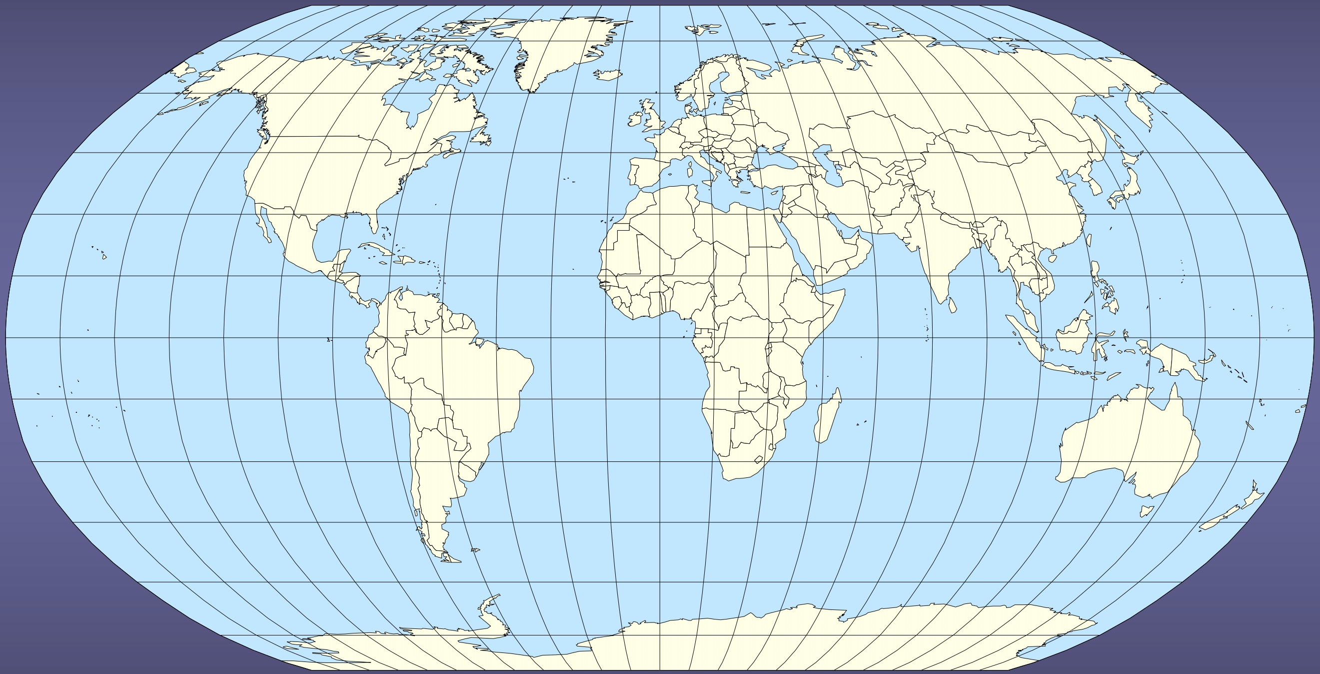


They are all freely available from URL:

http://www.gtk.fi/publ/foregsatlas/

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

Environmental Geochemistry for Global Survival



IUGS/IAGC project "Global Geochemical Baselines"

Geological Surveys consider it their obligation to provide to the present and future generations of humankind high quality geochemical databases in order to live in a better environment

Thank you for your attention