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

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General introduction
The Global Problem: 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.
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
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.

- Errors can be corrected by re-analysis of samples, provided enough sampling material is available.
Sampling
Field sampling manual was compiled by experienced applied geochemists in sampling in different morphoclimatic environments, and then tested in the field before finalisation.
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 km²)
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/km², Eastern Macedonia and Thrace, Hellas

Distribution of lead (Pb) in stream sediment
Eastern Macedonia and Thrace

Anomalous values due to mineralisation
Anomalous values due to anthropogenic activities - Contamination

Irene R.
Number of stream sediment samples = 862

Pb (mg/kg) in stream sediment

Pb (mg/kg) in overbank sediment

Depth in cm

0 79 104 195 234 303
0 159 169 26 16 14

Ore beneficiation plant
Alexandroupolis

Irene River
Athens
Irene River

Lead (Pb) in stream & floodplain sediment samples

Sample type

Pb (ppm)

Median of 862 stream sediment samples

Natural baseline conditions

Pollution

Present day stream sediment

Top floodplain sediment samples

Bottom floodplain sediment samples

Overbank sediment sample

Composite Stream sediment

Regional Overbank sediment

Topbottom
Distribution of Pb in overbank sediment layers, Bieber, Germany

(about 50 km to the east of Frankfurt)

Pb (mg/kg)

Depth in cm

0 15 30 45 60 75 90 105 120

285
228
209
331
1853
2777
3710
1980
2980

(Bolviken et al., 1996, Fig. 6, p.154)
Distribution of Zn in overbank sediment layers, Bieber, Germany

<table>
<thead>
<tr>
<th>Depth in cm</th>
<th>Zn (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>488</td>
</tr>
<tr>
<td>15</td>
<td>336</td>
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<tr>
<td>30</td>
<td>361</td>
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</tr>
<tr>
<td>55</td>
<td>1780</td>
</tr>
<tr>
<td>65</td>
<td>1620</td>
</tr>
<tr>
<td>80</td>
<td>4213</td>
</tr>
<tr>
<td>95</td>
<td>5640</td>
</tr>
<tr>
<td>110</td>
<td>4400</td>
</tr>
</tbody>
</table>

(Bolviken et al., 1996, Fig. 6, p.154)
Distribution of Co and Cu in overbank sediment layers, Bieber, Germany

![Distribution of Co and Cu](image)

(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)

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

Area: 320,000 km²
No. of sites: 690
Sample density: 1 site / 464 km²

Ottesen et al. (2000, p.85)

Lead in overbank sediment

Sample density: 1 site / 4,600 km²

Lead Floodplain

Pb

Environmental Geochemistry for Global Survival

IUGS/IAGC project "Global Geochemical Baselines"

Sample density: 1 site / 4,600 km²
Mean value of about 6400 stream sediment samples in each GRN cell

Average density: 1 site/14 km²

Mean value of 5 floodplain sediment samples in each GRN cell

Average density: 1 site/18,100 km²

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

Irene River
Ardas River
Thracian Sea
Bulgaria
Turkey
Pb contents in samples of post- and pre-industrial overbank sediments ….

(From Bolviken et al., 1996, Fig. 7, p.155)
….. Pb contents in samples of post- and pre-industrial overbank sediments

(From Bolviken et al., 1996, Fig. 7, p.155)
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
Analysis of **Reference Samples**, which must be inserted at regular intervals according to the number of samples analysed in each batch

**QUALITY CONTROL SCHEME**

**Randomisation of samples**

**Inter-laboratory checks**

**Sample site**

1. **Routine sample**
   - **Subsample 1A**
     - **Analysis 1A**
   - **Subsample 1B**
     - **Analysis 1B**

2. **Duplicate sample**
   - **Subsample 2A**
     - **Analysis 2A**
   - **Subsample 2B**
     - **Analysis 2B**

**Duplicate field samples**

**Environmental Geochemistry for Global Survival**

IUGS/IAGC project

“Global Geochemical Baselines”

**Geochemistry expert group**

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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 control chart at the 95% confidence interval.

Precision worse than ±10%

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

Results consistent with a precision of ±10%

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

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).
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

- Analytical
  - 10.88%
  - 7.25%

- Geochemical
  - 39.84%
  - 6.89%

- Sampling
  - 49.28%
  - 4.12%

Acceptable results

- Analytical
  - 18.24%
  - 6.89%

- Geochemical
  - 74.51%
  - 88.99%

- Sampling
  - 0%
  - 4.12%
Geostatistics ...Quantification of sources of variation

Analysis of Variance

**Arsenic (As)**

- Variogram function
- Range of influence = 1800 m
- Mean = 6.95 mg/kg
- Median = 6.29 mg/kg
- Stand. Dev. = 3.10 mg/kg
- Minimum = 2.44 mg/kg
- Maximum = 20.93 mg/kg
- Number of samples = 144

**Sampling**
- 0.74%

**Analytical**
- 1.78%

**Geochemical**
- 97.48%

**Variance 9.64**

Spatial variance = 4.14

Random variance or Nugget effect = 5.5

- **42.95%**
- **57.05%**
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 km²
925 sample sites
1 site/4,600 km²

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/
National guideline values:
1. to protect human health
2. to protect ecosystems
3. to protect groundwater

Levels $\gg$ Guideline values and Baseline $\rightarrow$ Remediation

Levels $<$ Guideline values, Baseline $\rightarrow$ Consider clean

Levels $\approx$ Guideline values
$\rightarrow$ Study chemical species, binding
$\rightarrow$ Potentially mobile form
$\rightarrow$ Study pathways
$\rightarrow$ 3D modelling

Geochemical baselines

Future land use

Potentially contaminated soil
Levels of pollutants (total)
Chemical species

Pathway to groundwater

Pathway to surface water, air, direct contact

Geochemistry expert group

www.eurogeosurveys.org
Samples should be stored carefully for future use.

The European sample archive is kept in storerooms of the Geological Survey of the Slovak Republic.
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.
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.
They are all freely available from URL:

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

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“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.