Geochemistry of European surface- and ground-water

Presented by

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***European ground water geochemistry**: Clemens Reimann, Manfred Birke and the EuroGeoSurveys EGG Project Team*

Water sustains all (Thales of Miletus, 600 B.C.)

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Sweden: K. Lax, SGU

Switzerland: P. Hayoz, Swisstopo

United Kingdom: D. Flight, S. Reeder, P. Smedley, BGS; D. Banks, HolyMoore Consultancy

Ukraine: V. Klos, M. Vladimirova, Geol. Surv.

+ samples from **Albania, Belarus, Georgia, Latvia, The Netherlands, Turkey**

Geochemistry of European surface- and ground-water

The work of the EuroGeoSurveys Geochemistry Expert Group

Presentation structure:

- **Introductory notes**
- **Geochemical Atlas of Europe (*results of stream water geochemistry*)**
- **Geochemical Atlas of Ground water geochemistry using *bottled mineral water as a sampling medium***
- **Conclusions**
- **Recommendations**
- **References**

2005-2015: International Decade for Action "Water for Life"

Based on the title of the first UN World Water Development Report "***'Water for People, Water for Life***" (http://www.unesco.org/water/wwap/wwdr/), the General Assembly of the United Nations decided to proclaim, in its resolution A/RES/58/217 (http://www.unesco.org/new/en/natural-sciences/environment/water/), **the period from 2005 to 2015 the International Decade for Action**, "**Water for Life**", commencing on World Water Day, 22 March 2005 (http://www.unesco.org/new/en/natural-sciences/environment/water/world-water-day/).

The Resolution states that the main goal of the Decade should be a greater focus on water-related issues at all levels and on the implementation of water-related programmes in order to achieve internationally agreed upon water-related goals contained in Agenda 21 (http://www.un.org/esa/dsd/agenda21**/), the United *Nations Millennium Development Goals*** (http://www.un.org/millenniumgoals/) ***and the Johannesburg Plan of Implementation*** (http://www.un.org/esa/sustdev/documents/WSSD_POI_PD/English/POIToc.htm).

Question: Have we done everything that should be done?

COM(2012) 673: A Blueprint to Safeguard Europe's Water Resources

"Water is essential for human life, nature and the economy. It is permanently renewed, but it is also finite and cannot be made or replaced with other resources. Freshwater constitutes only about 2% of the water on the planet and competing demands may lead to an estimated 40% global water supply shortage by 2030".

- Oceans and seas 95.96%
- Glaciers and polar ice 2.97%
- Ground water 1.05%
- Lakes and rivers 0.009%
- Atmosphere 0.001%
- Biosphere 0.0001%

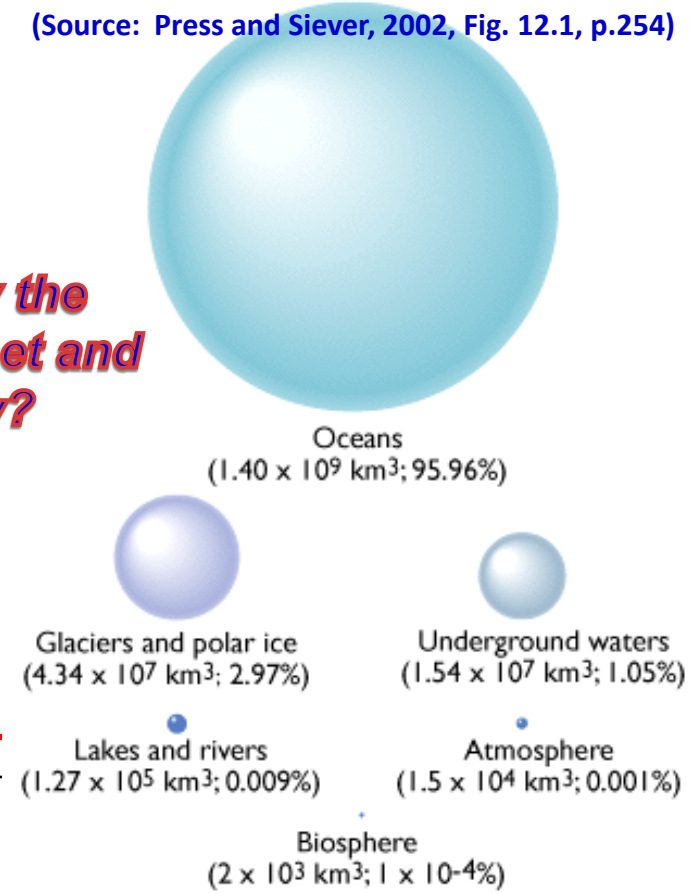
?

How much is finally the freshwater in our planet and what is its quality?

Therefore,

- ≈96% of the water on Earth is salty and is in the oceans and seas,
- ≈3% is in glaciers and polar ice, and
- ≈1% is fresh and available for use, and another assessment states ≈3% is fresh water

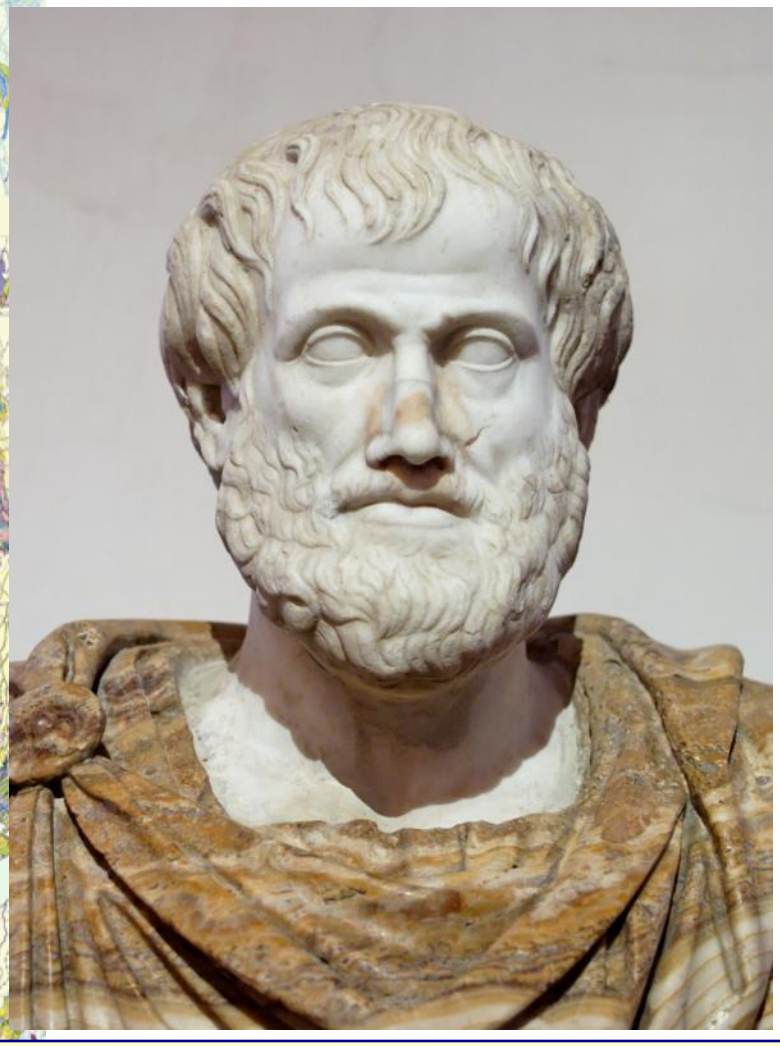
(Source: Press and Siever, 2002, Fig. 12.1, p.254)



This presentation is concerned with the inorganic chemical composition of European surface- and ground-water.

In fact , its chemical quality.

Water is soul of the Earth (Wystan H. Auden)



"*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*'.

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

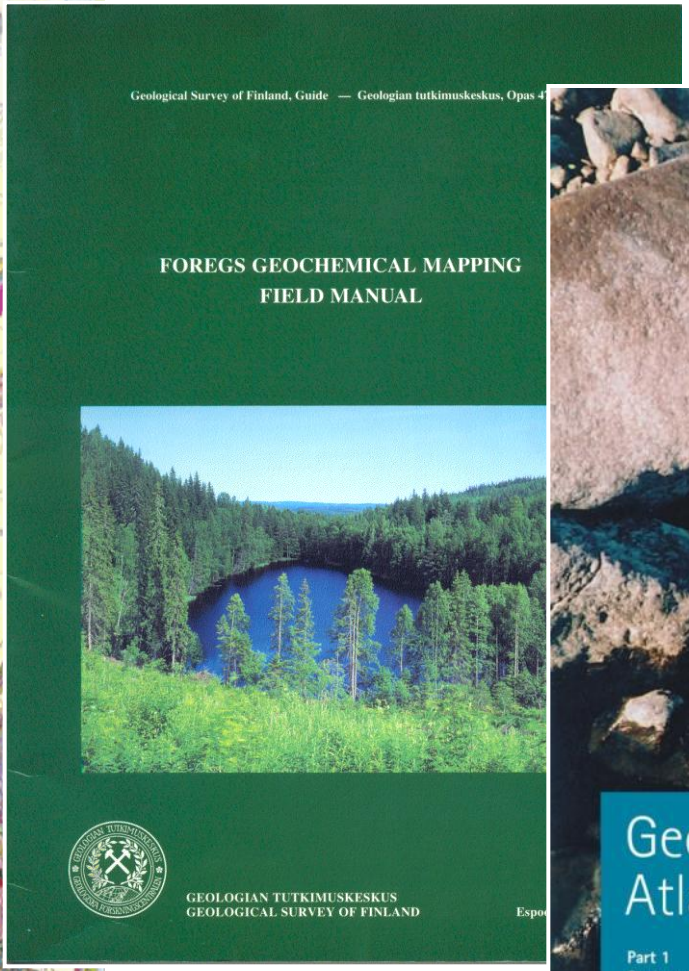
Sample preparation

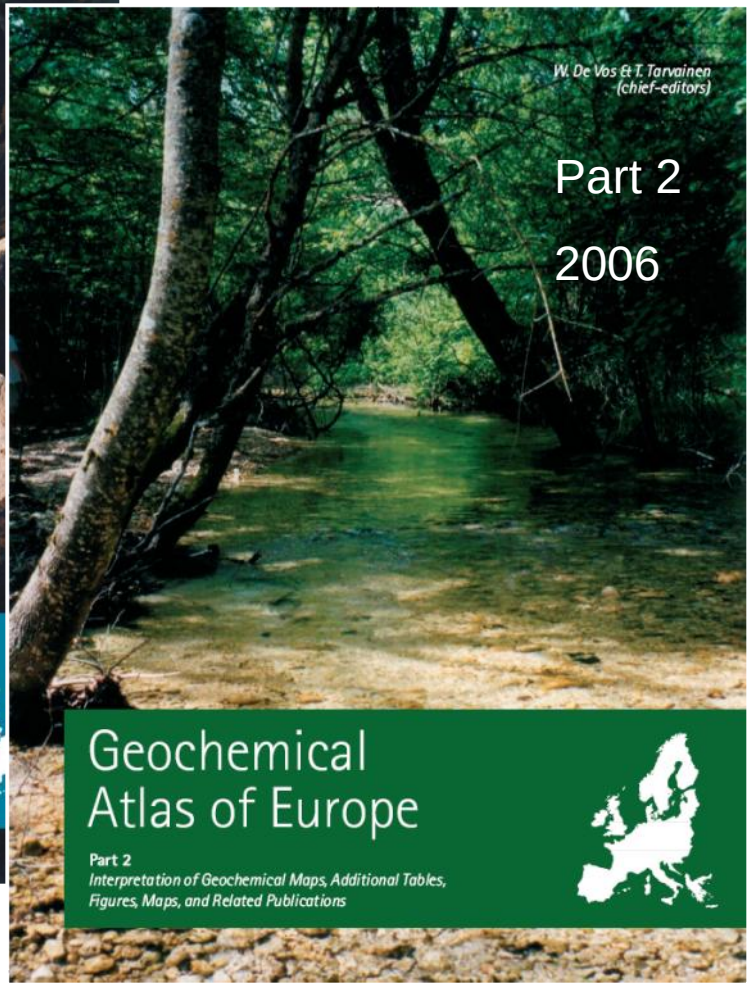
- **These are the two most crucial stages of any geochemical survey.**
- **Any errors during these two stages is carried forward, and can result in the failure of a whole survey.**

Laboratory analysis

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

Geochemical Atlas of Europe





http://arkisto.gsf.fi/op/op47/op47.pdf

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

Geochemical Atlas of Europe

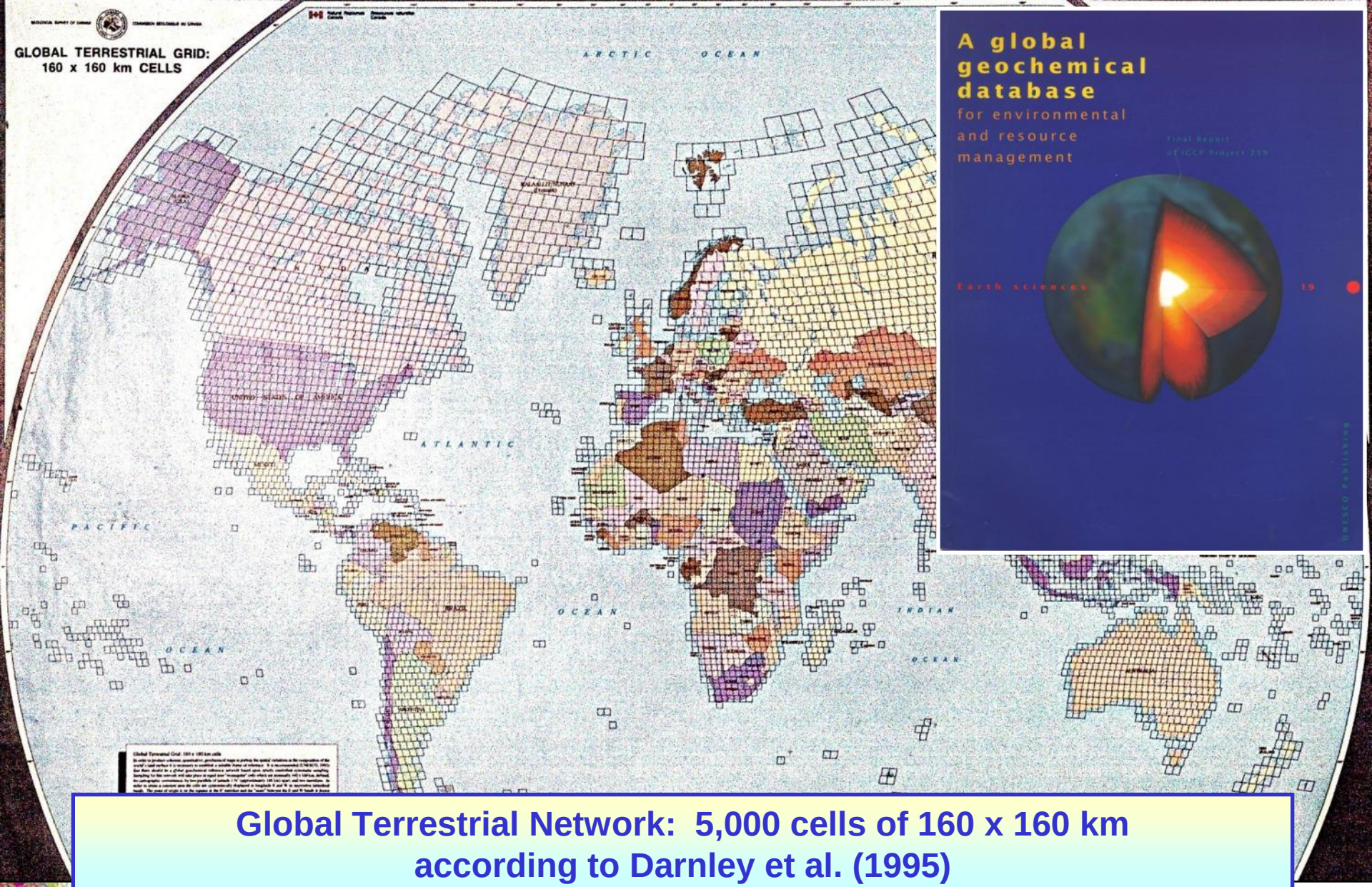
26 countries participated in the Geochemical Baseline Mapping of Europe

Area: 4,250,000 km^2

808 stream water samples collected during 1998 to 2000

1 site/≈5,000 km^2

Each country funded its own survey

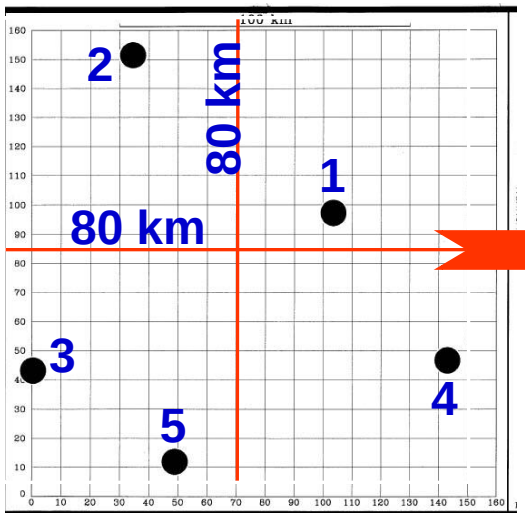


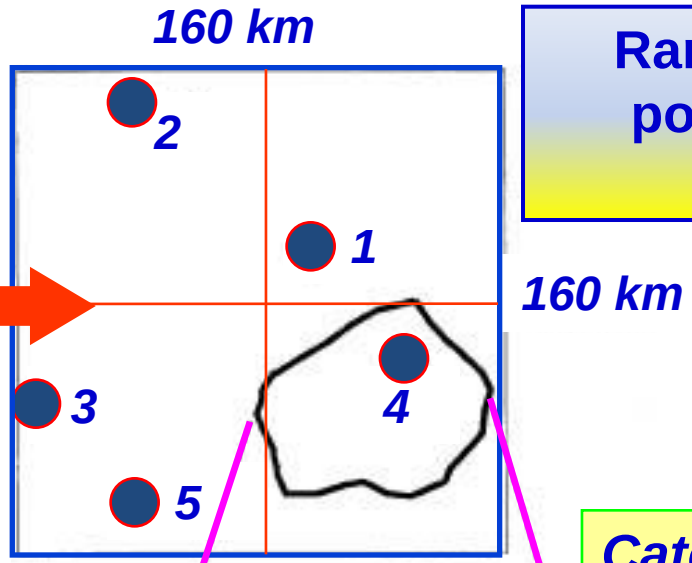
Global Terrestrial Network: 5,000 cells of 160 x 160 km according to Darnley et al. (1995)

http://www.globalgeochemicalbaselines.eu/wp-content/uploads/2012/07/Blue_Book_GGD_IGCP259.pdf

SAMPLING SCHEME

According to the specifications of IGCP 259
"*International Geochemical Mapping*" report (Darnley et al., 1995)

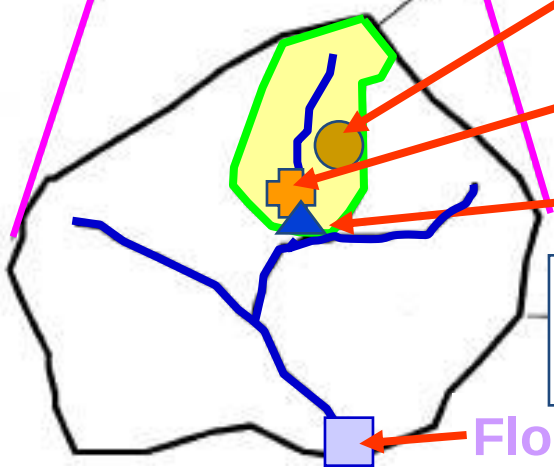




Randomly selected points in GTN cell N43E09

Catchment <100 sq.km

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.



Humus & Soil

Overbank sediment

Stream water & stream sediment

Large drainage basin 1000-6000 sq.km

Floodplain sediment

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Laboratory analysis of Stream water samples (n=808)

For the production of a harmonised and homogeneous database, all stream water samples were analysed for the same suite of determinands in the same laboratory

Federal Institute of Geosciences and Natural Resources
Bundesanstalt für Geowissenschaften und Rohstoffe

(BGR, Germany)

British Geological Survey

(BGS, United Kingdom)

Determinands measured & Quality control

BGR – Germany: ICP-QMS / ICP-AES

57 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

- **Accuracy of methods for all determinands is better than ±10%,**
- **the bias is within ±3%, and**
- **the repeatability at the 95% confidence interval is better than 5% at concentrations an order of magnitude above the limit of quantification.**

The noblest of the elements is water

(Pindar, *ca*. 522-438 B.C.)

Determinands measured & Quality control

BGS – U.K.: pH-meter, Conductivity meter, IC, DOC analyser

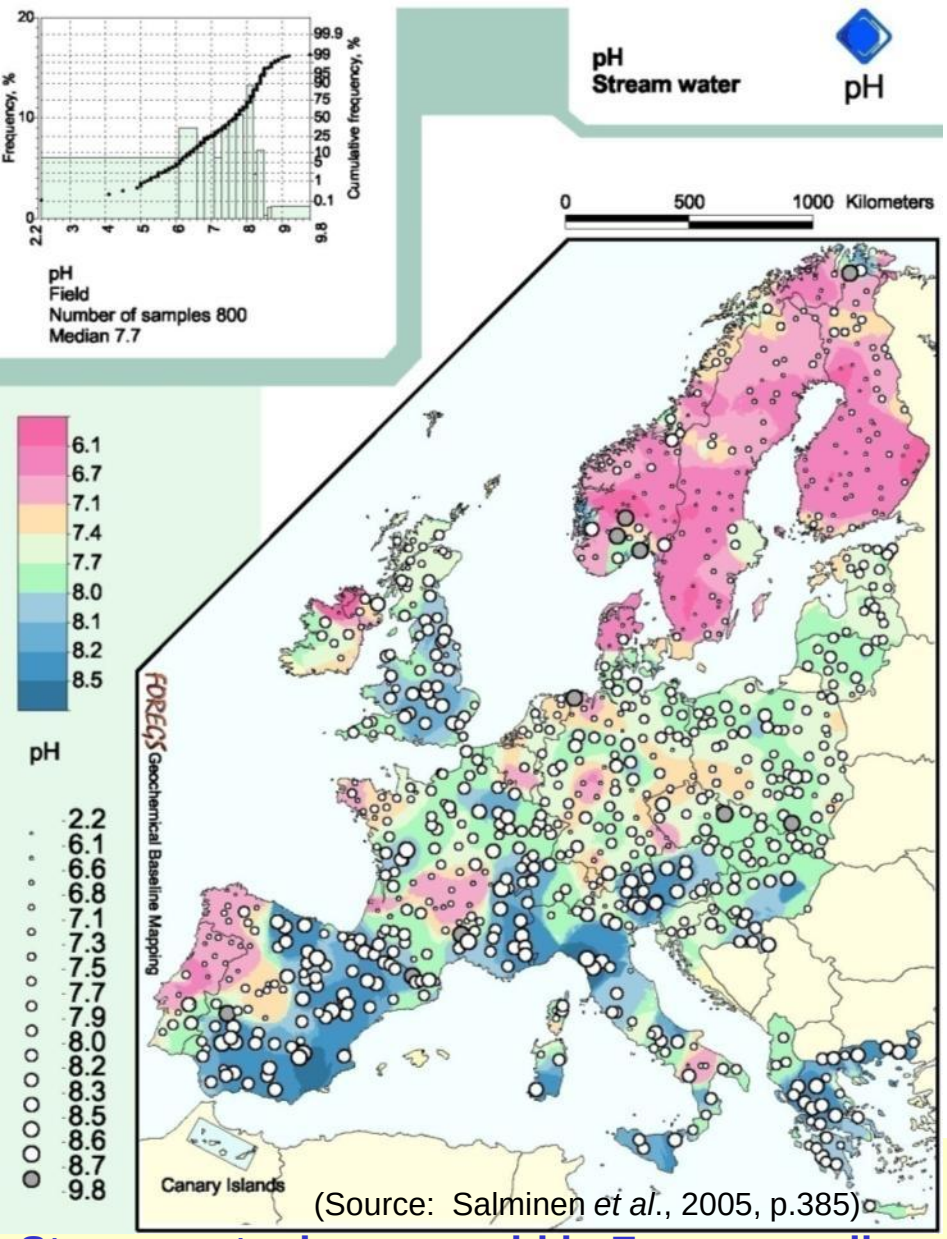
9 determinands: pH, EC,

HCO_3^-, Br^-, Cl^-, F^-, NO_3^-, SO_4^{2-},

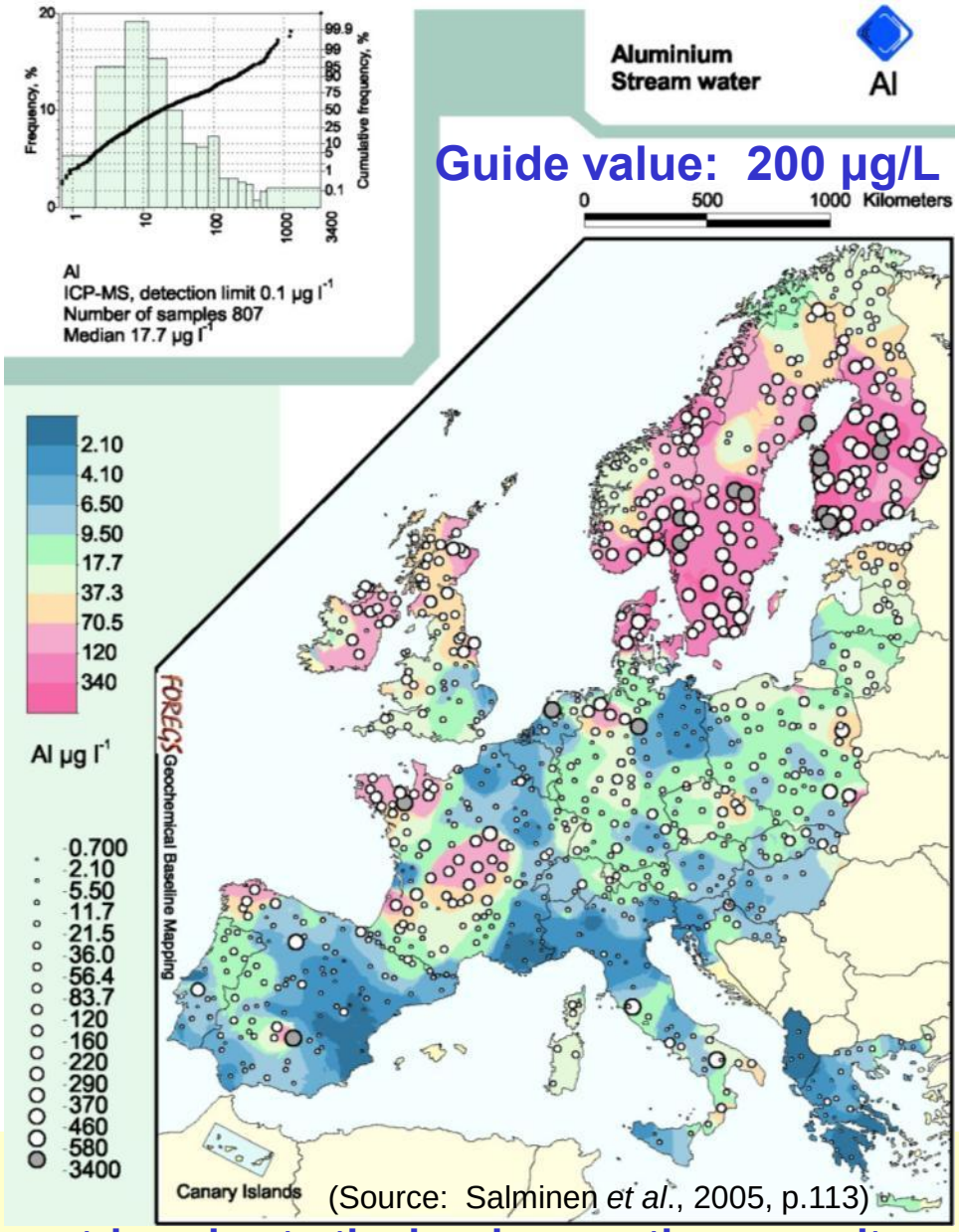
DOC

ANIONS: The accuracy of the method is better than ±10%, the bias is within ±3% and the precision at the 95% confidence interval is better than 5% at concentrations an order of magnitude above the limit of quantification.

DOC: The accuracy of the method is better than ±5%, the bias is within ±2%, and the precision at the 95% confidence interval is better than 6% at concentrations an order of magnitude above the limit of quantification (0.5 mg/L).



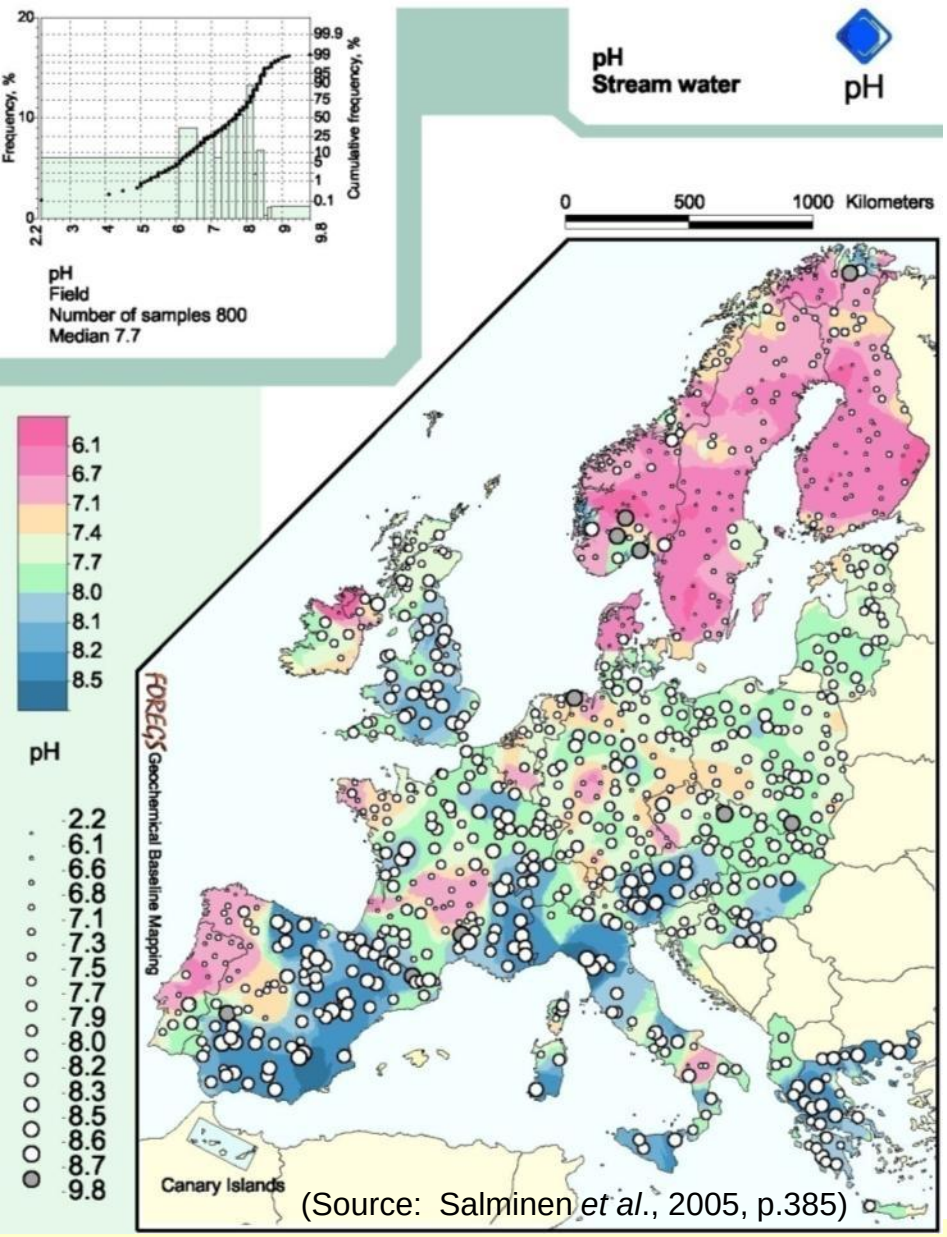
(Source: Salminen *et al*., 2005, p.385)



Guide value: 200 µg/L

(Source: Salminen *et al*., 2005, p.113)

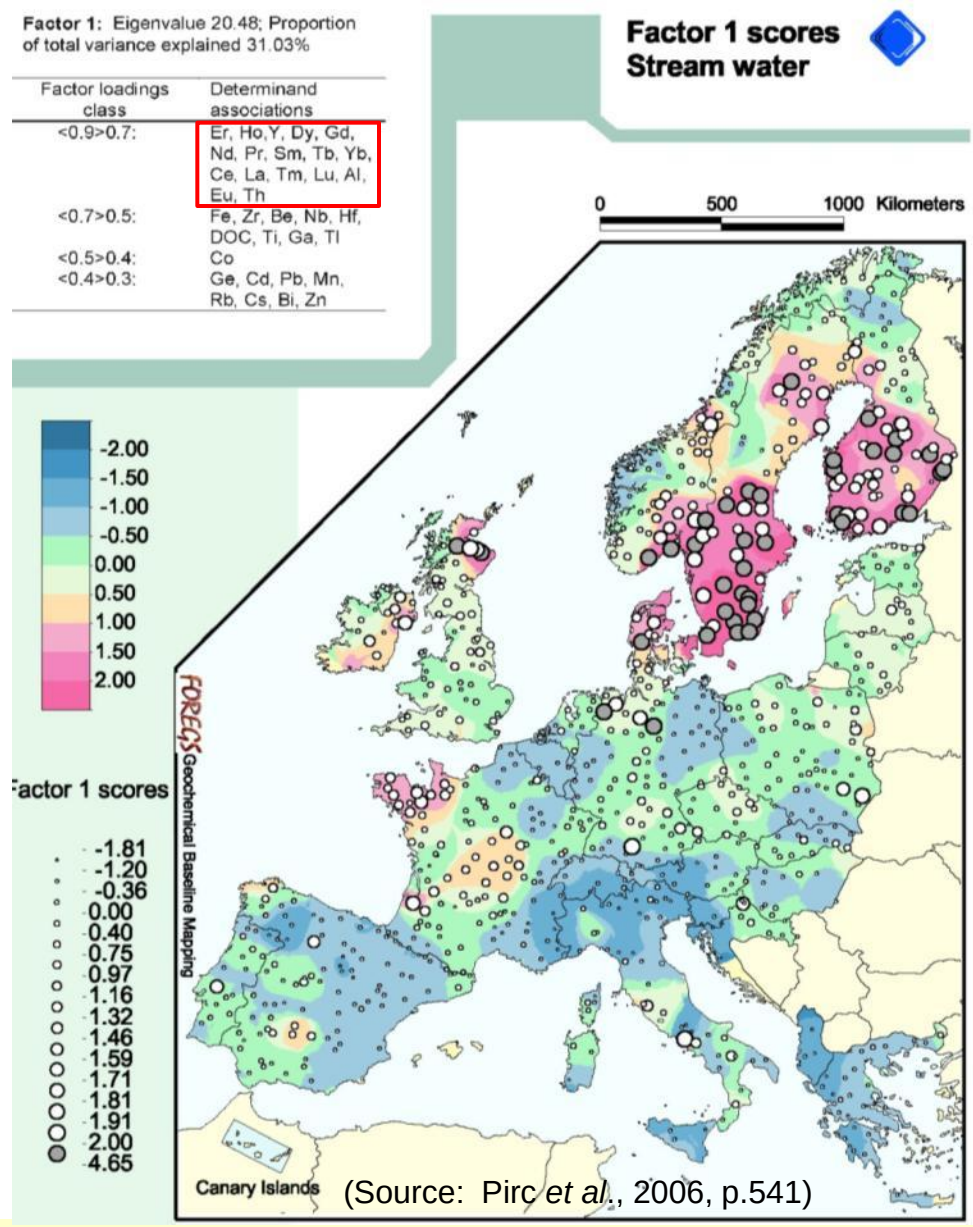
Stream water is more acid in Fennoscandian countries, due to the low base cation capacity of metamorphic basement rocks and high concentration of humic and fulvic acids, typical of boreal climate. Low pH values result in higher solubility of aluminum, REEs (Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) & some metals (*e.g.*, Cr, Fe, Pb, Th, Tl, Ti, Zr).



(Source: Salminen *et al*., 2005, p.385)

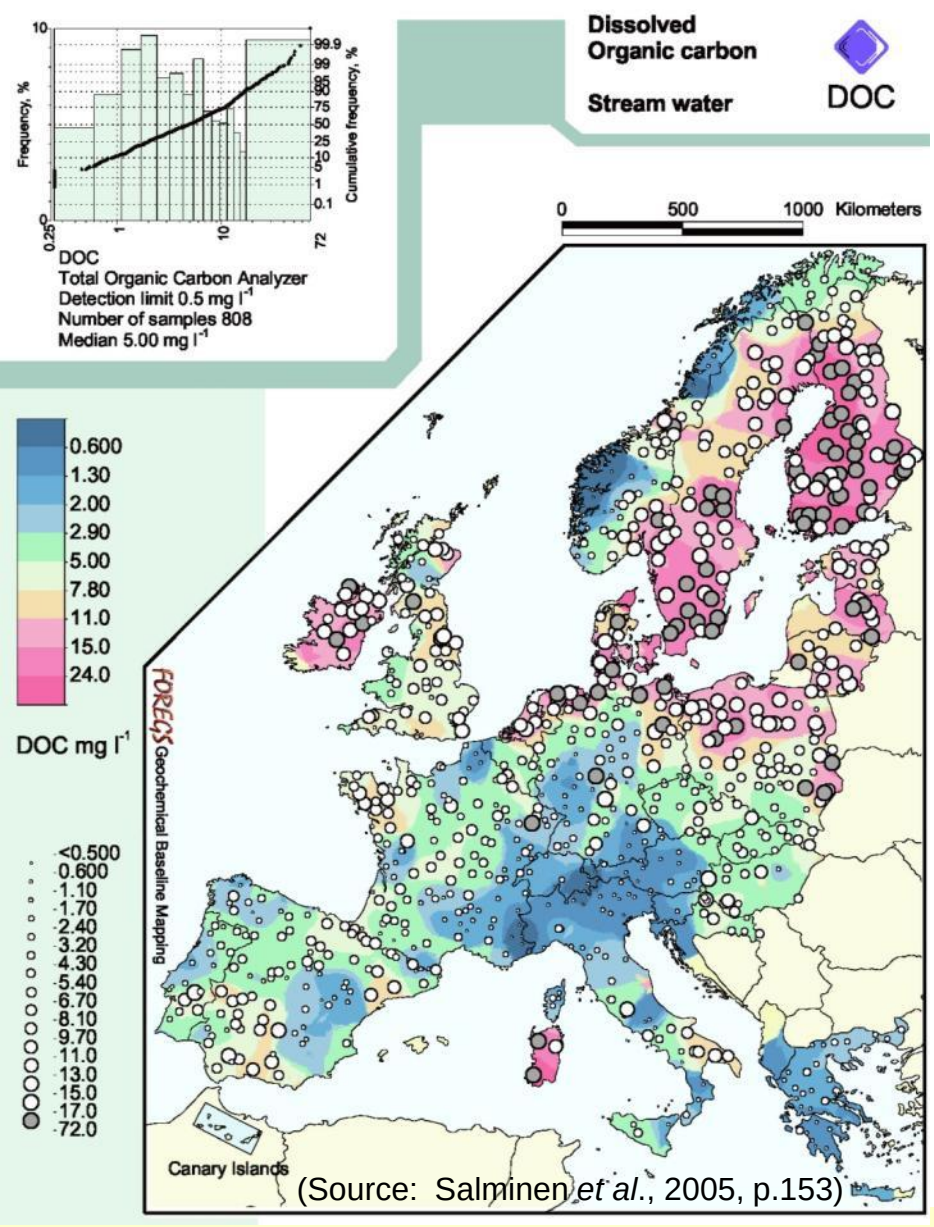
Factor 1: Eigenvalue 20.48; Proportion of total variance explained 31.03%

Factor loadings class	Determinand associations
<0.9>0.7:	Er, Ho,Y, Dy, Gd, Nd, Pr, Sm, Tb, Yb, Ce, La, Tm, Lu, Al, Eu, Th
<0.7>0.5:	Fe, Zr, Be, Nb, Hf, DOC, Ti, Ga, Tl
<0.5>0.4:	Co
<0.4>0.3:	Ge, Cd, Pb, Mn, Rb, Cs, Bi, Zn

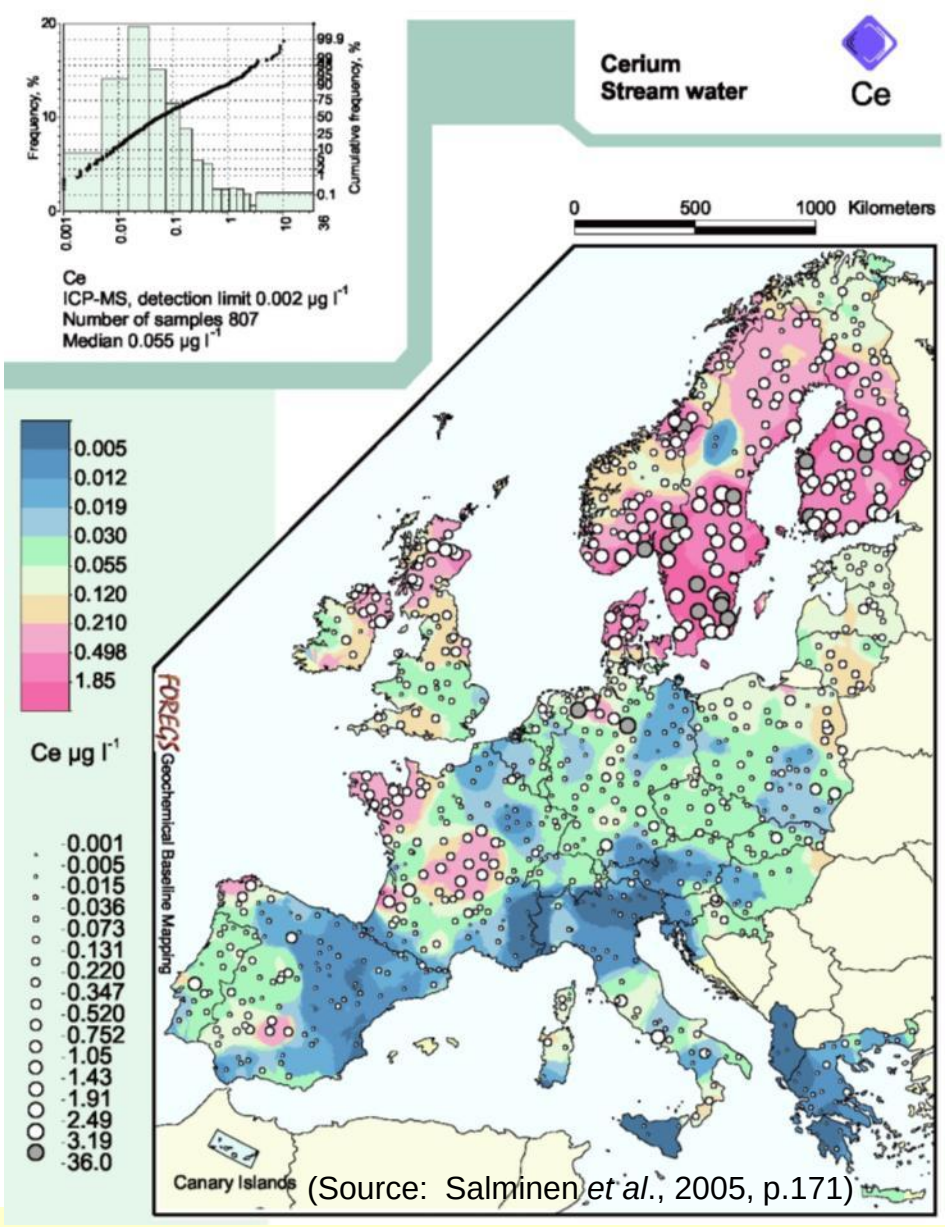


(Source: Pirc *et al*., 2006, p.541)

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



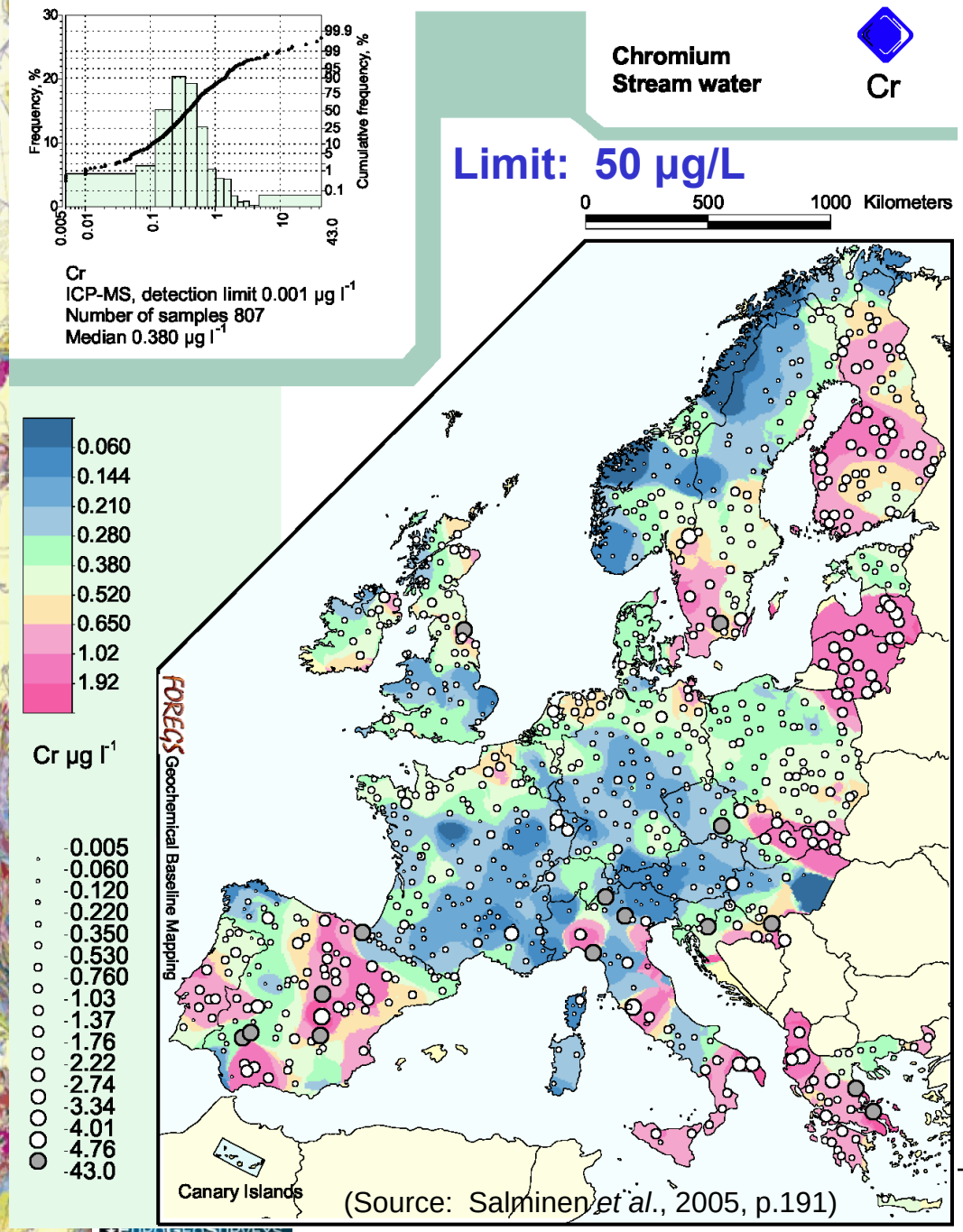
(Source: Salminen *et al.*, 2005, p.153)



(Source: Salminen *et al.*, 2005, p.171)

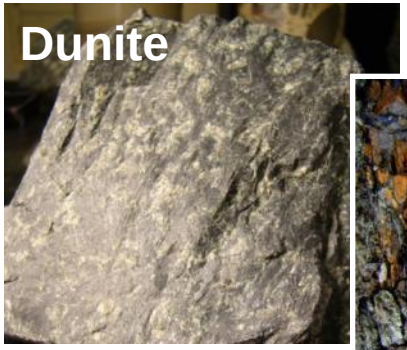
Rare earth elements (REE, *e.g.*, Cerium, Ce) and Aluminum are associated with low pH values and high Dissolved Organic Carbon (DOC).

Geochemical Atlas of Europe



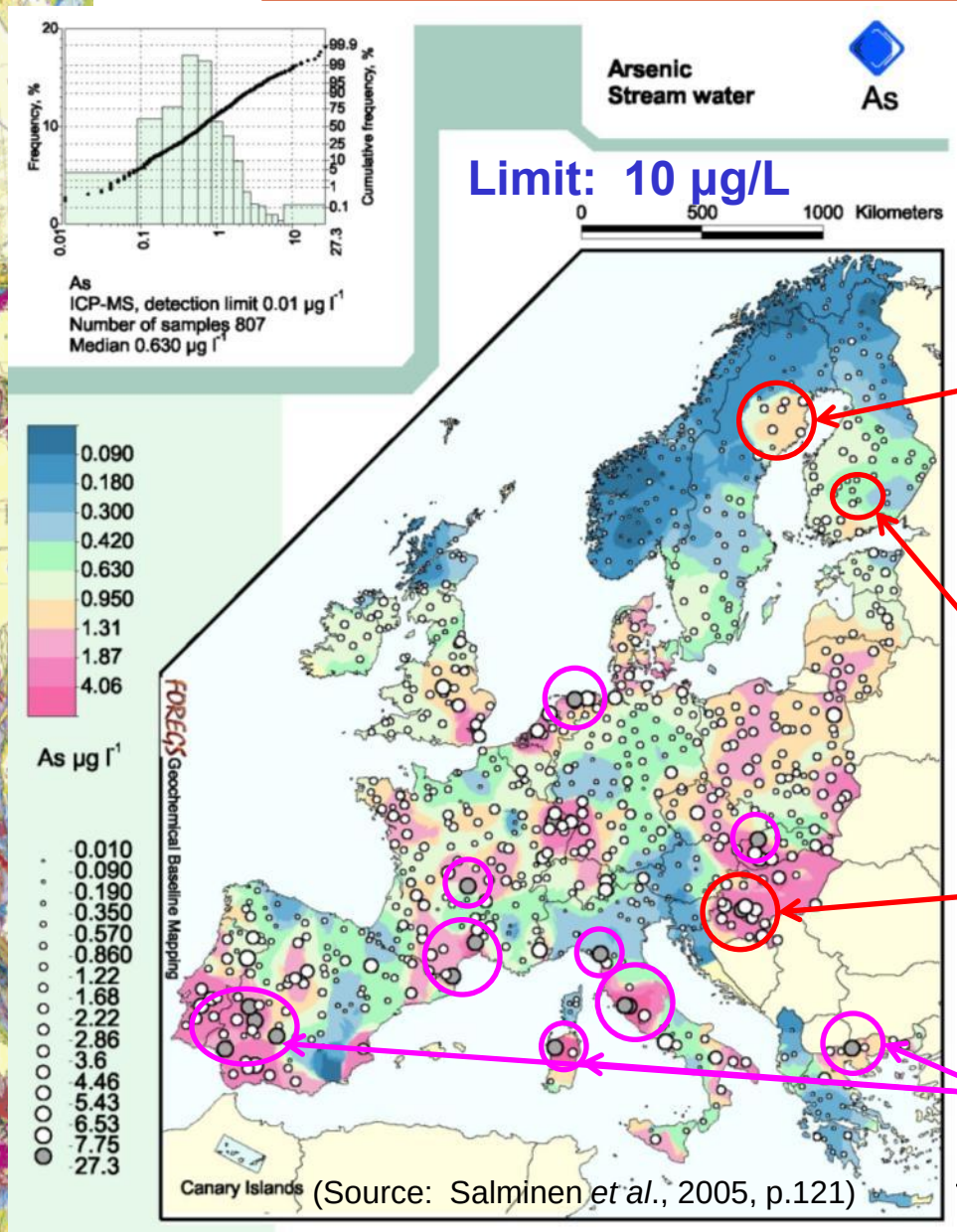
(Source: Salminen *et al.*, 2005, p.191)

Chromium is associated with ophiolite complexes (mafic & ultramafic rocks) and their derivates, alkaline rocks, and mineralised areas



Photographs from
http://geotripper.blogspot.com

Arsenic distribution in stream water



(Source: Salminen *et al.*, 2005, p.121)

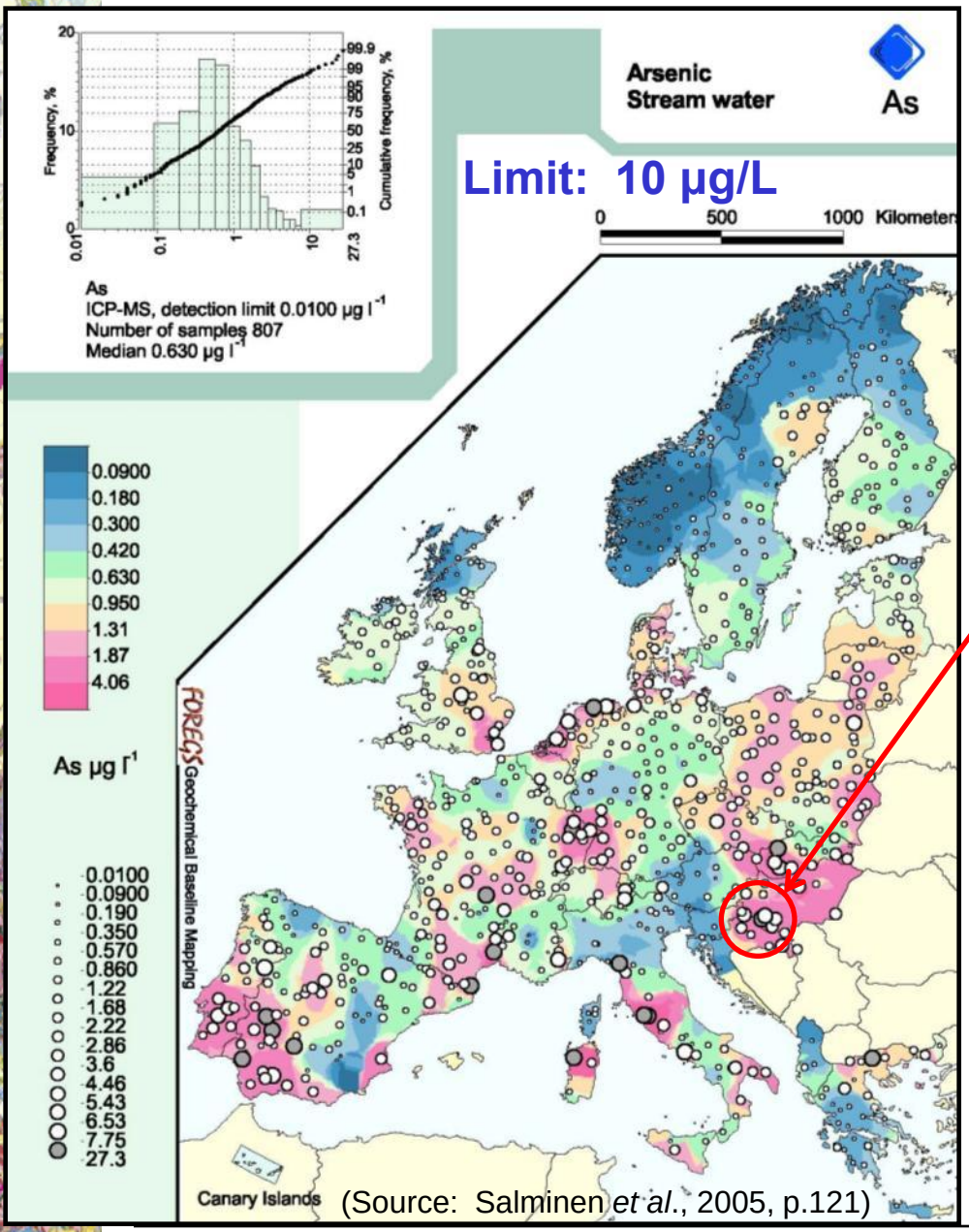
<10 µg/L Arsenic is the maximum admissible concentration in drinking water (WHO/EU)

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.

Balkan endemic nephropathy (BEN) area (or Danubian endemic familial nephropathy, DEFN)

There are, of course, other areas with potential As problems



(Source: Salminen *et al*., 2005, p.121)

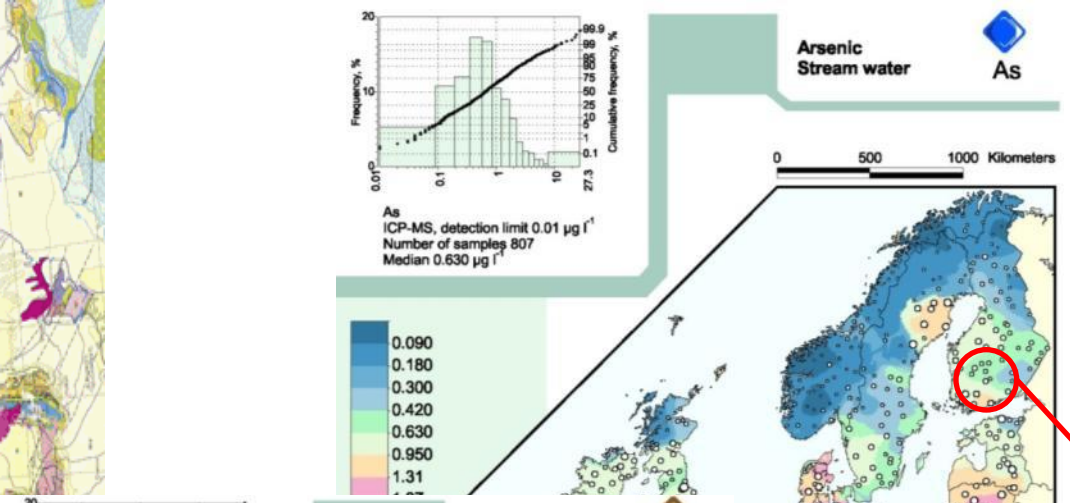
Balkan endemic nephropathy (BEN) is a severe, potentially fatal kidney disease leading to end-stage renal failure requiring blood dialysis, and is often associated with a particular kidney cancer (Tatu *et al*., 1998; Grollman *et al*., 2007). The disease only occurs amongst rural villagers in Bosnia & Herzegovina, Bulgaria, Croatia, Romania 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.

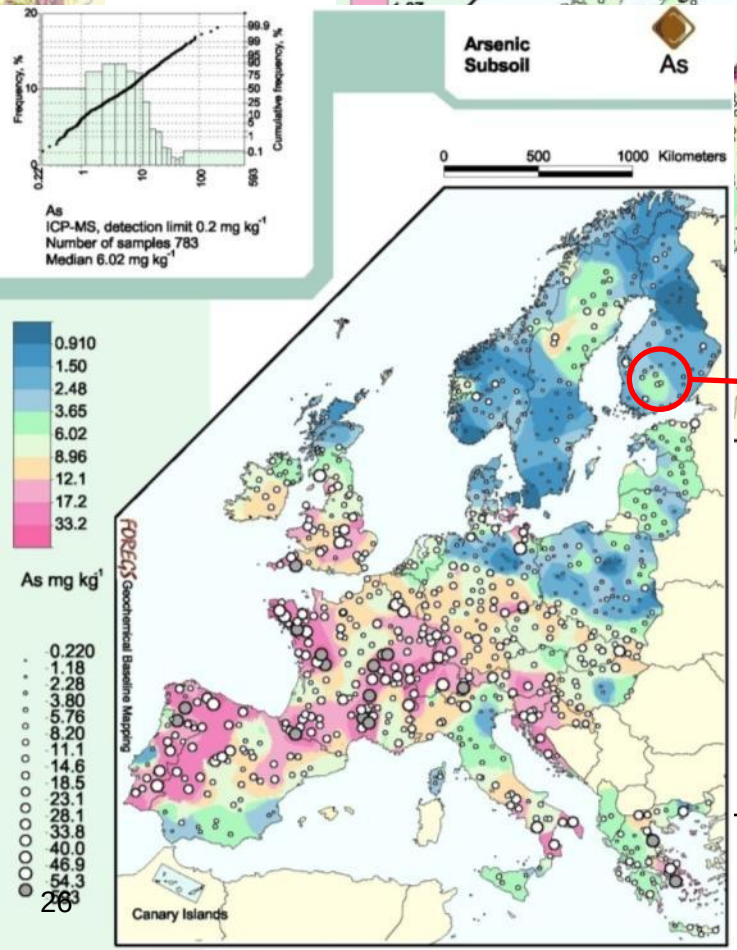
Balkan Endemic Nephropathy (BEN)

BEN patient in a dialysis clinic (Romania)

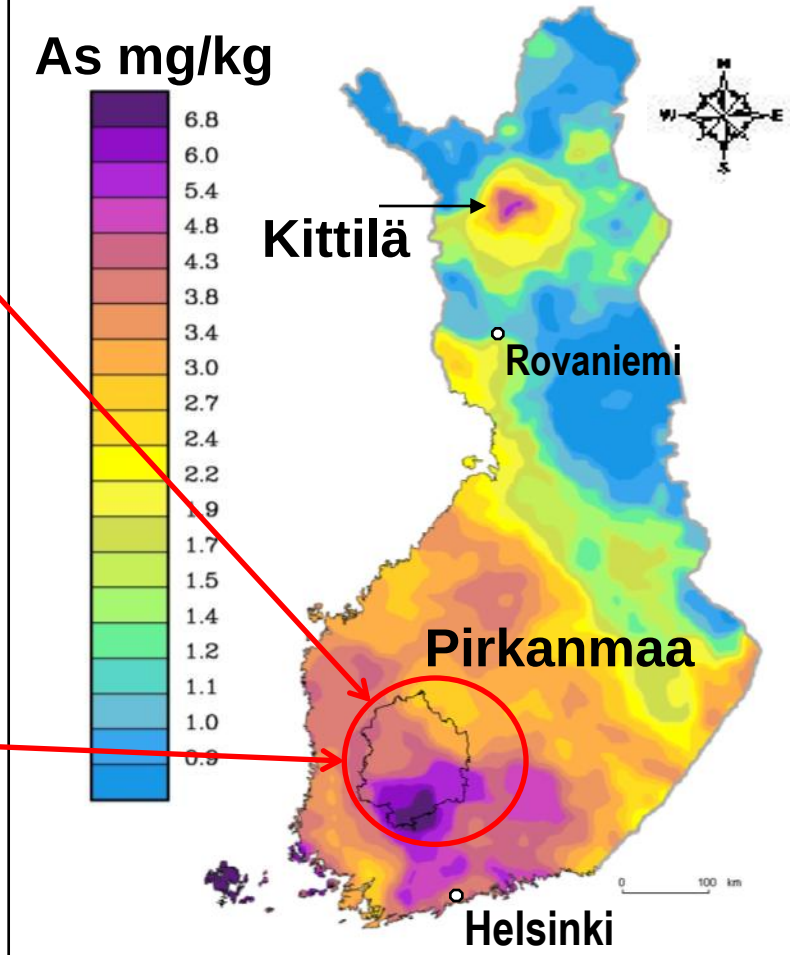
(Photographs provided by Olle Selinus, SGU, Sweden)

Arsenic concentrations in the fine fraction of till soil, Finland





(Source: Salminen *et al*., 2005, p.121)

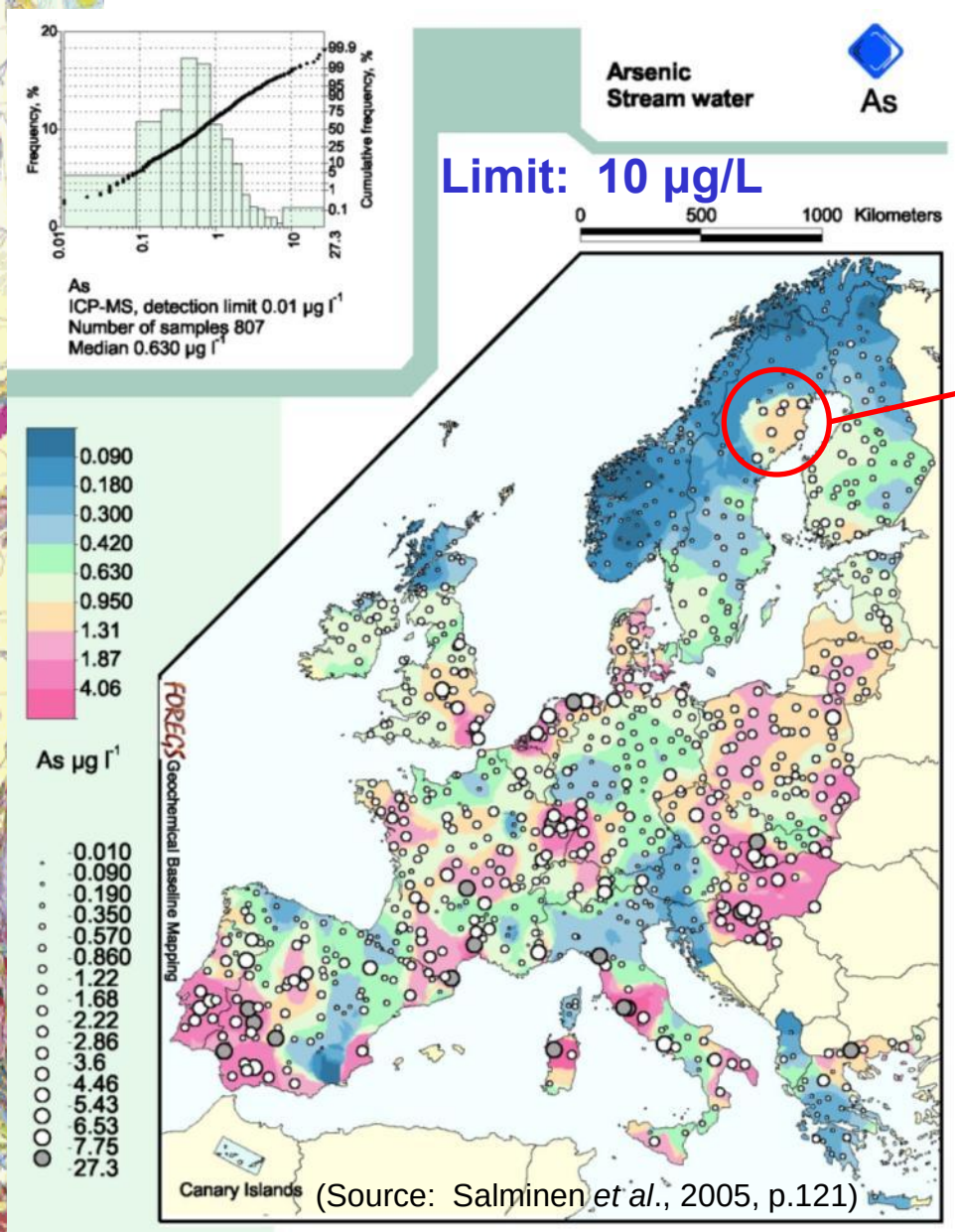


(Source: Koljonen, 1992, p.147)

Sample density: 1 site / 300 km^2

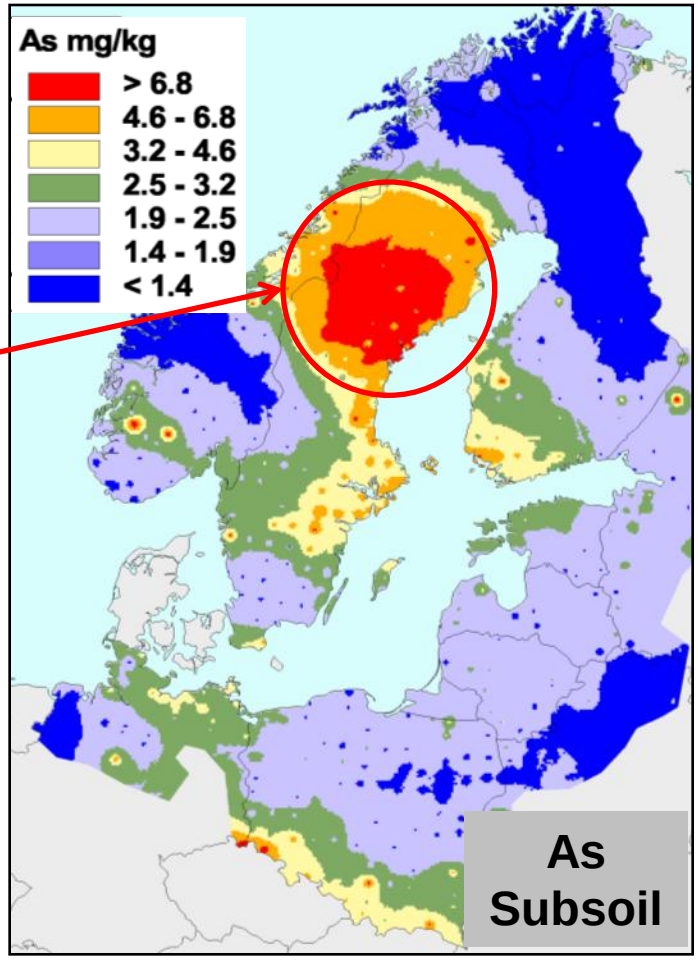
(Source: Salminen *et al*., 2005, p.117)

Other data sets are used for interpretation



(Source: Salminen *et al*., 2005, p.121)

Sample density: 1 site/≈5,000 km²

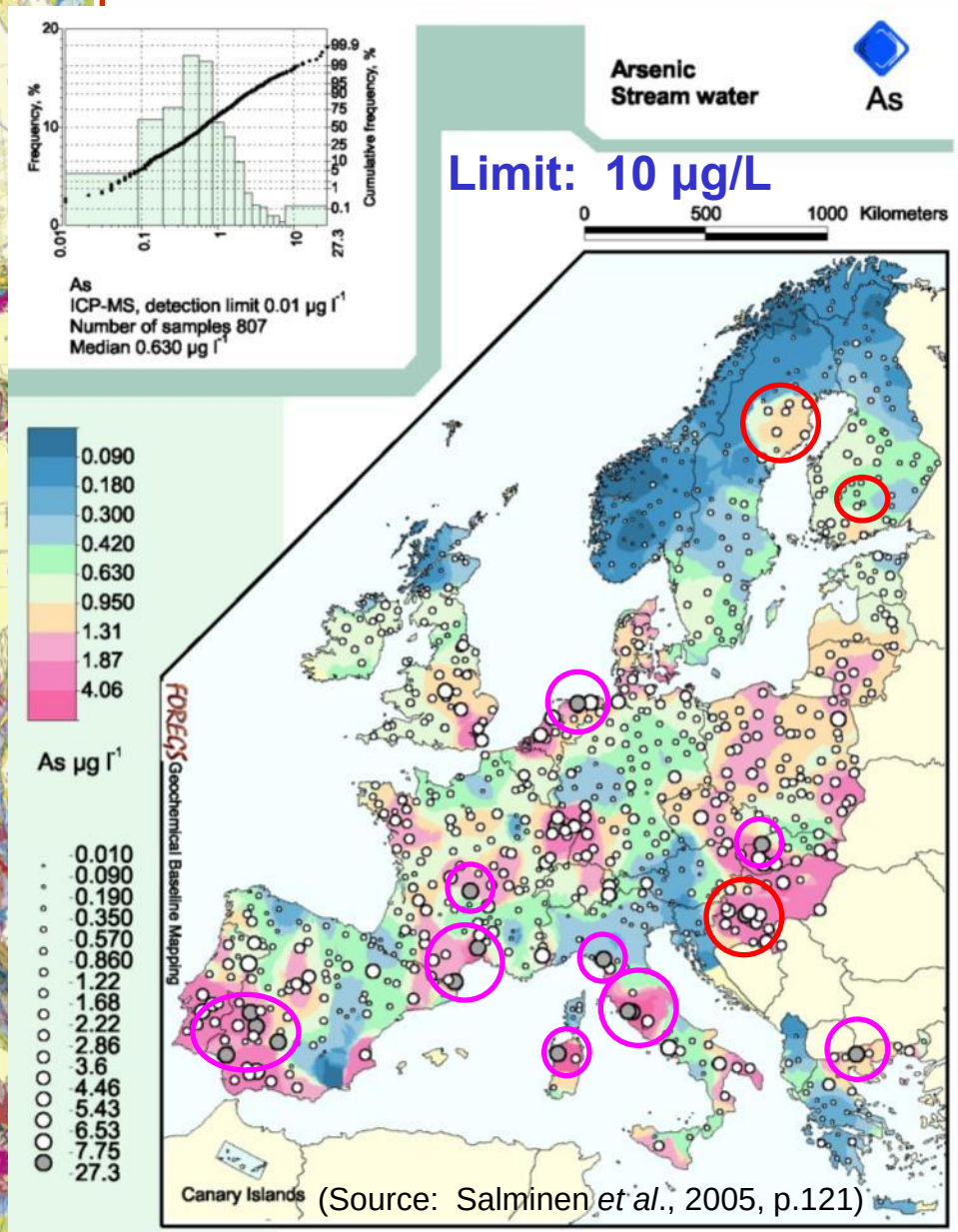


Baltic Soil Survey: As-concentrations in agricultural soil. Sample density: 1 site/2500 km²

(Source: Reimann *et al*., 2003, p.63)

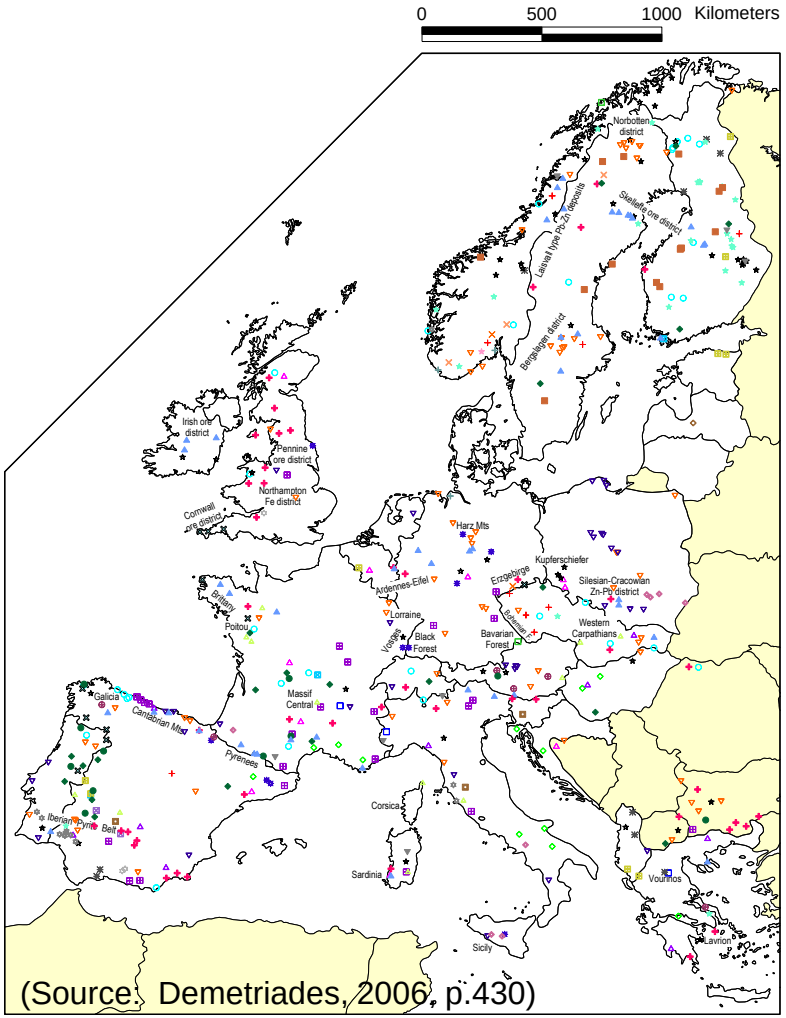
Other data sets are used for interpretation

Arsenic distribution is associated mainly with geogenic sources



(Source: Salminen *et al*., 2005, p.121)

Major mineral deposits of Europe



(Source: Demetriades, 2006, p.430)

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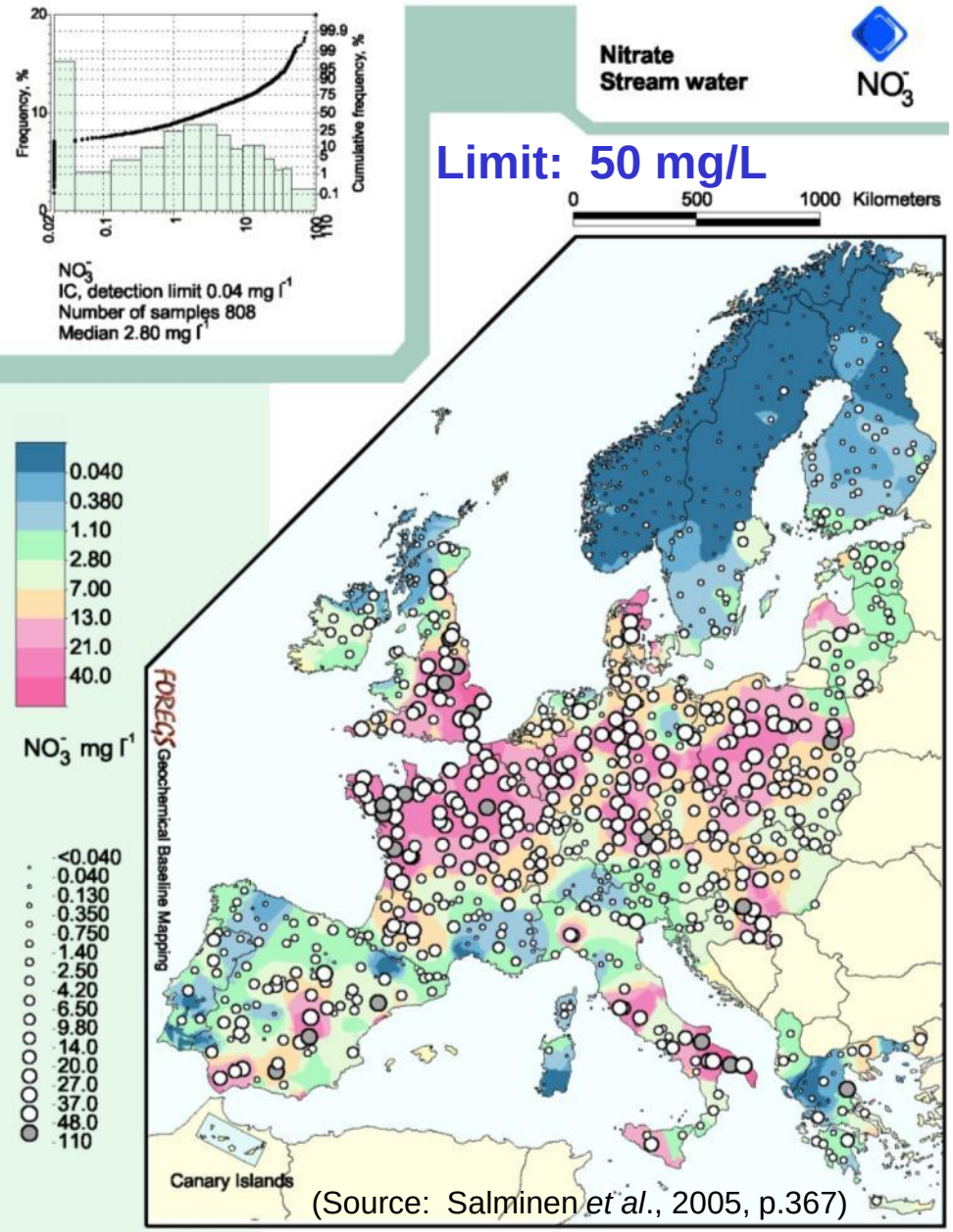
European Federation of Geologists

Geochemical Atlas of Europe



(Source: Salminen *et al*., 2005, p.367)

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

Limit value: 50 mg/L

Drinking water directive 98/83/EC

Natural Mineral water directive 2009/54/EC

The European Environmental Agency got in touch with us asking if a similar high quality geochemical database on groundwater was available

Ground water:

- **It is a difficult medium to sample (contamination issues)**
- **It is difficult to map [3D-regional distribution (aquifers)]**
- **It has a high local variation**

Ground water is, therefore, a medium that it is *impossible to sample systematically* and to analyse at a reasonable cost.

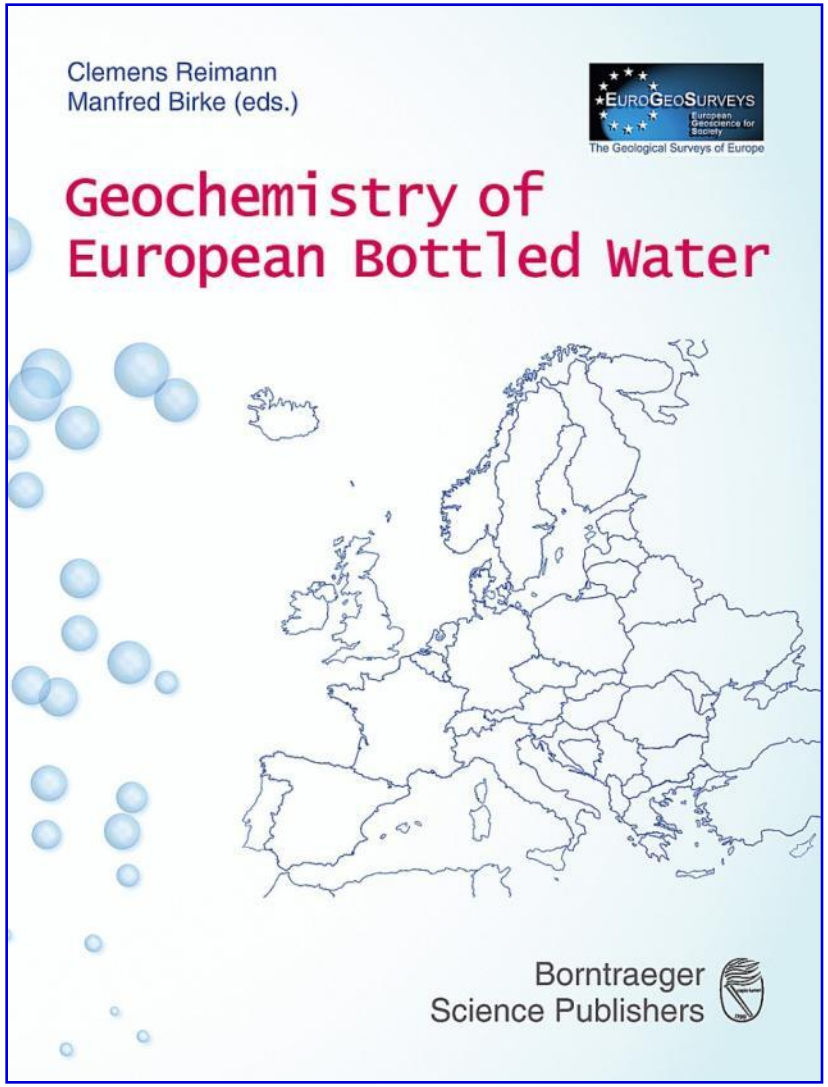
Manfred Birke (BGR)

Project idea:

Ground water can be bought readily sampled at the European scale – more than 1900 bottled mineral water brands are registered in Europe.

According to Manfred's experience, bottled water can be used as a "proxy" to ground water.

Geochemistry of ground water using mineral bottle water as the sampling medium



Publication date: 2010
268 pages
28 diagrams
6 tables
2 appendices
67 determinand distribution maps
CD-ROM with all analytical results, maps and diagrams

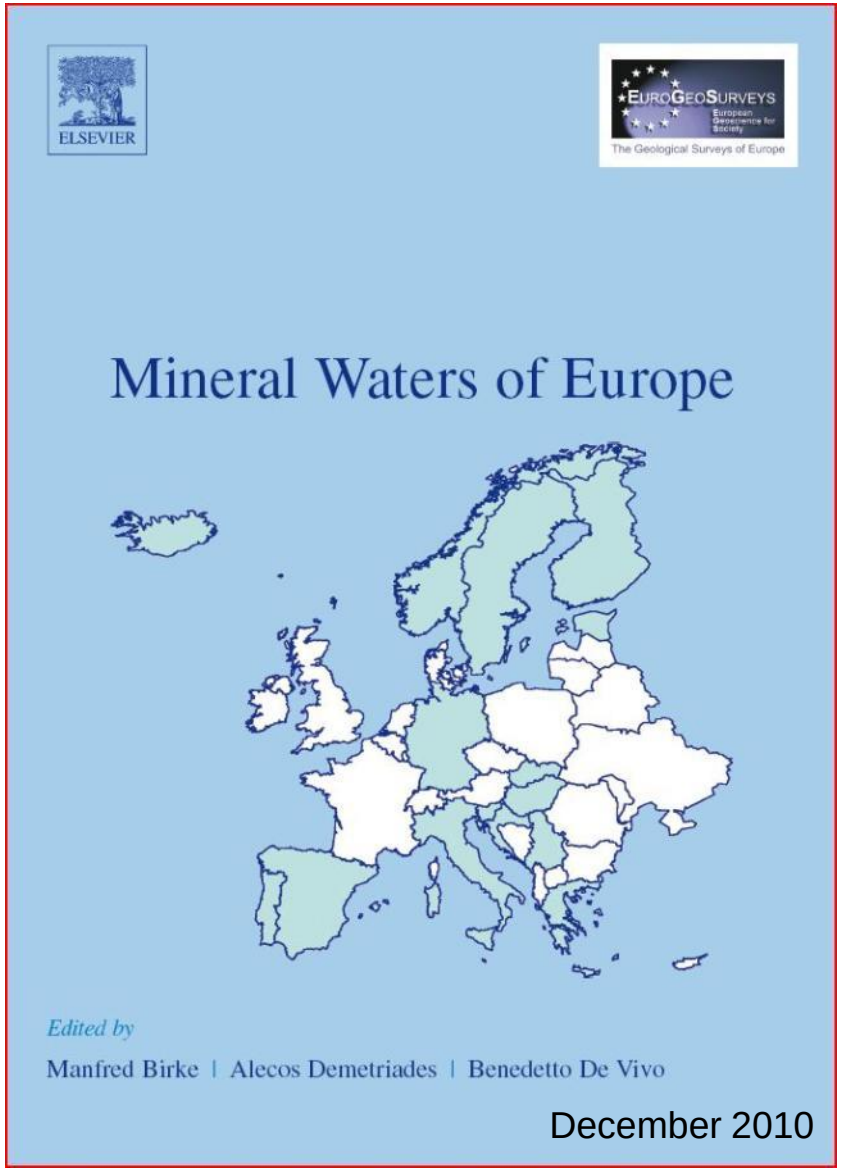
Language: English

ISBN 978-3-443-01067-6

Price: 78.00 €

http://www.schweizerbart.de/publications/detail/artno/001201002#

December 2010



December 2010

http://www.sciencedirect.com/science/journal/03756742/107/3

Atlas of European Ground water Geochemistry

The sampling or purchase of bottled water from supermarkets started in November 2007 and was completed by April 2008.

In total, 1785 "samples" of bottled water were purchased from supermarkets all over Europe (38 countries), representing 1247 boreholes/wells at 884 unique locations.

Sample storage at BGR, Berlin (Source: Reimann & Birke, 2010, Fig. 19, p.30)

Atlas of European Ground water Geochemistry

To obtain a fully harmonised and homogeneous data set all samples were analysed in just one laboratory for 72 parameters.

(Photograph provided by Manfred Birke, BGR, Germany)

Analytical programme, BGR-lab (72 determinands):

ICP-QMS: Ag, Al, As, B, Ba, Be, Bi, Cd, Ca, Ce, Co, Cr, Cs, Cu, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr

ICP-AES: Ba, Ca, K, Mg, Mn, Na, Sr, P, Si

IC: Br^-, Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-}

AFS: Hg

Titration: tAlk - HCO_3^-

Photometric: NH_4^+

Potentiometric: pH

Conductometric: EC

QUALITY CONTROL (1/2)

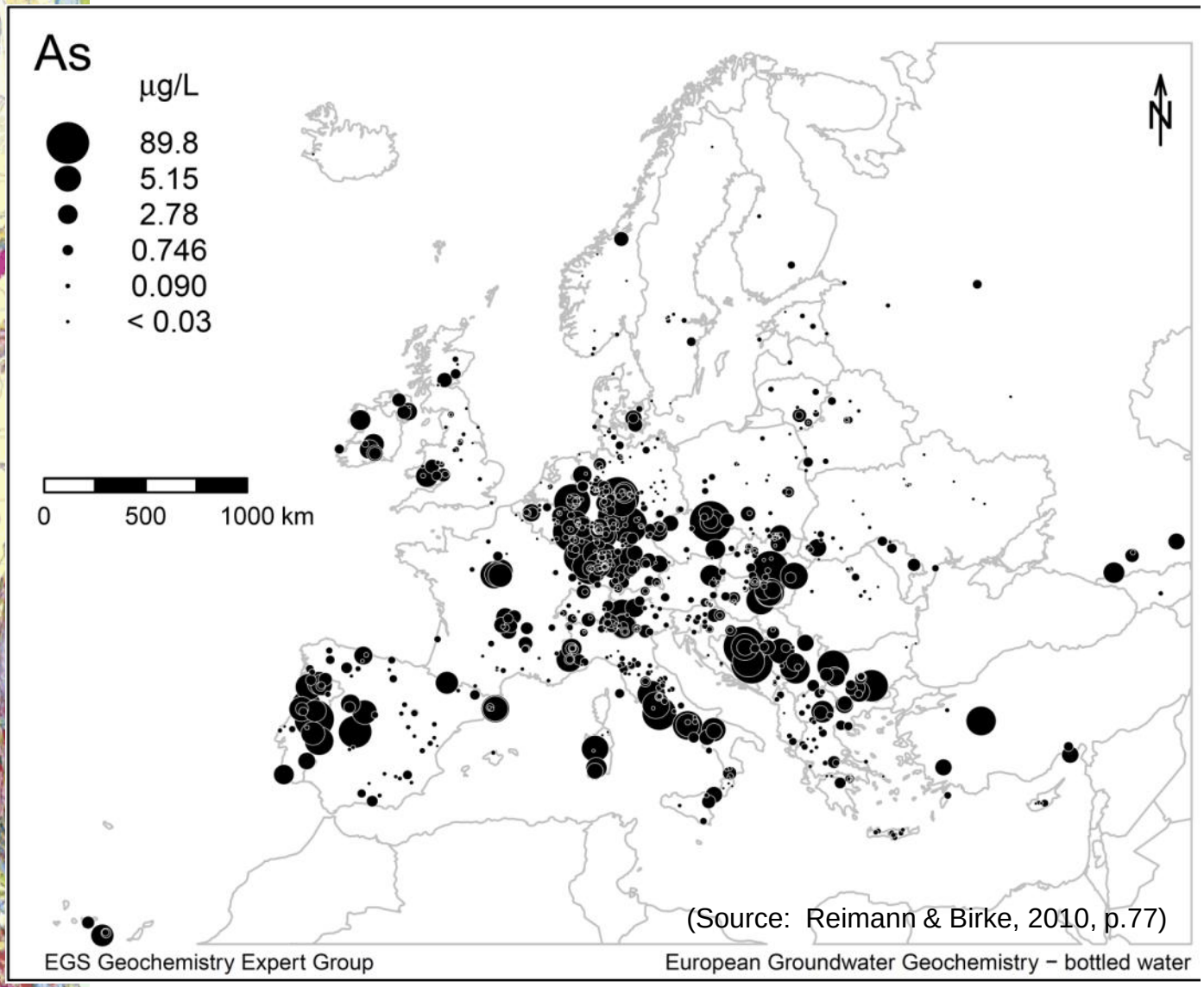
A very strict quality control programme was installed:

(1) Analysis of international reference samples to document the trueness of analytical results;
(2) Frequent analysis of an in-house project standard (MinWas) to check the accuracy of determined parameters;
(3) Frequent analysis of blank samples to detect any contamination issues, and to derive reliable detection limits;
(4) Frequent analysis of sample duplicates to determine precision of measurements;
(5) Comparison of analytical results of this study with those displayed on bottle labels;
(6) Determination of few parameters (Ba, Ca, K, Mg, Mn, Na & Sr) by ICP-QMS and ICP-AES, and Hg by ICP-QMS and AFS;

QUALITY CONTROL (2/2)

(7) Checking of bottled water samples with unusually high results for important parameters by buying another bottle and repeating the analysis.

- Accuracy of methods for most determinands is better than ±10%;
- Bias is within -4.9 to +1.6 for most elements, and
- the repeatability (precision) at the 95% confidence interval is better than ±10% at concentrations an order of magnitude above the detection limit, and for elements close to detection limit it varies between 11 to 29%.



(Source: Reimann & Birke, 2010, p.77)

Arsenic (As):

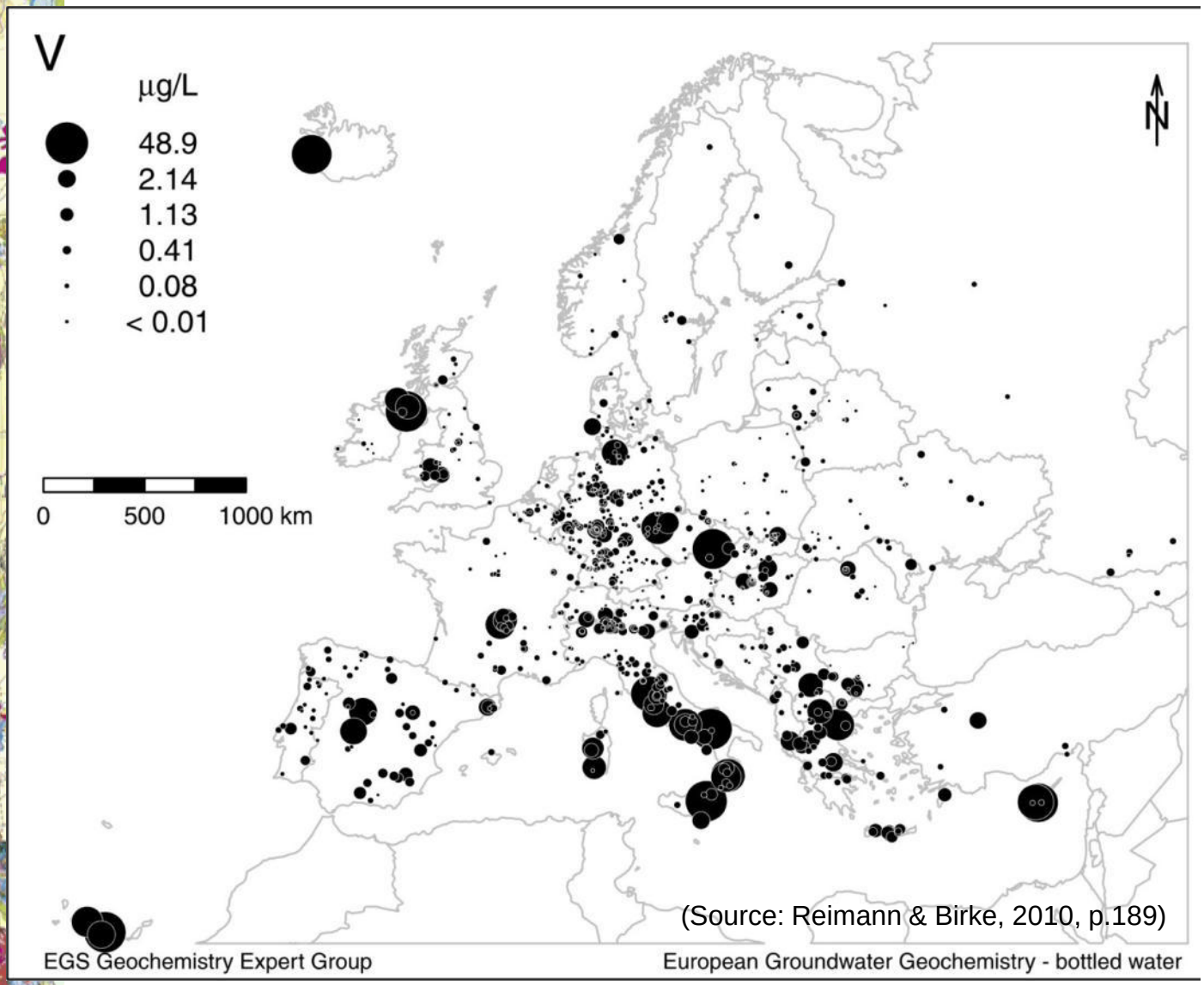
- **Sulphide mineralisation;**
- **fault zones;**
- **alkaline volcanic provinces in Italy.**

Limit value: 10 µg/L

Drinking water directive 98/83/EC

Natural Mineral water directive 2009/54/EC

9 samples have values exceeding the limit set by the drinking and mineral water directives.

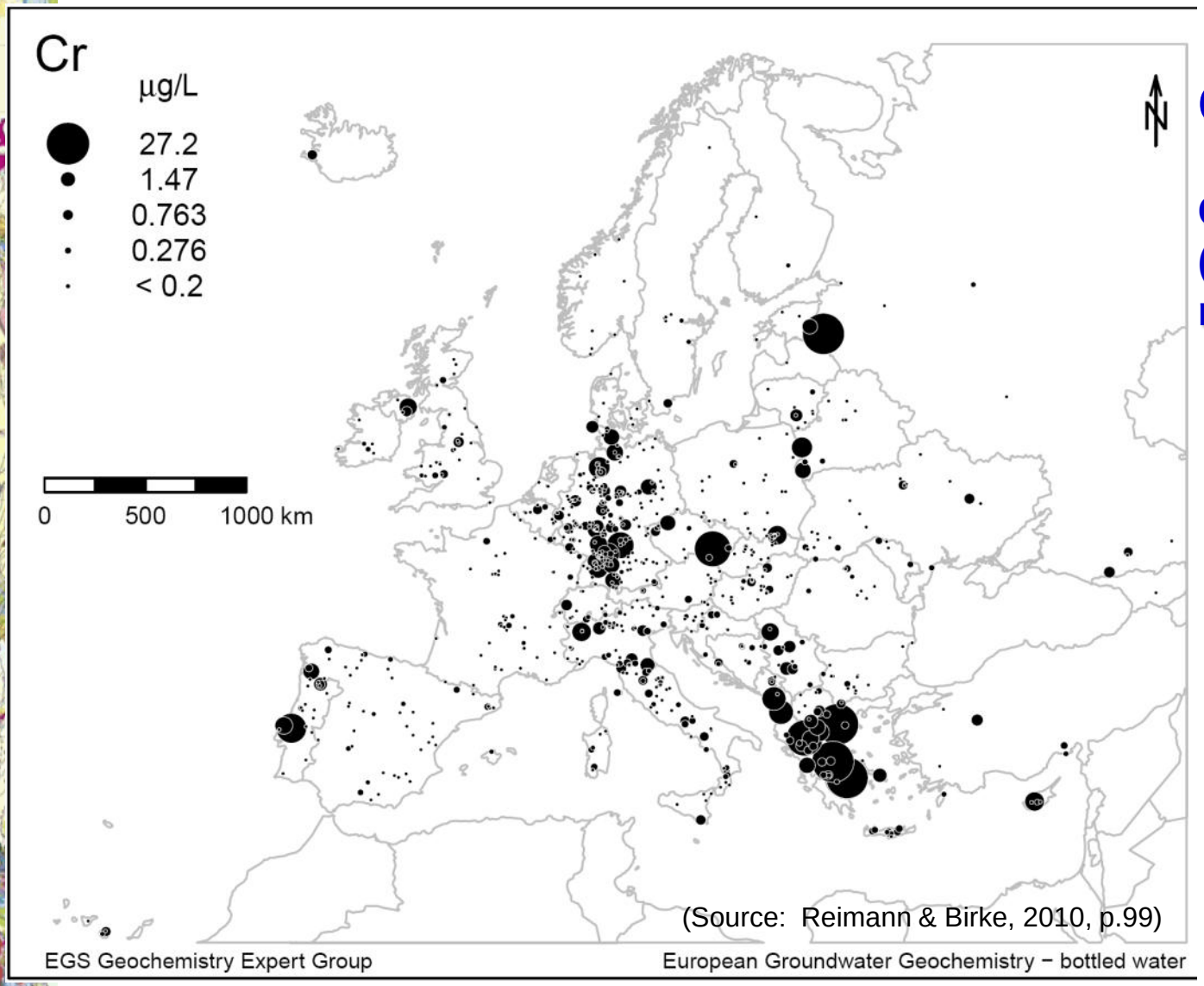


(Source: Reimann & Birke, 2010, p.189)

Vanadium (V):

Active volcanic centres and basaltic rocks are indicated, *e.g.*, Canary Isles, Cyprus, Hellas, Ireland (Antrim Plateau), Italy.

Limit value: none



(Source: Reimann & Birke, 2010, p.99)

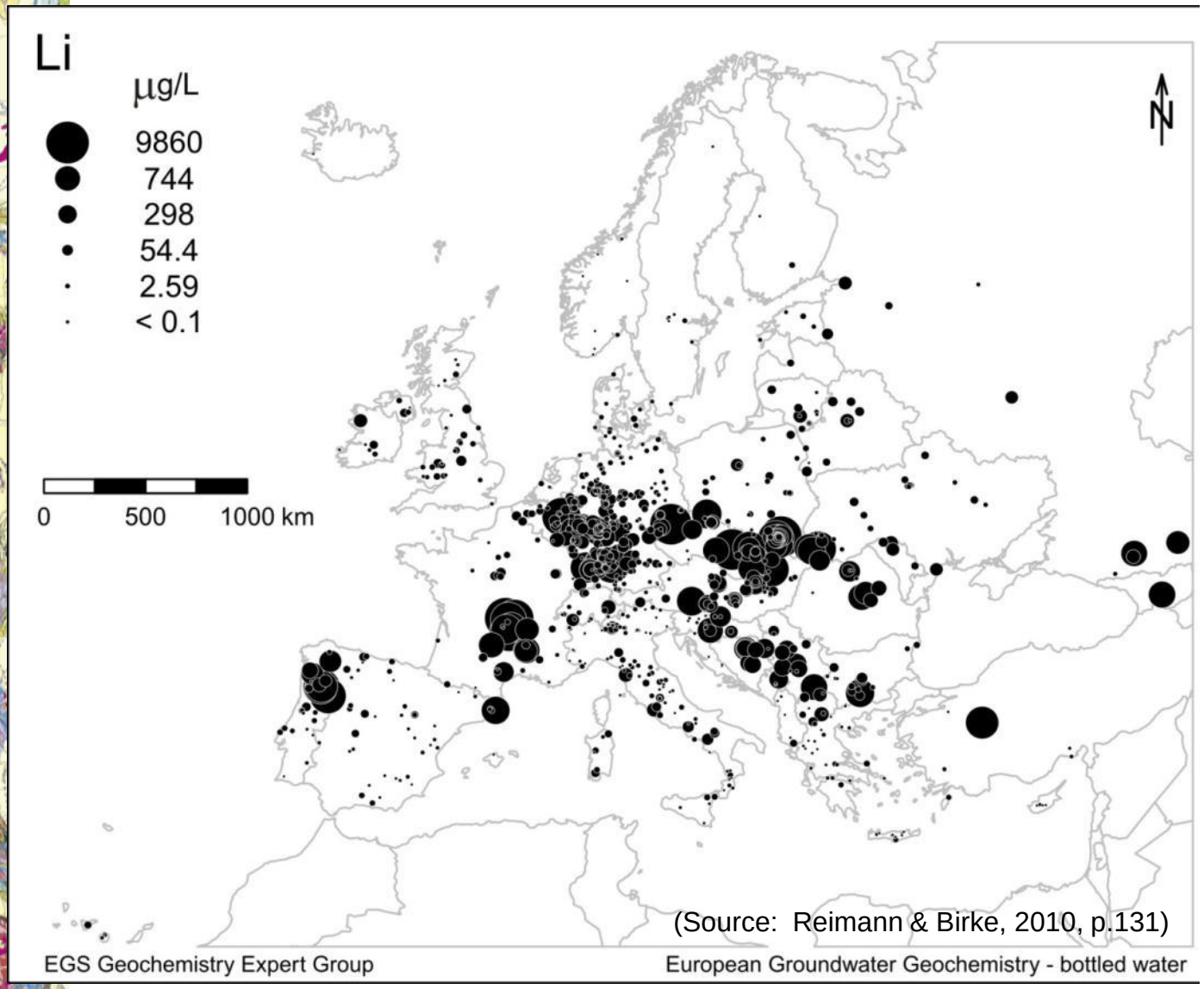
Chromium (Cr):

Ophiolite complexes (mafic-ultramafic rocks)

Limit value: 50 µg/L

Drinking water directive 98/83/EC

Natural Mineral water directive 2009/54/EC

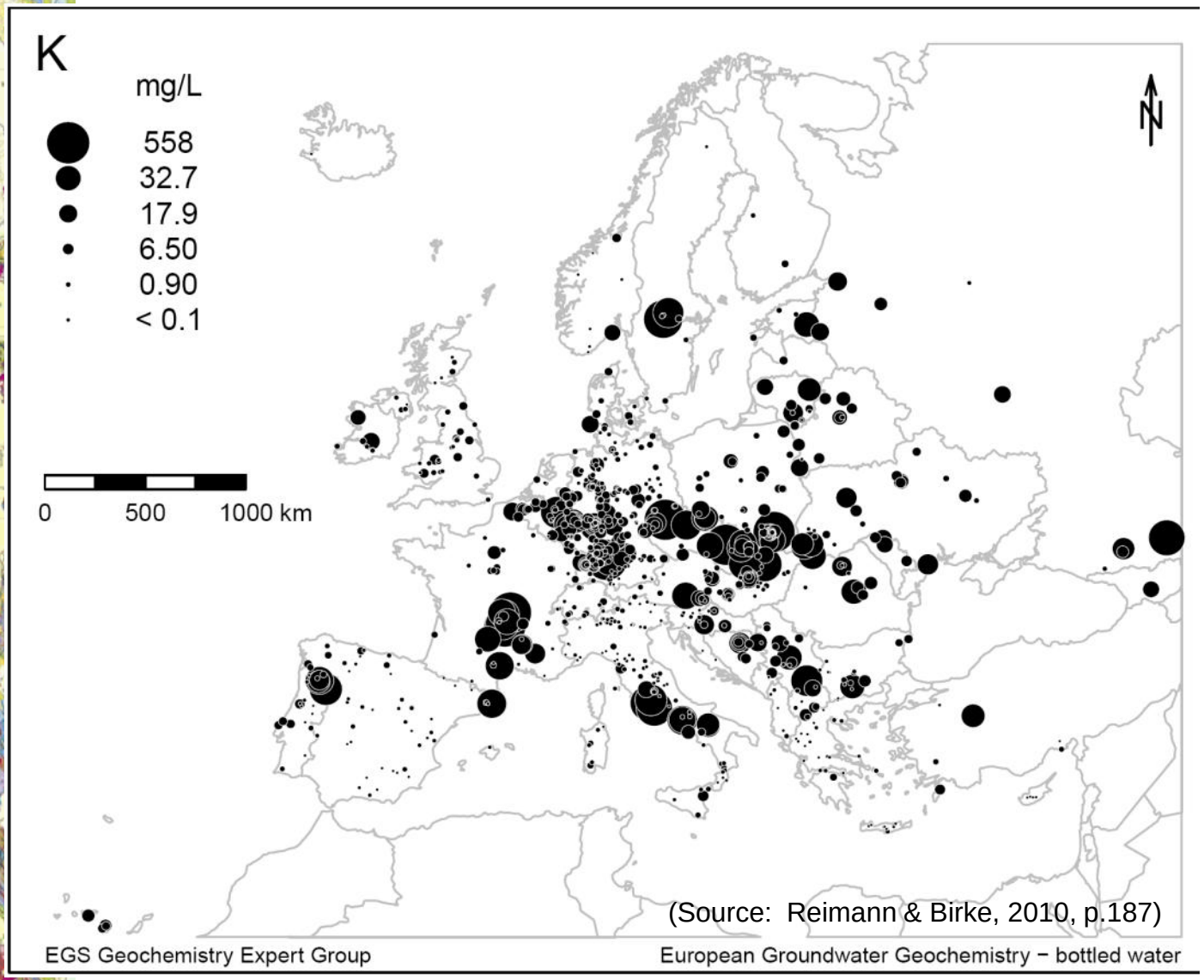


(Source: Reimann & Birke, 2010, p.131)

Lithium (Li):

Hercynian granite masses, Jurassic and Triassic sediments in Germany, and deep sourced water wells, *e.g.*, in the Carpathian Mountain Chain, Dinarides

Limit value: none



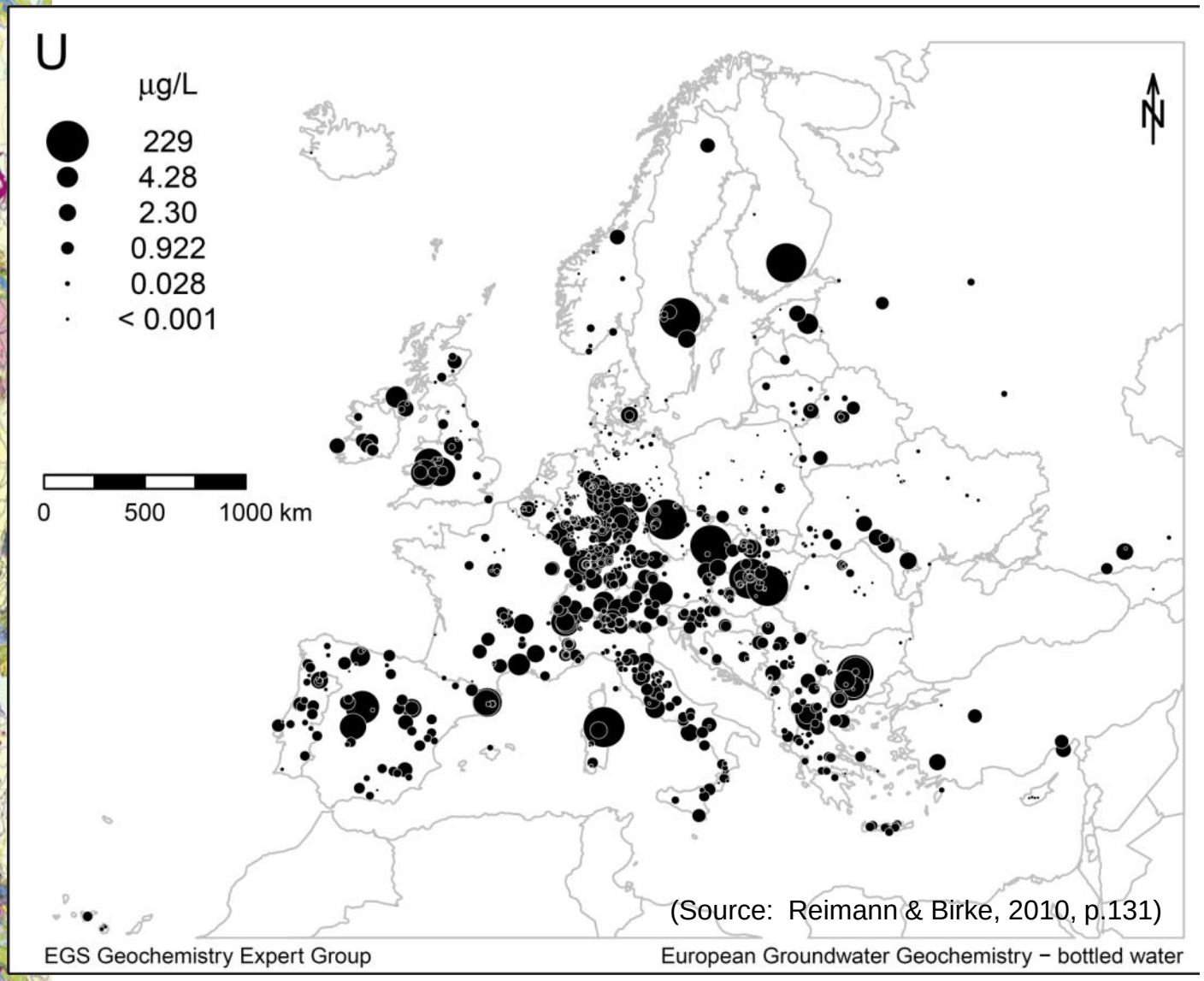
(Source: Reimann & Birke, 2010, p.187)

Potassium (K):

Distribution patterns similar to Li *with some minor differences*

Hercynian granite masses, Jurassic and Triassic sediments in Germany, and deep sourced water wells, *e.g.*, in the Carpathian Mountain Chain, *Alkaline volcanic provinces in Italy*

Limit value: none

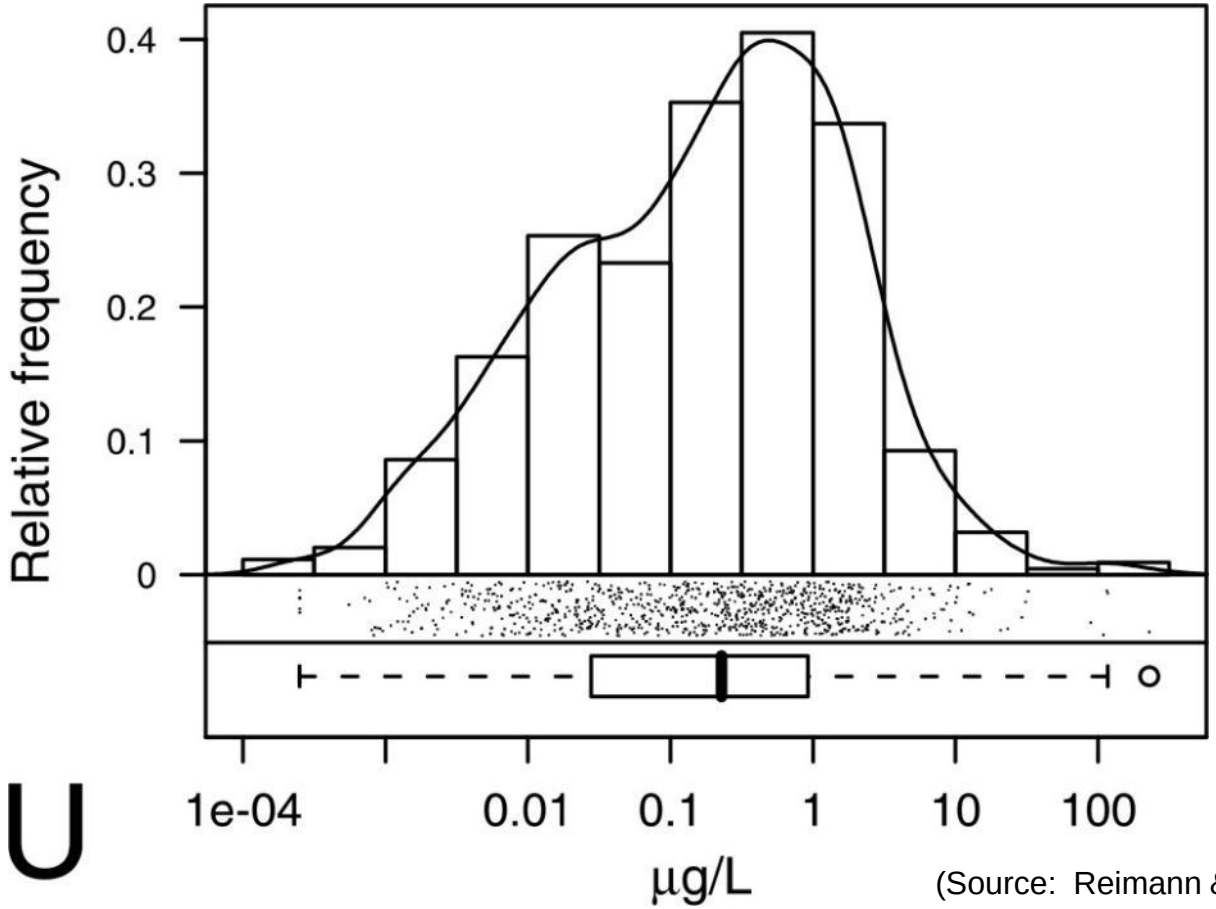


(Source: Reimann & Birke, 2010, p.131)

Uranium (U):

Granitic bedrock (*e.g.* , Sardinia, Sweden, Finland) or in sandstone (Keuper and Bunter formations)

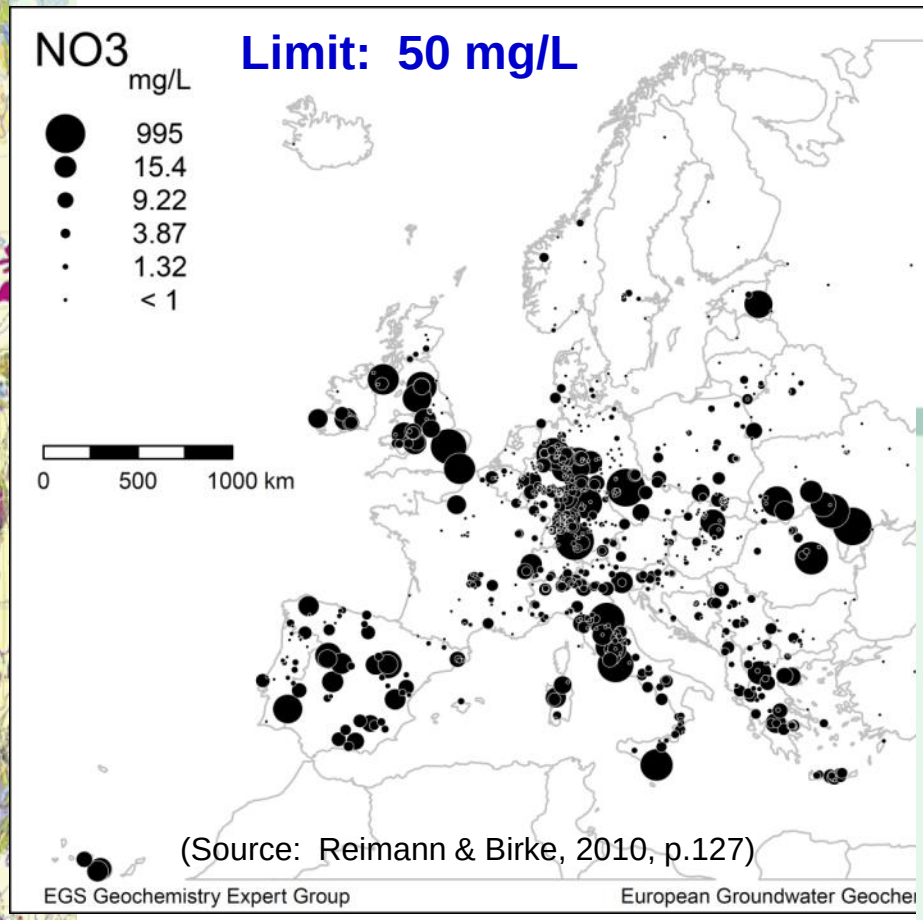
Limit value: none in EU countries



(Source: Reimann & Birke, 2010, p.187)

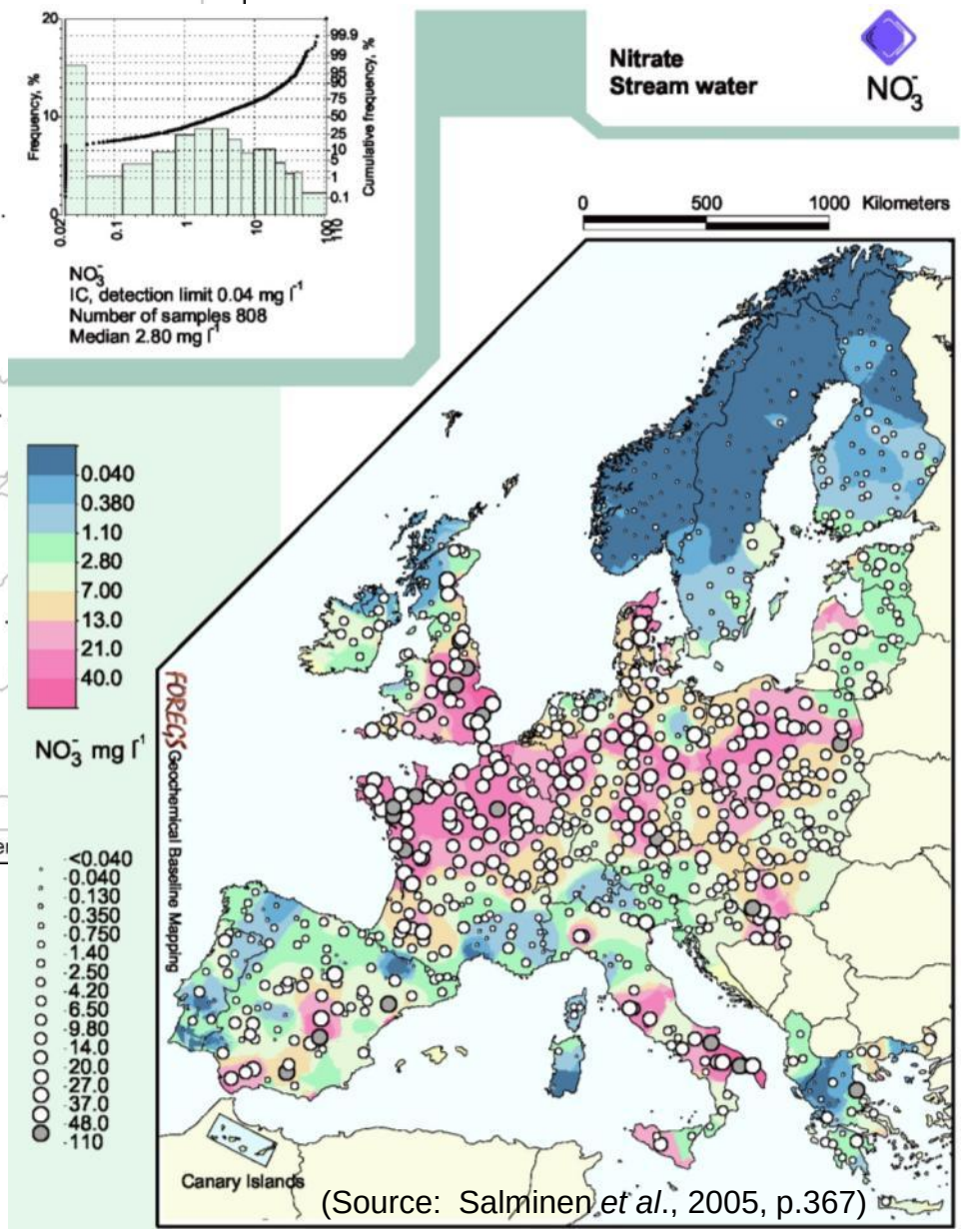
Distribution of U in samples of bottled water (N = 884). Observe the sudden drop of values at 10 µg/L.

The World Health Organisation has proposed a guideline value of 15 µg/L and it appears that the bottling companies are observing this limit.



Limit: 50 mg/L

(Source: Reimann & Birke, 2010, p.127)

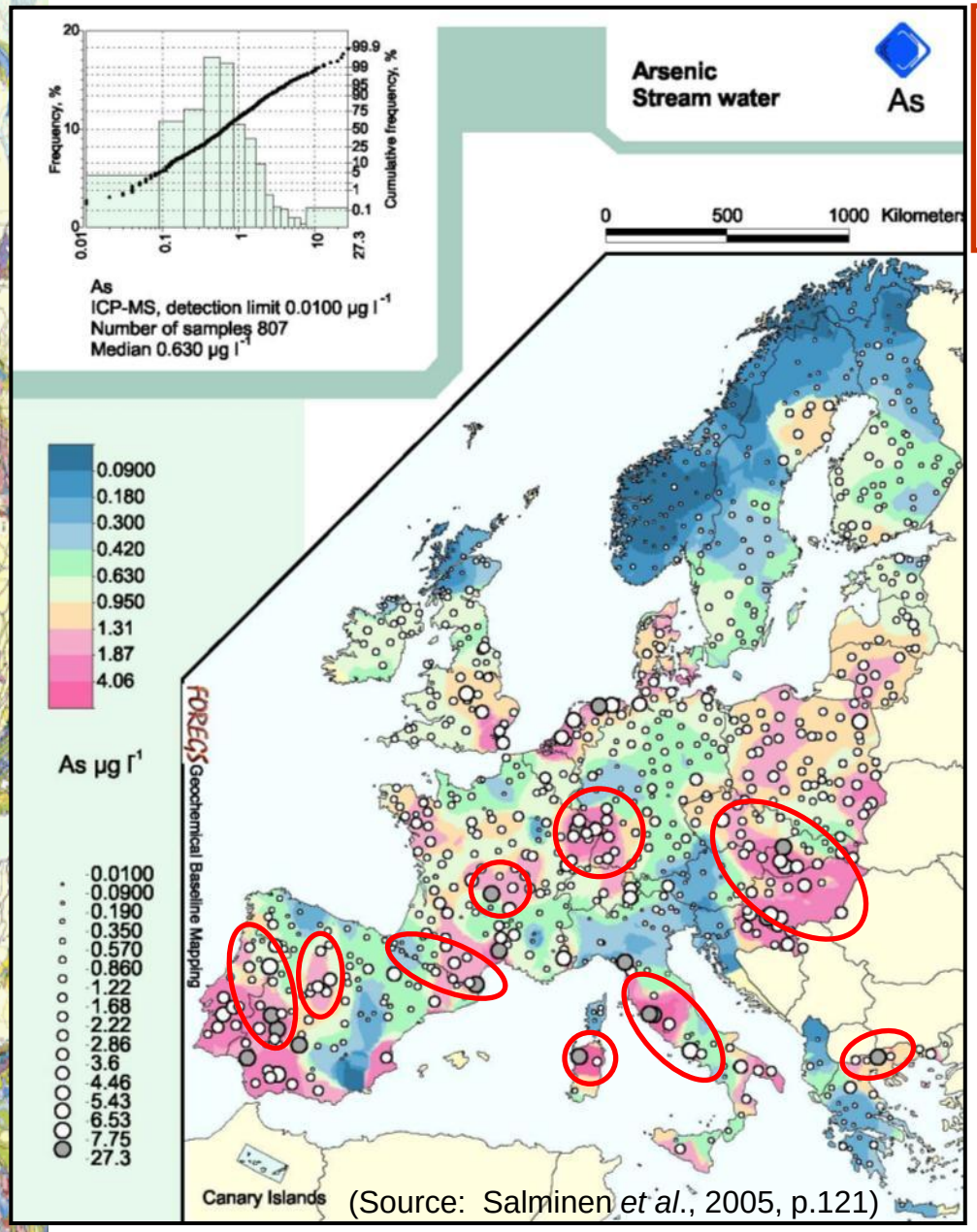


(Source: Salminen *et al.*, 2005, p.367)

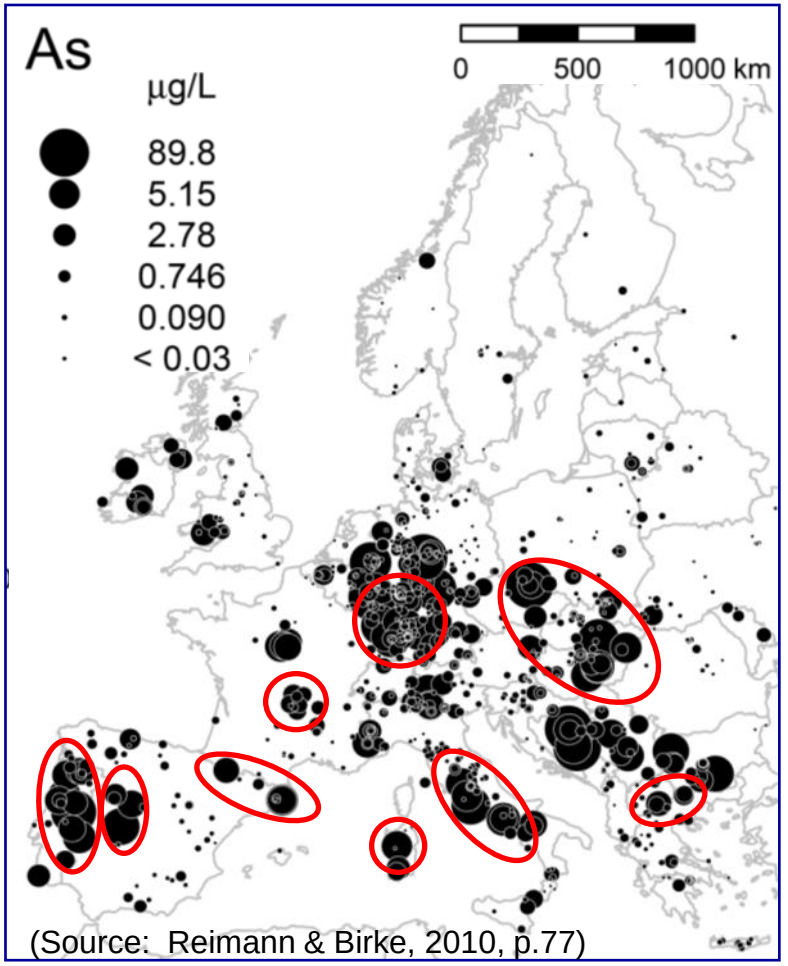
Nitrate concentrations in stream- and ground-water are elevated in central Europe, possibly due to intensive agriculture

Only two bottled water samples have values >50 mg/L

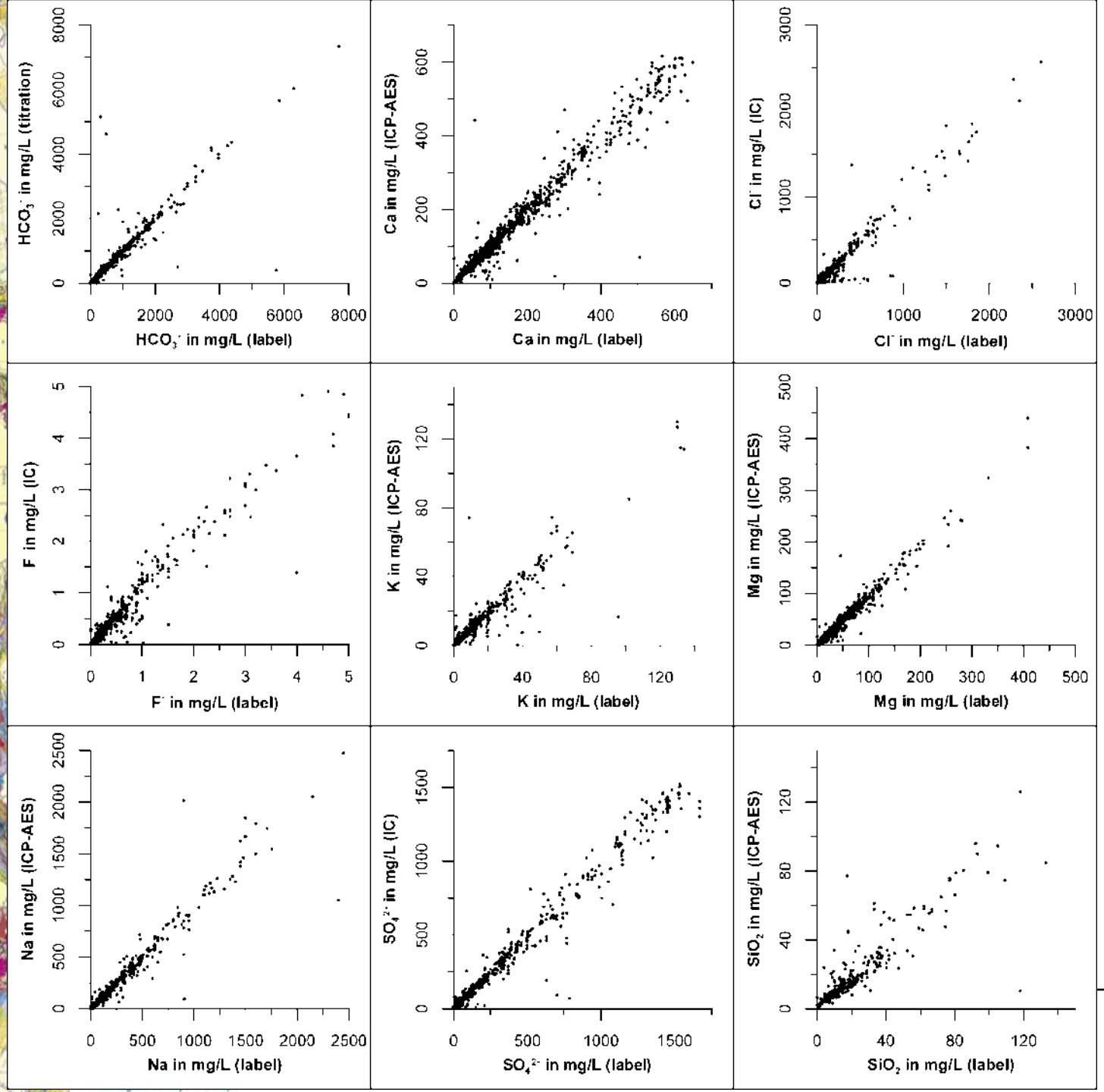
An interesting relationship of As in surface- and ground-water



(Source: Salminen *et al.*, 2005, p.121)



(Source: Reimann & Birke, 2010, p.77)



Comparison of analytical data of the EuroGeoSurveys study with those displayed on bottle labels show a fairly good linear correlation.

Chemical composition stability over time of source aquifers for mineral bottle water is a necessary prerequisite of European legislation

(Source: Reimann & Birke, 2010, Fig. 20, p.44)

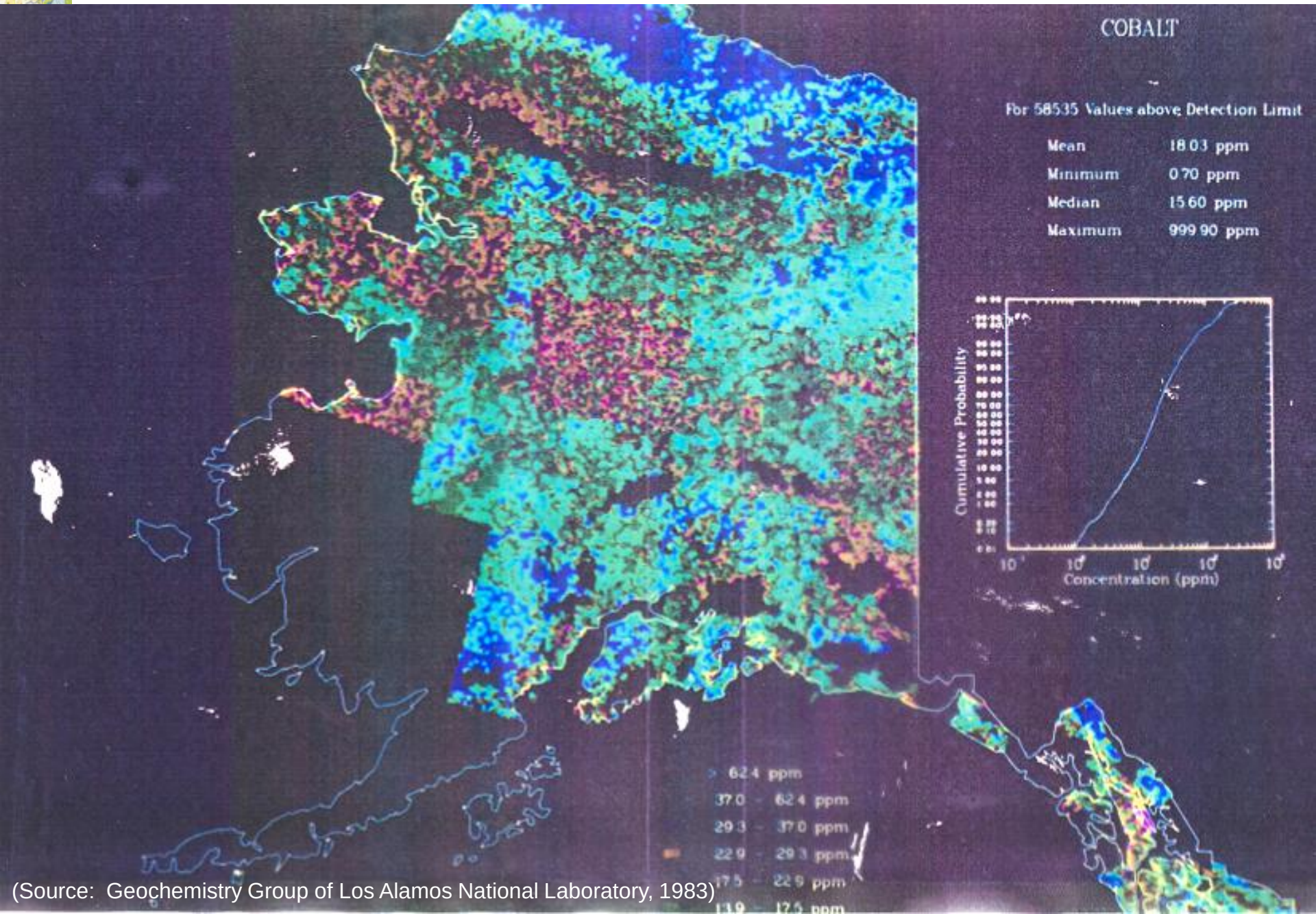
Conclusions (1/6)

- **The only harmonised and homogeneous geochemical databases that exist in Europe at the present time for surface- and ground-water are the ones that were developed by the Geochemistry Expert Group of EuroGeoSurveys.**
- **The geochemistry of stream water of the Geochemical Atlas of Europe provides the end of 20th century time line for comparison with future surveys about the state of surface water in Europe.**
- **The geochemistry of ground water, as depicted by bottled mineral water samples, provides the 2007-8 time line for comparison with future surveys about the state of ground water in Europe.**
- **These databases provide the general continental scale picture, which forms the necessary background for the more detailed studies carried out at the catchment basin level.**

Conclusions (2/6)

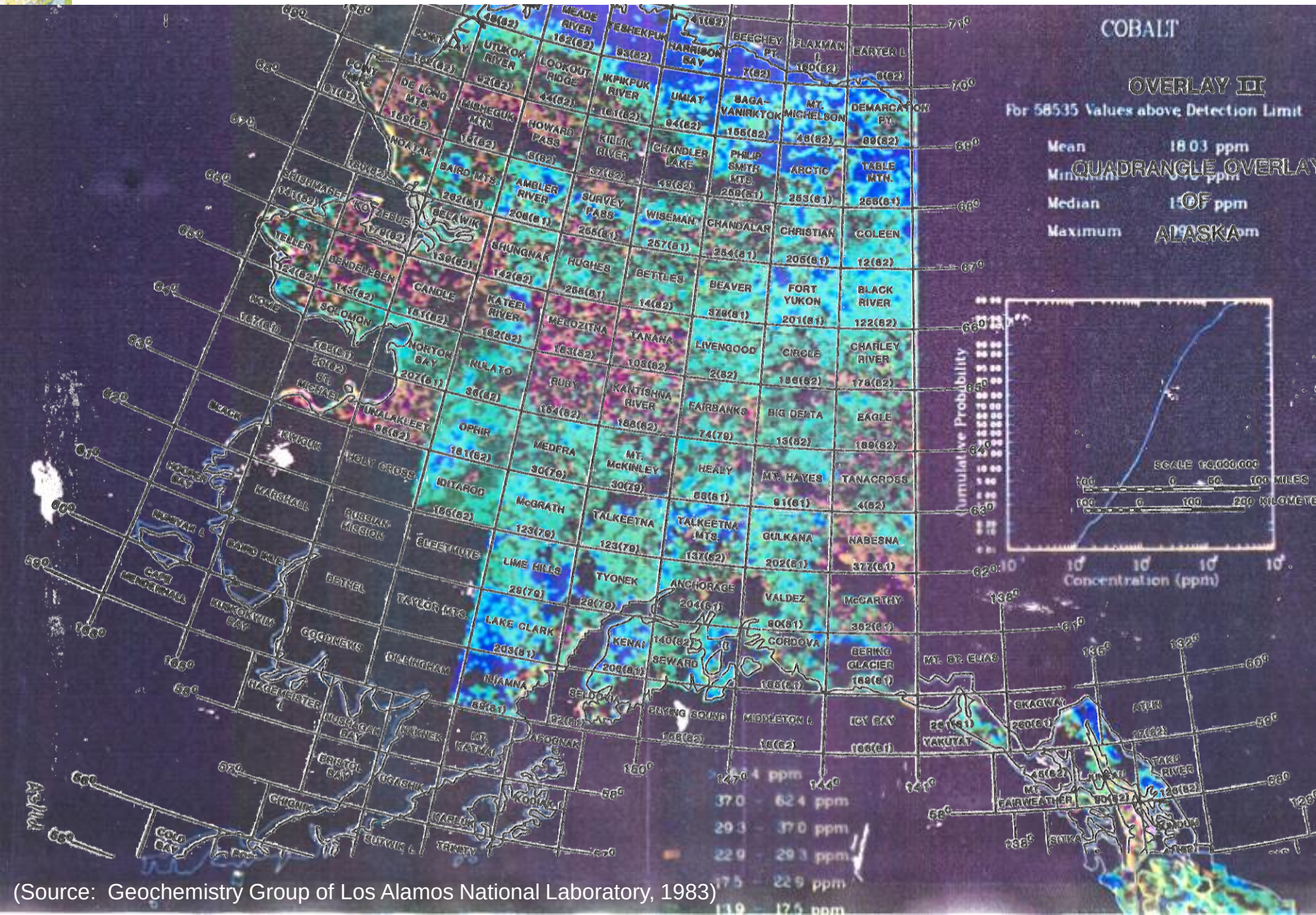
- "*Low density geochemical sampling and mapping*", as developed during the last 15-20 years for detecting large-scale geochemical processes at the Earth's surface, can also be applied to ground water.
- Geochemical mapping at the continental scale permits cost-effective selection of scale and location of monitoring sites.
- To obtain a fully harmonised and homogeneous data set at the European scale for both surface- and ground-water high-quality measurements in a single laboratory are required.
- Also, strict quality control procedures from sampling in the field to laboratory analysis, must be installed, otherwise serious issues will emerge about the validity and integrity of the data as the following:

Geochemical Survey of Alaska – Cobalt (Co)



(Source: Geochemistry Group of Los Alamos National Laboratory, 1983)

Geochemical Survey of Alaska – Cobalt (Co)



(Source: Geochemistry Group of Los Alamos National Laboratory, 1983)

Conclusions (3/6)

- **In the majority of cases, elevated concentrations in stream water are related to geogenic sources and climatic factors, except in the case of NO_3^- in central Europe, which is ascribed to agricultural practices, and locally stream water is polluted by industrial activities.**
- **Natural variation is enormous for both surveys and for most elements, usually 3-5 and for a few elements up to 7 orders of magnitude, were observed.**
- **Some brands of "natural bottled mineral water" are enriched in Ag, B, Be, Br, Cl, Cs, F, Ge, I, K, Li, Na, Rb, Sr, Te, Tl & Zr, and are clearly not representative of "normal" shallow groundwater, and the high values are typical of "mineral water" from deep aquifers.**
- **For most elements, the bottled mineral water data set provides a realistic picture of their median value and variation in (ground)water at the European scale.**

Conclusions (4/6)

- **When discussing water quality, natural variation must be documented first; the present focus on "pollution" is misleading in view of the observed high background variation.**
- **It may be necessary to study more seriously the problems that are related to deficiency in ground water, since water is an important source of elements, such as F, I, Se, Ba.**
- **Using bottled mineral water as a 'proxy' for ground water was more successful than initially anticipated.**

Conclusions (5/6)

Geological characteristics which are visible on the geochemical maps include:

- **ophiolites (Cr, V)**
- **Alkaline volcanics, and generally areas of active volcanicity (Al, As, Be, F, K, Mn, Mo, P, Rb, Se, Si, Tl, V)**
- **Hercynian granite (Al, B, Be, Cs, F, Ge, K, La, Li, Rb, Si, Sn, tAlk, Th, Ti, Zr)**
- **Deep structures (Sr)**
- **Deep sedimentary basins (B, Ba, Br, Cl, I, K, Li, Mg, Na)**

Conclusions (6/6)

- **Bottled water standards: The majority of bottled water brands fulfil the requirements of European Union legislation for mineral (and drinking) water. However, for some determinands, a few brands of bottled water exceed the potable water standards, *e.g.*, the maximum values observed for Al, As, Ba, F^-, Mn, Ni, NO_2^-, NO_3^-, Se and U.**

- **Comparison of bottled mineral water analytical results of the EuroGeoSurveys project with those displayed on bottle labels show a fairly good linear correlation, suggesting *chemical stability of source aquifers over time*, a necessary prerequisite of European legislation for bottled mineral water.**

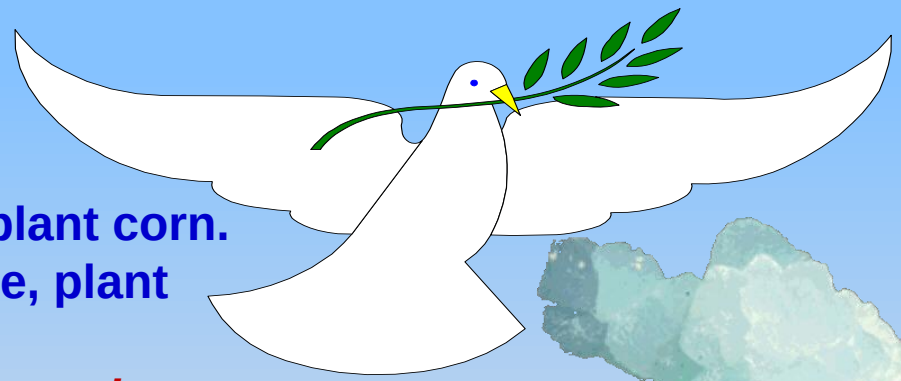
Finally, the Geochemical Atlas of Europe and the new bottled-(ground-)water atlas provide European policy makers, scientists and other interested parties with valuable information about the geochemistry of stream- and ground-water at the continental scale.

Recommendations

- **Directive 2000/60/EC: "*Water is not a commercial product like any other but, rather, a heritage which must be protected, defended and treated as such*." We should, therefore, treat it as such, and water distribution companies should be managed by State-run companies without profit (*i.e.*, running costs and modernisation of infrastructures).**
- **A single State institution should be responsible for the monitoring of the quantity and quality of surface- and ground-water resources, since there is an agreement that there is an interaction between surface- and ground-water.**
- **Since, it is impossible to propose the analysis of all surface- and ground-water samples in a single central European laboratory, one laboratory in each country must be responsible. If possible the same analytical instruments and methodologies should be used, and inter-laboratory validation checks made.**

Quotations:

- *"When the well is dry, we know the worth of water"* **(Benjamin Franklin)**
- *"Anyone who can solve the problems of water will be worthy of two Nobel prizes - one for peace and one for science"* **(John F. Kennedy, President of U.S.A.)**



Chinese proverb:

- **When planning for a year, plant corn.**
- **When planning for a decade, plant trees.**
- ***When planning for life, train and educate people.***

Thank you for your attention

http://www.eurogeologists.de/

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http://www.eurogeosurveys.org/

European Federation of Geologists

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EUROPEAN FEDERATION OF GEOLOGISTS

EFG WORKSHOP

European water policy: challenges for Hydrogeologists

Date: 22-23 November 2013

Venue: Royal Belgian Institute of Natural Sciences, Rue Vautier 29, 1000 Brussels, Belgium

Organised by

European Federation of Geologists
(http://www.eurogeologists.de/)

Supported by: International Association of Hydrogeologists (http://iah.org/); EC Water supply and sanitation Technology Platform (http://www.wsstp.eu/); EuroGeoSurveys (http://www.eurogeosurveys.org/); Geological Survey of Belgium (http://www.naturalsciences.be/geology); Museum of Natural Sciences (http://www.naturalsciences.be/)

Presentation on Saturday, 23rd November 2013