EGG: European Groundwater Geochemistry

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Fellow of the Society for Environmental Geochemistry and Health

EuroGeoSurveys
European Geoscience for Society
The Geological Surveys of Europe

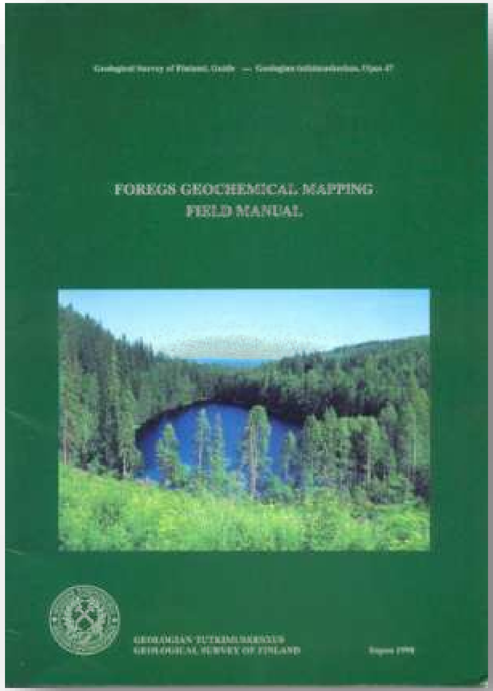
European Groundwater Geochemistry

http://www.eurogeosurveys.org/
Geochemistry Expert Group

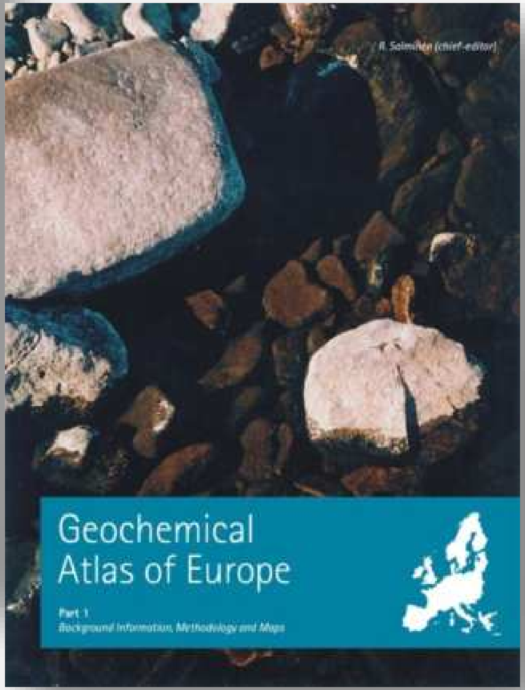
EGG: European Groundwater Geochemistry – Seminar Contents

FOREGS Geochemical Atlas of Europe

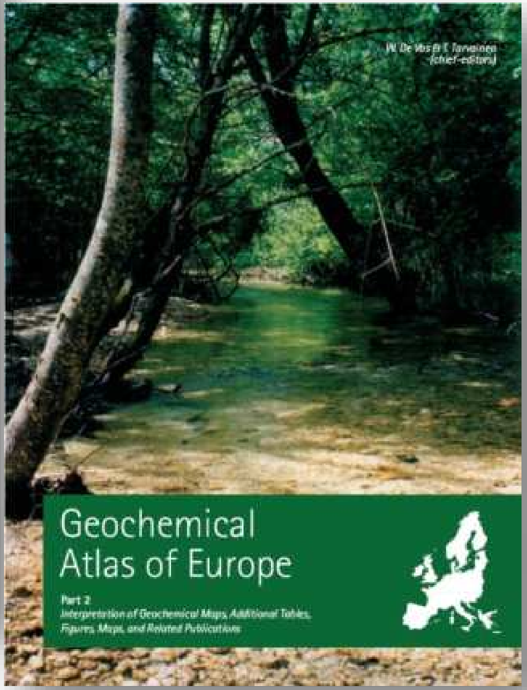
1998



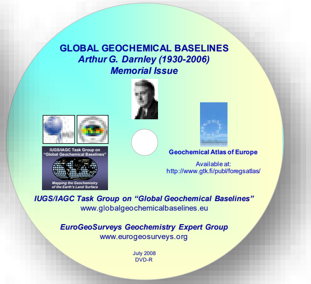
2005



2006



https://tupa.gtk.fi/julkaisu/opas/op_047.pdf



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

Work of the EuroGeoSurveys Geochemistry Expert Group

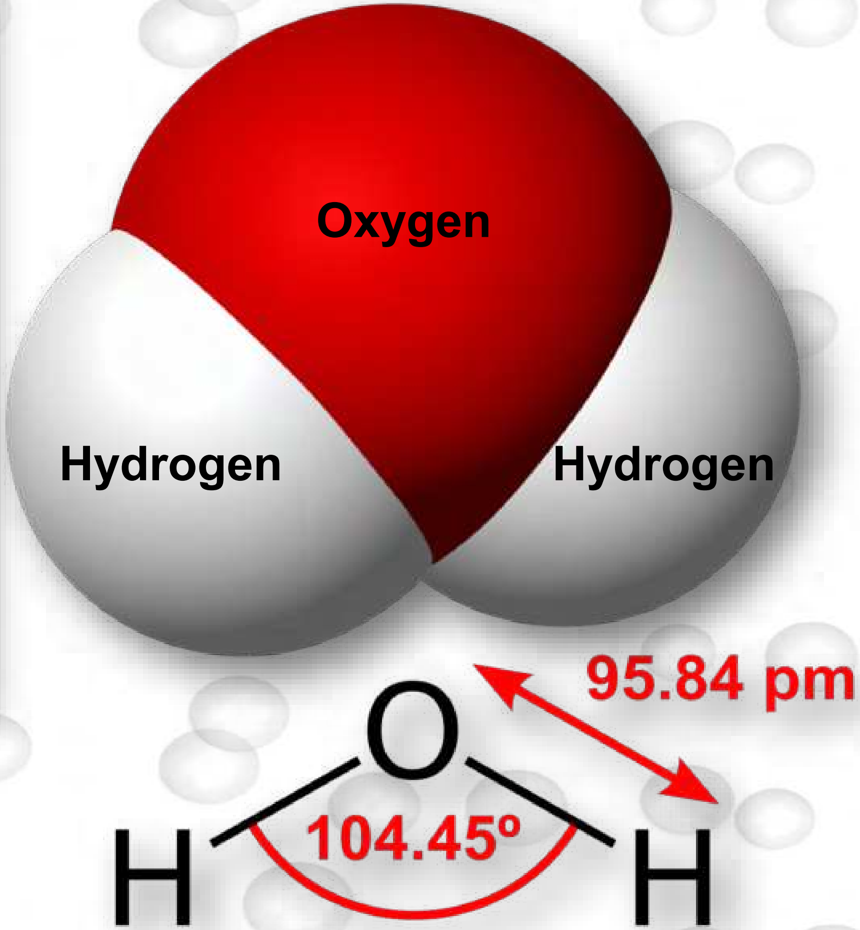
Collected sample types:

- Stream water
- Stream sediment
- Floodplain sediment (0≈25 cm)
- Topsoil (A horizon: 0≈25 cm)
- Subsoil (C horizon >75 cm)

Missing: Groundwater

Castalia spring,
Delphi, Hellas

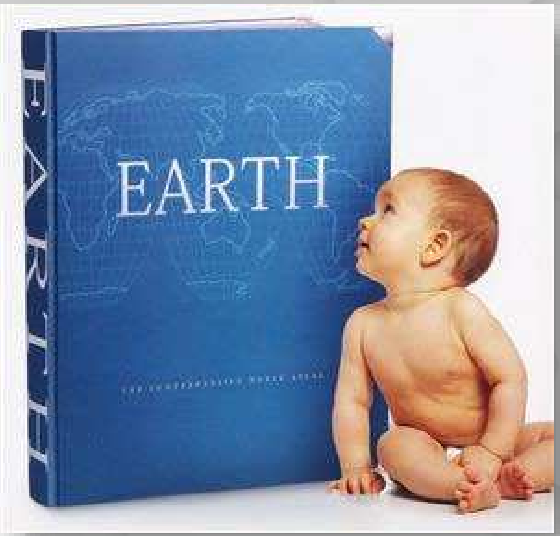
Water is the most valuable natural resource for our quality of life



H_2O

http://en.wikipedia.org/wiki/Properties_of_water

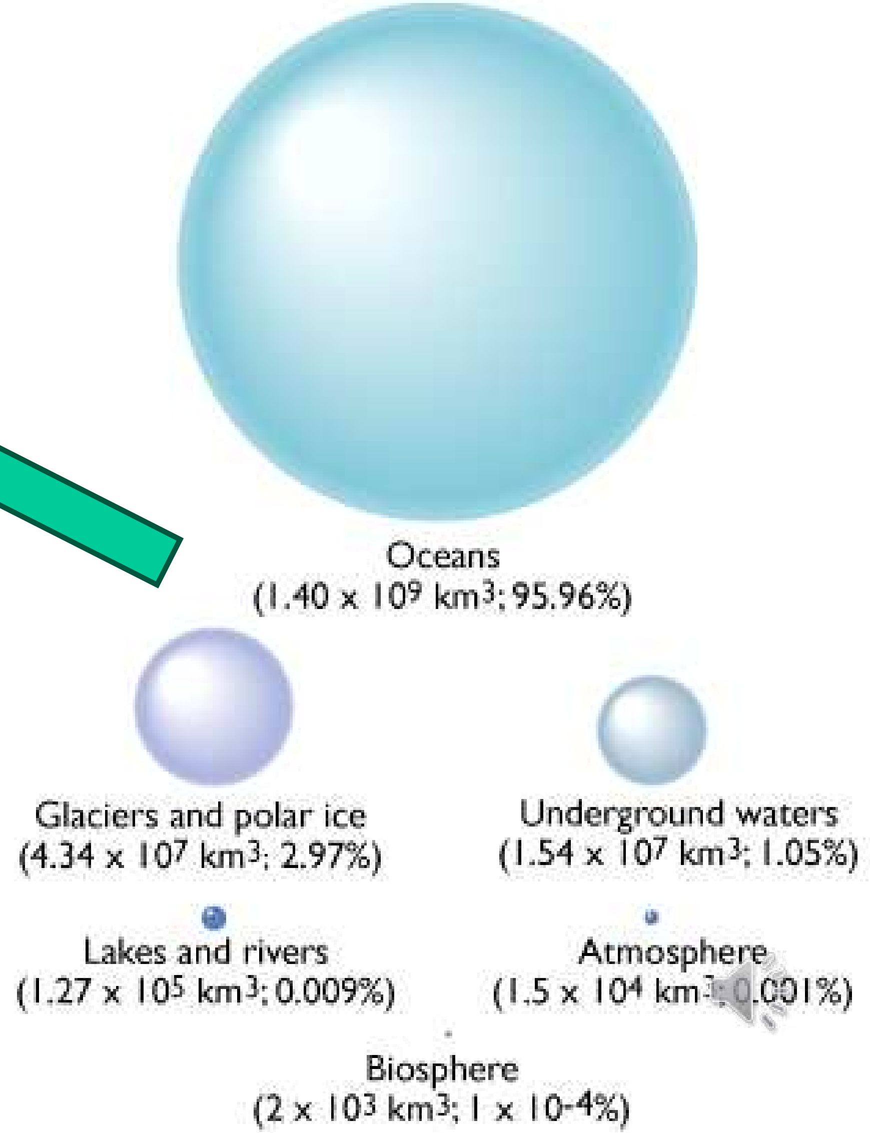
https://www.weforum.org/agenda/2024/02/wildlife-photographer-2023-polar-bear/



Distribution of water on Earth

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

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



According to Press and Siever (2002):

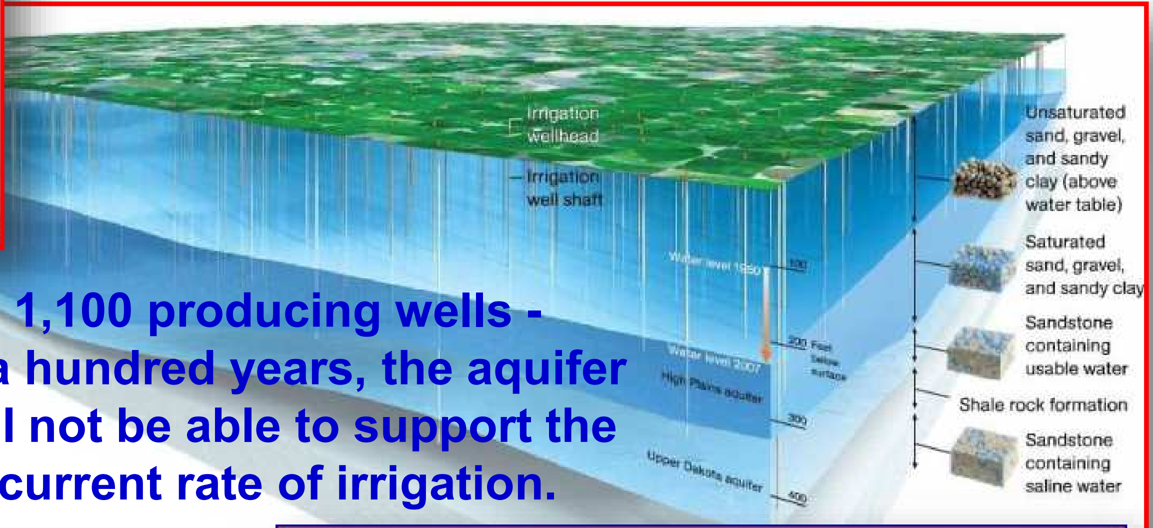
- **≈96% of the water on Earth is salty and is in the oceans and seas,**
- **≈3% is in glaciers and polar ice, and**
- ***slightly more than 1% is fresh and available for use*.**

Available fresh water and its use

- *"Nearly 70% of the World's fresh water is locked in ice.*
- *Most of the remaining is in aquifers that we are draining much more rapidly than the natural recharge rate.*
- *Two-thirds of our water is used in agriculture to grow our food.*
- *With 83 million more people on Earth each year, water demand will keep going up, unless we change the ways we use it."*

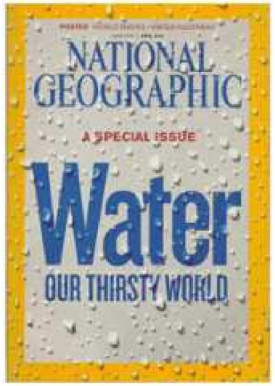
[Photograph on p. 53]

Haskell County aquifer, Kansas, U.S.A.
Nation's breadbasket



1,100 producing wells - In a hundred years, the aquifer will not be able to support the current rate of irrigation.

[Figure on pp. 130-131]



(National Geographic, April 2010. Water our thirsty World - A special issue:- text on p.52)

Imperial Valley, California, U.S.A.

[Photograph on pp. 136-137]

Human interference on the hydrological cycle

According to Press and Siever (2002, p.257):

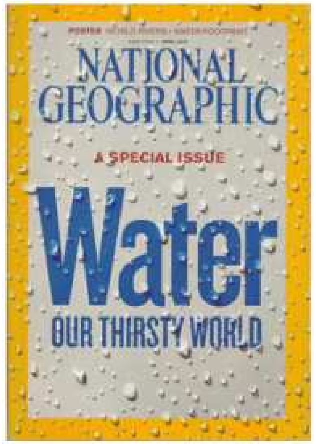
"Human activities constitute a massive interference in the operations of the natural hydrological cycle. Some of these interferences are:

- ***Evaporation is increased by the use of irrigation waters in dry areas.***
- ***Runoff patterns are altered where water is diverted from one region to another.***
- ***Paving that covers the Earth's surface with motorways, car parks, and buildings decreases infiltration.***
- ***Human contribution to global and local warming can lead to melting of glacial ice and changes in the balance of water in the other reservoirs.***

As threats of water shortages loom, water usage enters the arena of public policy debate."

Water and health

- *"One out of eight people lacks access to clean water.*
- *3.3 million people die each year from water-related health problems.*
- *Washing hands with soap can reduce diarrheal disease by 45%.*
- *An eradication campaign that includes a simple water filter has reduced the number of guinea worm cases by 99.9% since 1986."*

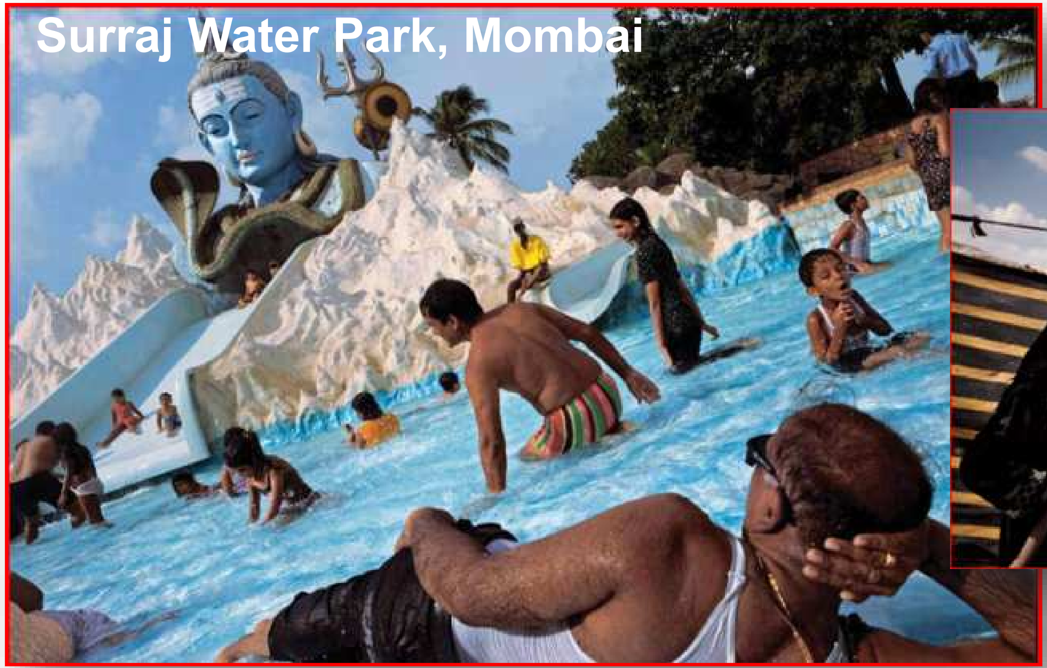


(National Geographic, April 2010. Water our thirsty World - A special issue:- text on p.112)

Well in the village of Natwargadh, Gujarat, India [Photograph on pp. 16-17]

[Photograph on p. 28]

Surraj Water Park, Mombai



[p.56-57]

Palestine

[p. 166]

Slum dwellers in Delhi, India

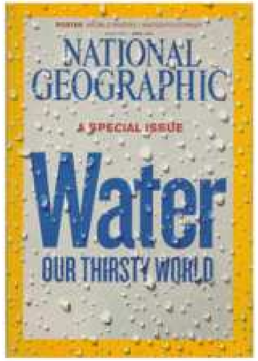
[p. 75]

Gabra women in northern Kenya walk every day up to 5 hours for their water

[pp. 96-97]

Rendille villagers in northern Kenya

[pp. 101-102]



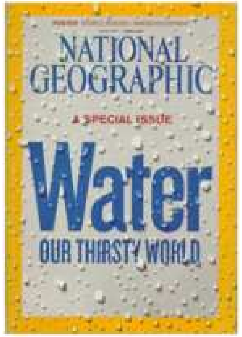
(National Geographic, April 2010. Water our thirsty World - A special issue)

Chemical element prevalence in the Human Body (listed by percentage)

Oxygen	65.0%
Carbon	18.5%
Hydrogen	9.5%
Nitrogen	3.3%
Calcium	1.5%
Phosphorus	1.0%
Potassium	1.0%
Sulphur	0.3%
Sodium	0.3%
Chlorine	0.2%
Magnesium	0.05%
Iron	0.01%
Fluorine	< 0.01%
Zinc	< 0.01%
Silicon	< 0.01%
Rubidium	< 0.01%
Strontium	< 0.01%
Bromine	< 0.01%
Lead	< 0.01%
Copper	< 0.01%

Oxygen + Hydrogen: 74.5%

Milk, egg, vegetables and human blood consist of 70 to 93% of water



The body of this baby in the swimming pool is 75% water.

(Photograph: National Geographic, April 2010. Water our thirsty World - A special issue, p.45)

2005-2015
UN 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***" (https://unesdoc.unesco.org/ark:/48223/pf0000129556), the General Assembly of the United Nations decided to proclaim, in its resolution A/RES/58/217 (https://sdgs.un.org/documents/ares58217-international-decade-action-20915), the period from 2005 to 2015 the International Decade for Action, "**Water for Life**", which commenced on World Water Day, 22nd March 2005, and is celebrated on the 22nd of March every year (https://www.un.org/en/observances/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).

Words, words, words…!!! Question: *Is this enough?*

Young Europeans Discuss Sustainable Development (YEDS) in Athens (Hellenic Republic) on the 10th and 11th of May 2011

Their worries and concerns 13 years ago

Ensuring our survival: Water and Food!

"*We are talking about a water crisis...* : 1.1 billion people in developing countries have inadequate access, and 2.6 billion people lack basic sanitation. About 1.4 million children will die each year from lack of access to safe drinking water and adequate sanitation.

- *What are the water management methods that could ensure sustainable access to water and food for everyone?*
- *What are the strategies to deal with naturally occurring or anthropogenic water-related hazards?* Hazards can result from too much water (floods, erosion, landslides and so on) or too little (droughts, desertification and loss of wetlands or habitat), and from the effects of chemical and biological *pollution* on *water quality*."

Question: *Has anything changed during the past 13 years?*

Access to clean and safe water

With an ever-growing world population and drastic global climatic changes, groundwater will become a valuable resource for our well-being.

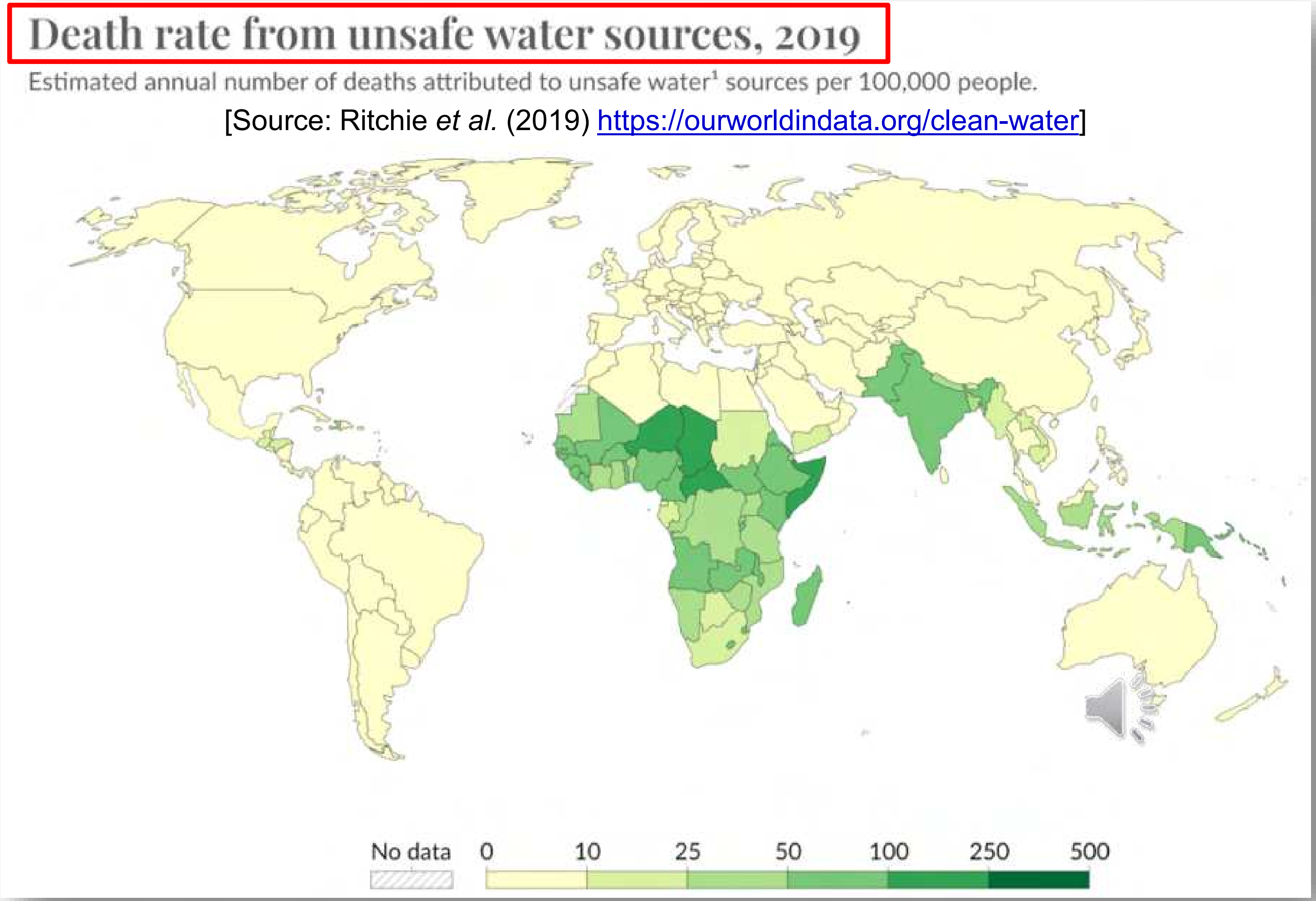
Clean and safe water is important for our health.

According to Ritchie *et al*. (2019):

"One in four people in the world do not have access to safe drinking water.

This is a major health risk.

Unsafe water is responsible for more than a million deaths each year."

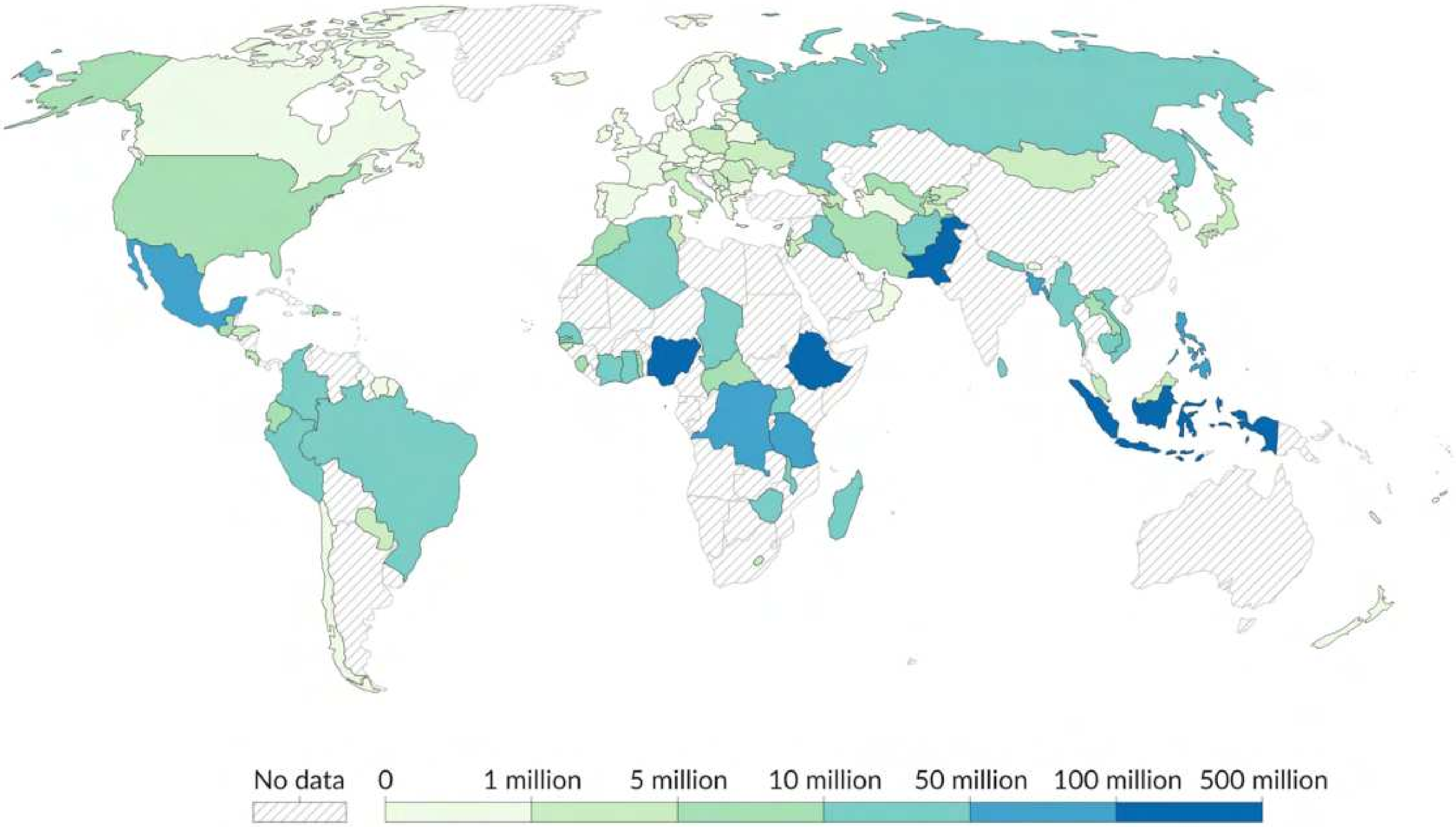


[Source: Ritchie *et al.* (2019) https://ourworldindata.org/clean-water]

[Source: Ritchie *et al.* (2019) https://ourworldindata.org/clean-water]

People not using safe drinking water facilities, 2022

Safely managed drinking water is defined as an “Improved source located on premises, available when needed, and free from microbiological and priority chemical contamination.”



Data source: WHO/UNICEF Joint Monitoring Programme for Water Supply, Sanitation and Hygiene (JMP) (2024)
OurWorldInData.org/water-access | CC BY

[Source: Ritchie *et al.* (2019) https://ourworldindata.org/clean-water]

Development of project idea: Problems & solution

The European Environmental Agency contacted in 2007 the EuroGeoSurveys Geochemistry Expert Group (EGS-GEG) whether there was a *harmonised geochemical data set* for groundwater, similar to the stream water geochemical data set produced during the multi-sample media project of the Geochemical Atlas of Europe (Salminen *et al*., 2005; De Vos, Tarvainen *et al*., 2006).

Of course, the answer was negative.

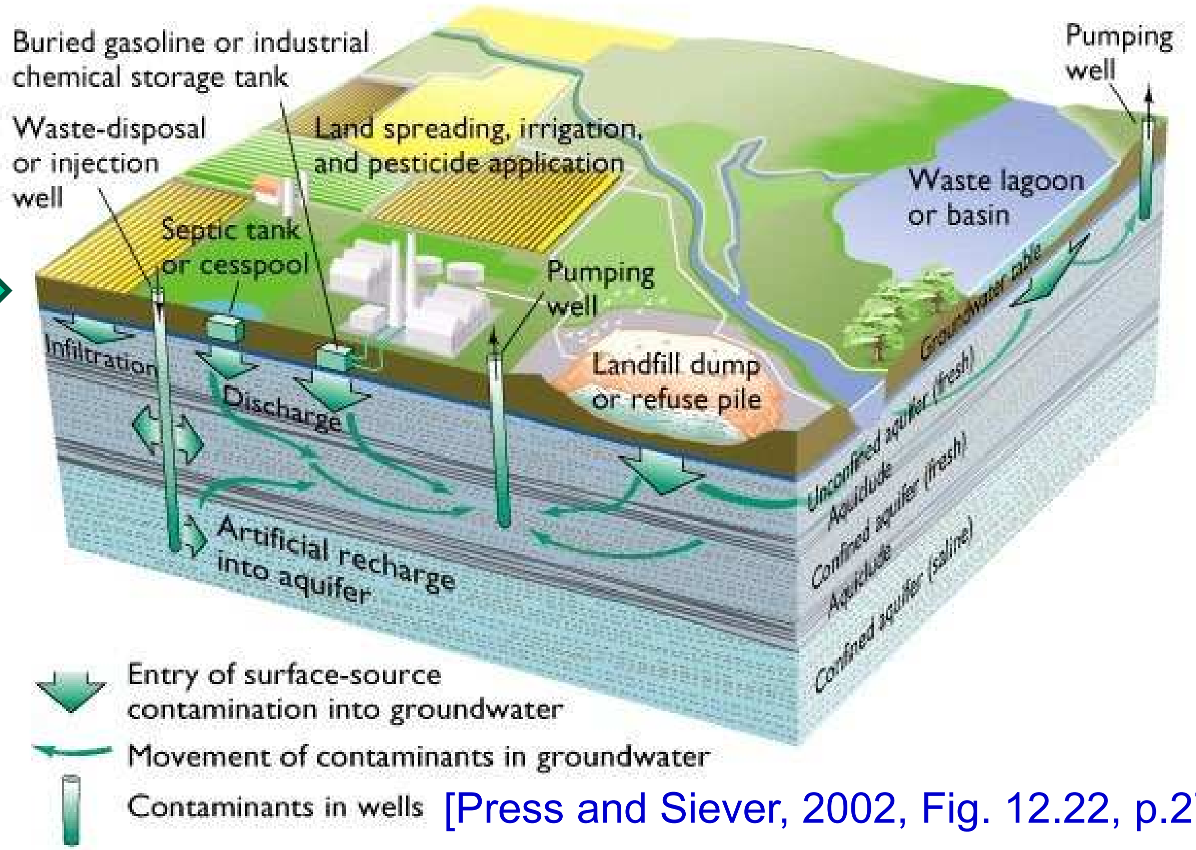
However, there were discussions among the members of EGS-GEG if such a project was possible to be carried out cost-effectively.

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

Development of project idea: Problems & solution

Groundwater:

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

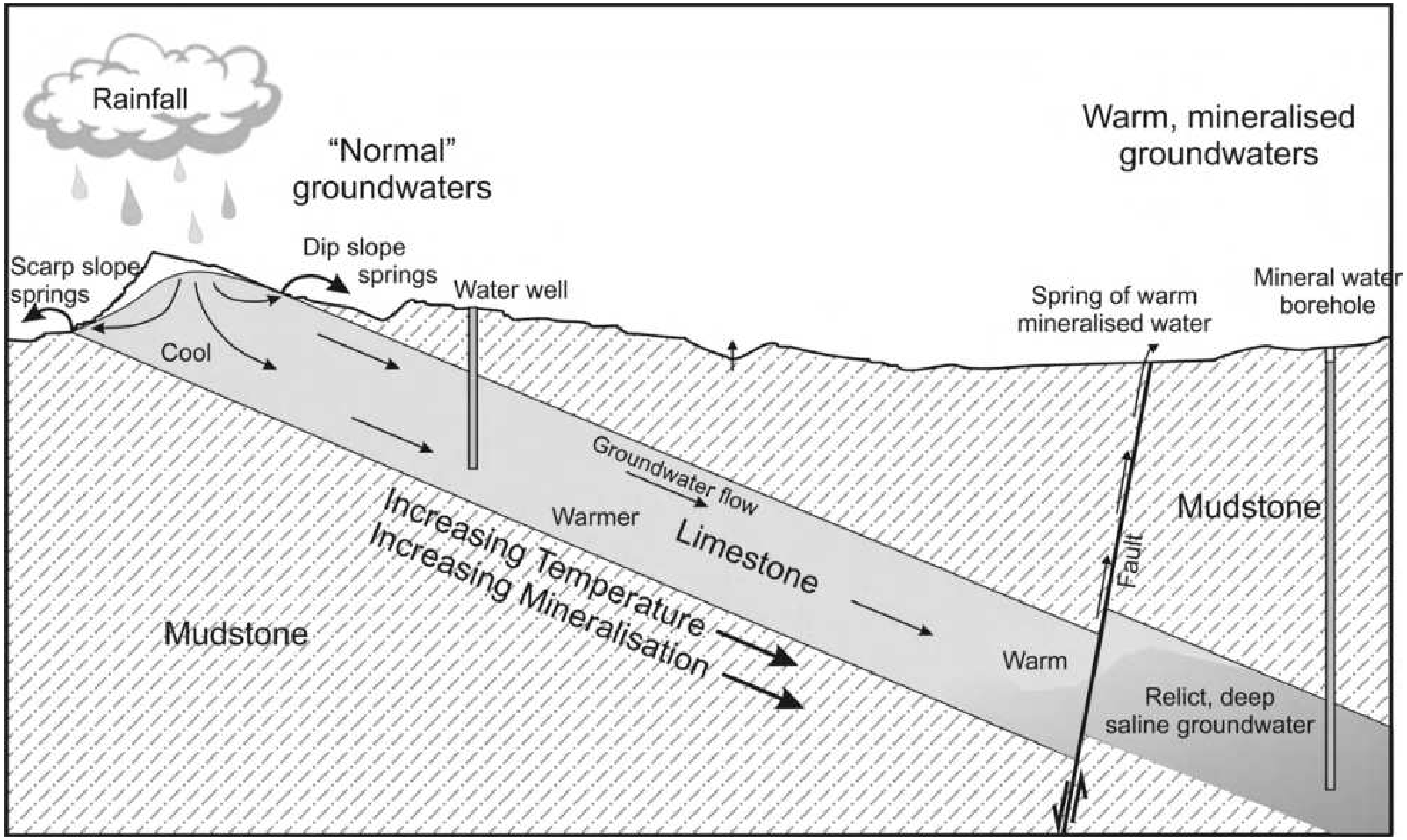


[Press and Siever, 2002, Fig. 12.22, p.273]

"Human activities can contaminate groundwater. Contaminants from surface sources, such as dumps and subsurface sources (e.g., septic tanks) enter aquifers through normal groundwater flow. Contaminants may be introduced into water supplies through pumping wells. Waste-disposal wells are designed to pump contaminants into deep saline aquifers, but they may accidentally leak into freshwater aquifers above."

Conclusion: ***Groundwater is a medium that is impossible to sample systematically and analyse at a reasonable cost.***

Groundwater



[Reimann and Birke, 2010, Fig. 1, p.5]

Simplified diagram of the hydrogeological cycle of an idealised strata-bound sedimentary aquifer (*a limestone sandwiched between layers of low permeability mudstone*).

Rainfall seeps into the outcrop area of the limestone to form groundwater. The groundwater dissolves calcite in the limestone to result in a fresh, cold, typical calcium-bicarbonate (Ca^{++}-HCO_3^-) groundwater – this type of water would be favoured by producers of bottled spring water in many Western European nations. As the water flows down-dip through the aquifer it becomes warmer and increasingly mineralised. It may even mix with relict saline groundwater in the deepest parts of the aquifer to form a "true" mineral water in the classic tradition.

Development of project idea: Problems & solution

The German Federal Institute for Geosciences and Natural Resources (B.G.R.) offered to analyse free of charge all collected groundwater samples from all European countries.

There was, however, an almost impossible problem:

No funds were available to carry out systematic sampling of groundwater in Europe.

The main reason was that the European Geological Surveys were committed at the time to planning the sampling of agricultural and grazing land soil, the GEMAS project (Refer to SEGHLive Fellows Seminar 1st March 2024:- "GEMAS: Geochemistry of Agricultural and Grazing land soil for healthy food production in Europe" - https://youtu.be/xOQP3XLuo5k?si=N7gQ9zLoNcQ83M49).

Development of project idea: Problems & solution

Manfred Birke from the German Federal Institute for Geosciences and Natural Resources (B.G.R.), came up with the idea that '*bottled mineral water*' can be used as a proxy for the geochemistry of groundwater.

According to Manfred's experience, the geochemistry of bottled mineral water can be used as a '*proxy*' for that of groundwater.

In Europe, there are more than 1900 registered bottled water brands. Therefore, "*bottled groundwater*" can be bought readily sampled at the European scale from supermarkets.

Manfred's idea was considered absurd and that the EuroGeoSurveys Geochemistry Expert Group would be criticised for carrying out such an unconventional project.

Manfred Birke insisted and supported his proposal with reference to European Commission legislation. In Europe, there are 3 categories of bottled water:−

(1) ***Natural mineral water*** (Directives 80/777/EC & 2003/40/EC, 2009/54/EC for limit values): It is drinking water of underground origin with a stable chemical composition, and it is bottled at source (spring/well/borehole). *It is not subjected to any treatment*, and differs from common drinking water by its mineral content, trace elements or other constituents.

(2) ***Spring water*** (Directives 96/70/EC & 98/83/EC for limit values): It is drinking water of underground origin, and is bottled at source (spring/well/ borehole). *It is not subjected to any treatment. It is not required to have a stable chemical composition*. Its physicochemical characteristics (parameters) must satisfy the standards of drinking water for human consumption.

(3) ***Table water*** (Directive 98/83/EC for limit values): It is bottled water for human consumption. Its physicochemical characteristics (parameters) satisfy those of common drinking water. It can even be normal tap water or treated and disinfected river water. [NOT SUITABLE for the project].

Issues considered when using 'Bottled Mineral Water' as a proxy for groundwater geochemistry:

Bottled mineral water:

- May come from non-representative, quite special and unusual aquifers.
- Can be contaminated from well and bottling installations, and
- Can be contaminated from the bottle material itself.

- Bottled table water is treated prior to bottling (filtered, carbonated, de-ironed, *etc*.). ***Hence, Bottled table water is unsuitable for sampling***.

No

Decision time!!!

Do we go ahead with the project?

Yes

It is noted that most members of the EuroGeoSurveys Geochemistry Expert Group are Applied Geochemists with experience in mineral exploration, where they learnt to sample and measure systematically any natural medium to meet project objectives in a cost-effective manner.

Manfred's proposal was discussed, and although it was met with considerable scepticism, the *explorationists* among the group decided that it was worth a try, since the cost of sampling was minimal, *i.e.*, just the cost of purchasing the bottled mineral water from supermarkets and of posting the samples to Germany.

Sampling of Bottled Mineral Water from supermarkets

Instructions were sent to all members of the EuroGeoSurveys Geochemistry Expert Group, as well as to friends and colleagues travelling to European countries, to purchase from supermarkets as many different bottled mineral water brands as possible. In case the same bottled water was available with and without gas, both varieties were purchased. If bottled water was marketed in different bottle types (*e.g.*, glass and PET), or in bottles of different colour, all varieties were bought whenever possible.

To keep shipping costs down 0.5 litre bottles were preferentially bought. However, if a brand was exclusively marketed in larger capacity containers of 1, 1.5 or even 5 litres were purchased.

Before shipping to Germany, the analytical results recorded on bottle labels were transferred to an Excel worksheet together with other pertinent information.

Collection of project samples in 40 European countries by 85+ scientists

Albania: F. Koller (U. Vienna); K. Onuzi (U. Tirana)
Austria: G. Hobiger (G.B.A.); P. Filzmoser (TU Wien); F. Koller (U. Wien)
Belarus: P. Filzmoser (TU Wien); V. Gregorauskiene (Geol. Surv. Lithuania)
Belgium: I. Schoeters (Rio Tinto); W. De Vos (Geo. Surv.); C. Reimann (N.G.U.)
Bosnia & Herzegovina: H. Hrvatovic, N. Miosic, F. Skopljak & N. Samardzic (Geol. Surv.)
Bulgaria: V. Trendavilov (Min. of Environment and Water)
Croatia: J. Halamic & A. Šorša (Geol. Surv.)
Czechia: M. Duris & R. Kadlecova (Geol. Suv.)
Cyprus: A. Demetriades (I.G.M.E.)
Denmark: R.T. Ottesen & C. Reimann (N.G.U.)
Estonia: J. Kivisilia & V. Petersell (Geol. Surv.); L. Bityukova (Tallinn U.)
Finland: T. Tarvainen & J. Jarva (G.T.K.)
France: I. Salpeteur & C. Innocent (B.R.G.M.)
F.Y.R.O.M.: S. Stafilov (U. Skopje)
Georgia: M. Birke (B.G.R.)
Germany: M. Birke, U. Rauch, L. Kaste & H. Lorenz (B.G.R.)
Hellas: A. Demetriades (I.G.M.E.)
Hungary: G. Jordan, U. Fugedi & L. Kuti (Geol. Surv.)
Iceland: B. Wigum (Manvit HF) & M. Birke (B.G.R.)
Ireland: R. Flynn (Queens Univ. Belfast)
Italy: B. De Vivo, S. Albanese, A. Lima (U. Napoli); E. Dinelli (U. Bologna); D. Cicchela (U. Sannio) & P. Valera (U. Cagliari)
Latvia: A. Gilucis (L.E.G.M.A.)
Lithuania: V. Gregorauskienne (Geol Surv.)
Luxembourg: R. Maquil (S.G.L.)
Moldova: M. Titovet (Min. Ecology)
Montenegro: N. Devic (Geol. Surv.)
Norway: C. Reimann, B. Frengstad & R.T. Ottesen (N.G.U.)
Poland: L. Smietanski (P.G.I.)
Portugal: C. Lourenço & Maria João Batista (INETI)
Romania: A. Ion (Geol. Surv.) & C. Ionesco (U. C-Napoca)
Russia: N. Philippov (SC Mineral); O. Karnachuk (U. Tomsk); R. Salminen (G.T.K.)
Serbia: A. Gulan, T. Petrovic, B. Vukicevic & M.Z. Mandic (Geol. Inst.); N. Veljkovic (Env. Agency)
Slovakia: P. Malik (Geol.Surv.)
Slovenia: M. Gosar (Geol. Surv.)
Spain: A. Bel-lan, J. Locotura & M. Corral (I.G.M.E.)
Sweden: K. Lax & M. Andersson (S.G.U.)
Switzerland: P. Hayoz (Swisstopo)
The Netherlands: R.T. Ottesen & C. Reimann (N.G.U.)
United Kingdom: D. Flight, S. Reeder & P. Smedley (B.G.S.); D. Banks (HolyMoore Consultancy)
Ukraine: V. Klos & M. Vladimirova (Geol. Surv.)
(Turkey): M. Birke (B.G.R.)

Sampling of Bottled Mineral Water from supermarkets

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

Duplicate bottled mineral water samples of the same brand were purchased from different supermarkets.

Bottled Mineral Water was not purchased from kiosks

The reason is that bottled mineral water is exposed to the ambient temperature.

Storage of collected Bottled Mineral Water samples

Storage of bottled mineral water samples in refrigerators at BGR, Berlin (Reimann & Birke, 2010, Fig. 19, p.30)

In total, 1785 'samples' of bottled mineral water were purchased from supermarkets all over Europe (40 countries), representing 1247 boreholes/wells at 884 unique locations.

Upon arriving in Germany, all bottled mineral water samples were stored in refrigerators until their analysis.

So, Manfred Birke had to buy many refrigerators to store the 1785 bottles of mineral water.

Atlas of European Groundwater Geochemistry

To obtain a fully harmonised geochemical data set all bottled mineral water samples were analysed for 72 parameters in just one laboratory, the B.G.R. laboratory in Germany.

Atlas of European Groundwater Geochemistry: Analytical programme

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

Ion Chromatography (IC): Br^-, Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-}

Atomic Fluoresce Spectrometry (AFS): Hg

Titration: tAlk - HCO_3^-

Photometric: NH_4^+

Potentiometric: pH

Conductometric: Electrical Conductivity (EC)

Analytical results received from the laboratory

Sample	pH	EC	Ag	Al	As	B	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Fe	Ga
HEL001-1	7.4	460	-0.001	-0.3	0.122	10.6	0.006	-0.001	0.000506	96.3	0.00382	-0.0005	0.0173	0.754	0.0369	0.187	0.00025	0.000109	0.000251	0.279	0.00154
HEL002-1	7.55	385	-0.001	1.05	0.32	9.63	0.033	-0.001	-0.0005	73.3	0.00464	-0.0005	0.0217	0.305	0.0382	0.185	0.00065	0.000146	0.000759	0.303	0.00771
HEL003-1	7.4	498	-0.001	0.481	0.0903	9.3	0.141	-0.001	0.000621	100	0.00262	0.000567	0.0102	1.99	0.00286	0.136	0.000551	0.000512	0.0038	0.236	0.00154
HEL003-2	7.4	475	-0.001	3.44	0.102	8.64	0.207	-0.001	0.000623	94.4	0.00101	0.00465	0.0102	1.89	0.00227	0.276	0.000802	0.000806	0.00361	0.23	0.00618
HEL004-1	7.7	451	-0.001	0.58	0.317	18	0.031	-0.001	-0.0005	59	0.00161	-0.0005	0.0104	14	0.00169	0.0792	0.000872	0.000622	0.000631	0.173	0.00163
HEL004-2	7.65	469	-0.001	1.37	0.336	19.9	0.031	-0.001	0.00139	59.2	0.0056	0.0336	0.0173	14	0.00185	0.403	0.00261	0.00215	0.00203	0.135	0.00563
HEL005-1	7.25	560	0.00432	0.495	0.0382	19.2	0.001	-0.001	0.00413	51.4	0.00513	-0.0005	0.00681	1.58	0.00598	3.99	0.00139	0.00138	-0.0002	0.503	-0.0005
HEL006-1	7.85	394	-0.001	0.541	0.0902	27.9	0.069	-0.001	0.00116	65.8	0.00117	-0.0005	0.0126	0.212	0.00497	0.226	0.000278	0.000244	0.00112	0.362	0.00188
HEL006-2	7.7	399	-0.001	6.11	0.122	27	0.067	-0.001	0.000977	67.1	0.00281	0.0182	0.0136	0.284	0.00529	0.392	0.00145	0.00114	0.000948	0.341	0.00751
HEL007-1	8.25	891	-0.001	5.48	0.393	143	0.081	0.0127	0.00171	17.9	0.00211	0.00105	0.0283	0.291	0.00243	0.0933	0.00502	0.00326	0.00147	0.187	0.00376
HEL008-1	8.35	391	-0.001	0.842	0.135	44.9	0.007	-0.001	0.00104	58	0.00304	0.000973	0.0225	2.07	0.00275	0.495	0.00151	0.00131	0.000363	0.404	0.00376
HEL009-1	9.2	180	-0.001	0.514	0.0194	3.61	-0.001	-0.001	-0.0005	2.87	-0.001	-0.0005	0.0126	7.39	0.00141	0.143	0.000336	0.000204	-0.0002	0.221	-0.0005
HEL010-1	7.65	594	-0.001	-0.3	0.499	74.7	0.016	-0.001	-0.0005	71.2	0.00469	-0.0005	0.0141	2.55	0.00448	0.285	0.00028	0.000164	0.000203	0.513	-0.0005
HEL011-1	7.95	434	-0.001	3.19	0.16	14.6	0.031	0.00146	-0.0005	63.9	0.00235	-0.0005	0.0189	0.445	0.00269	0.247	0.000393	0.000328	0.000825	0.243	0.00941
HEL012-1	8.25	261	0.00123	2.79	0.21	11.6	0.015	0.00122	0.000929	27.6	0.0223	-0.0005	0.0105	0.247	0.00365	0.114	0.000281	-0.0001	-0.0002	0.116	0.0132
HEL013-1	8.1	251	-0.001	3.17	0.201	11.6	0.014	0.0017	0.00354	26.1	0.00306	-0.0005	0.0162	0.281	0.00391	0.359	0.000338	0.000123	0.000624	0.108	0.0339
HEL014-1	8.1	280	-0.001	1.59	0.198	9.57	0.008	-0.001	0.00118	29.3	0.0033	-0.0005	0.00839	0.444	0.00462	0.637	0.000113	0.00033	0.000304	0.157	0.0132
HEL015-1	7.9	432	-0.001	0.806	0.128	16.8	0.005	-0.001	-0.0005	58.9	0.00283	0.00305	0.0713	0.447	0.0162	0.551	0.00186	0.00107	0.000558	0.282	0.00754
HEL015-2	7.9	432	-0.001	0.575	0.113	16.3	0.006	-0.001	0.000503	57.9	0.00142	0.00298	0.0671	0.514	0.0163	0.355	0.00215	0.00116	0.000469	0.349	0.0113
HEL016-1	7.9	557	-0.001	0.666	0.201	34.2	0.068	0.00122	0.000504	54.9	0.00496	-0.0005	0.00629	0.0419	0.028	1.01	0.000907	0.000828	0.00115	0.177	0.00566
HEL017-1	8.1	265	-0.001	2.06	0.207	9.22	0.019	-0.001	0.00119	27.2	-0.001	-0.0005	0.00524	0.425	0.00425	0.432	0.00017	0.000166	0.00026	0.164	0.0189
HEL017-2	8.15	265	-0.001	2.77	0.177	9.26	0.019	-0.001	-0.0005	28.2	-0.001	-0.0005	0.00576	0.447	0.00483	0.495	-0.0001	-0.0001	-0.0002	0.162	0.0113
HEL018-1	8.1	268	-0.001	2.62	0.192	8.98	0.019	-0.001	0.00107	28.6	0.00403	-0.0005	0.0414	0.455	0.004	0.421	0.000342	0.000582	0.00043	0.391	0.017
HEL019-1	7.8	446	-0.001	0.524	0.202	15.9	0.185	-0.001	-0.0005	68.5	0.00403	-0.0005	0.0189	0.6	0.0348	0.516	0.00177	0.00112	0.00374	0.304	0.00567
HEL020-1	7.8	429	-0.001	0.569	0.186	14.4	0.174	0.00121	0.000511	65.6	0.00142	-0.0005	0.032	0.537	0.0272	0.73	0.00103	0.001	0.00241	0.231	0.00567
HEL021-1	7.5	733	-0.001	1.68	0.12	84.8	0.033	0.00387	-0.0005	101	0.0231	0.00063	0.0202	0.0772	0.0411	1.39	0.000464	0.000634	0.000602	0.348	-0.0005
HEL021-2	7.45	764	-0.001	5.25	0.107	83	0.034	0.00242	-0.0005	103	0.0362	0.0123	0.0486	0.144	0.0393	1.72	0.00221	0.00114	0.000883	0.433	0.00743
HEL022-1	7.6	415	-0.001	0.347	0.323	8.33	0.043	-0.001	-0.0005	86	0.00309	-0.0005	0.0196	1.09	0.051	0.41	0.000407	-0.0001	0.000683	0.227	-0.0005
HEL023-1	7.6	415	-0.001	0.324	0.336	7.84	0.042	-0.001	0.000847	86	0.00166	-0.0005	0.0129	1.08	0.0546	0.368	-0.0001	-0.0001	0.000983	0.235	0.00555
HEL023-2	7.53	359	-0.001	-0.3	0.125	6.9	0.006	0.00141	0.0011	95.8	0.00386	0.00111	0.00669	0.758	0.0331	0.0911	0.000204	0.000366	0.000589	0.329	0.00537
HEL024-1	7.6	414	-0.001	-0.3	0.35	6.93	0.042	0.00121	0.00156	85.7	0.00214	-0.0005	0.0129	1.12	0.0471	0.407	0.000291	-0.0001	0.000617	0.174	0.0111
HEL025-1	7.65	413	-0.001	0.578	0.339	6.83	0.043	-0.001	0.000524	84.6	0.00166	-0.0005	0.0154	1.11	0.051	0.442	0.000175	-0.0001	0.000624	0.315	0.00551
HEL025-2	7.7	423	-0.001	0.469	0.31	6.72	0.043	-0.001	-0.0005	88	0.00356	-0.0005	0.0225	1.05	0.0486	0.444	0.000233	0.000169	0.000957	0.237	0.00367
HEL026-1	8.3	649	-0.001	0.637	0.354	18.5	0.002	-0.001	-0.0005	10.2	-0.001	-0.0005	0.00818	22.4	0.0203	0.697	0.00035	0.000169	0.000297	0.53	-0.0005
HEL027-1	8.4	717	0.112	1.21	0.0762	12.1	0.002	-0.001	-0.0005	3.88	0.00166	0.000513	0.00868	19.6	0.00919	0.675	0.000642	0.00017	0.000269	0.711	0.00182
HEL028-1	8.4	719	-0.001	0.526	0.0724	11.8	0.002	-0.001	-0.0005	3.86	0.00189	-0.0005	0.0229	20.1	0.00912	0.542	0.000409	0.000424	0.000201	0.365	-0.0005
HEL029-1	8.3	655	-0.001	0.501	0.518	14.1	0.004	0.00145	0.00273	9.44	-0.001	-0.0005	0.0127	17.8	0.0263	0.294	0.000117	-0.0001	-0.0002	0.133	-0.0005
HEL030-1	8.3	647	-0.001	0.77	0.363	18.9	0.003	-0.001	0.000656	9.97	0.00118	-0.0005	0.00912	23.6	0.0212	0.503	0.000645	0.000213	0.000288	0.232	-0.0005

Quality control, Data processing, map plotting, interpretation and report writing

1) The quality of results was first checked
2) Data processing – basic statistics
3) Plotting of maps
4) Interpretation
5) Report writing (Atlas book)
6) Publications

Detection Limit

The Instrument Detection Limit (IDL) was estimated at three times the standard deviation of sample blank determinations.

The Reported Detection Limit (RDL) was calculated at ten times the standard deviation of sample blanks. The conservative RDL was used as the cut-off value for all statistical graphics and tables, as well as for producing the distribution maps.

The duplicate analyses were also used to estimate the Practical Detection Limit (PDL) (Demetriades 2010, 2011; Demetriades *et al.*, 2022). In this case, the PDL was used for the verification of the Reported Detection Limit (RDL).

Element	IDL	RDL	PDL	Precision
	µg/l			%
Ag	0.001	0.002	0.002	13
Al	0.2	0.5	0.2	5
As	0.01	0.03	0.001	10
B	0.1	2	0.2	4
Ba	0.005	0.05	1*	5
Be	0.001	0.01	0.005	5

Extract from Table 5 (p. 43).

Note: The lower PDL values indicate that if uncensored values were provided a much lower detection limit could have been estimated.

* Too large a concentration range and too many high values to reliably calculate PDL.

QUALITY CONTROL (1/6)

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 estimate reliable detection limits.**
4) **Frequent analysis of sample duplicates to determine the precision of measurements.**
5) **Comparison of analytical results of this study with those displayed on bottle labels.**
6) **Determination of a few parameters (Ba, Ca, K, Mg, Mn, Na & Sr) by ICP-QMS and ICP-AES, and Hg by ICP-QMS and AFS.**
7) **Checking bottled mineral water samples with unusually high results for important parameters by buying another bottle and repeating the analysis.**

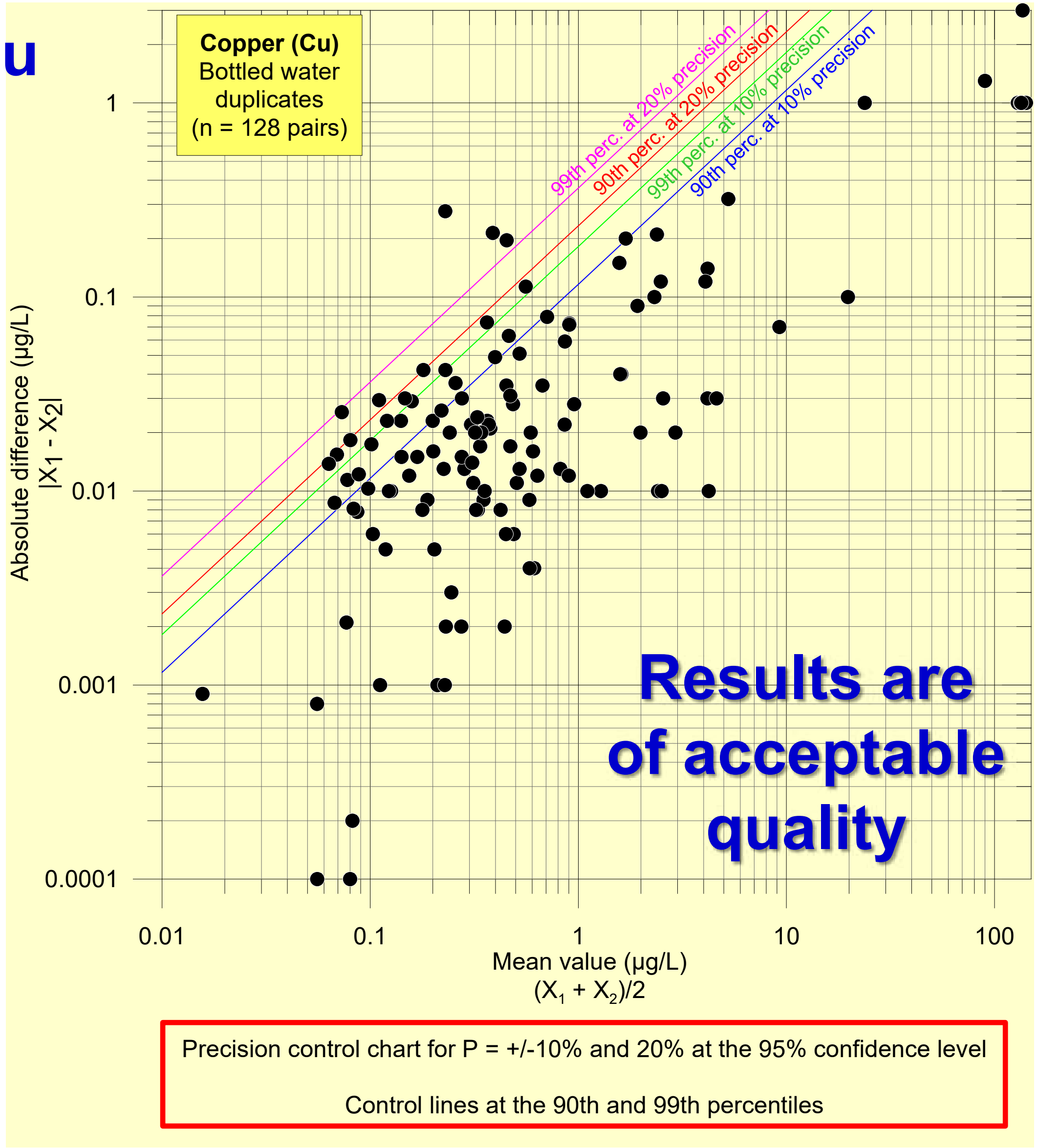
QUALITY CONTROL (2/6)

8) The international sample SLRS-4 was analysed 103 times.
9) The low fortified standards for trace elements TM-26.3, TM-27.2, TM-28.2 and TM-28.3 were randomly analysed from 25 to 91 times.
10) The in-house laboratory reference sample 'MinWas' was randomly analysed 261 times, and
11) The blank samples of deionised water (SERALPUR-90; 18.2 MΩ) and 4 ml 69% HNO_3 (Roth, ultrapure) were randomly analysed 10 to 12 times.

The only problems that were detected, during the study of quality control results, concerned the reproducibility of Hf, Nb, Sn, Ta and W at low concentrations. *Consequently, the results of these elements up to concentrations 10 times their detection limit should be considered with some caution*. However, the results of reference samples at higher concentrations showed that these are reliable.

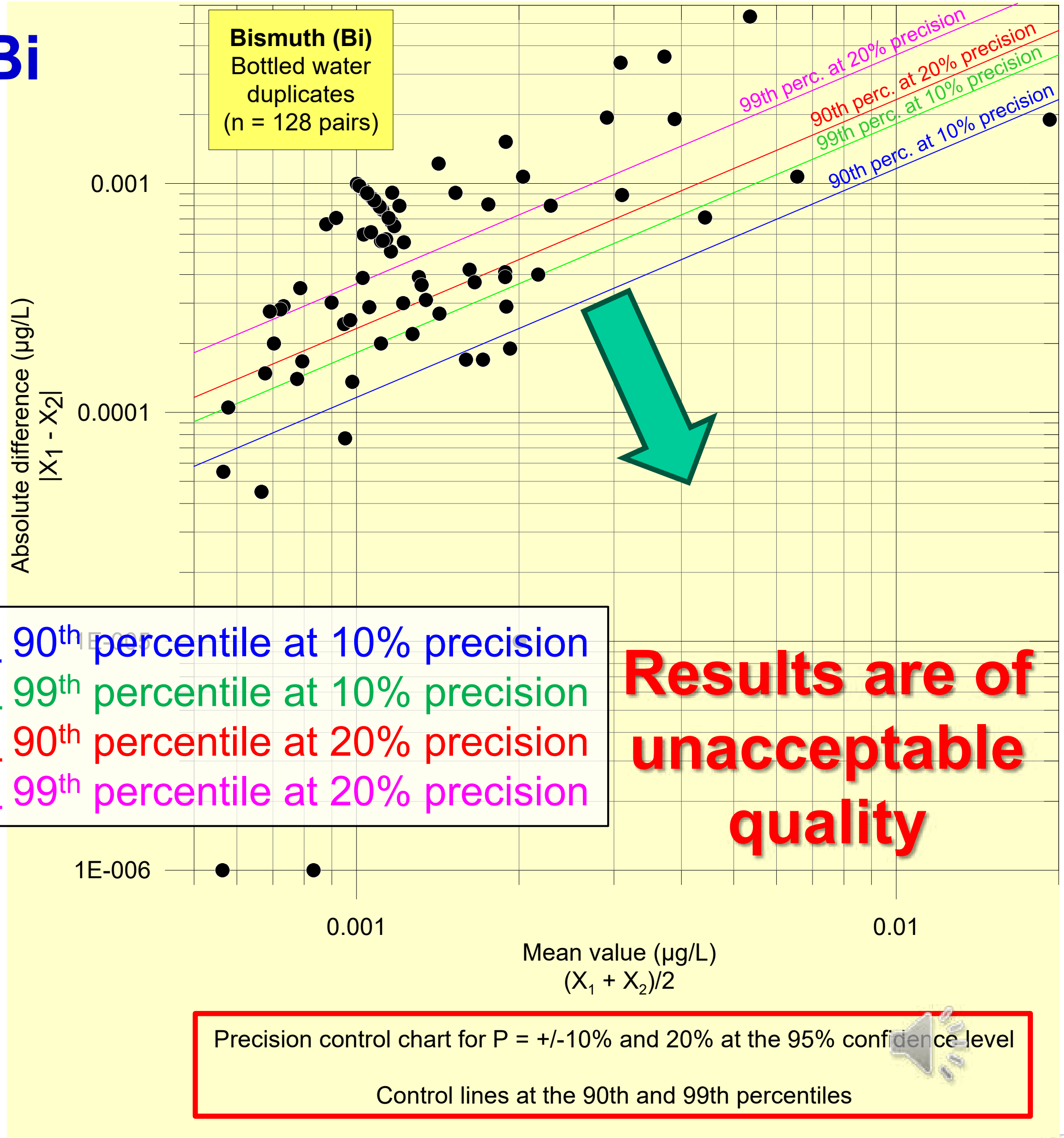
Quality control (3/6): Thompson-Howarth precision charts

Cu



Results are of acceptable quality

Bi

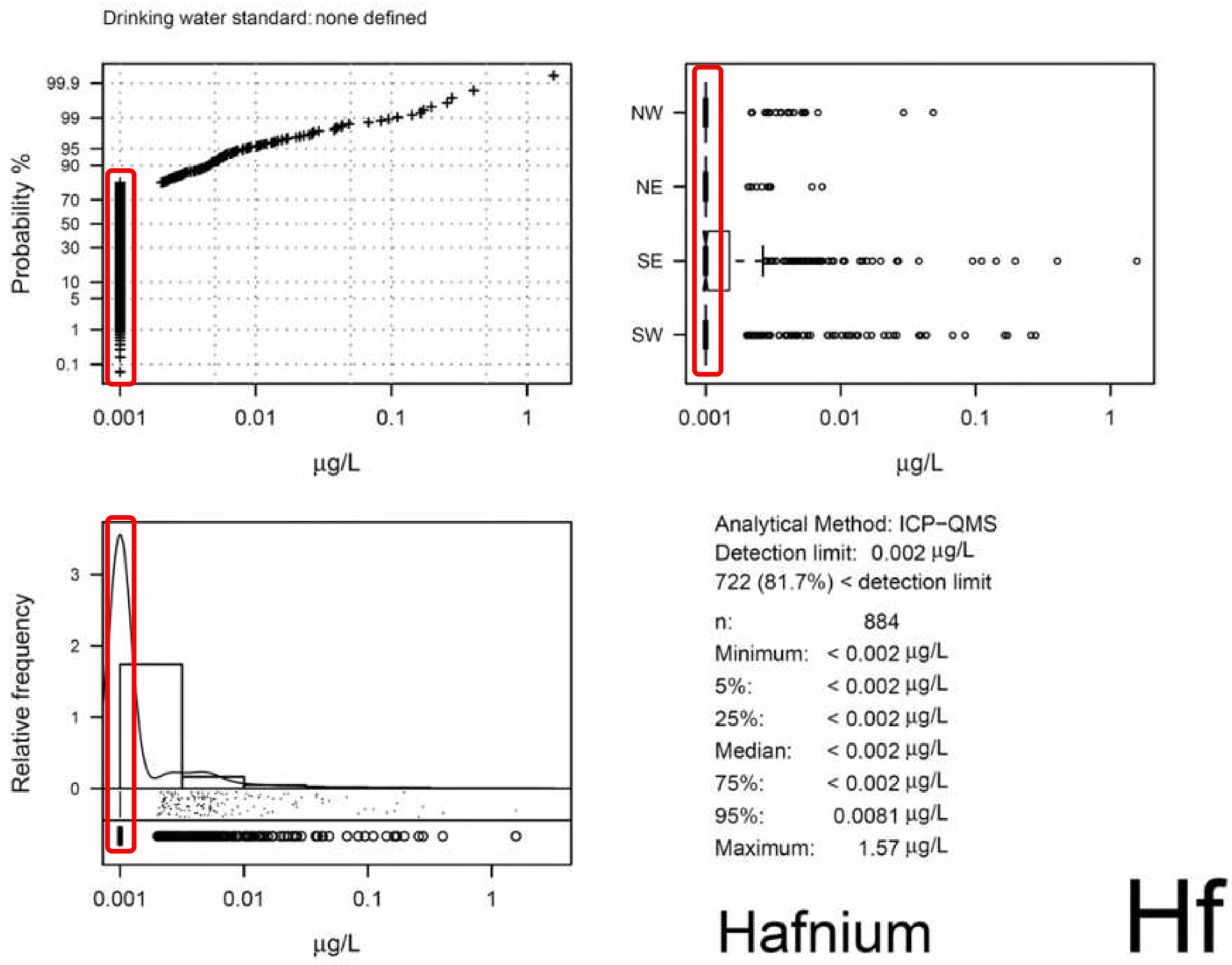


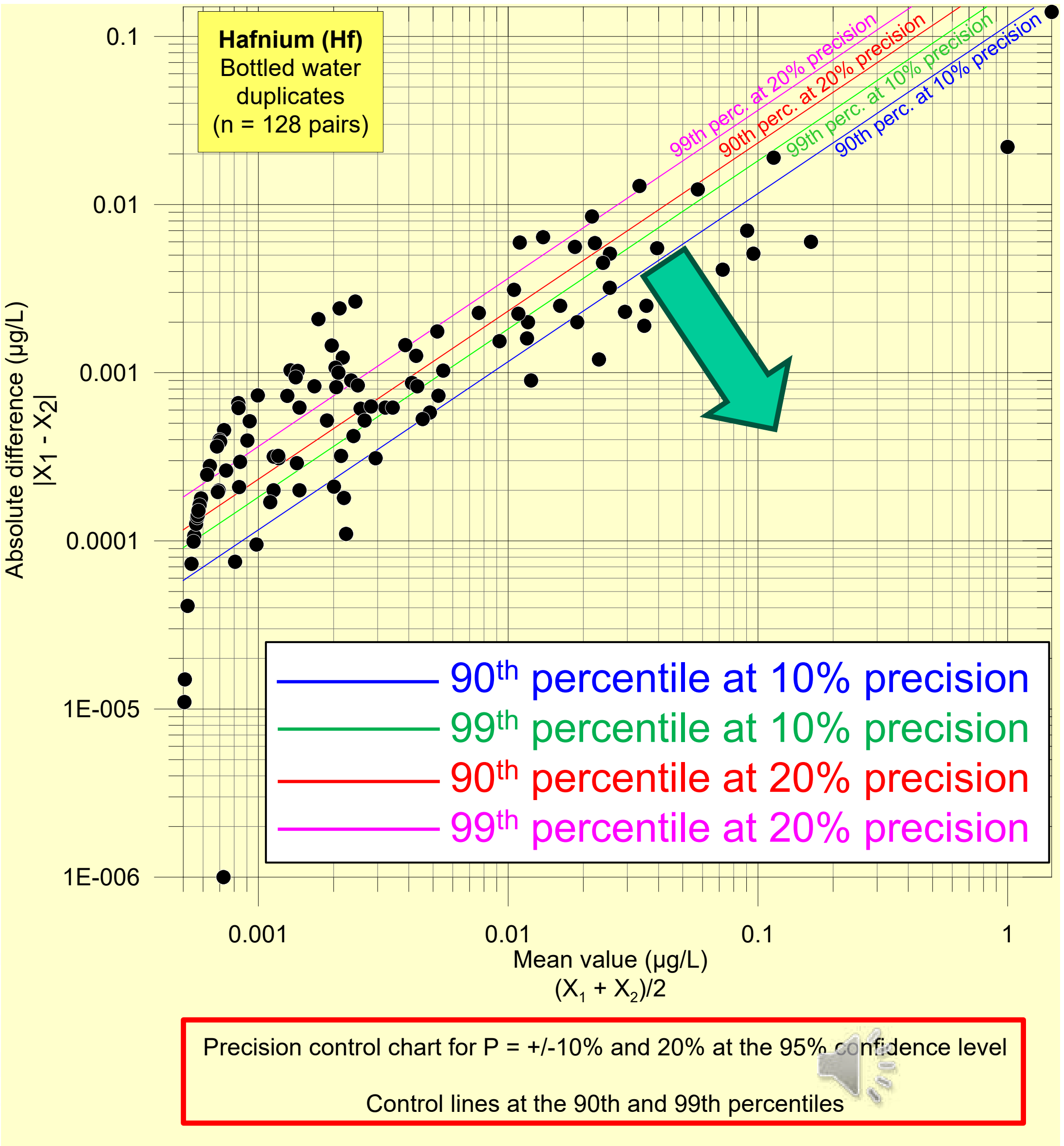
90th percentile at 10% precision
99th percentile at 10% precision
90th percentile at 20% precision
99th percentile at 20% precision

Results are of unacceptable quality

QUALITY CONTROL (4/6)

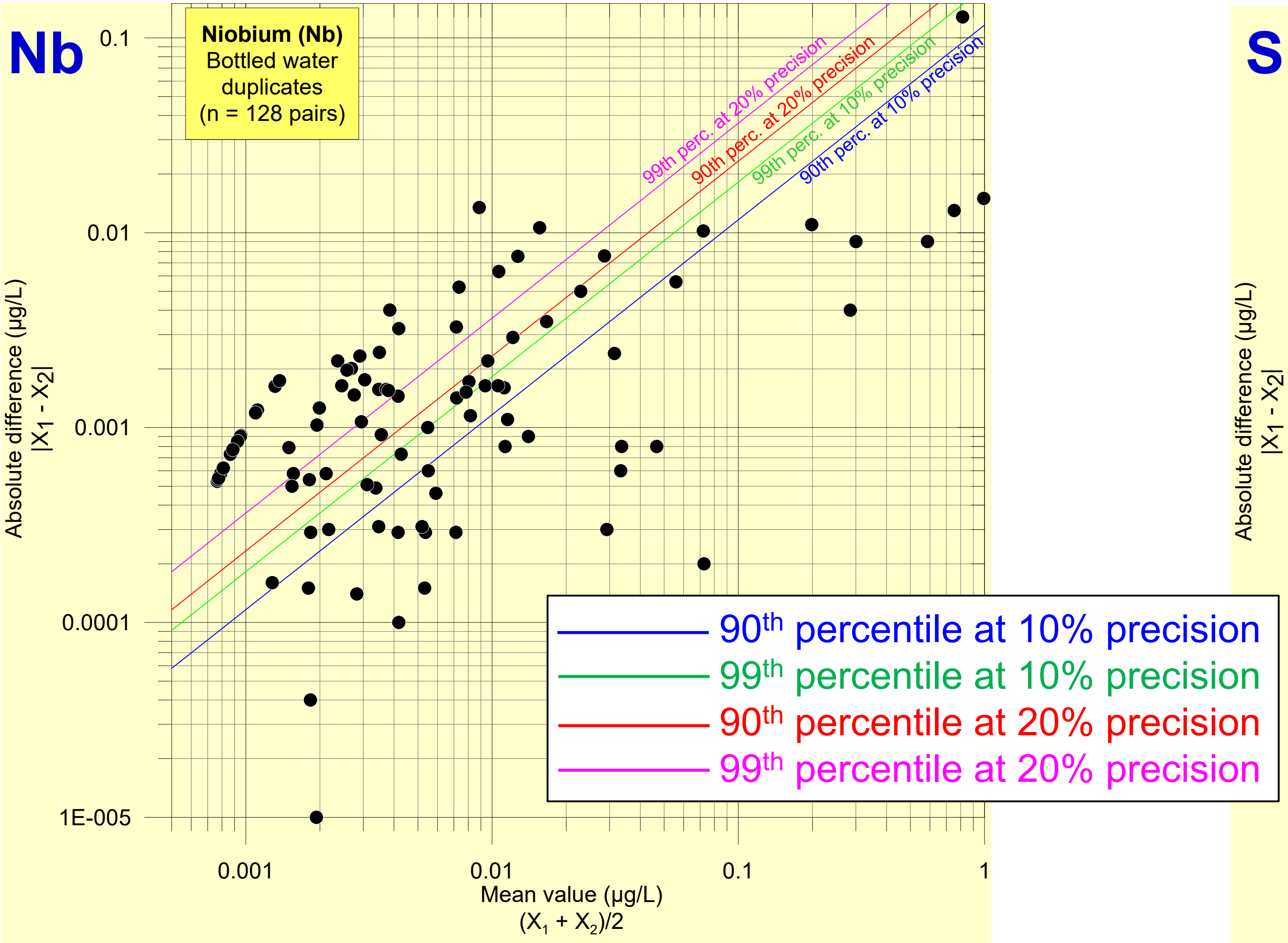
Thompson-Howarth precision chart





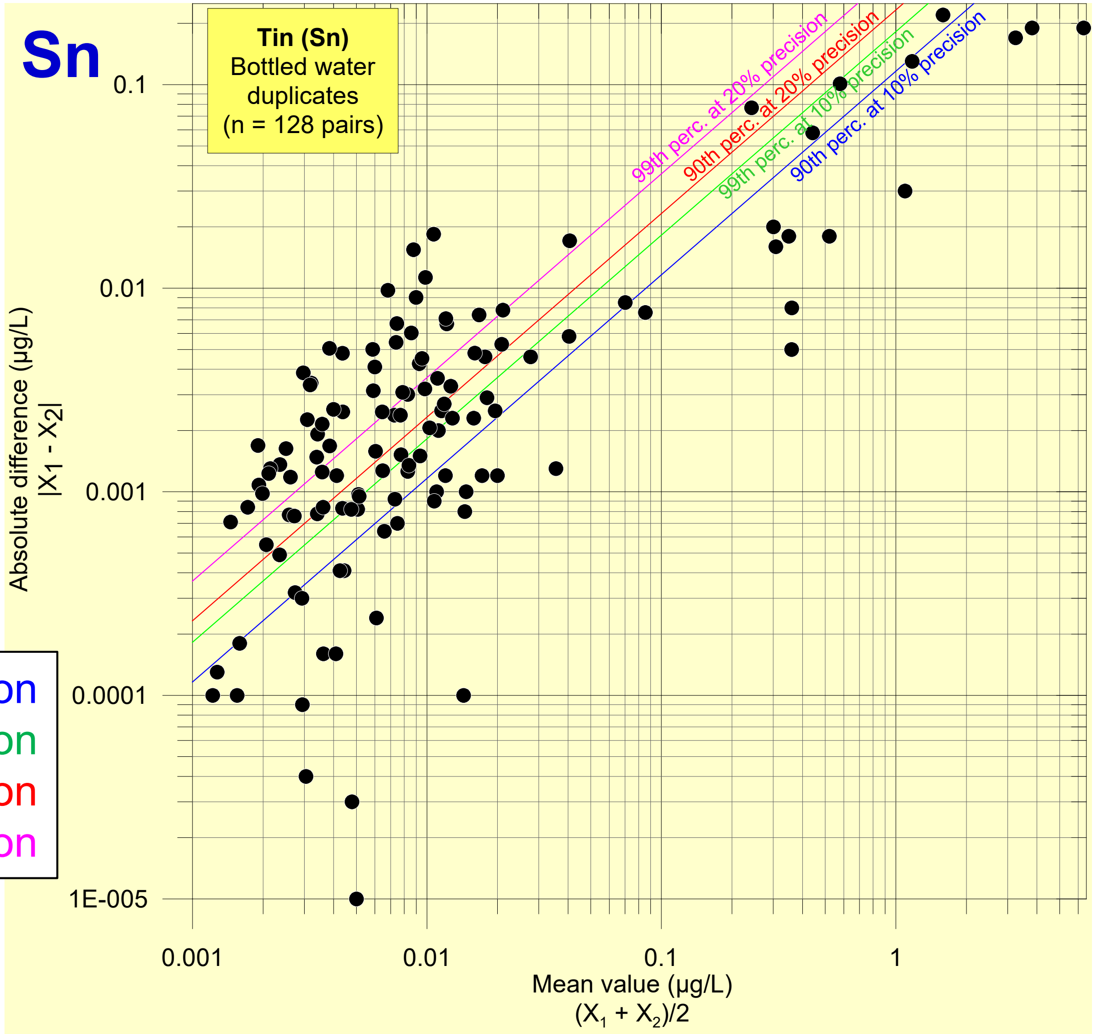
(Reimann & Birke, 2010, p.121)

Quality control (5/6): Thompson-Howarth precision charts



Precision control chart for P = +/-10% and 20% at the 95% confidence level

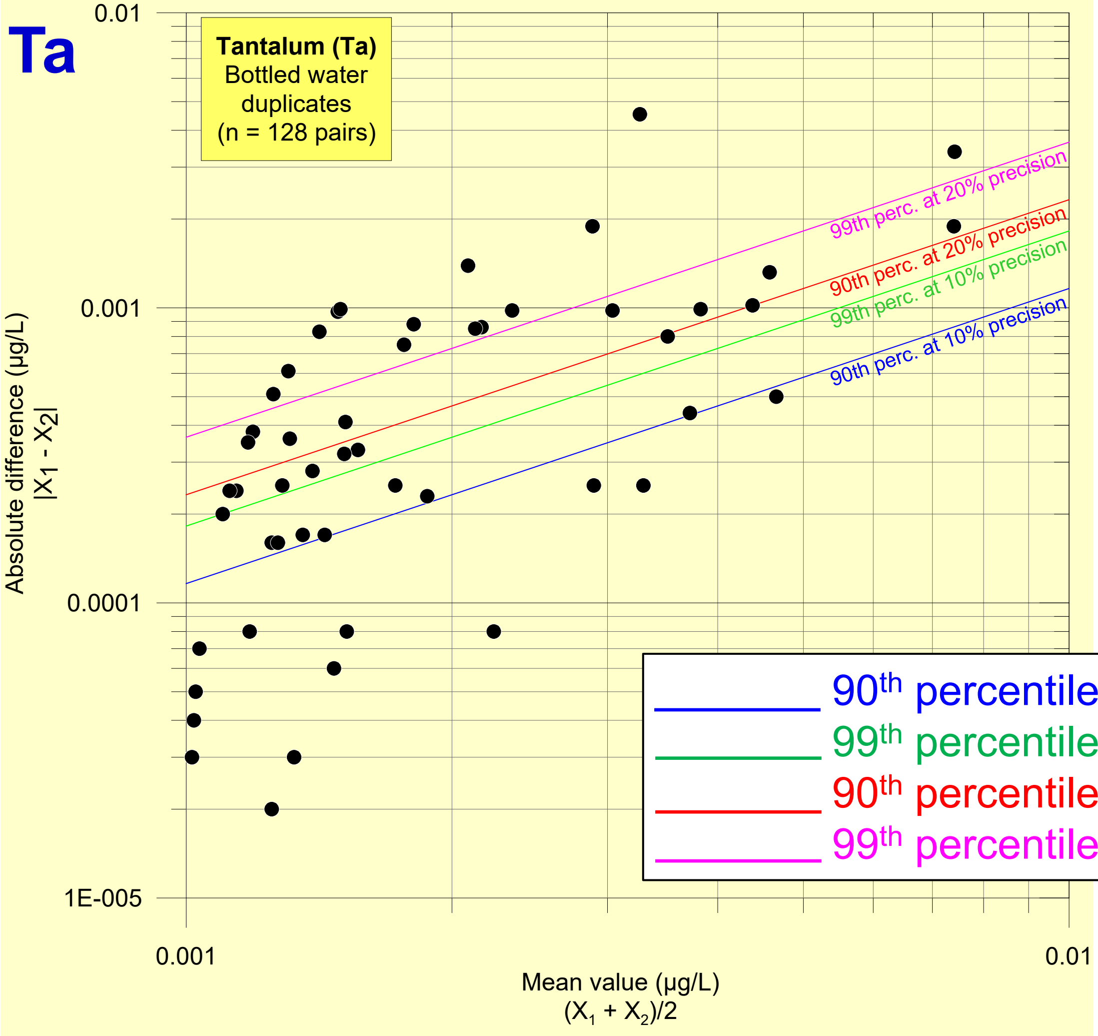
Control lines at the 90th and 99th percentiles



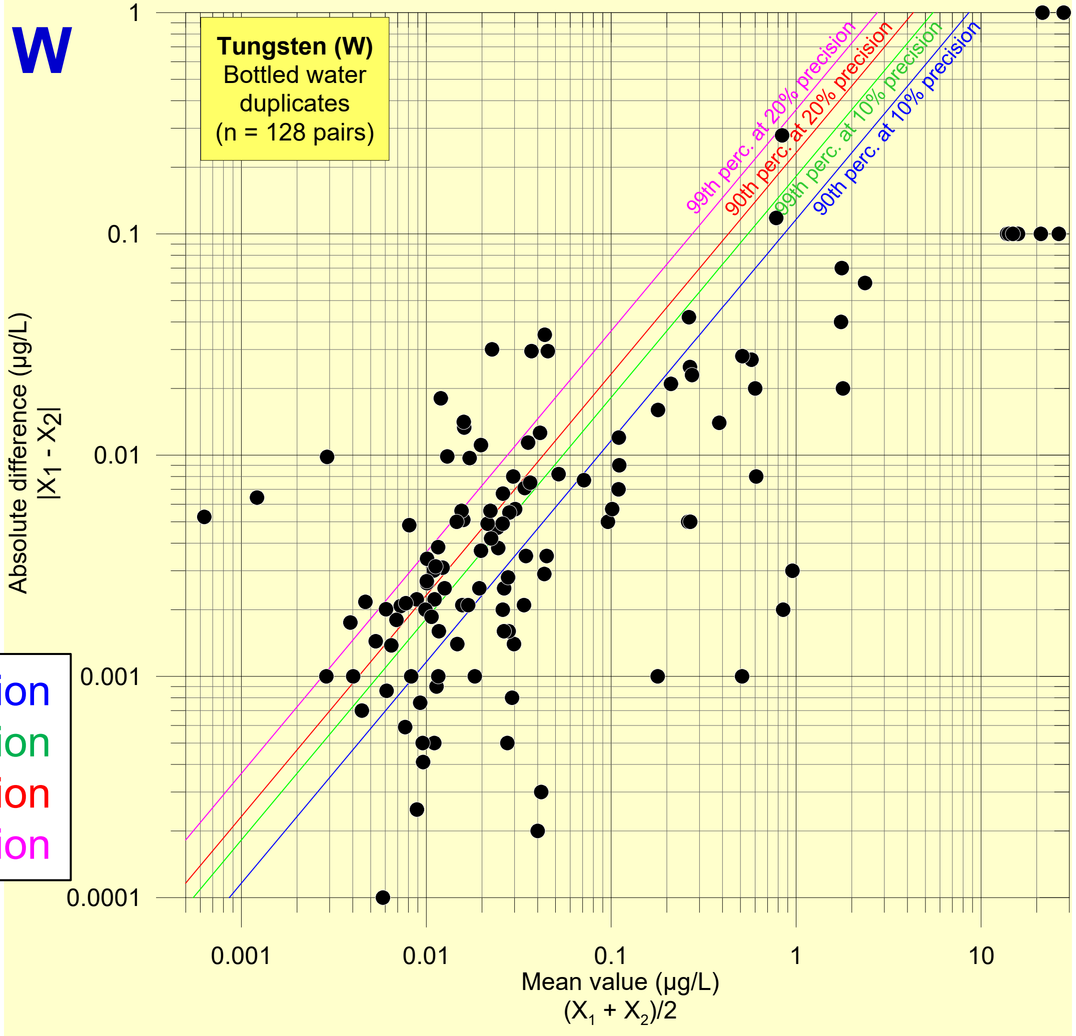
Precision control chart for P = +/-10% and 20% at the 95% confidence level

Control lines at the 90th and 99th percentiles

Quality control (6/6): Thompson-Howarth precision charts



90th percentile at 10% precision
99th percentile at 10% precision
90th percentile at 20% precision
99th percentile at 20% precision



Precision control chart for P = +/-10% and 20% at the 95% confidence level

Control lines at the 90th and 99th percentiles

Precision control chart for P = +/-10% and 20% at the 95% confidence level

Control lines at the 90th and 99th percentiles

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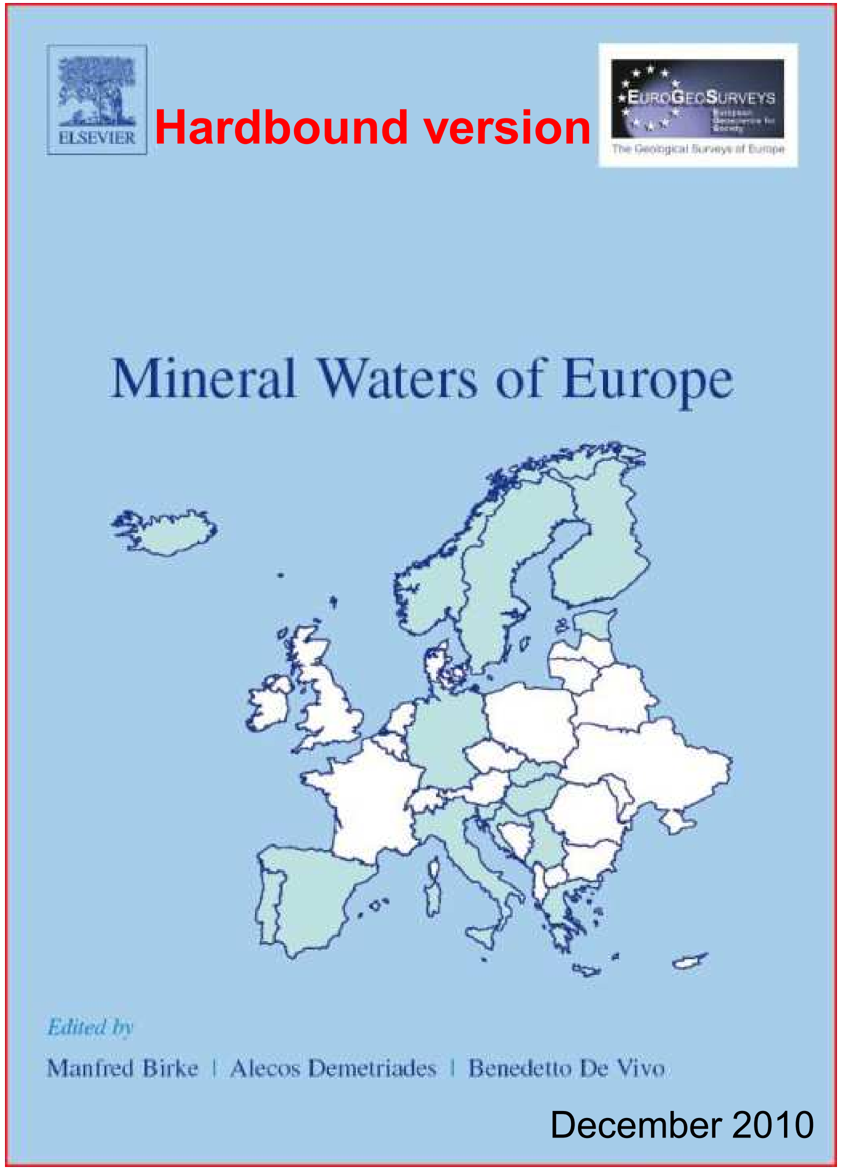

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EGG: European Groundwater Geochemistry

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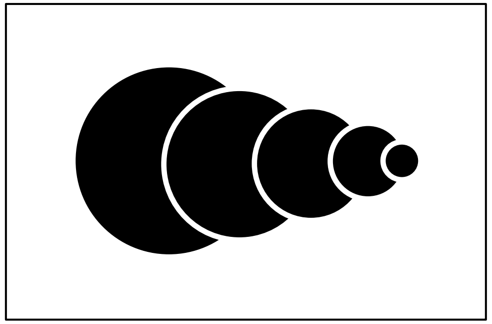
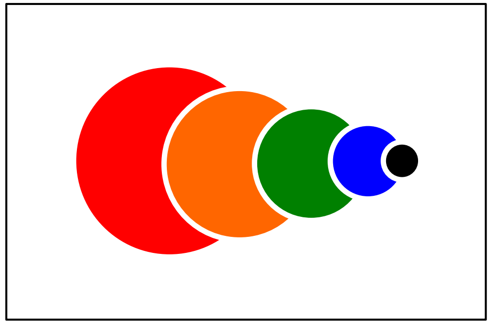
EuroGeoSurveys Geochemistry Expert Group
October 2010 Annual meeting in Athens, Hellenic Republic

Distribution maps and interpretation text

Distribution maps were prepared using the ‘variable-size’ or ‘growing’ dots

Black dots used in printed Atlas





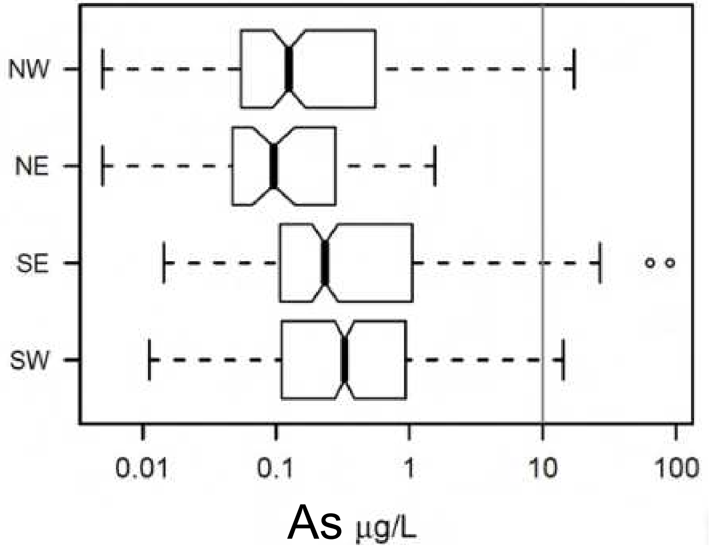
Colour dots used in new maps

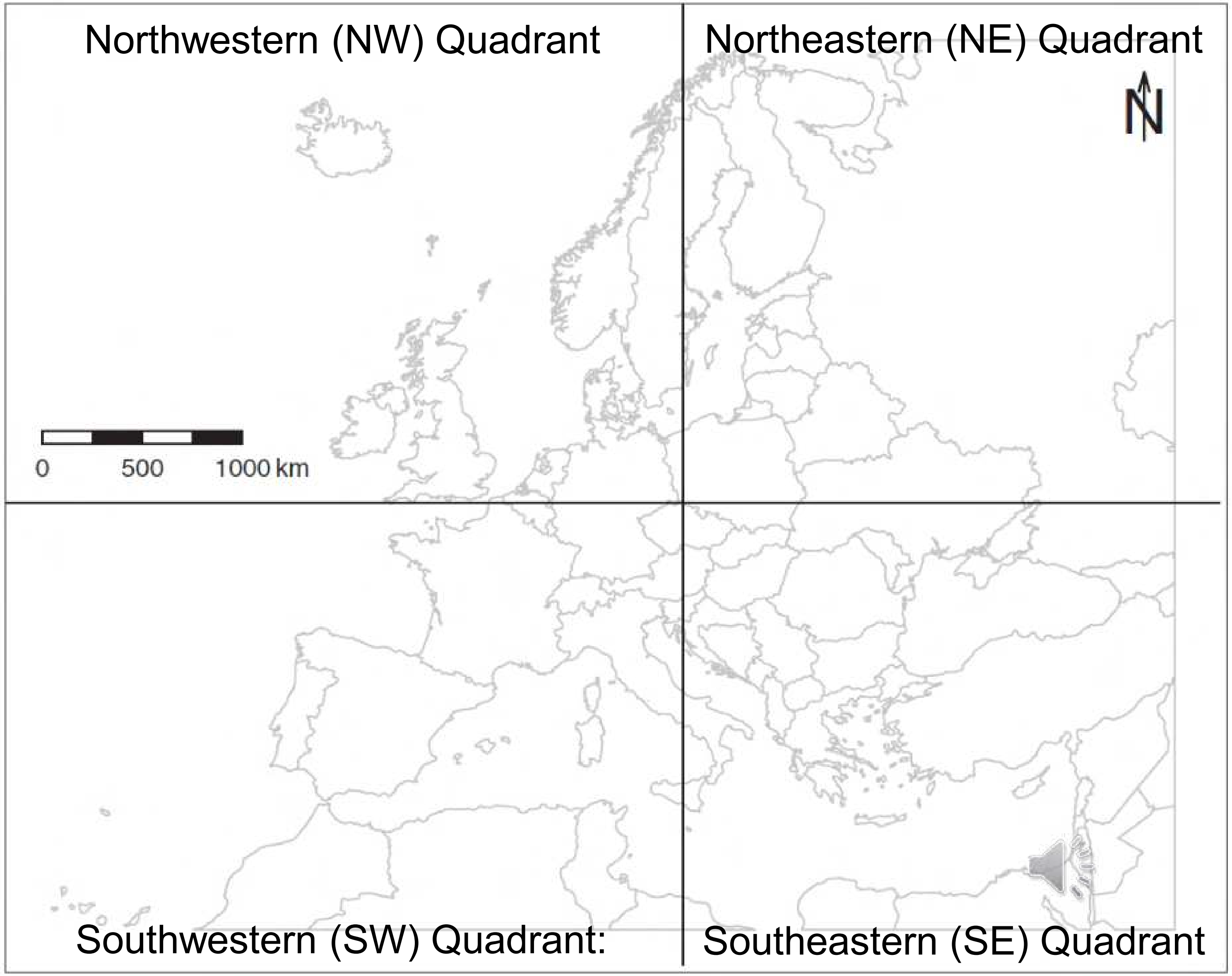
Clear regional patterns emerge for the majority of elements

Plotting of notched-box-and-whisker plots

To be able to get a more objective impression of whether there exist regional scale differences in the observed element concentration and/or variation in Europe, the data set was subdivided into four quadrants:-

Northwestern (NW), Northeastern (NE), Southeastern (SE) and Southwestern (SW):-





Atlas pages

Arsenic is a trace element with a predominantly non-metallic character (atomic number 33). It occurs in oxidation states -3, +3 and +5 in nature. Arsenopyrite (FeSAs) is a common As mineral. Many ore minerals (e.g. galena, pyrite, sphalerite) contain high concentrations of As, but also common silicates (like feldspars) can contain traces of As. Because of the possible substitution of P^{V} by As^{V} phosphate minerals can also contain As.

Many As-minerals are relatively soluble, however, the mobility of As in the secondary environment is limited because of its strong tendency to sorb to clays, secondary hydroxides (especially ferric oxyhydroxides) and organic matter. Hydrothermal processes lead to an enrichment of As. It is, together with Sb, a typical element enriched in hydrothermal waters and an indicator of hydrothermal alteration zones (Banks et al., 2004). It is also often enriched in coal and black shales. Arsenic can be released to the groundwater environment as ferric oxyhydroxides (with a possible loading of sorbed arsenic) are converted by reductive dissolution to dissolved ferrous iron under chemically reducing conditions. This process is believed to be one of the dominant mechanisms for the evolution of arsenic-rich groundwater in some aquifers in Bangladesh. Conversely, when oxidation causes the precipitation of ferric hydroxides from solution, arsenic can also be removed from solution by sorption to the precipitate (this aeration process is one of the few permitted treatments of mineral / spring waters, in order to remove iron and manganese, and it would be expected to also remove arsenic from the water, if present).

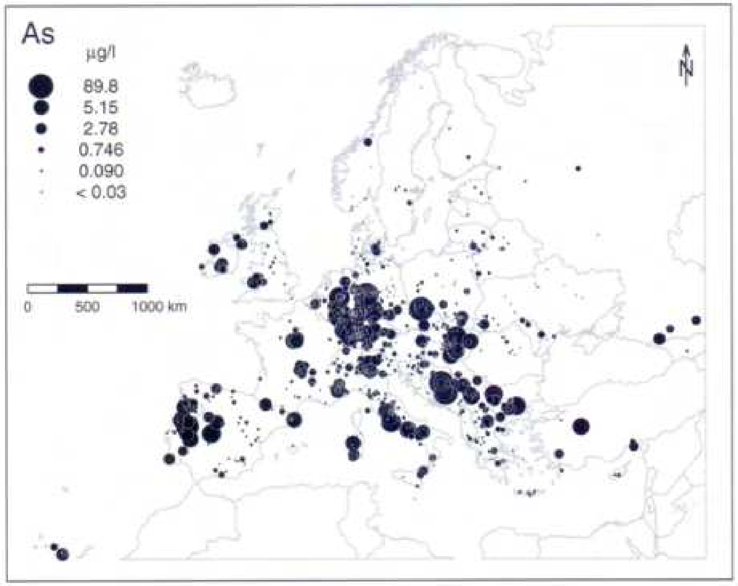
As-compounds are used in many herbicides, insecticides and fungicides, combustion processes, ore roasting and even pig and poultry farming can lead to an anthropogenic load of As. However, due to the strong redox- and pH-dependence of As solubility, the question of whether such contamination will reach groundwater will be very dependent on local conditions. The many incidences of high As in drinking water wells reported in literature (e.g. Smith et al., 2002; Smedley and Kinniburgh, 2002) are invariably connected to special redox- and geological conditions, are usually natural, and no "contamination".

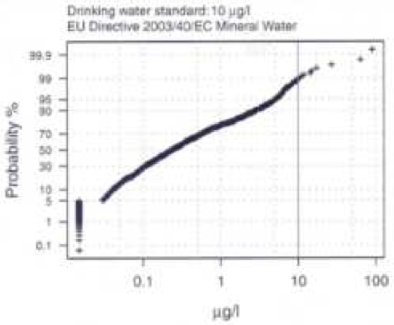
The mean concentration of As in surface water has been estimated to be 4 µg/l (see Koljonen, 1992), a value that is likely to be too high in the light of the results for European surface water (0.63 µg/l – Salminen et al., 2005) and the values presented here (0.24 µg/l) for bottled water.

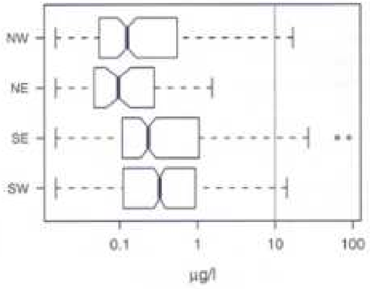
The map of As in bottled water shows quite a number of areas with enhanced As-values. Of the interesting patterns observed for As in the geochemical atlas of Europe were generally the higher concentrations in Southern than in Northern Europe (a factor 3 difference in the median value). The same can be seen for the bottled water. As values are clearly higher in the Southern European countries (see boxplots, median Northern Europe = 0.07, Southern Europe = 0.28 µg/l). Many of the high values displayed on the map occur in parts of Europe that are known for the occurrence of sulphide mineralization. Furthermore, the alkaline volcanic provinces in Italy are marked by higher than usual As values. The highest value (89.8 µg/l) was reported in a Polish mineral water, abstracted in an area with known mineralization. Even four samples from Germany are above the drinking water standards, one is abstracting the water from Palaeozoic rocks, another drawing water from a major fault zone. It is important to mention what is not seen on the map: in the Southern parts of the Great Hungarian Plain occurs groundwater with high natural concentrations of As (e.g. Smedley and Kinniburgh, 2005), which are of course not bottled, but would add on another order of magnitude to the natural variation observed for As. Bedrock groundwater with high As concentrations from Finland and Sweden are also not seen in this low density sample map.

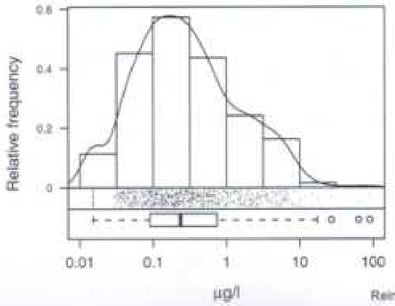
Bottle leaching should have no influence on the observed As concentrations (up to 0.09 µg/l from glass bottles).

The water standard defined for As in mineral water and drinking water in general is 10 µg/l in the EU. Nine samples exceed this level. In the CP-diagram in Figure 26 all samples show very comparable As values and variation, with a slight enrichment of As in the European surface water in the lower and middle concentration range. The CP-diagram suggests that the natural variation of As concentration in European bottled water (and European water in general) covers four orders of magnitude (+2 orders of magnitude from natural As-provinces).









Analytical Method: ICP–QMS
Detection limit: 0.03 µg/l
45 (5.09%) < detection limit

n:	884
Minimum:	< 0.03 µg/l
5%:	< 0.03 µg/l
25%:	0.090 µg/l
Median:	0.235 µg/l
75%:	0.746 µg/l
95%:	5.15 µg/l
Maximum:	89.8 µg/l

Reimann & Birke (Eds.) (2010): Geochemistry of European Bottled Water
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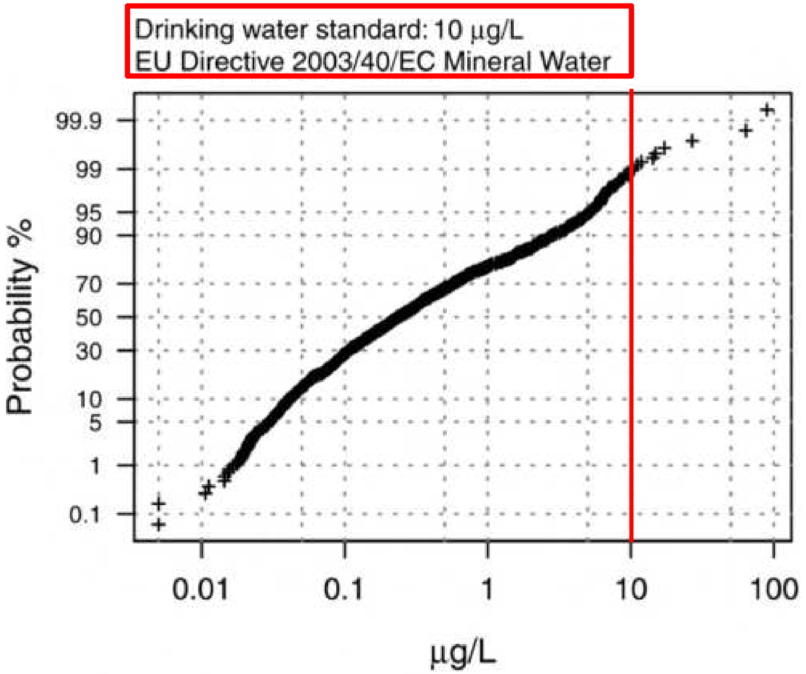
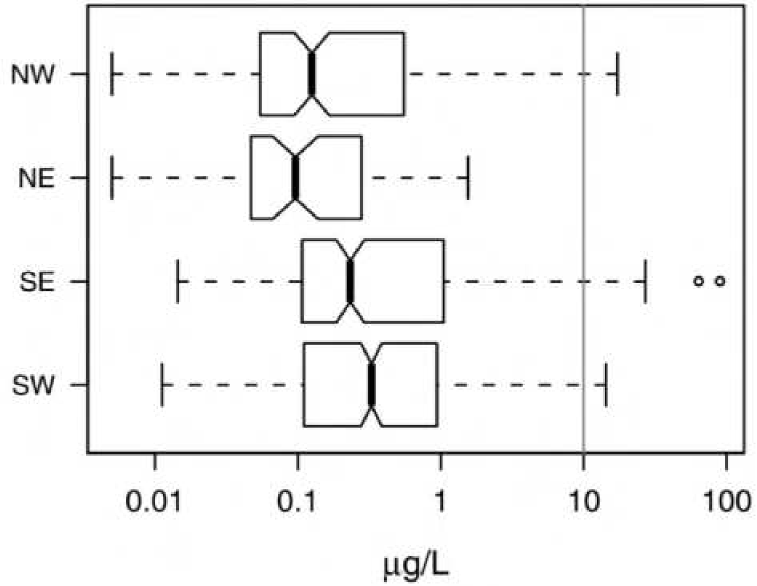
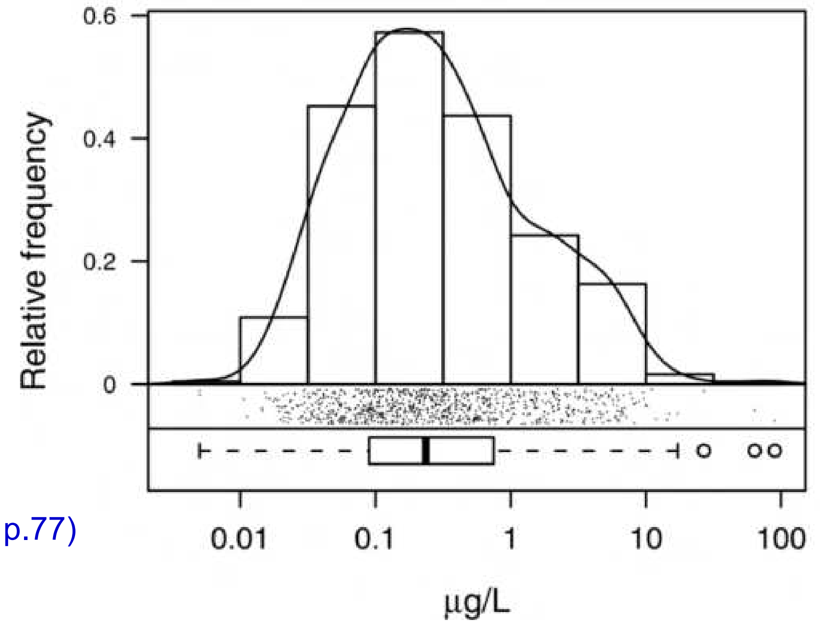
(Reimann & Birke, 2010, p.76-77)







(Reimann & Birke, 2010, p.77)

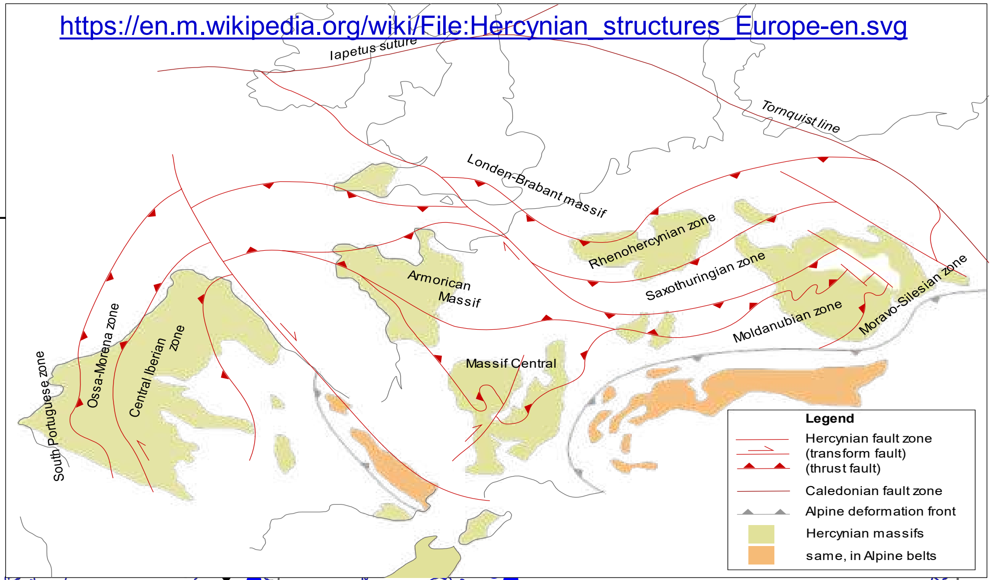
Analytical Method: ICP-QMS
Detection limit: 0.01 µg/L
2 (0.23%) < detection limit

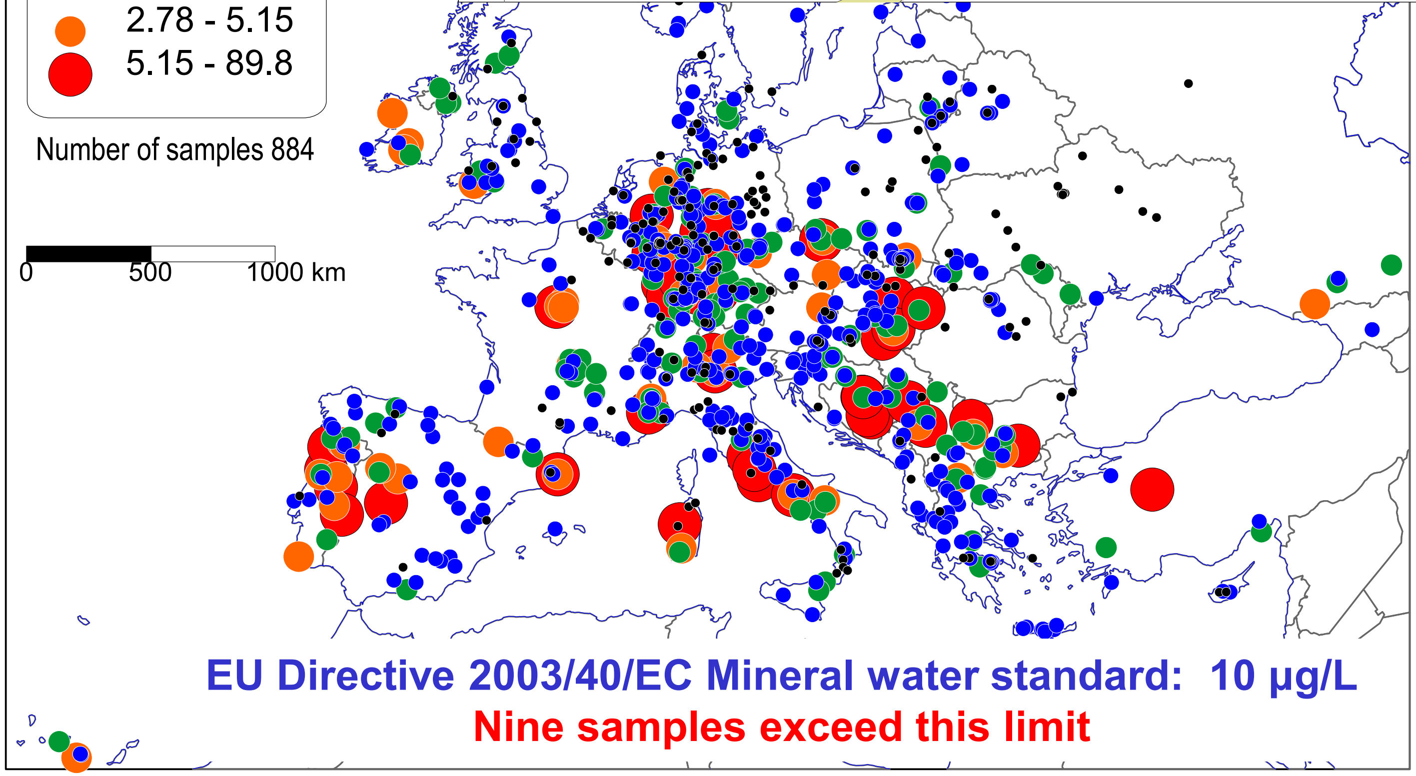
n:	884
Minimum:	< 0.01 µg/L
5%:	0.030 µg/L
25%:	0.090 µg/L
Median:	0.235 µg/L
75%:	0.746 µg/L
95%:	5.15 µg/L
Maximum:	89.8 µg/L

Arsenic As

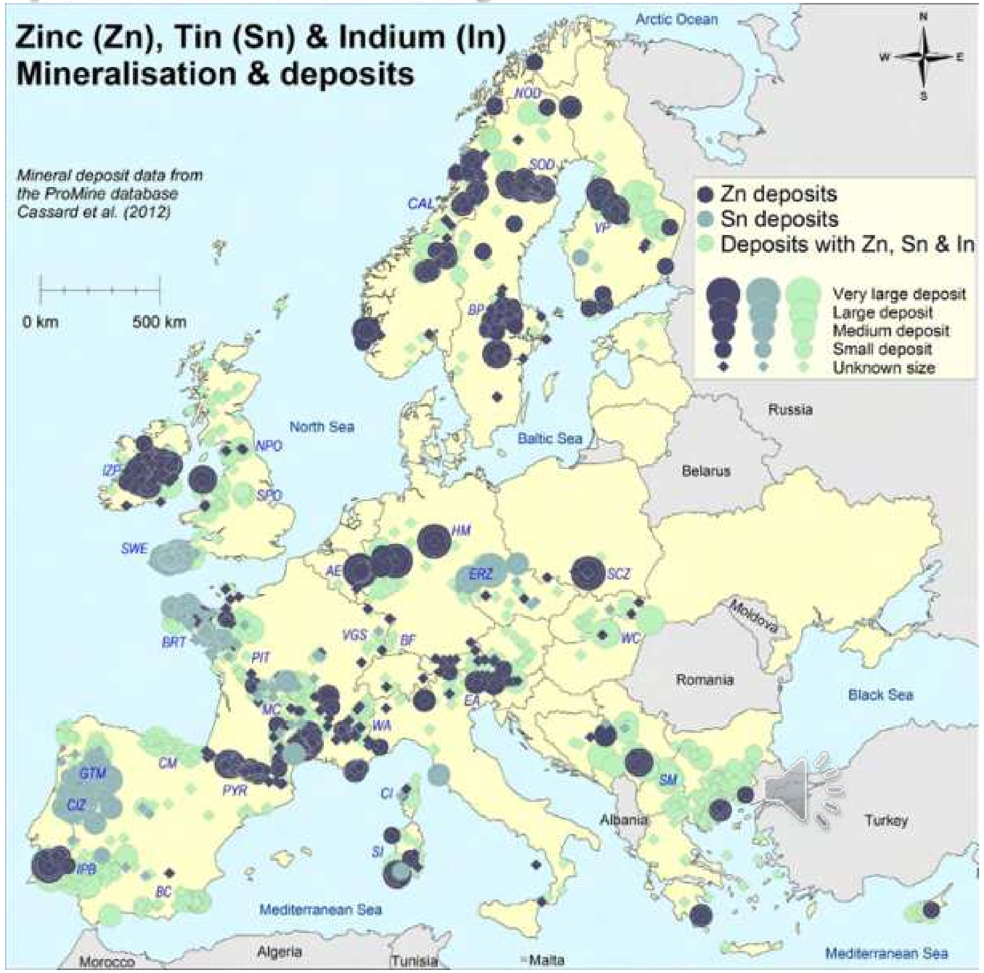
Arsenic (As):-

Anomalous samples occur near Sulphide mineralisation, fault zones, and the alkaline volcanic provinces in Italy.



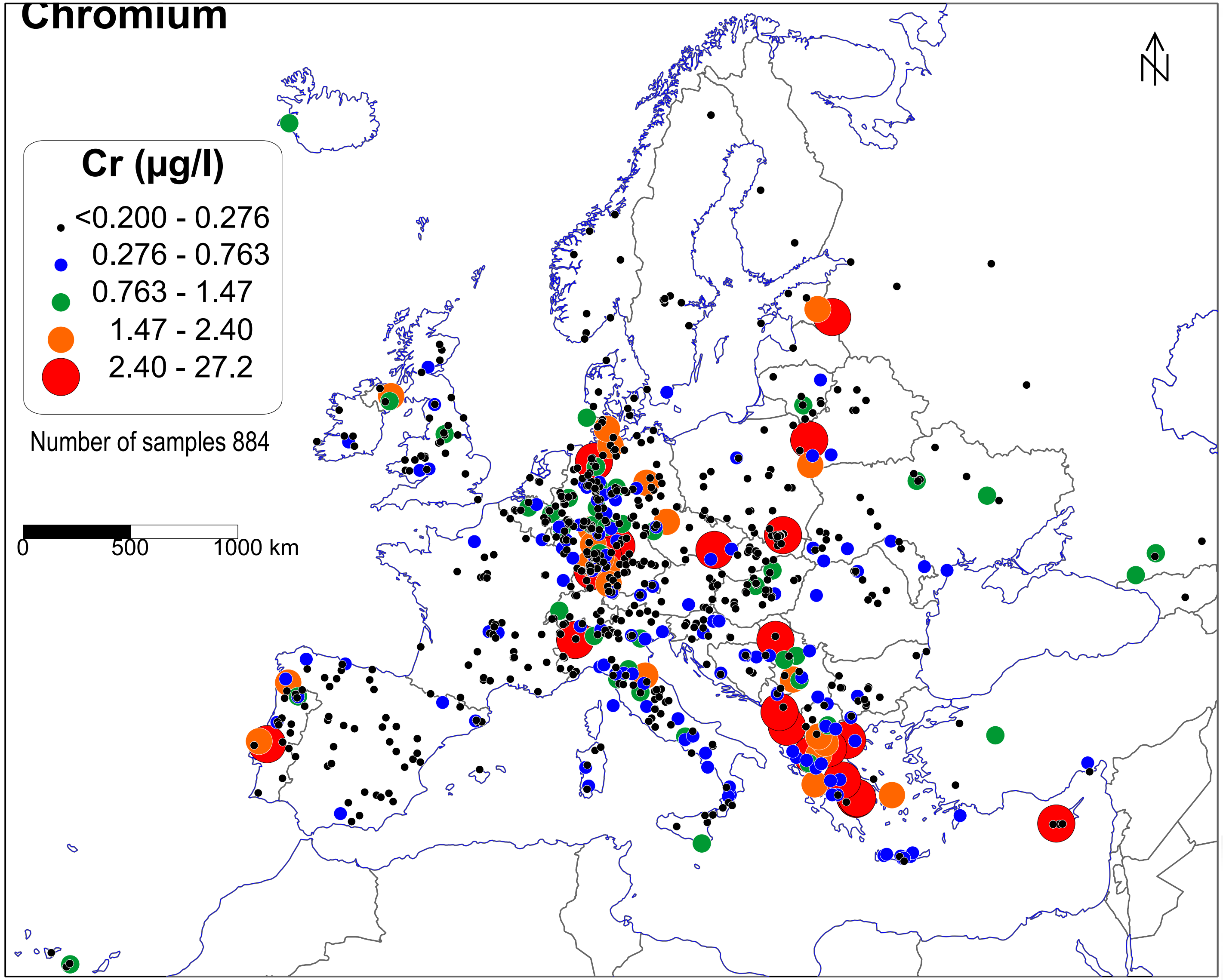


(Reimann & Birke, 2010, p.77, modified)

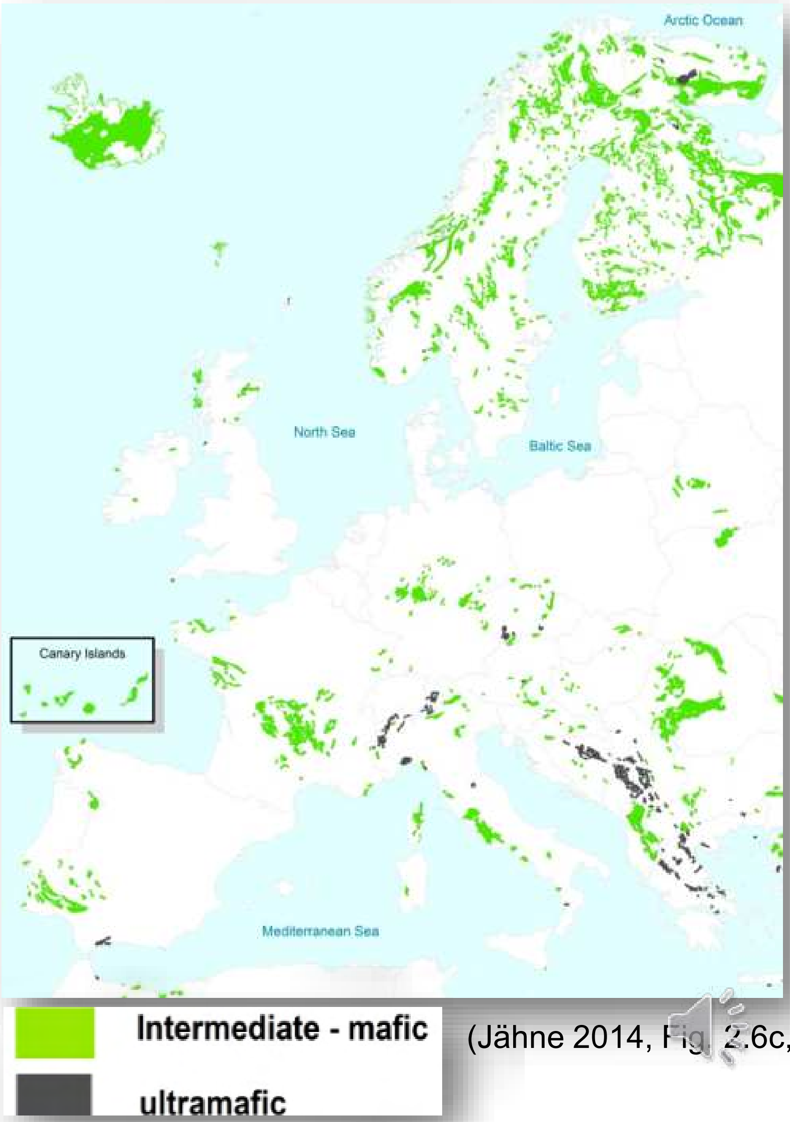


(Ladenberger *et al.*, 2015, Fig. 1, p.64)

Chromium (Cr):- Anomalous samples occur in areas with Ophiolites (mafic-ultramafic rocks).



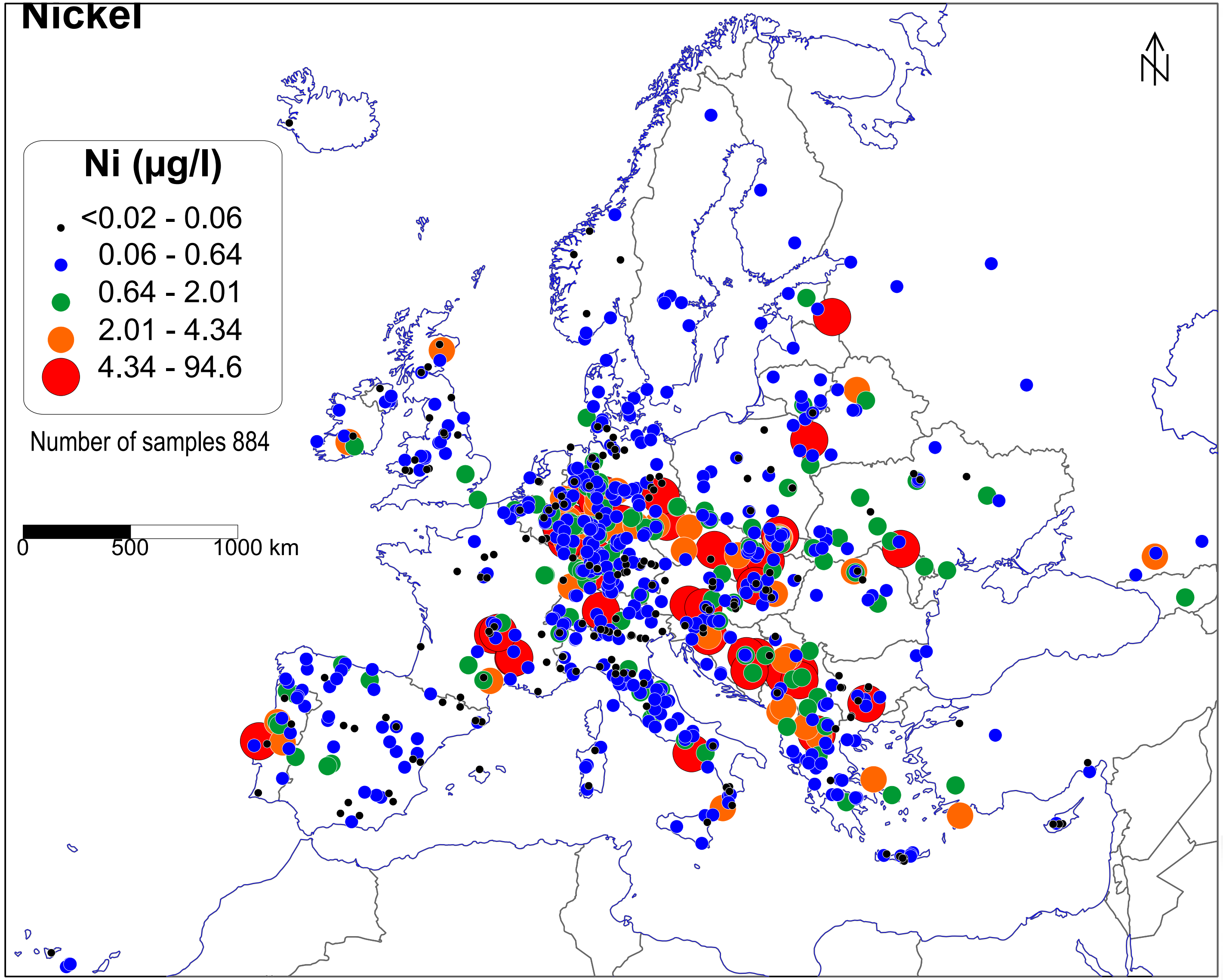
(Reimann & Birke, 2010, p.99, modified)



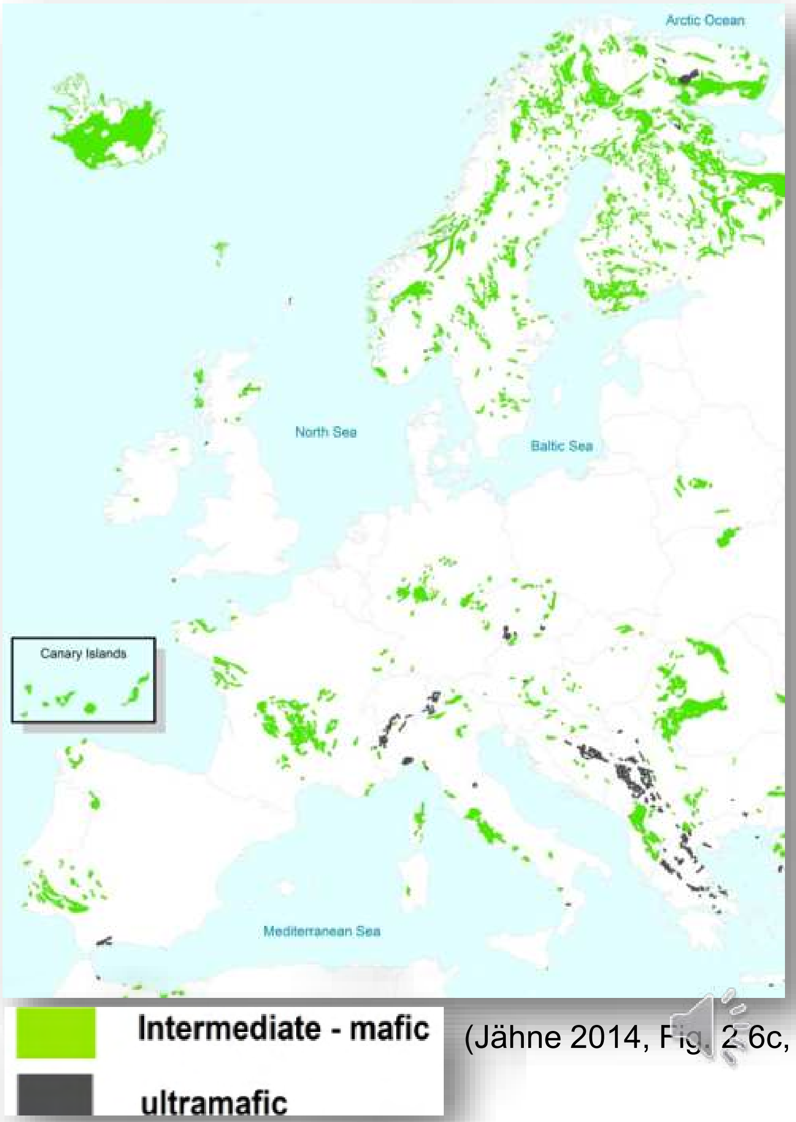
(Jähne 2014, Fig. 2.6c, p.59)

EU Directive 2003/40/EC Mineral water standard: 50 mg/L

Nickel (Ni): Anomalous samples occur in areas with Ophiolites (mafic-ultramafic rocks)



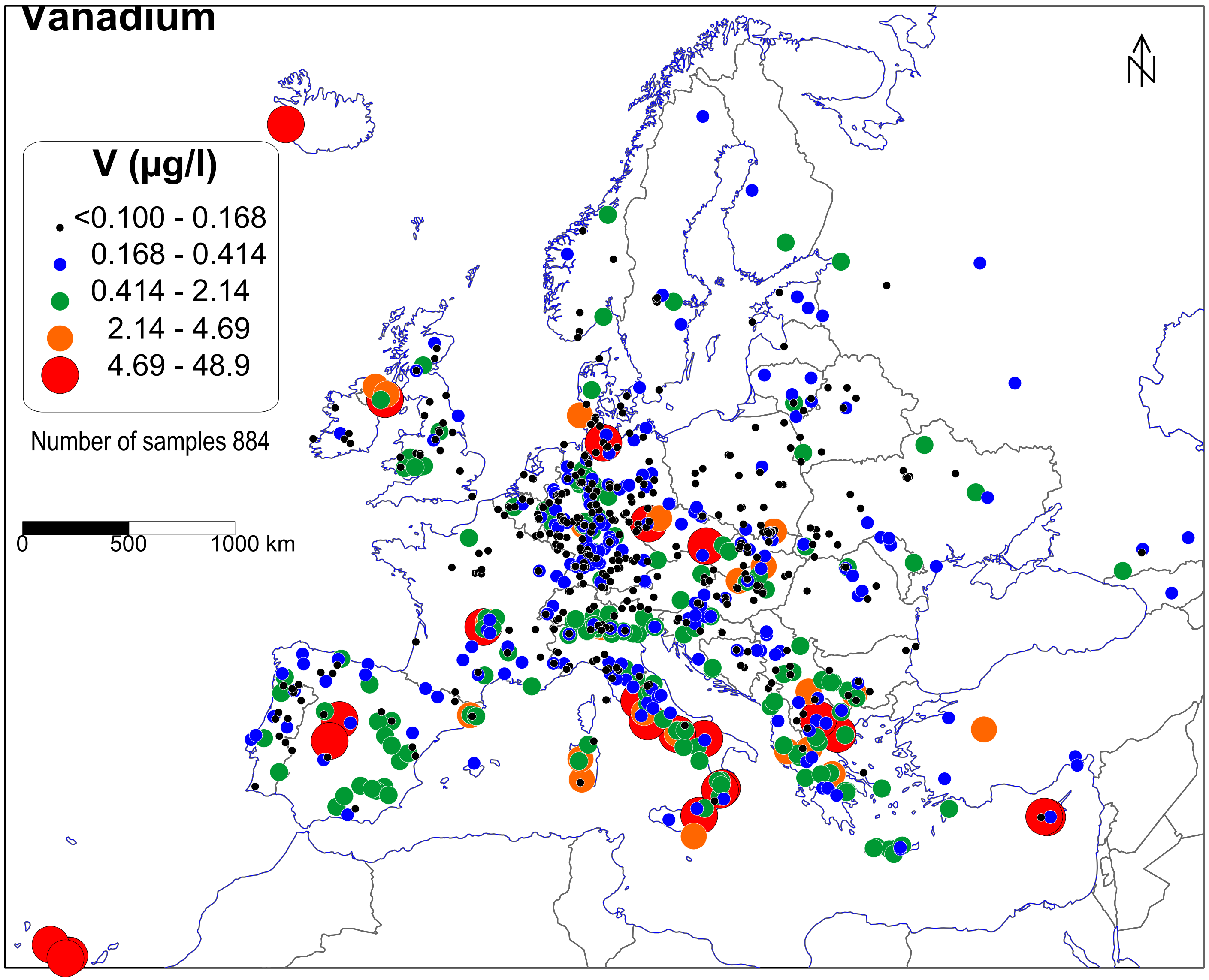
(Reimann & Birke, 2010, p.149, modified)



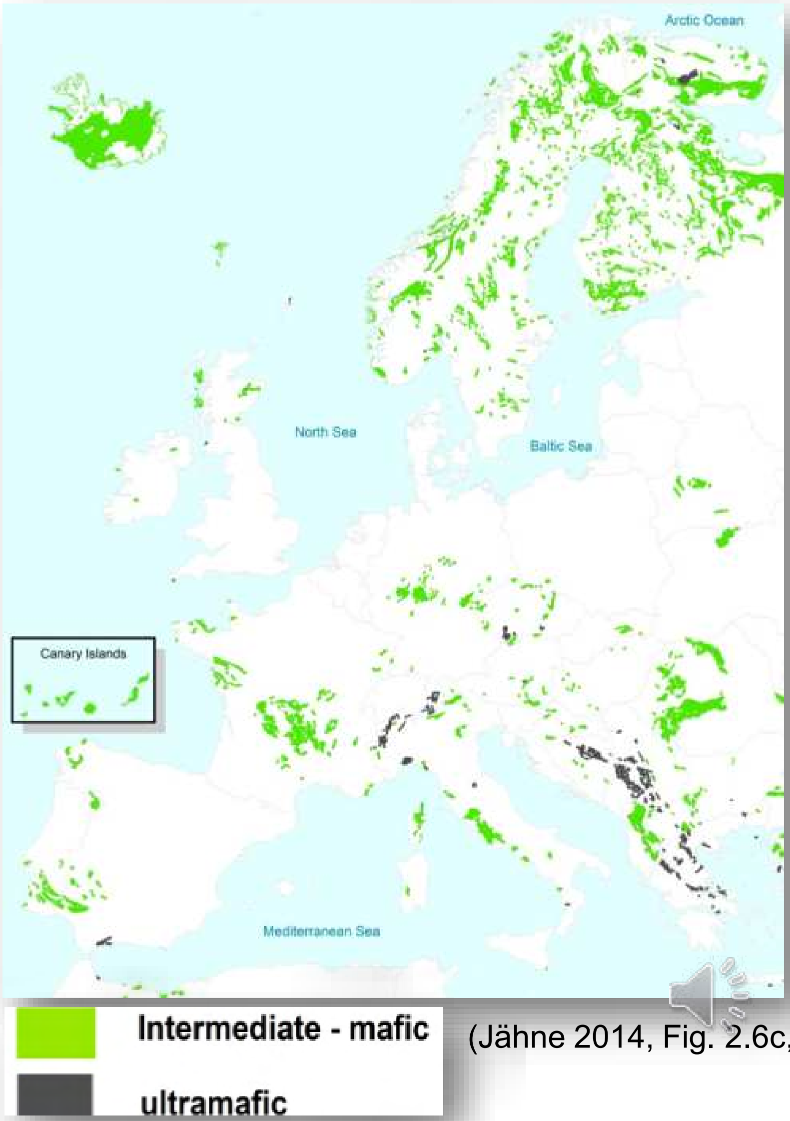
(Jähne 2014, Fig. 2.6c, p.59)

EU Directive 2003/40/EC Mineral water standard: 20 mg/L; 6 samples exceed this limit

Vanadium (V):- Anomalous samples occur in the vicinity of active volcanic centres and basaltic rocks.



(Reimann & Birke, 2010, p.189, modified)



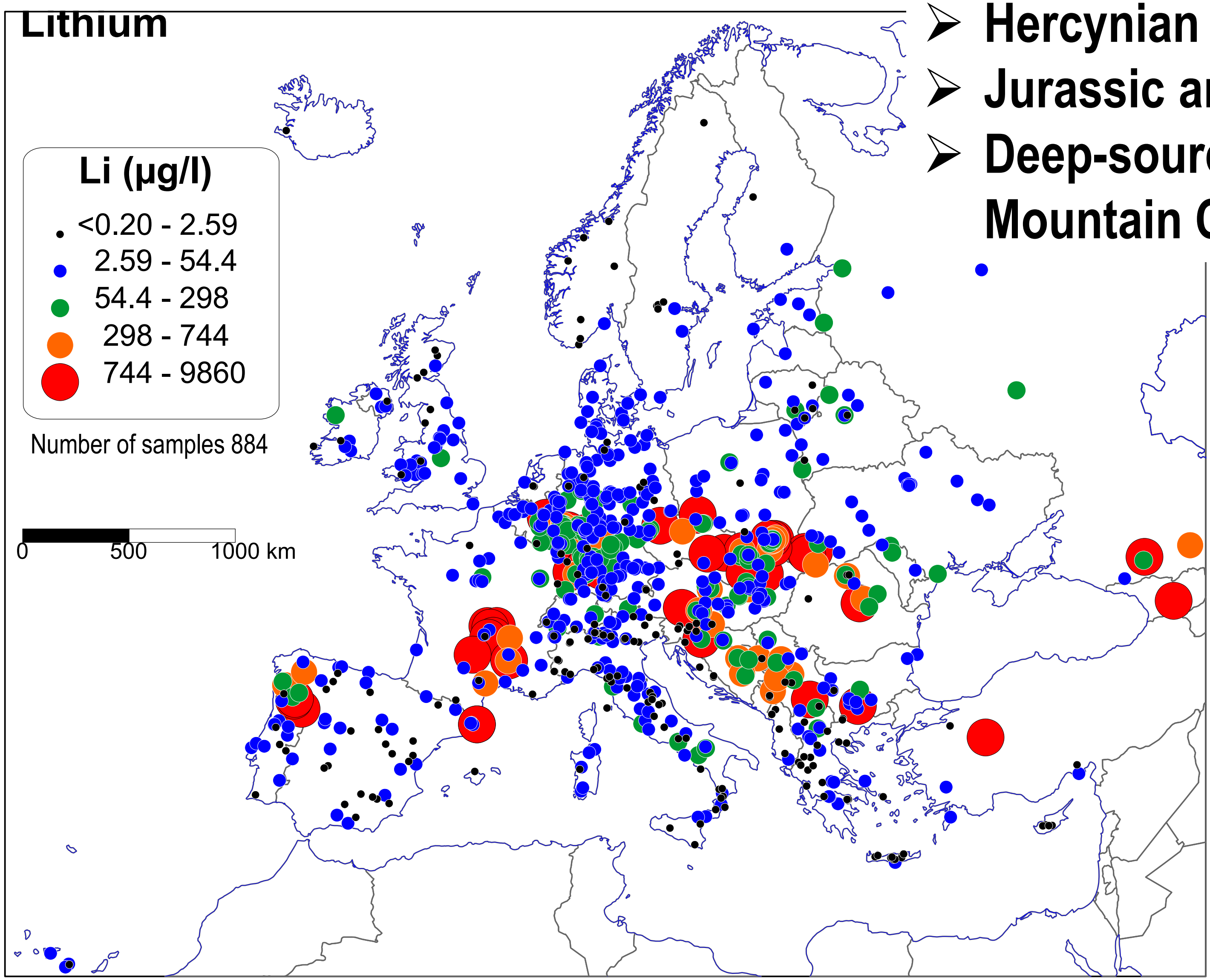
(Jähne 2014, Fig. 2.6c, p.59)

Drinking water standard: None defined

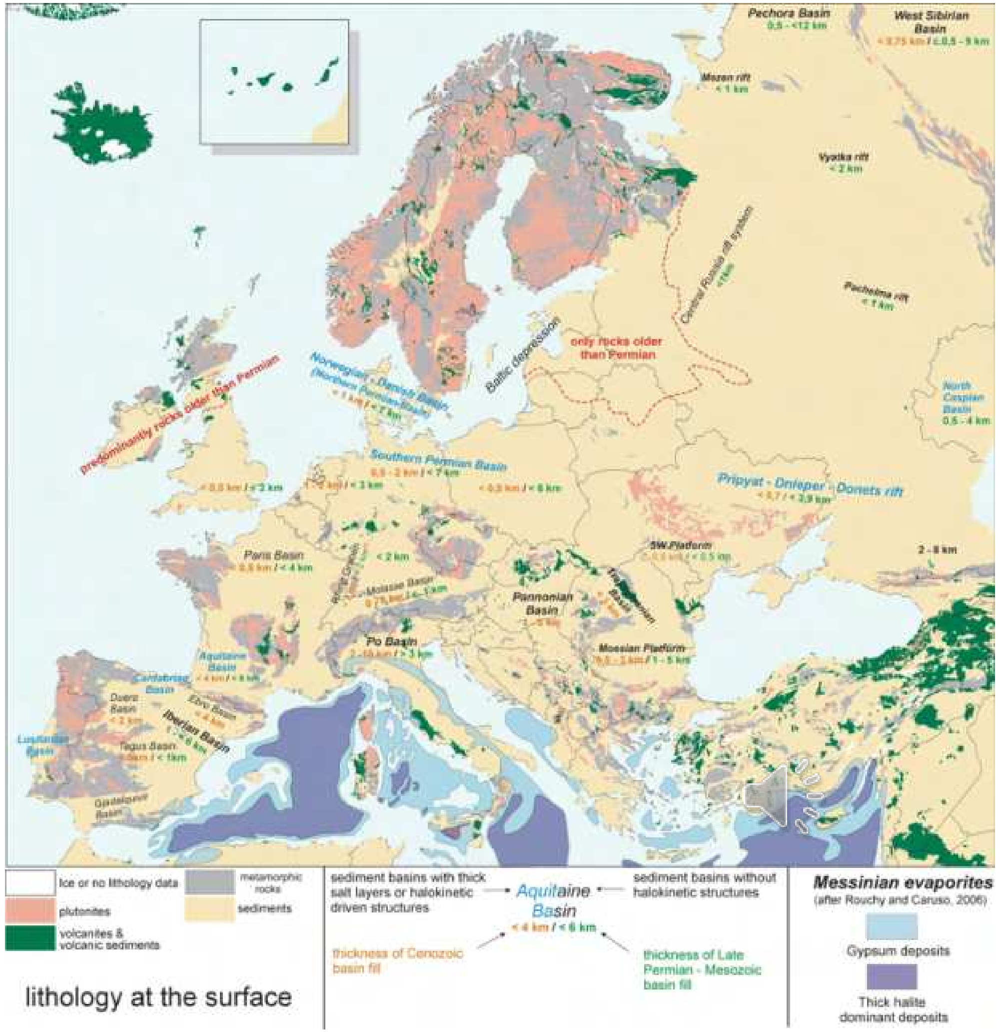
Lithium (Li):- Anomalous samples occur in areas with

- ➢ Hercynian granites,
- ➢ Jurassic and Triassic sediments in Germany, and
- ➢ Deep-sourced water wells, *e.g.*, in the Carpathian Mountain Chain & Balkans.

(Reimann & Birke, 2010, Fig. 15, p.25)

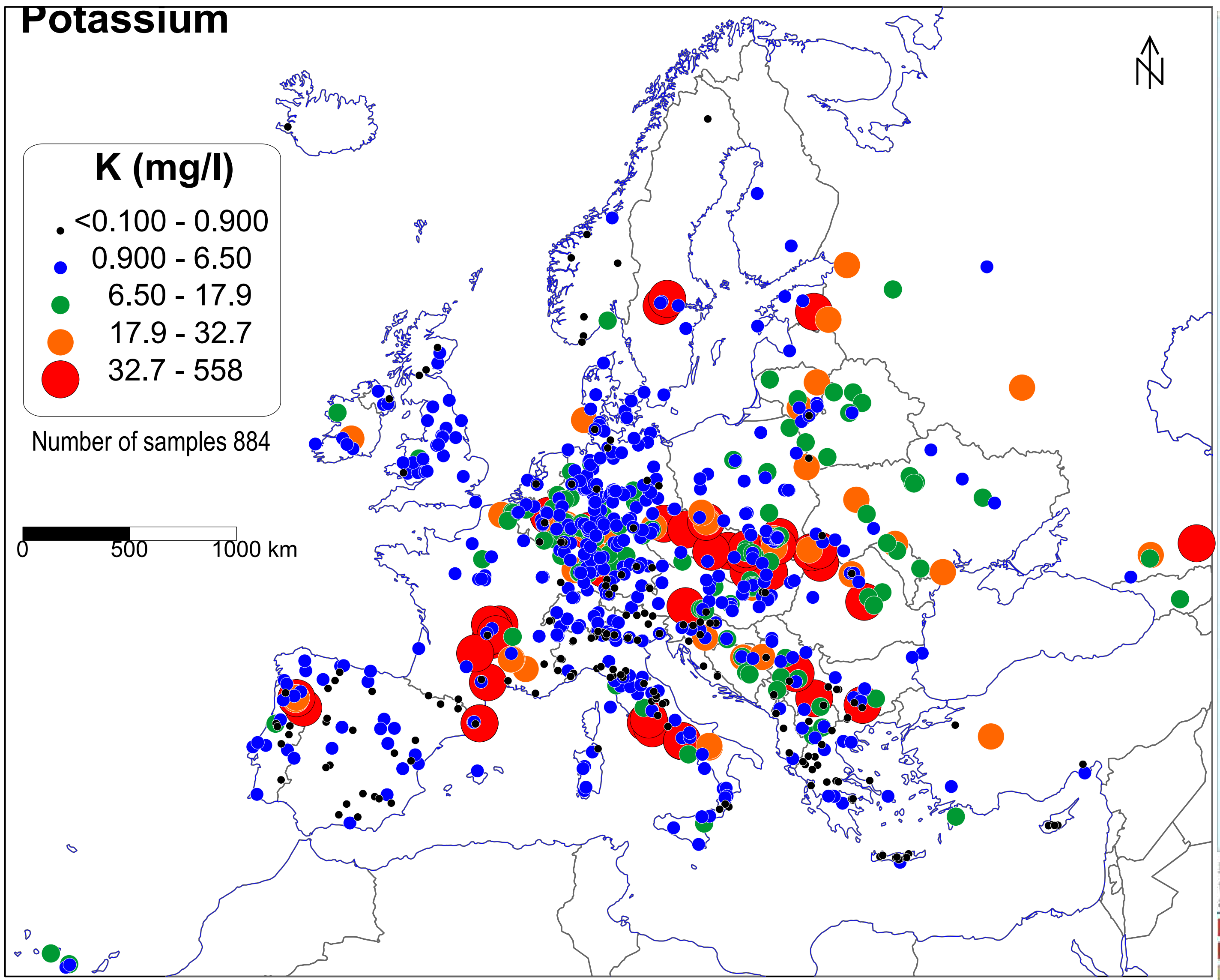


(Reimann & Birke, 2010, p.131, modified)

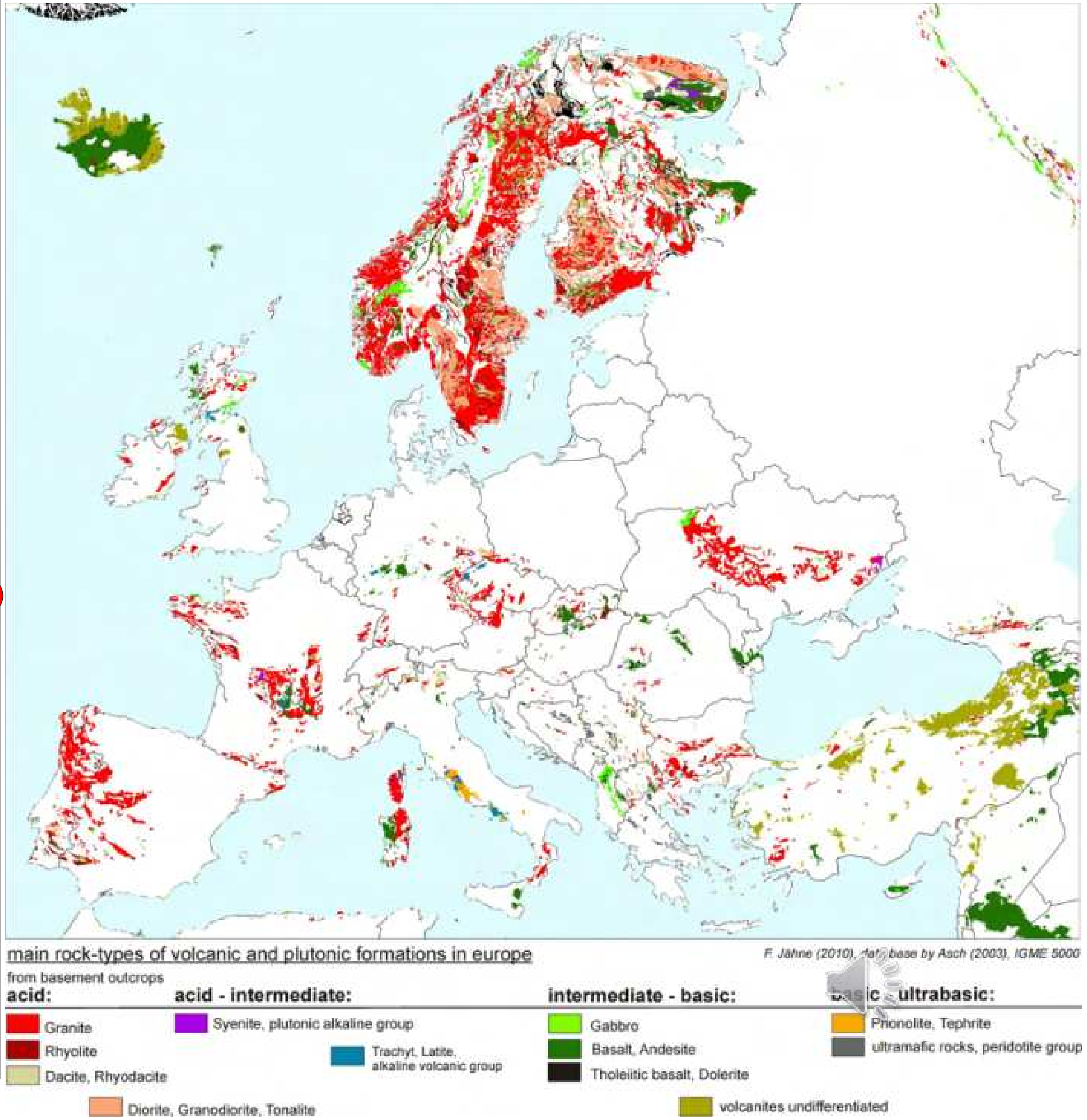


Drinking water standard: None defined

Potassium (K):- Distribution patterns are similar to those of Li.



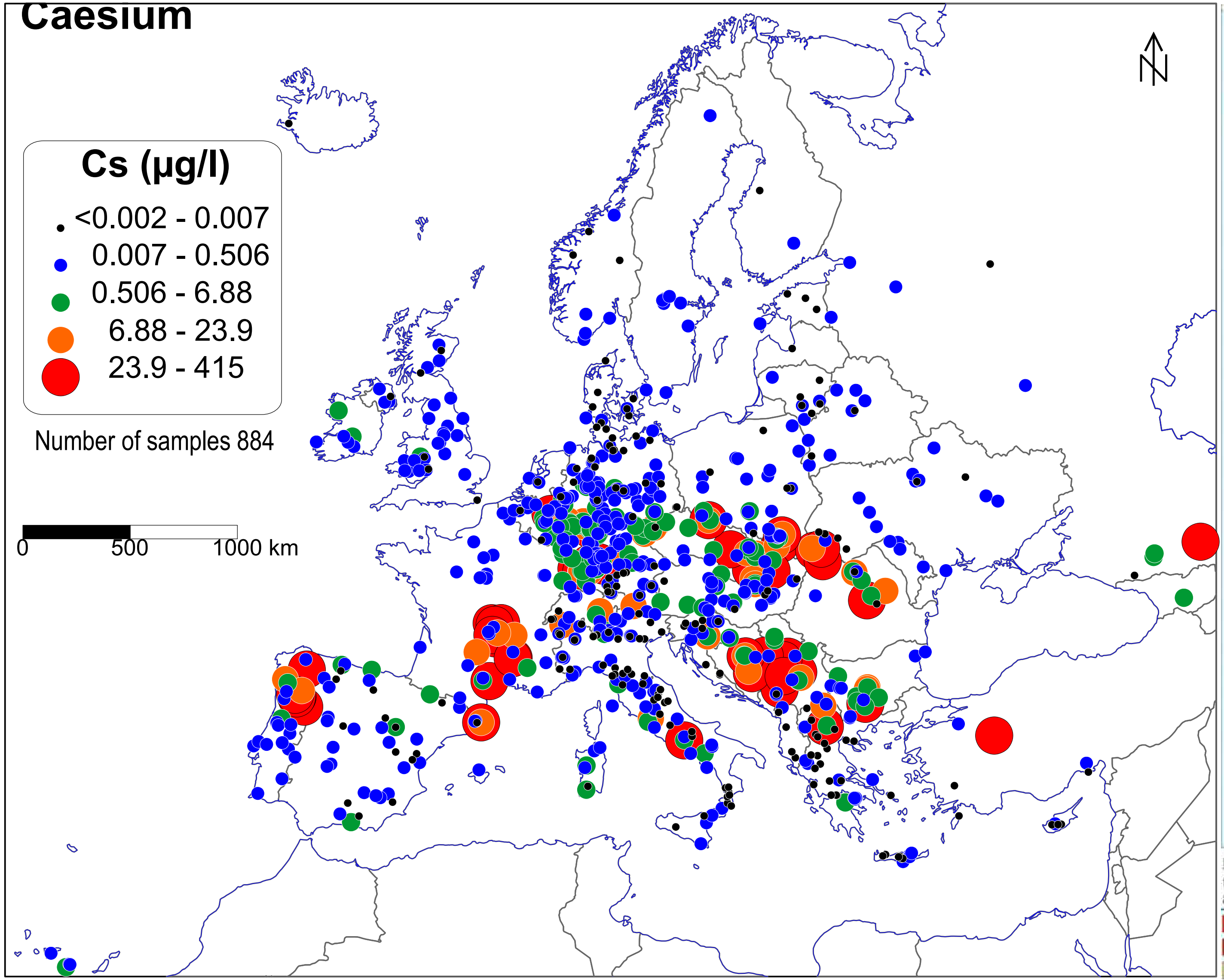
(Reimann & Birke, 2010, p.127, modified)



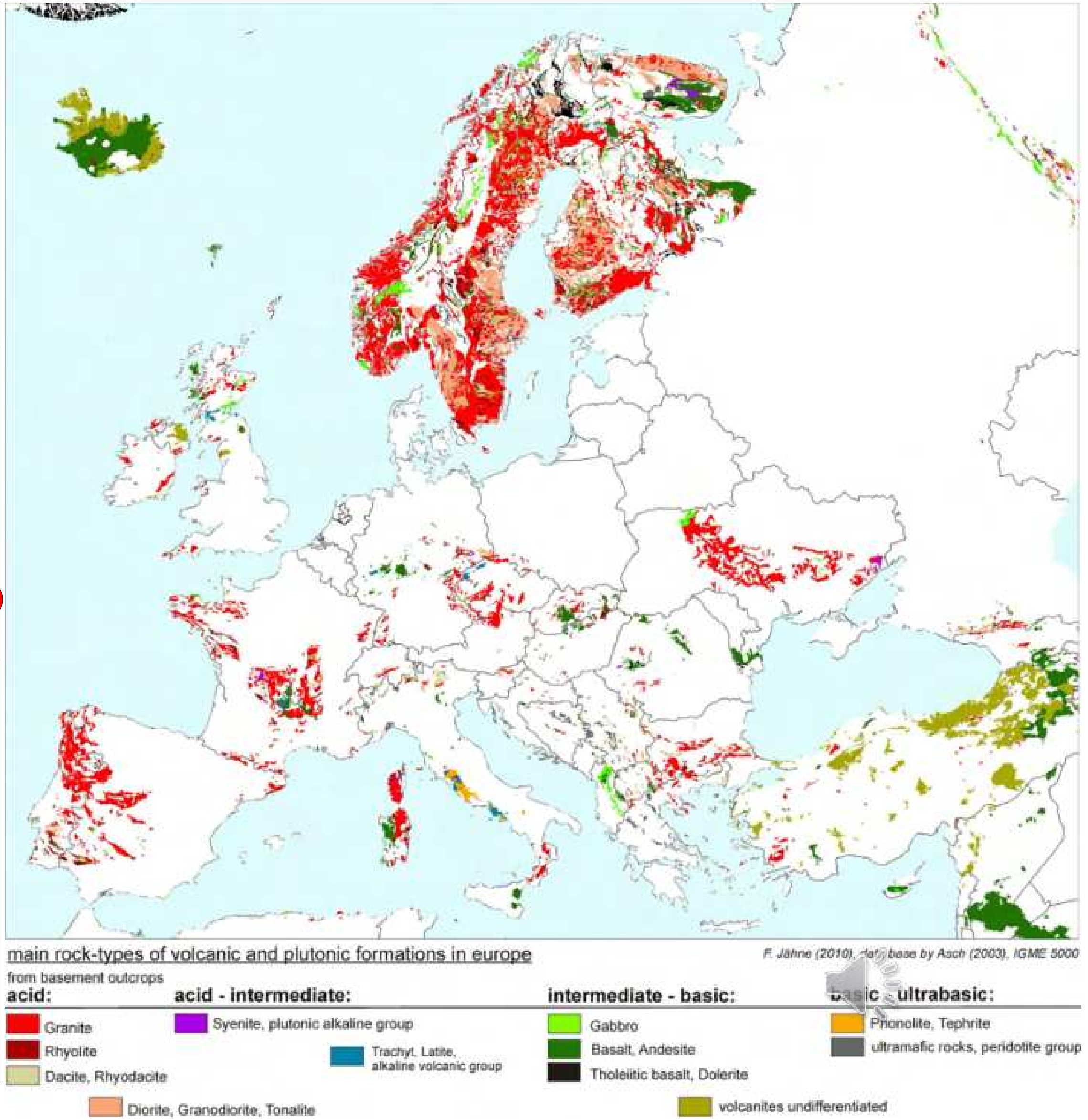
(Reimann & Birke, 2010, Fig. 14, p.24)

Drinking water standard: None defined

Caesium (Cs):- Distribution patterns are similar to those of Li and K.



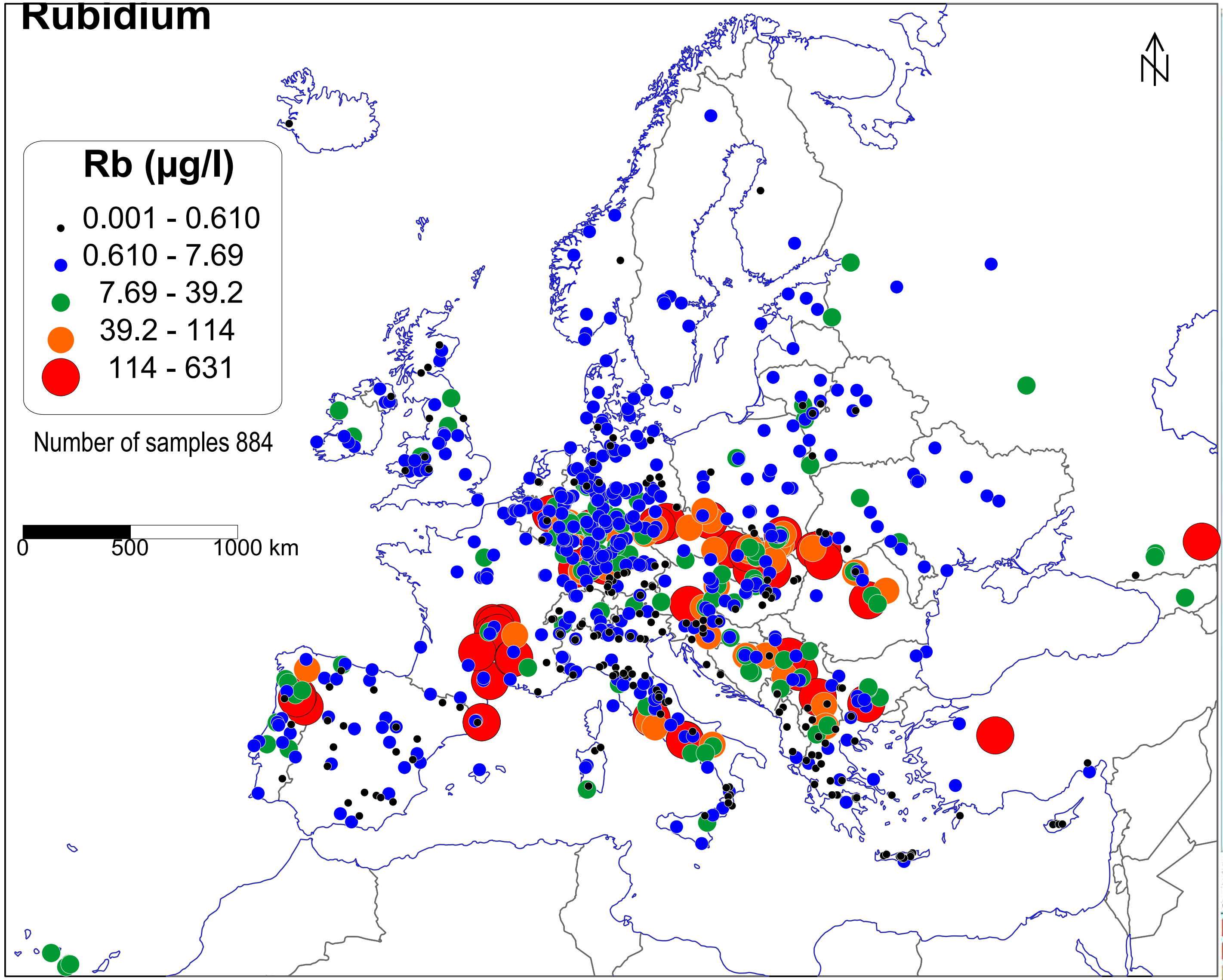
(Reimann & Birke, 2010, p.101, modified)



(Reimann & Birke, 2010, Fig. 14, p.24)

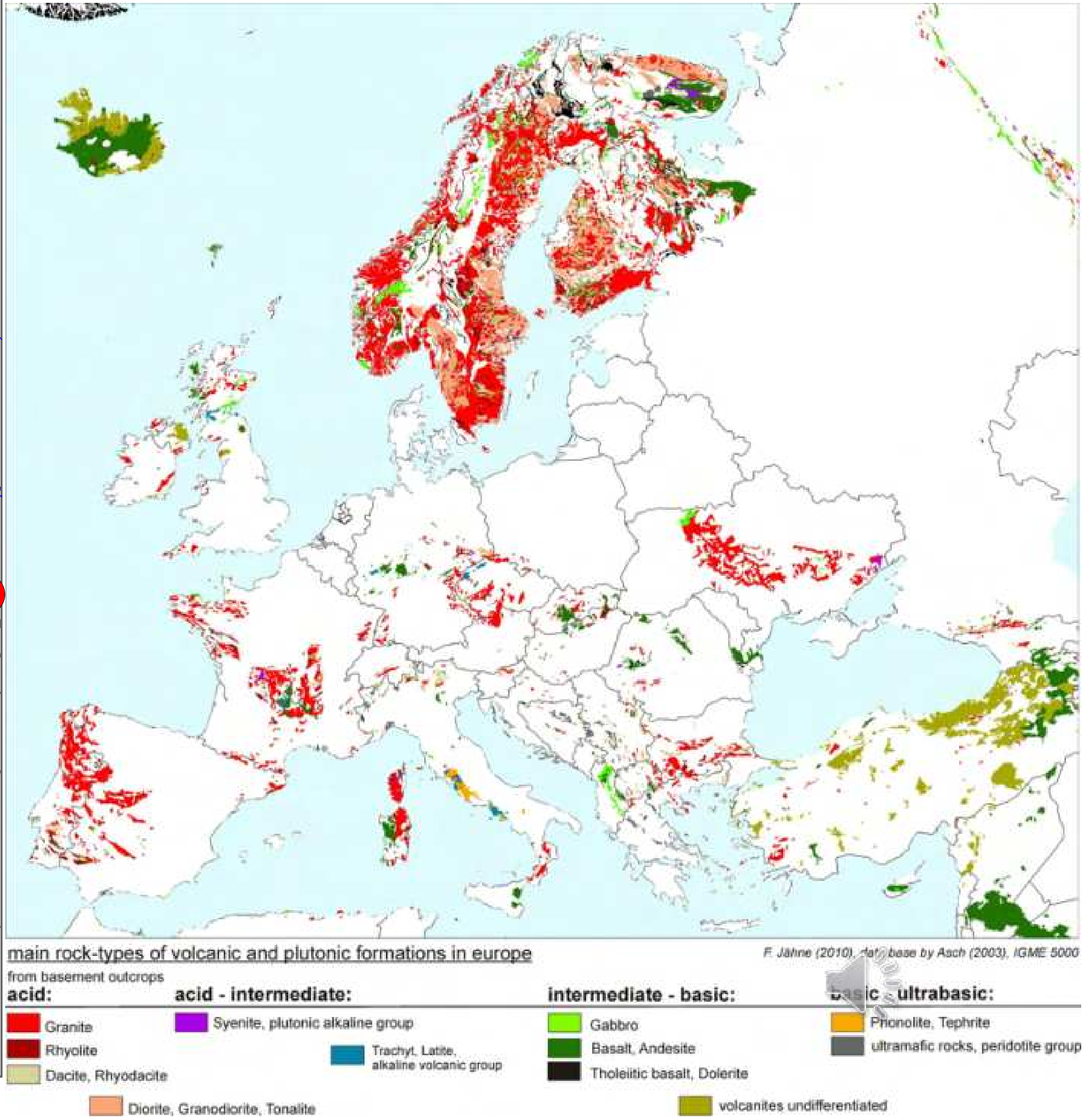
Drinking water standard: None defined

Rubidium (Rb):- Distribution patterns are similar to those of Li, K and Cs.



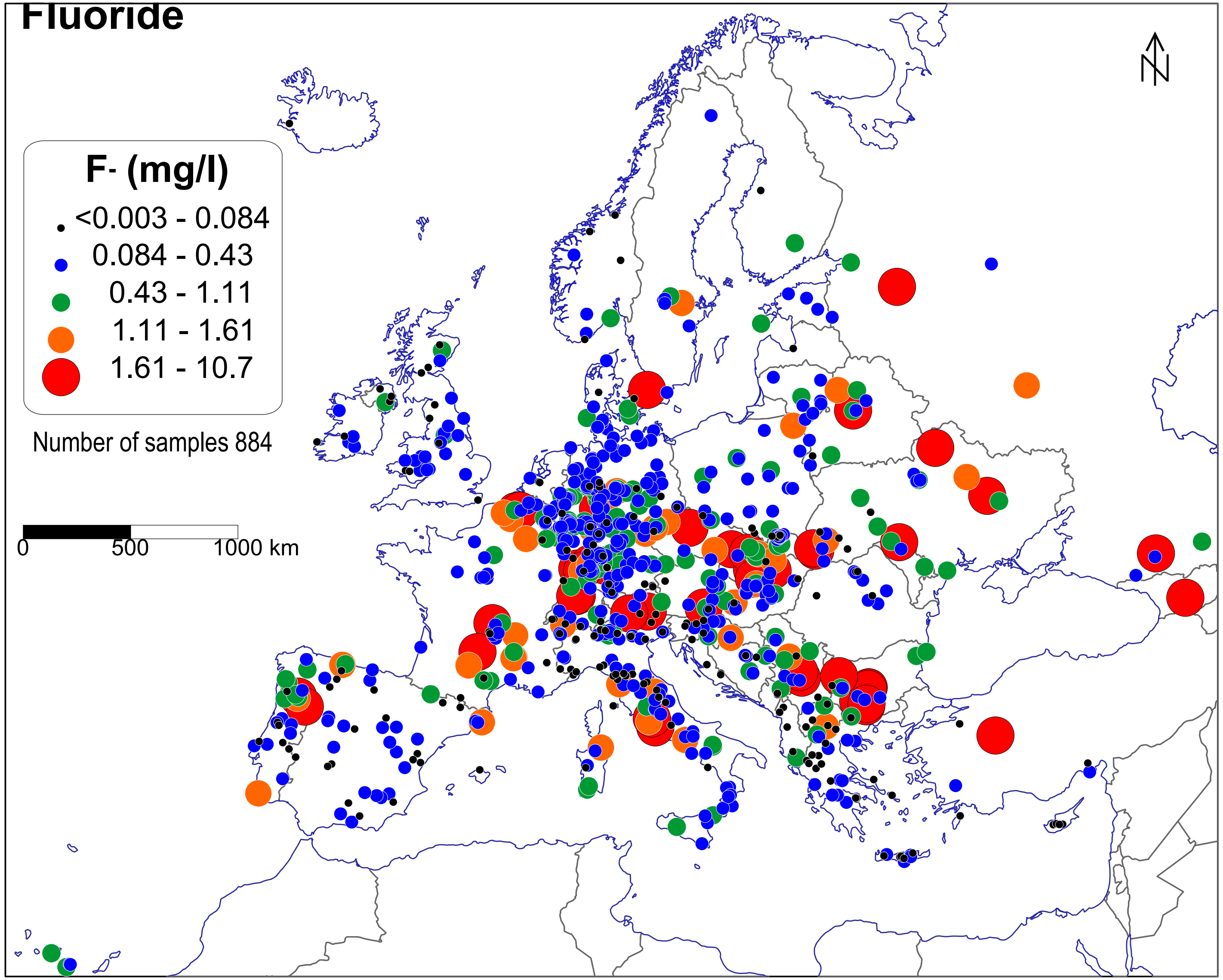
(Reimann & Birke, 2010, p.159, modified)

Drinking water standard: None defined



(Reimann & Birke, 2010, Fig. 14, p.24)

Fluoride (F):-



(Reimann & Birke, 2010, p.111, modified)

Drinking water standard: 5 mg/L F^-.

One sample exceeds this limit.

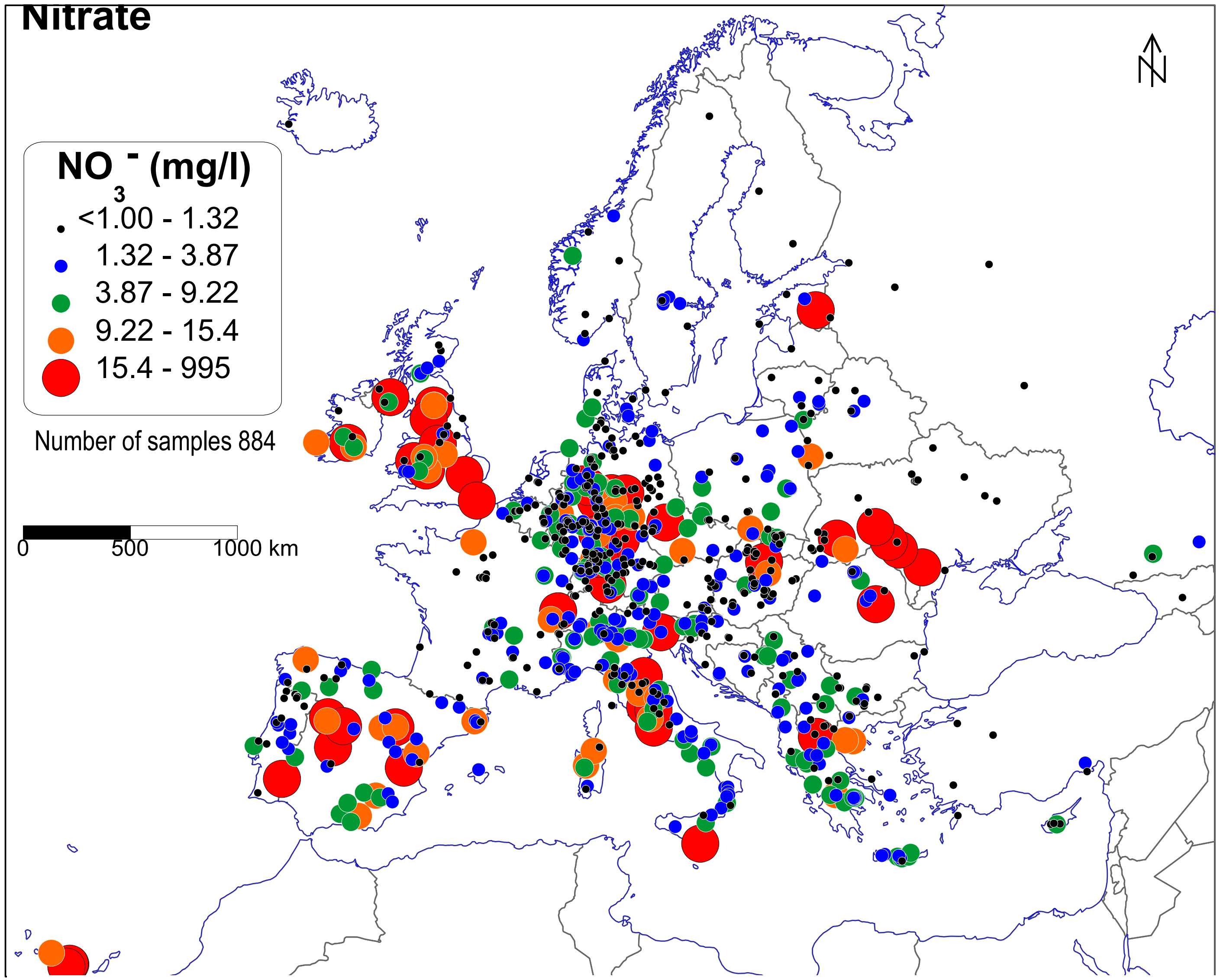
Most bottled mineral waters show high F^- values in Northeastern Europe, where many "true" (*i.e.*, highly mineralised) mineral waters are bottled. Several wells abstracting water in areas underlain by young granites exhibit unusually high F^- concentrations (*e.g.*, Portugal, France).

In Italy, waters extracted from wells in areas with Tertiary alkaline volcanic rocks show elevated F^- concentrations.

In Bulgaria, the high F^- concentrations are possibly due to Palaeozoic granites and fluoride mineralisation (*e.g.*, Mihalkovo deposit).

The highest value of 10.7 mg/L F^- was reported from a well from Georgia and it was marked as "*medicinal water*".

Many of the anomalous wells can be traced to deep fault zones.



(Reimann & Birke, 2010, p.151; modified)

Drinking water standard: 50 mg/L NO_3^-. This level is set with respect to the perceived risk of infantile methaemoglobinaemia.

Only two bottled mineral water samples have values >50 mg/L NO_3^-.

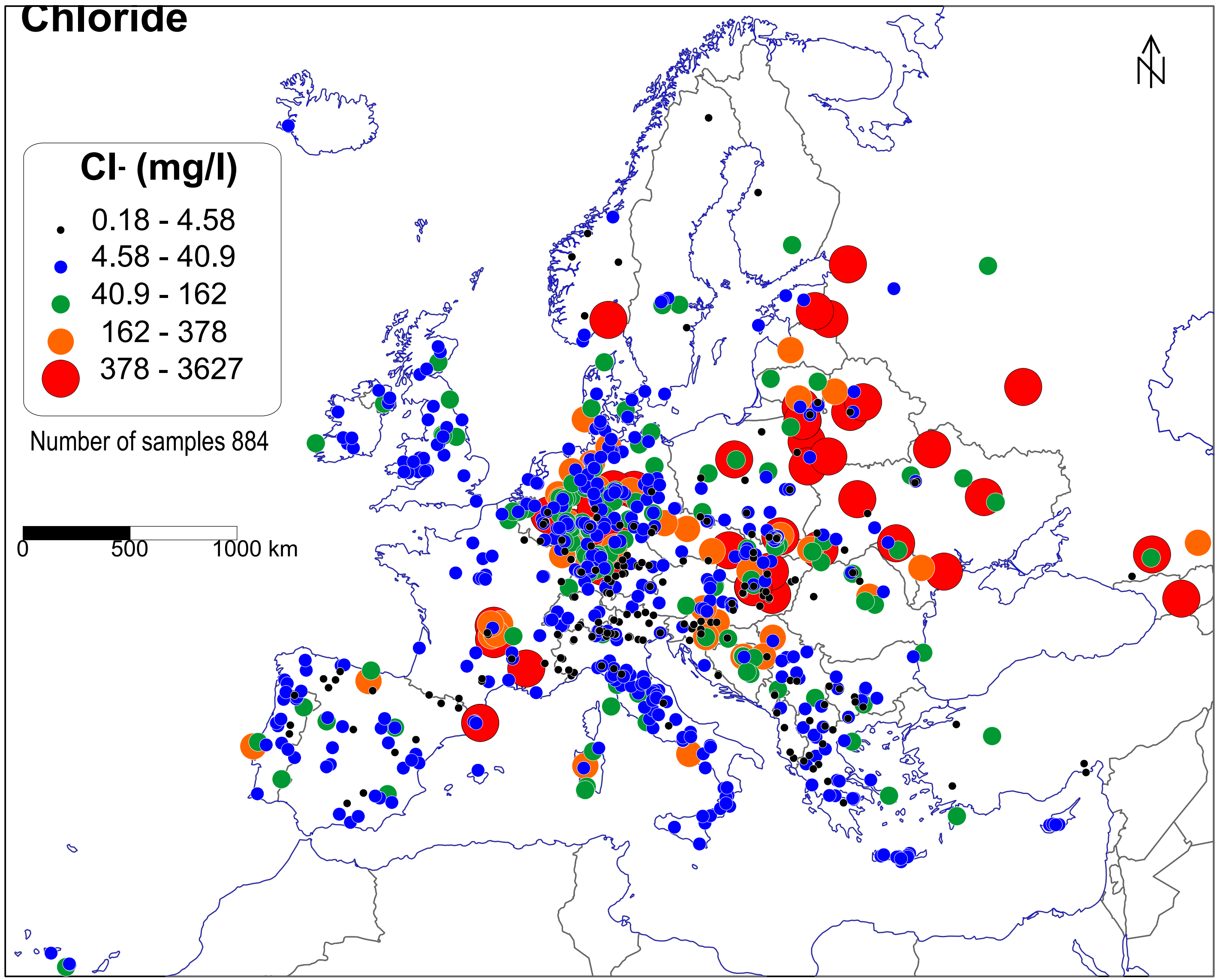
Nitrate (NO_3^-)

Samples from Southern and Eastern Europe, and the British Isles have the highest NO_3^- concentrations.

The spatial distribution cannot be linked to known geological features, nor would such a correlation be expected, as NO_3^- is typically released by surface and atmospheric processes.

The highest value of 995 mg/L was reported in a bottled mineral water from the Czech Republic.

The elevated NO_3^- concentrations are ascribed to human activities.



(Reimann & Birke, 2010, p.95, modified)

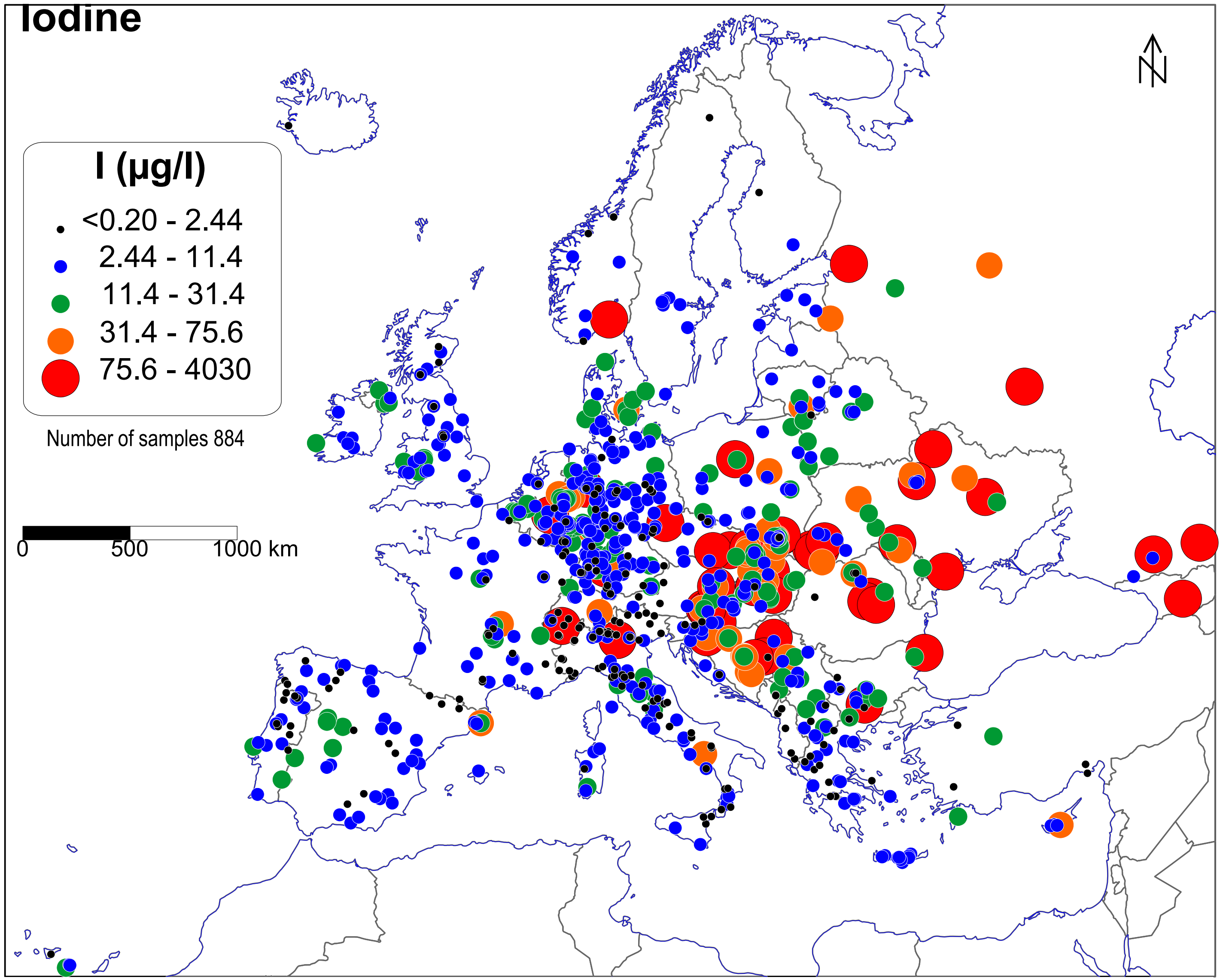
Chloride (Cl^-)

Most of the anomalously high-chloride wells can be traced to deep formation waters, although chlorine derived from hydrothermal and volcanic activity may also be a source of elevated chloride.

The highest value of 3627 mg/L Cl^- was reported from a Slovakian well.

The highest value in Norway is influenced by saline pore waters from marine clays.

Drinking water standard: 250 mg/L; 68 samples exceed this limit



(Reimann & Birke, 2010, p.125; modified)

Drinking water standard: None defined

Iodine (I)

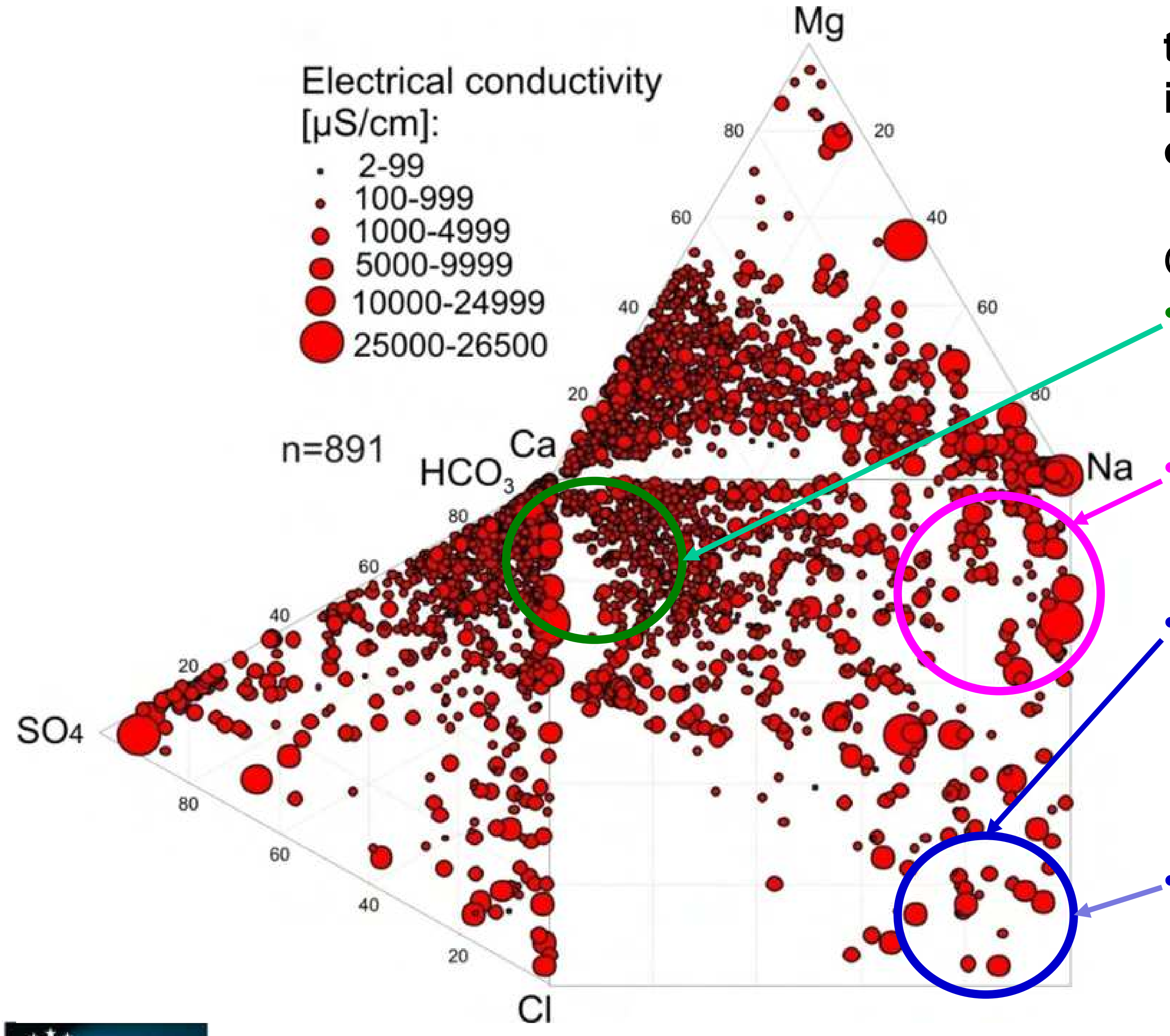
Similar to Cl^-, most of the anomalously high iodine can be traced to deep formation waters.

The highest value of 4030 mg/L Iodine was reported from the same Slovakian well.

The highest value in Norway is influenced by saline pore waters from marine clays.

It is stressed that iodine is a difficult element to analyse with ICP-MS, and due to its importance for human health special care was taken to obtain reliable results.

Durov diagram for the bottled mineral water data set (N=884)



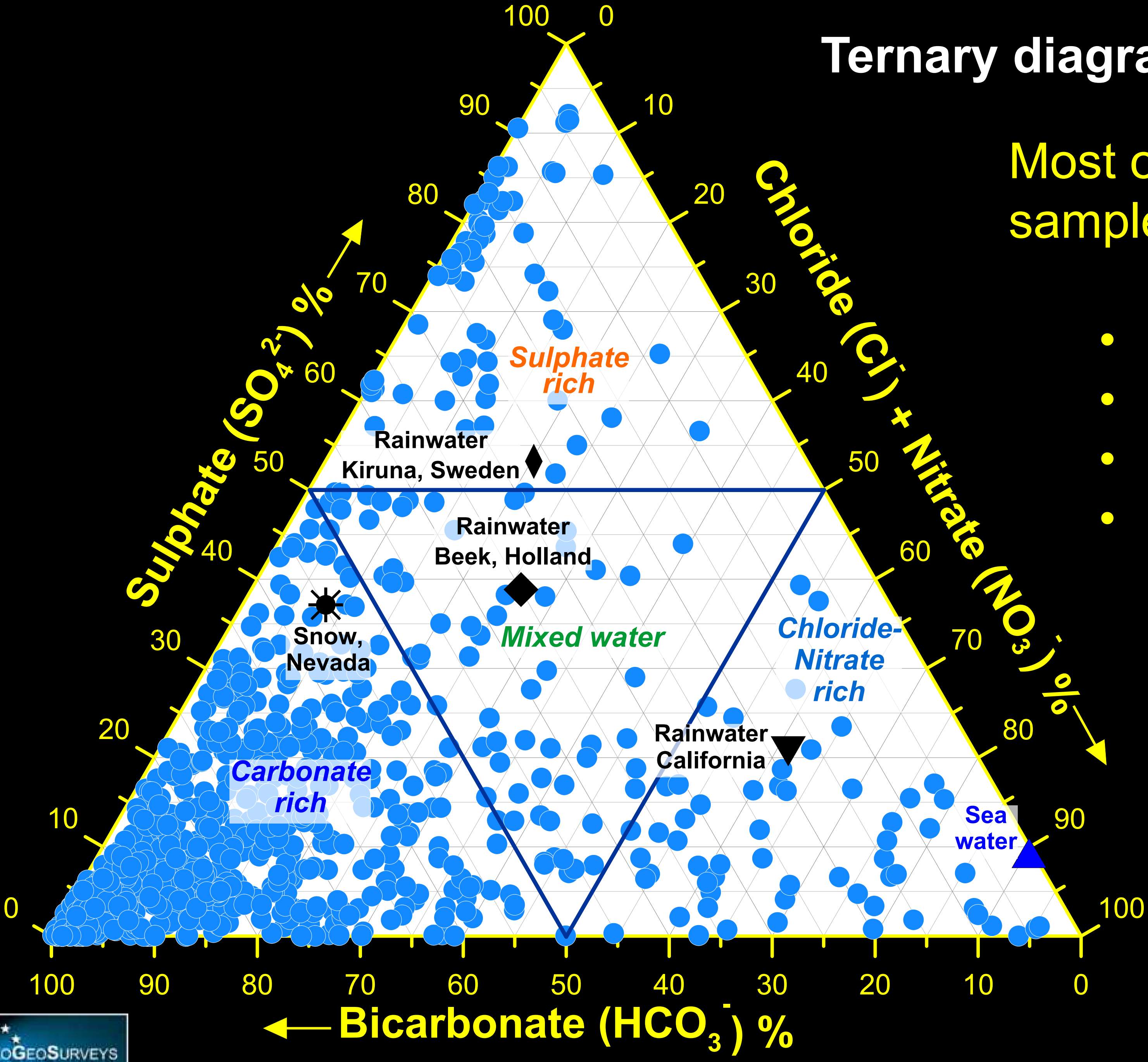
(Reimann & Birke, 2010, Fig. 7, p.16)

The diagram is based on milliequivalent fractions of the major cations and anions. The size of the symbol is related to the total dissolved solutes (on the basis of electrical conductivity).

On this diagram:-

- **More 'normal' groundwaters of Ca–HCO_3 type, derived from calcite hydrolysis, plot in the top left corner.**
- **More evolved granitic groundwaters, characterised by prolonged aluminosilicate weathering, might be of Na–HCO_3 type and plot at the top right corner.**
- **Dilute, newly recharged waters, possessing a weak signature of marine salts in coastal areas, would plot as small dots (*i.e.*, low electrical conductivity) in the lower right field – they would be termed a "*low ionic strength Na–Cl*" water type.**
- Deep saline brines would most likely be of Na–Cl composition and plot as large-diameter dots (high electrical conductivity) near the bottom right corner of the diagram.

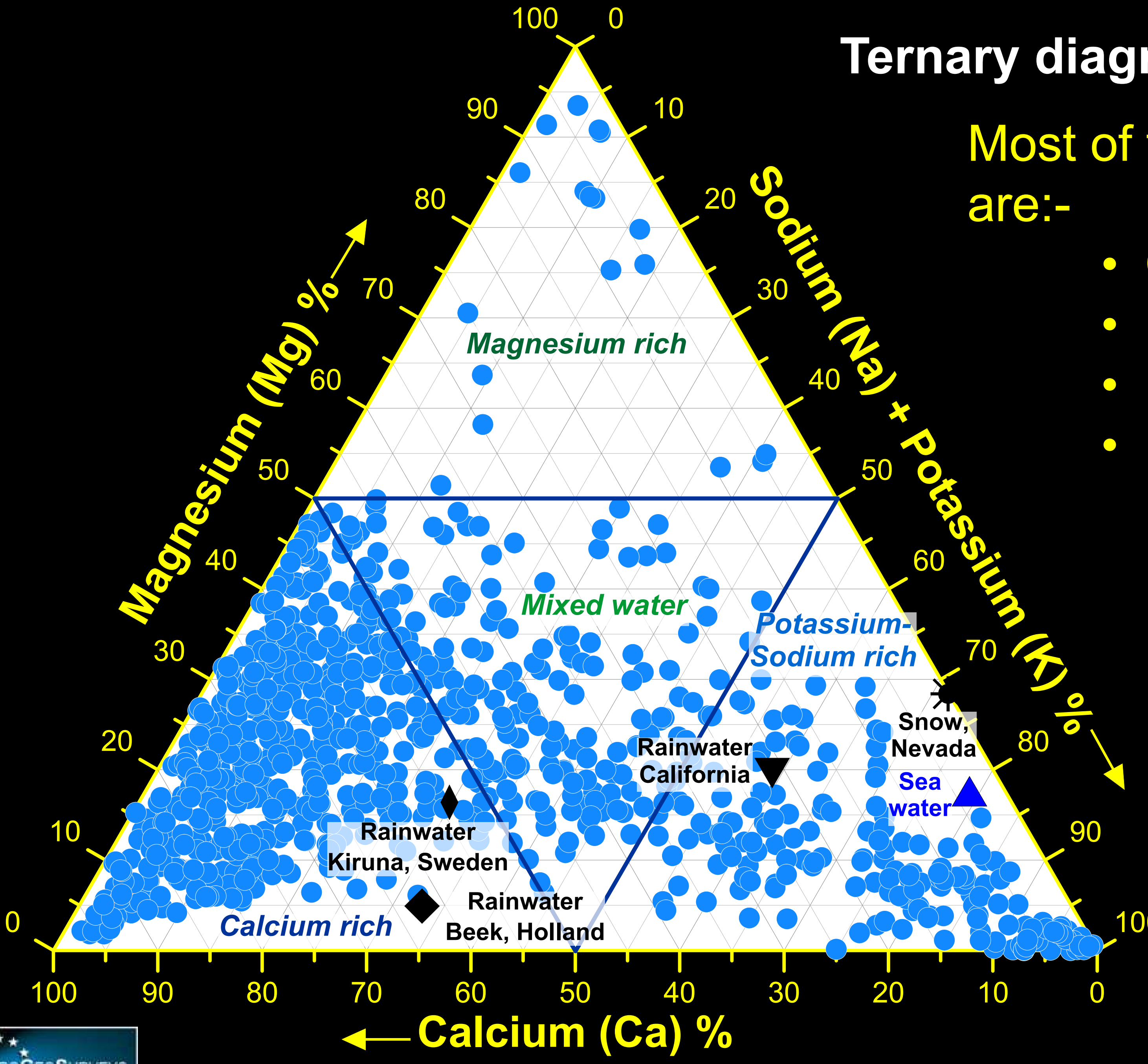
Ternary diagram of HCO_3^- – (Cl^-+NO_3^-) – SO_4^{2-}



Most of the Bottled mineral water samples are:-

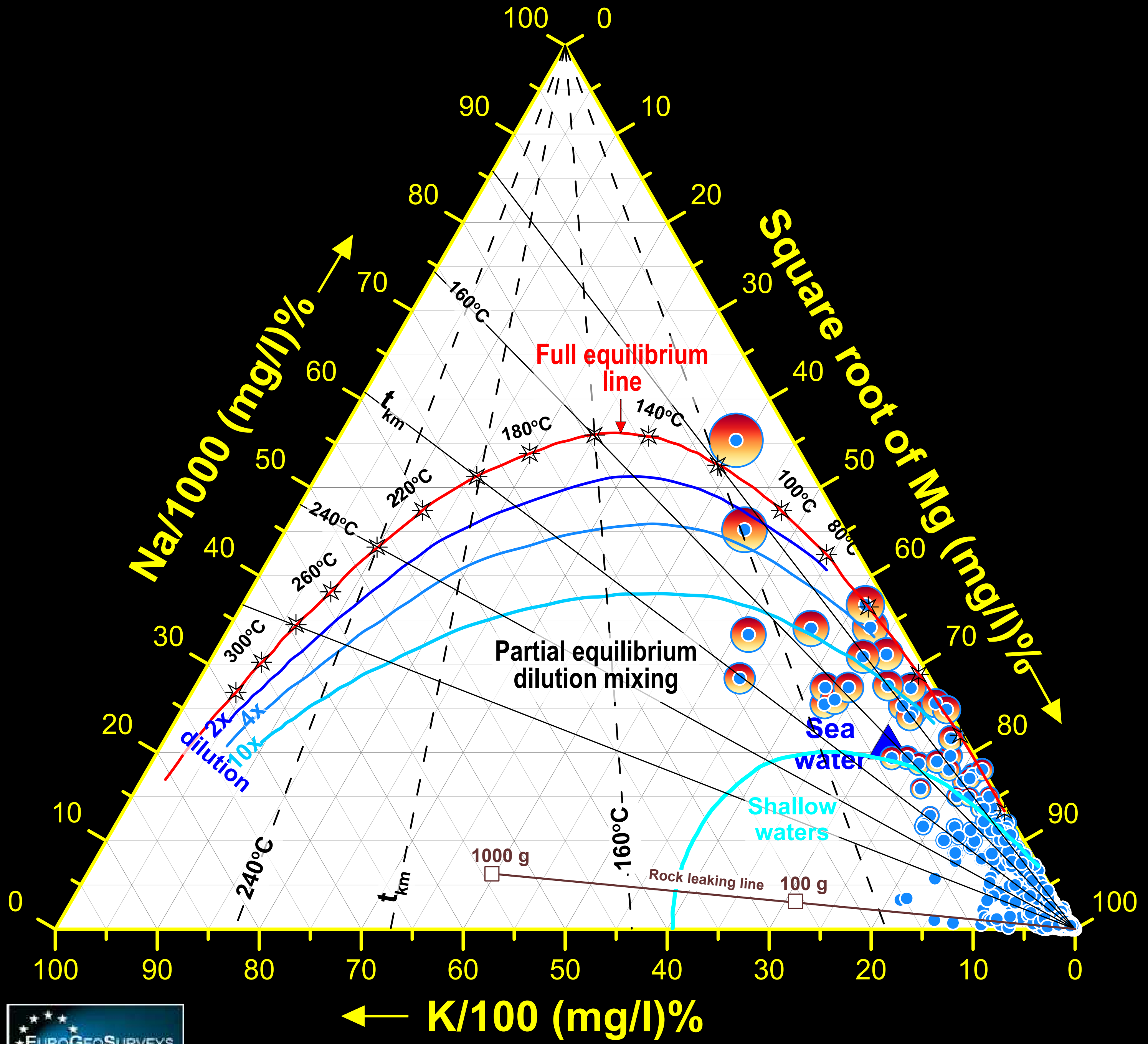
- Carbonate rich, followed by
- Sulphate rich,
- Chloride-Nitrate rich and
- Mixed water

Ternary diagram of Ca − (Na+K) – Mg



Most of the Bottled mineral water samples are:-

- Ca rich, followed by
- K-Na rich,
- Mixed water and
- Mg rich water.

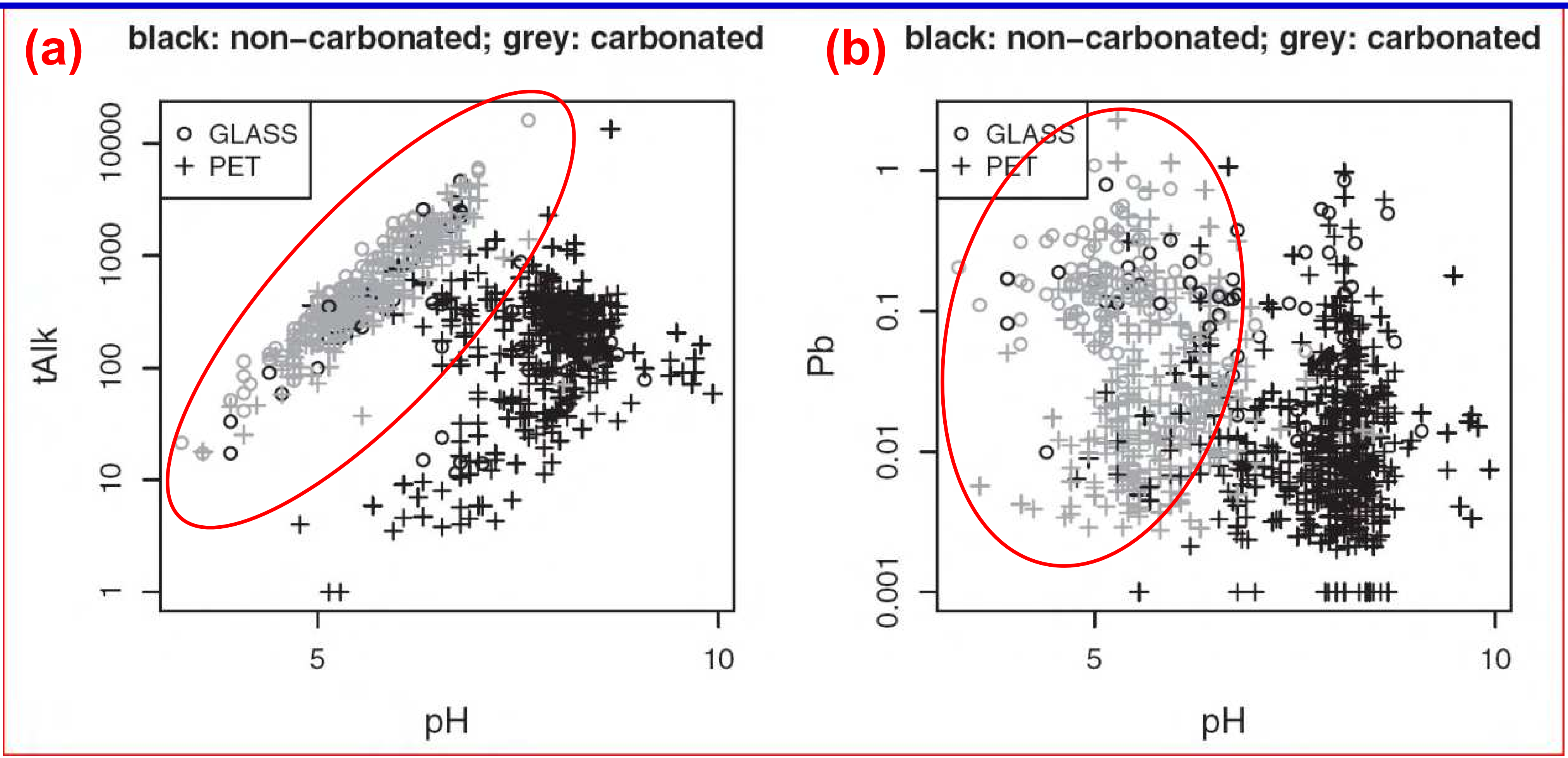


The Giggenbach (K-Mg-Na) Triangle verifies the extent to which water-rock equilibrium has been attained. It combines the Na-K and K-Mg geothermometres.

Most of the European bottled mineral water samples are of shallow origin.

A few samples are sourced from deeper wells/boreholes reaching a temperature of up to 130°C.

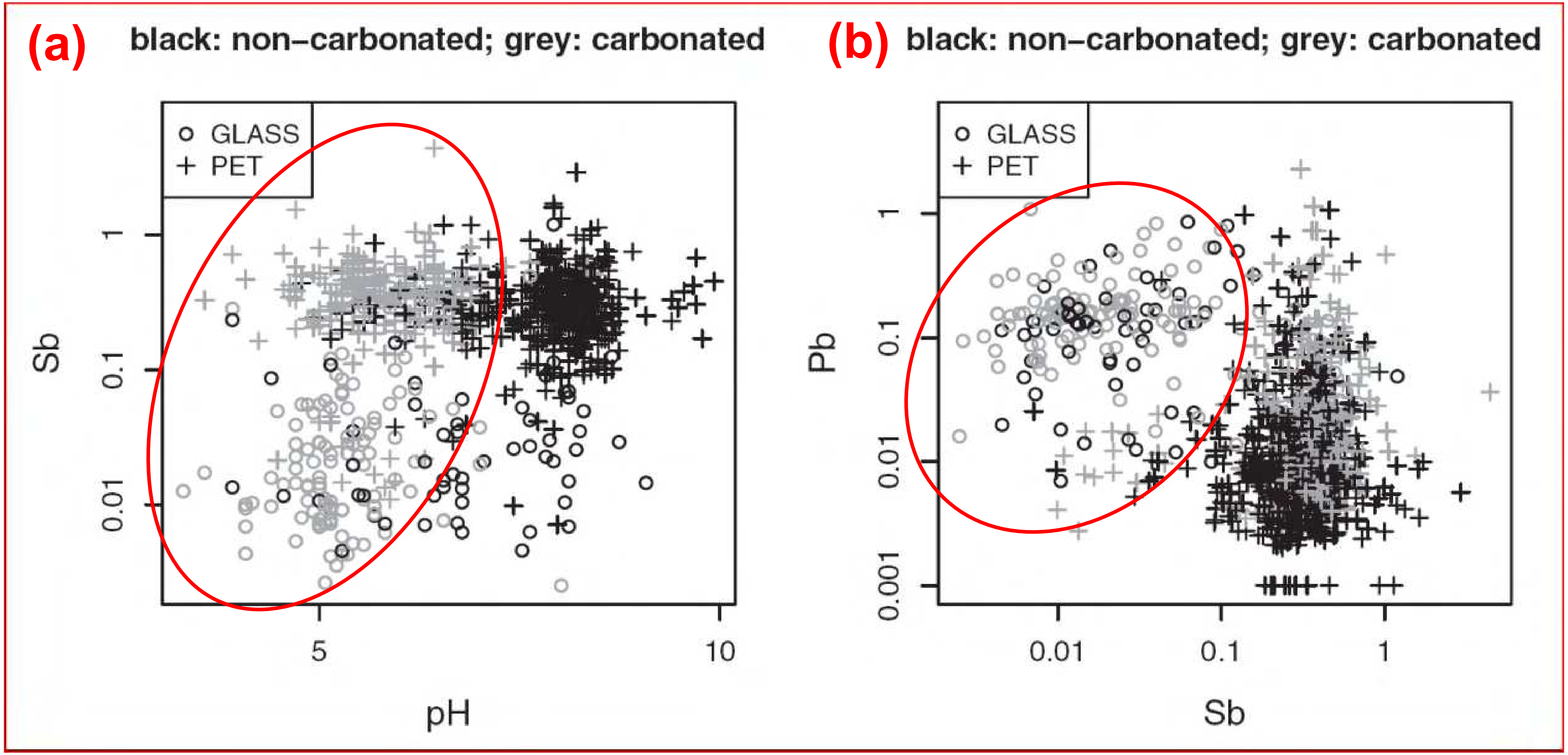
Leaching of elements from bottle materials (1/5)



Scattergrams showing the dependence of (a) pH in relation to total alkalinity [tAlk meq/L], and (b) pH in relation to Pb [µg/L], according to bottle type [o glass & + PET] and whether Still (in black) or Carbonated water (in grey)

(Reimann & Birke, 2010, Fig. 21, p.47)

Leaching of elements from bottle materials (2/5)

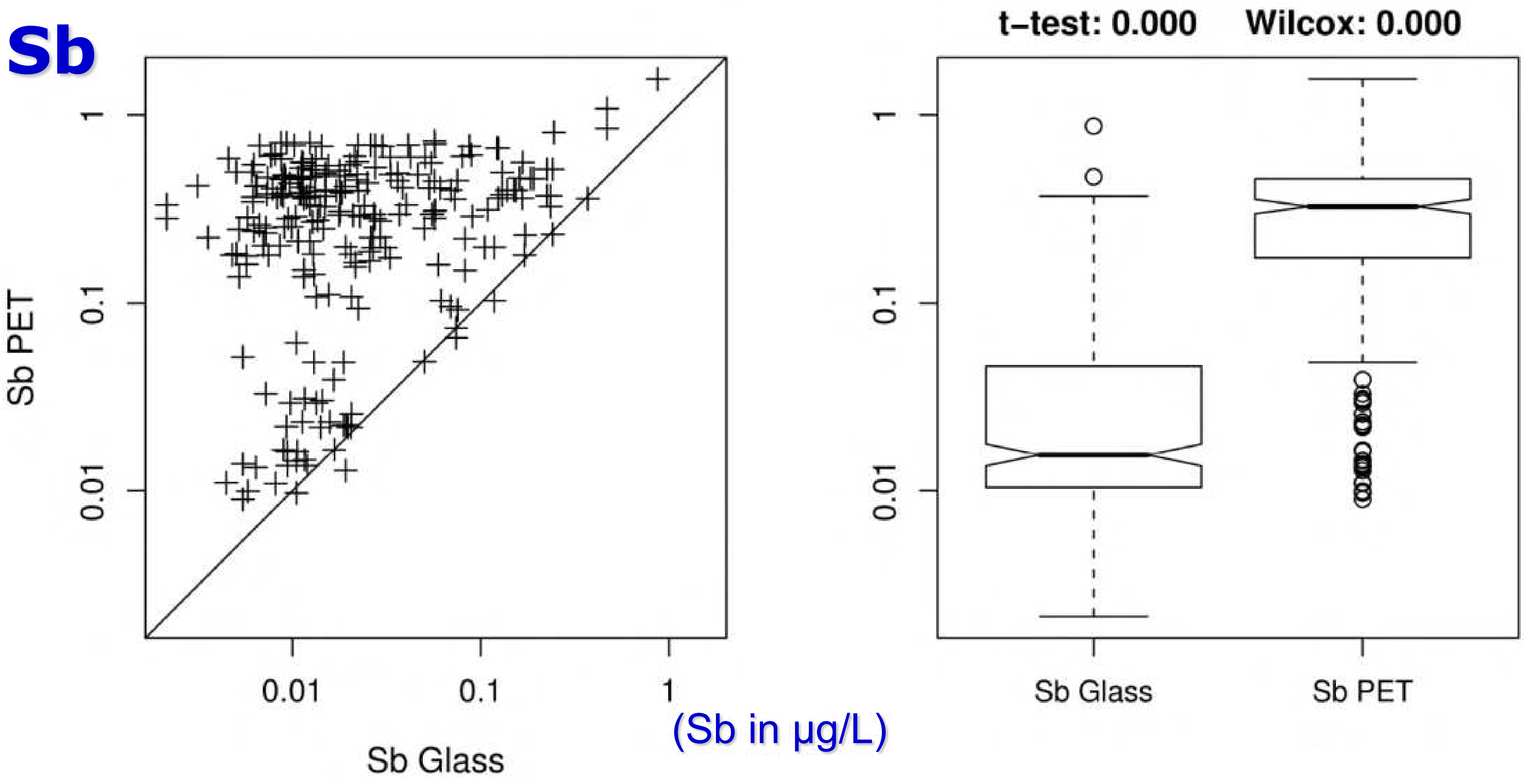


Scattergrams showing the dependence of (a) pH in relation to Sb [µg/L], and (b) Sb [µg/L] in relation to Pb [µg/L], according to bottle type [o glass & + PET) and whether Still (in black) or Carbonated water (in grey)

(Reimann & Birke, 2010, Fig. 21, p.47).

Leaching of elements from bottle materials (3/5)

Sb



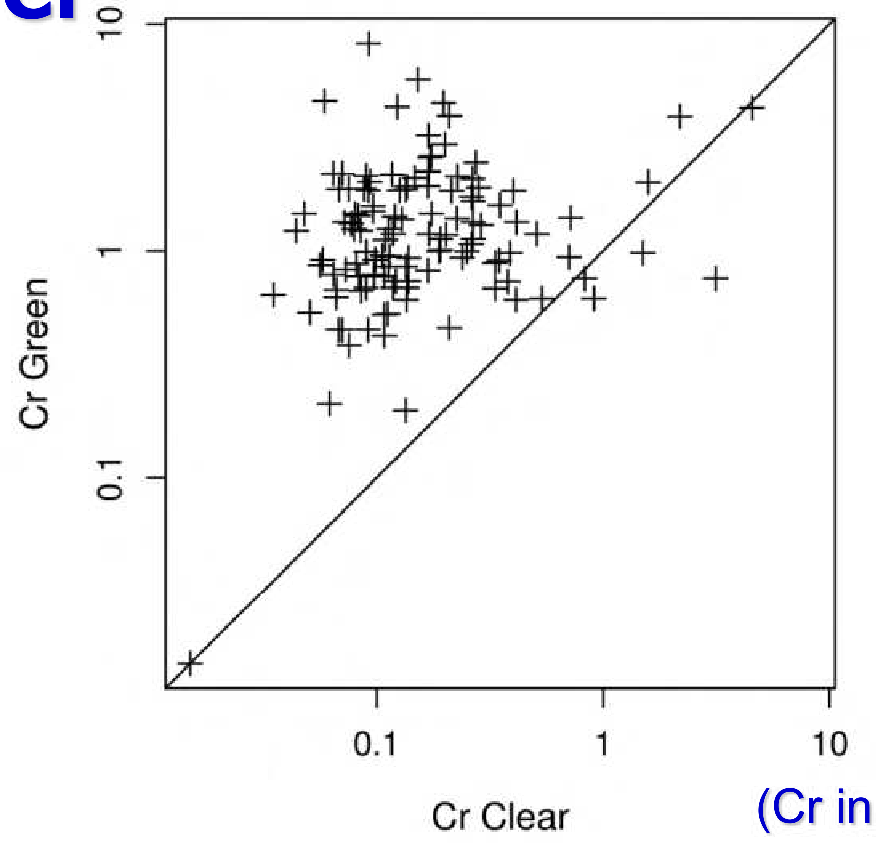
(Sb in µg/L)

Comparison of Sb concentrations in the same type of bottled mineral water sold in Glass and PET bottles (N=131)

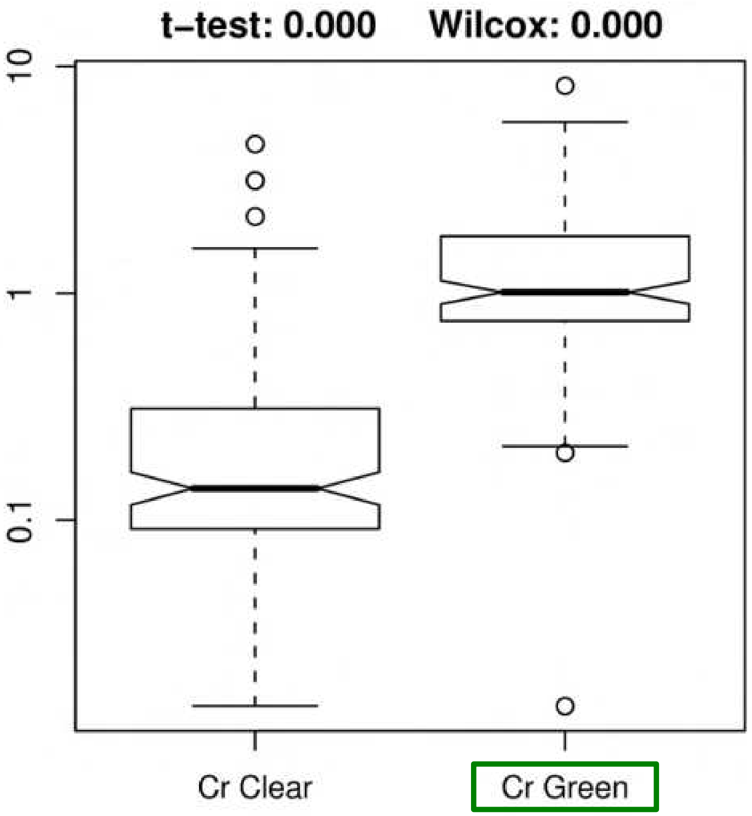
(Reimann *et al*., 2010, Fig. 1, p.1033)

Leaching of elements from bottle materials (4/5)

Cr



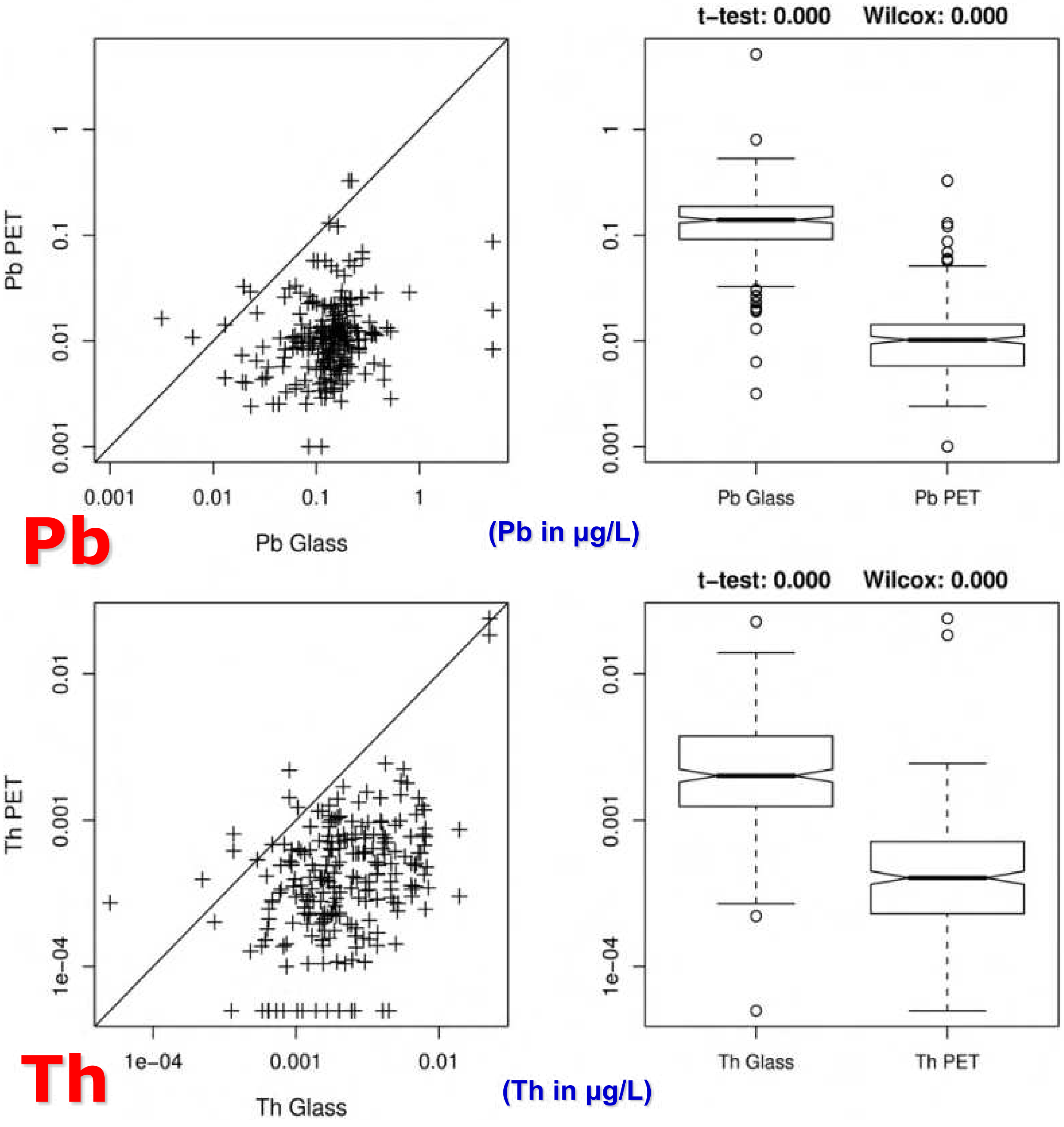
(Cr in µg/L)



Green glass bottles release more Cr to the water than clear bottles

(Reimann *et al*., 2010, Fig. 4, p.1036)

Leaching of elements from bottle materials (5/5)



Glass affects more the concentrations of elements such as Ce, Pb, Al, Zr, Ti, Hf, Th and La

(N=131)

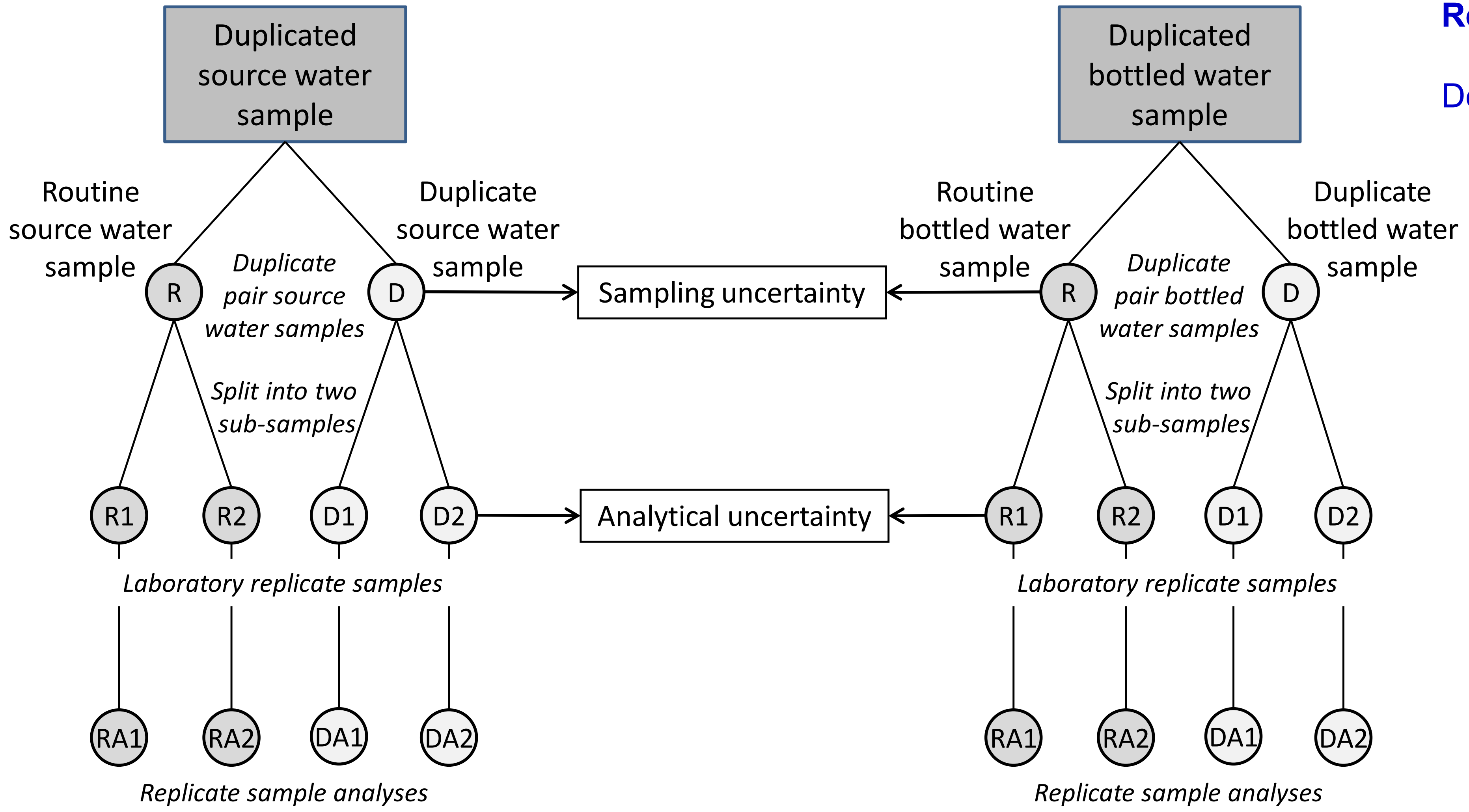
(Reimann *et al.*, 2010, Fig. 2, p.1033)

Use of measurement uncertainty to assess compliance of bottled mineral water with drinking water standards

Ramsey (1998)

(a) Balanced ANOVA design for bottle source water, e.g., spring or well

(b) Balanced ANOVA design for bottled water after bottling

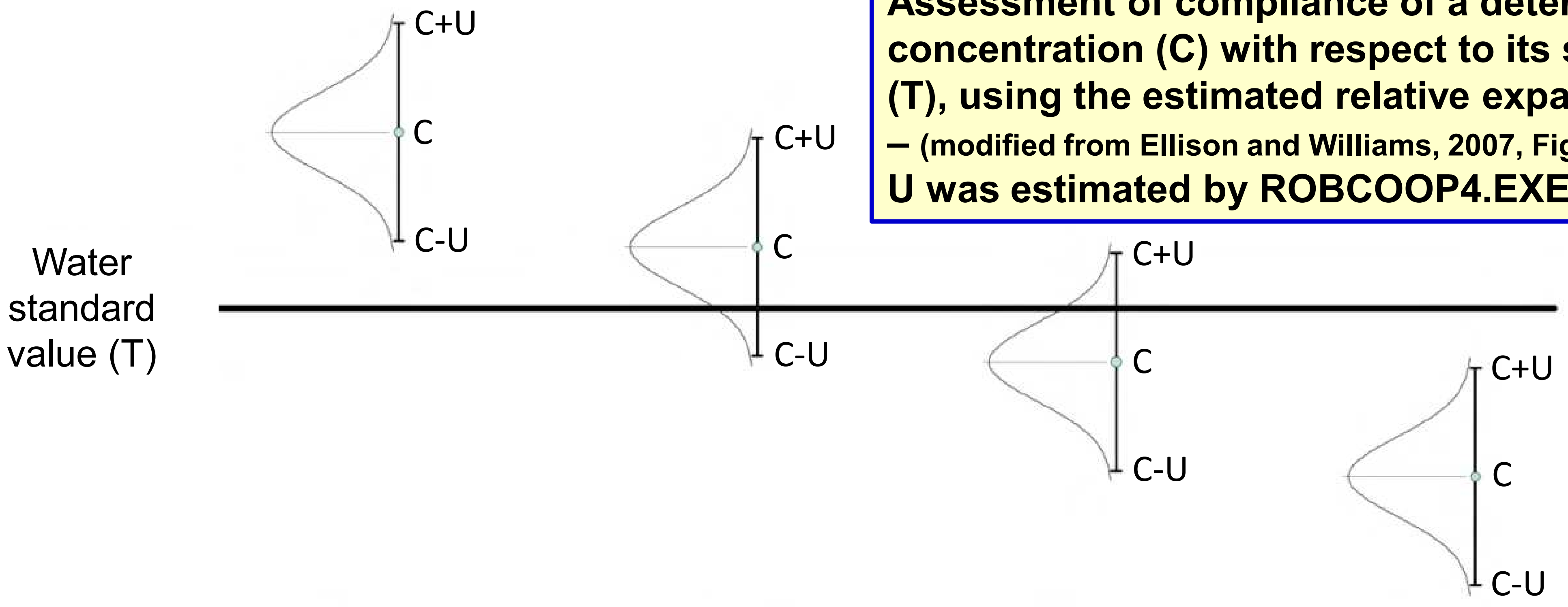


Refer to:

Demetriades, A., 2010. *Use of measurement uncertainty in a probabilistic scheme to assess compliance of bottled water with drinking water standards*. In: M. Birke, A. Demetriades, B. De Vivo (Guest Editors), Mineral Waters of Europe. Special Issue, Journal of Geochemical Exploration, 107(3), 410−422. https://doi.org/10.1016/j.gexplo.2010.11.001.

Use of measurement uncertainty to assess compliance of bottled mineral water with drinking water standards

Assessment of compliance of a determinand concentration (C) with respect to its statutory standard (T), using the estimated relative expanded uncertainty (U) – (modified from Ellison and Williams, 2007, Fig. 1, p.2).
U was estimated by ROBCOOP4.EXE (Ramsey, 1998).



(i) Result (C) minus expanded uncertainty (U) above limit (T)

(ii) Result (C) above limit (T); limit within expanded uncertainty (U) interval

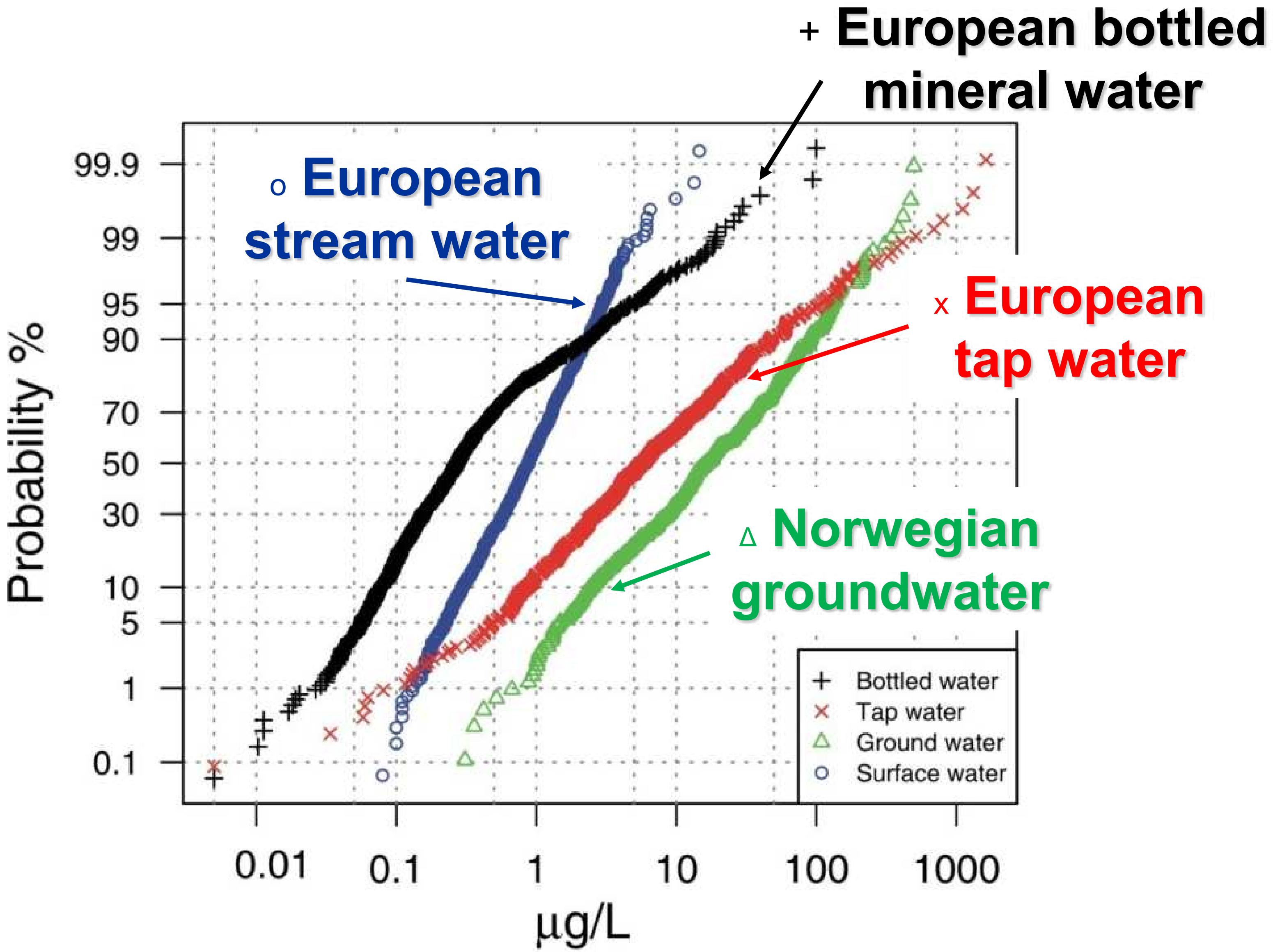
(iii) Result (C) below limit (T); limit within expanded uncertainty (U) interval

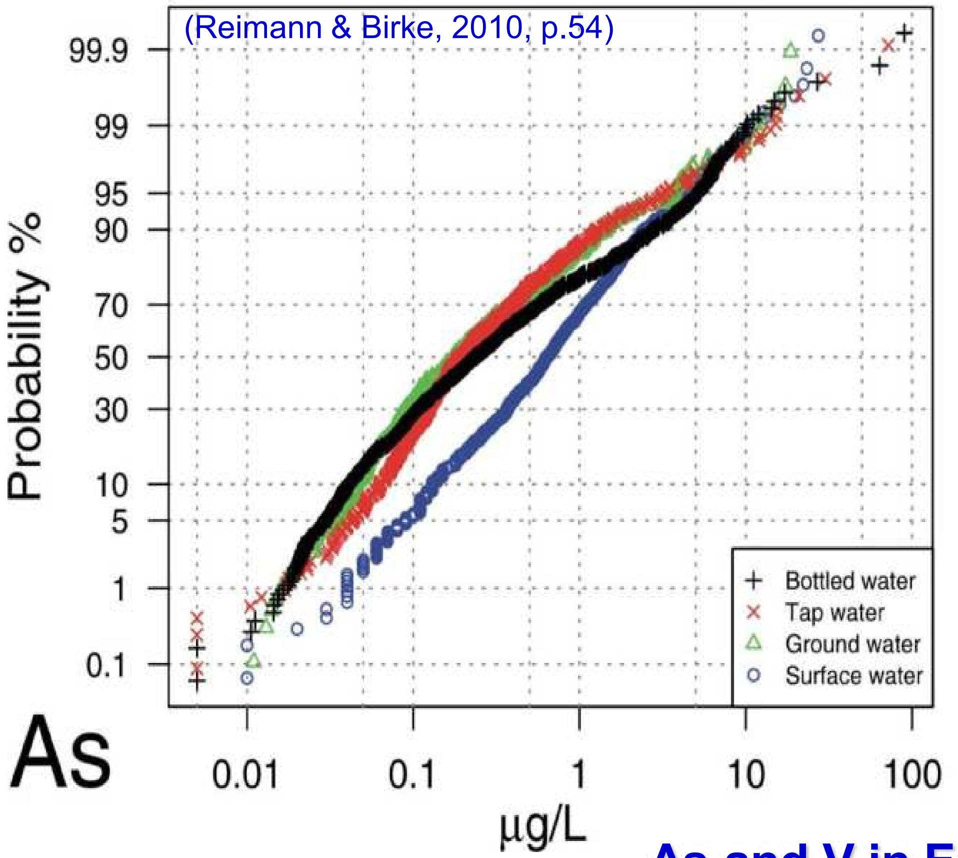
(iv) Result (C) plus expanded uncertainty (U) below limit (T)

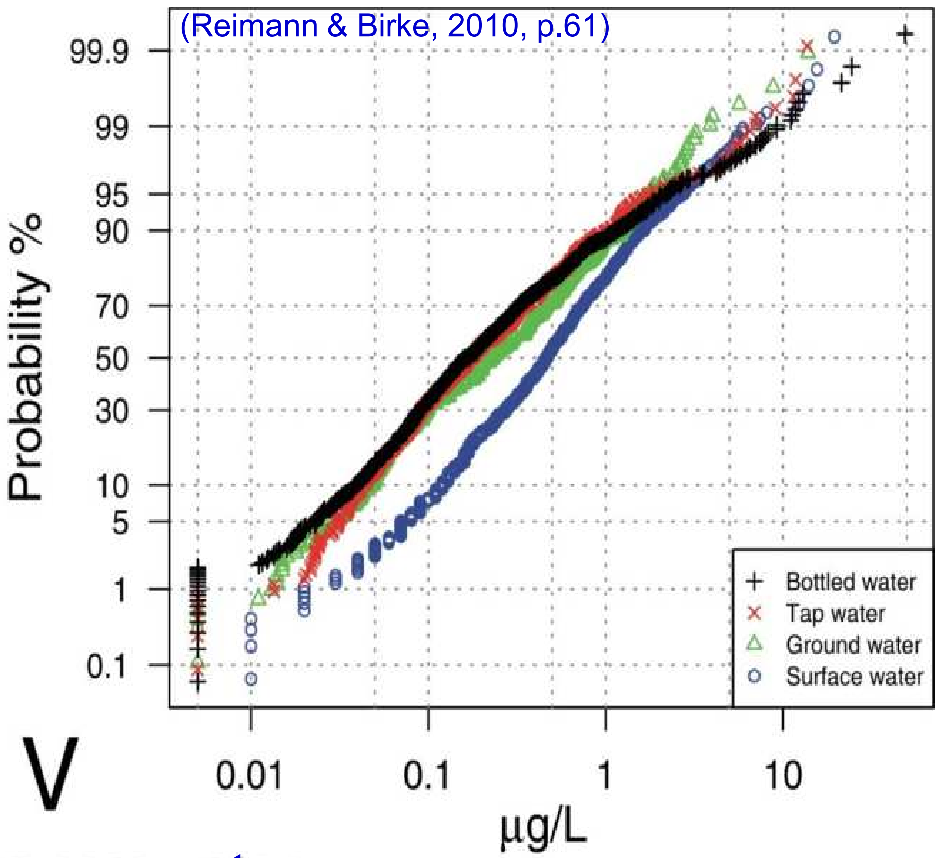
Bottled mineral water in the set of 1785 samples exceeding the minimum EU statutory water Standard Value with respect to Al, As, B, Ba, Fe, Mn, Ni and Se

Element	Standard Value (µg/L)		Upper Threshold Limit (µg/L)	Bottled waters exceeding Upper Threshold Limit	
	Directive 98/83/EC (EC, 1998)	Directive 2003/40/EC (EU, 2003)		Total number	Number of bottles in each country
Aluminium	200	-	217.5	3	Belgium (1), Germany (1), Italy (1)
Arsenic	10	10	10.6	14	Bosnia and Herzegovina (3), Germany (7), Hungary (1), Poland (2), Portugal (1)
Boron	1000	-	1101.4	105	Austria (3), Belarus (5), Belgium (2), Bosnia and Herzegovina (5), Bulgaria (1), Croatia (1), Czech Republic (3), Estonia (1), France (7), Georgia (2), Germany (19), Hungary (3), Italy (1), Montenegro (1), Poland (1), Portugal (1), Romania (13), Russia (6), Serbia (3), Slovakia (10), Spain (2), Turkey (1), Ukraine (11)
Barium	-	1000	1076.5	16	Belarus (2), Czech Republic (1), Georgia (1), Germany (1), Poland (1), Romania (2), Russia (1), Slovakia (2), Ukraine (5)
Iron	200	-	212.8	15	Belarus (2), Poland (5), Russia (1), Slovakia (4), Ukraine (3)
Manganese	50	-	51.7	235	Austria (7), Belarus (4), Bosnia and Herzegovina (6), Croatia (3), Czech Republic (7), F.Y.R.O.M. (1), Finland (1), France (3), Germany (108), Hungary (16), Italy (5), Lithuania (7), Moldova (1), Montenegro (1), Norway (2), Poland (15), Portugal (4), Romania (13), Russia (3), Serbia (1), Slovakia (15), Spain (2), Turkey (1), U.K. (1), Ukraine (8)
Nickel	20	20	23.4	6	Bosnia and Herzegovina (1), Czech Republic (2), Germany (2), Slovakia (1)
Selenium	10	10	11.4	4	Czech Republic (2), Moldova (2)

COMPARISON OF RESULTS AMONG FOUR DATA SETS OF WATER SAMPLES (1/4)



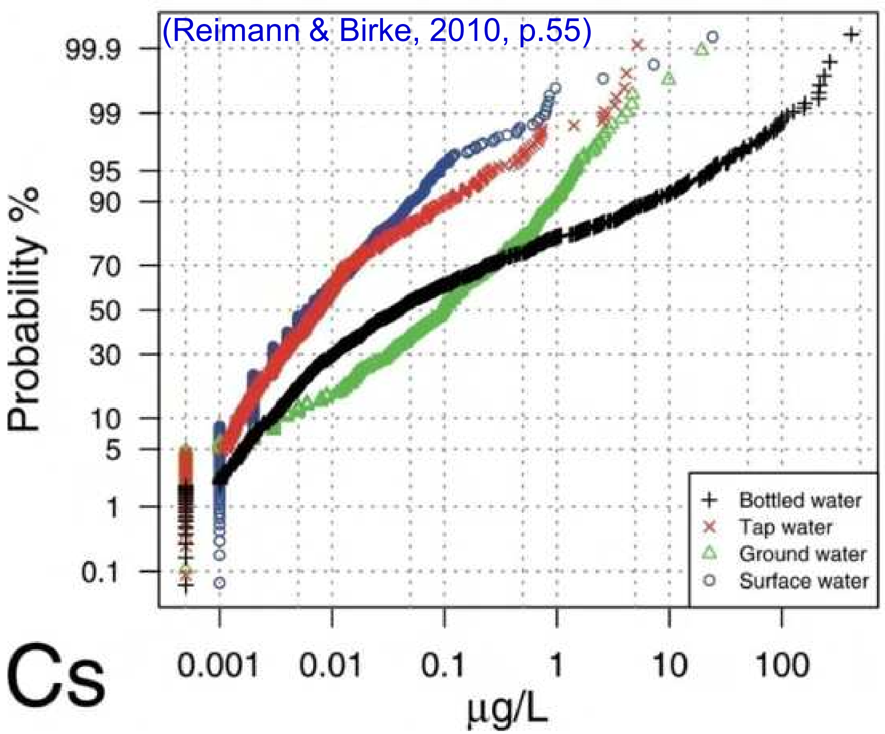


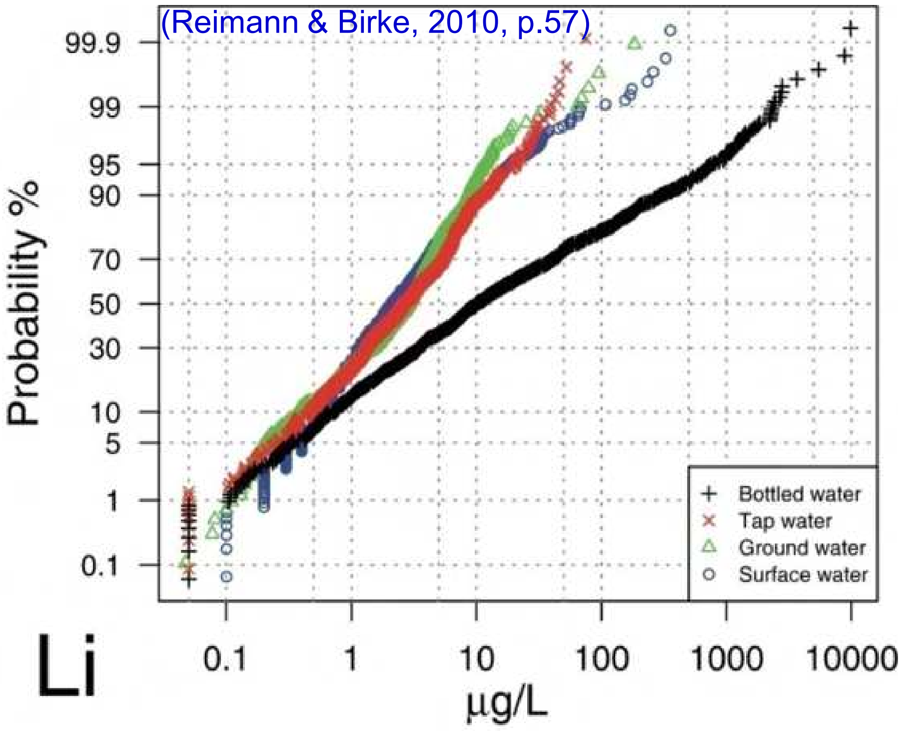


As and V in European water

Most elements show a surprising comparable distribution in all 4 data sets

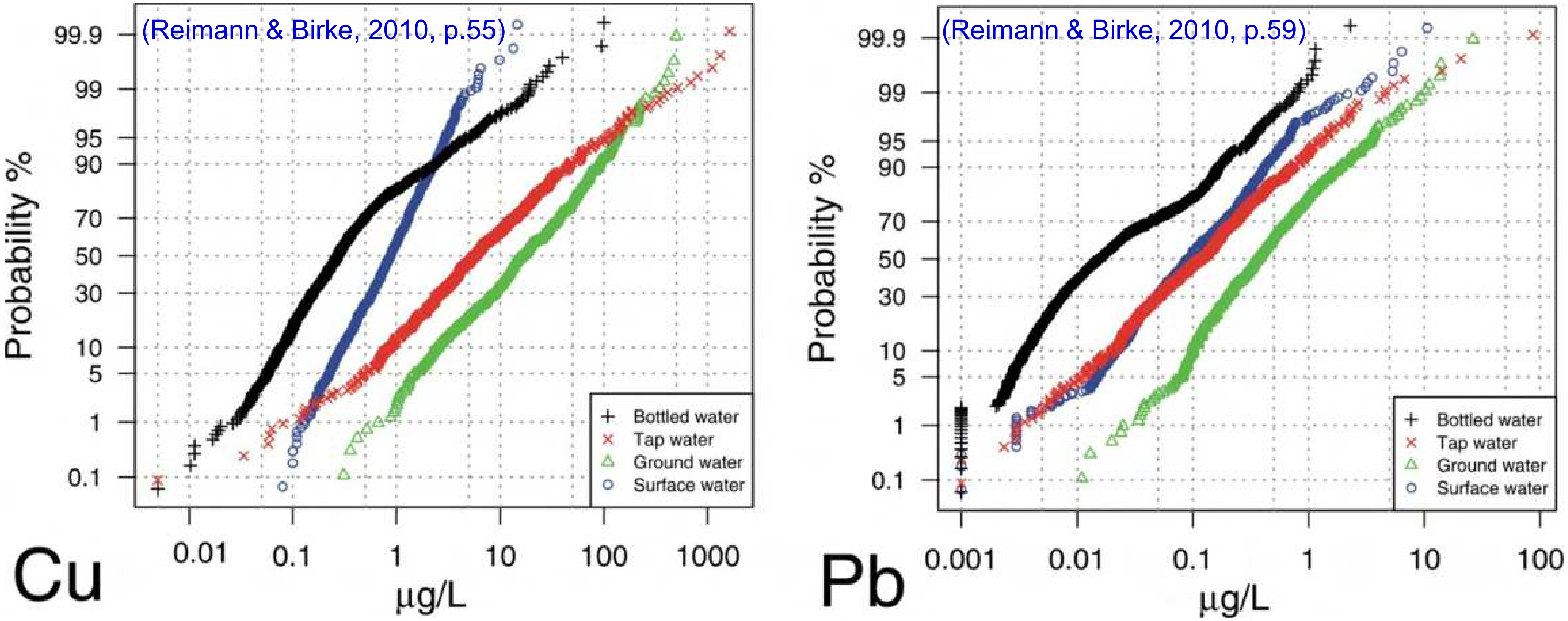
European bottled mineral water (+ black, N=884),
European tap water (x red, N=586),
Norwegian groundwater (Δ green, N=808) [Frengstad *et al*., 2000],
European stream water (o blue) from the FOREGS project (Salminen *et al*., 2005)





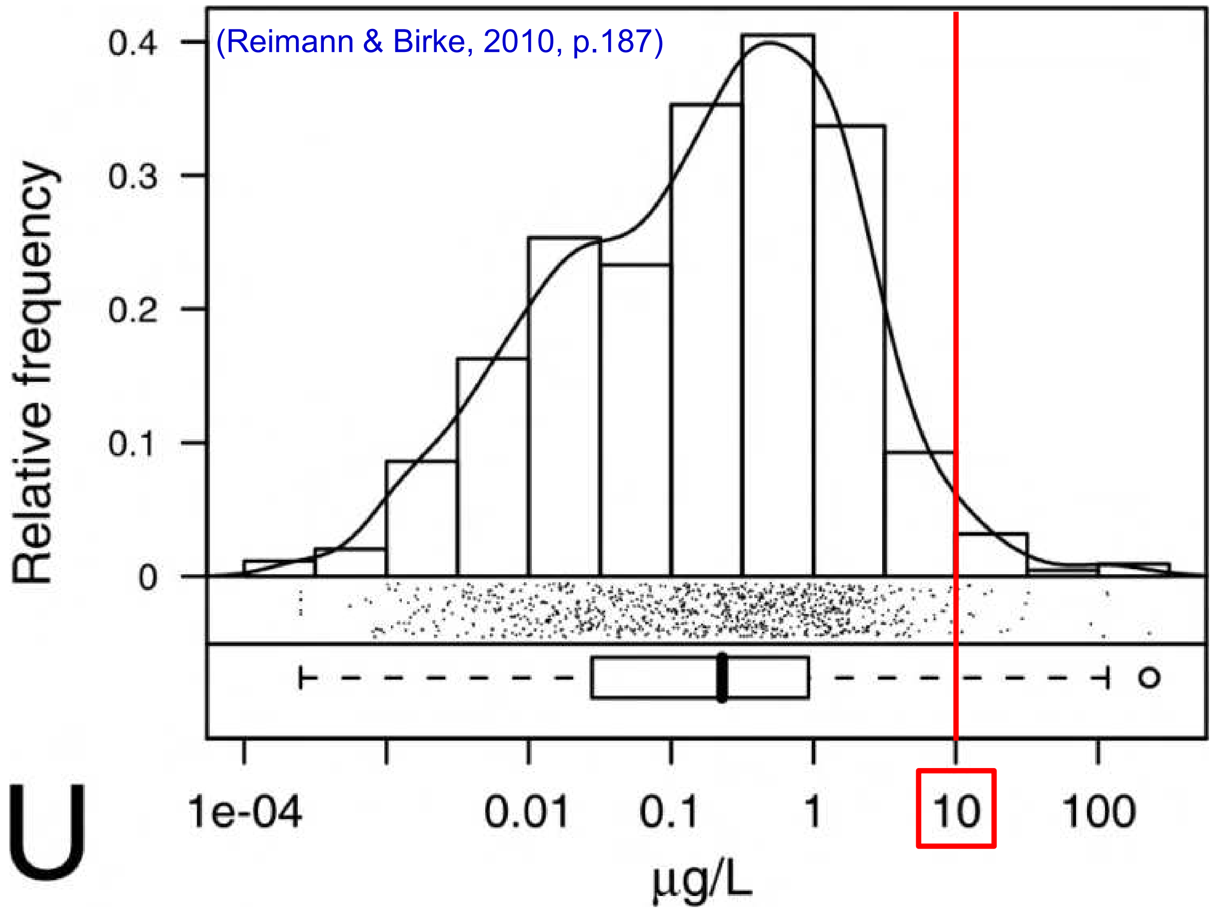
Some elements (*Ag, B, Be, Br, Cl, Cs, F, Ge, I, K, Li, Na, Rb, Sr, Te, Tl, Zr*) show a 'mineral water' specific enrichment (+1 to +2 orders of magnitude variation).
These are from deep sources (brines and hydrothermal water).

European bottled mineral water (+ black, N=884),
European tap water (x red, N=586),
Norwegian groundwater (Δ green, N=808) [Frengstad *et al*., 2000],
European stream water (o blue) from the FOREGS project (Salminen *et al*., 2005)



Some elements (Cu, Pb, Zn) show definite indications that European tap water and Norwegian groundwater are contaminated by well installations and water piping – over the whole concentration range.

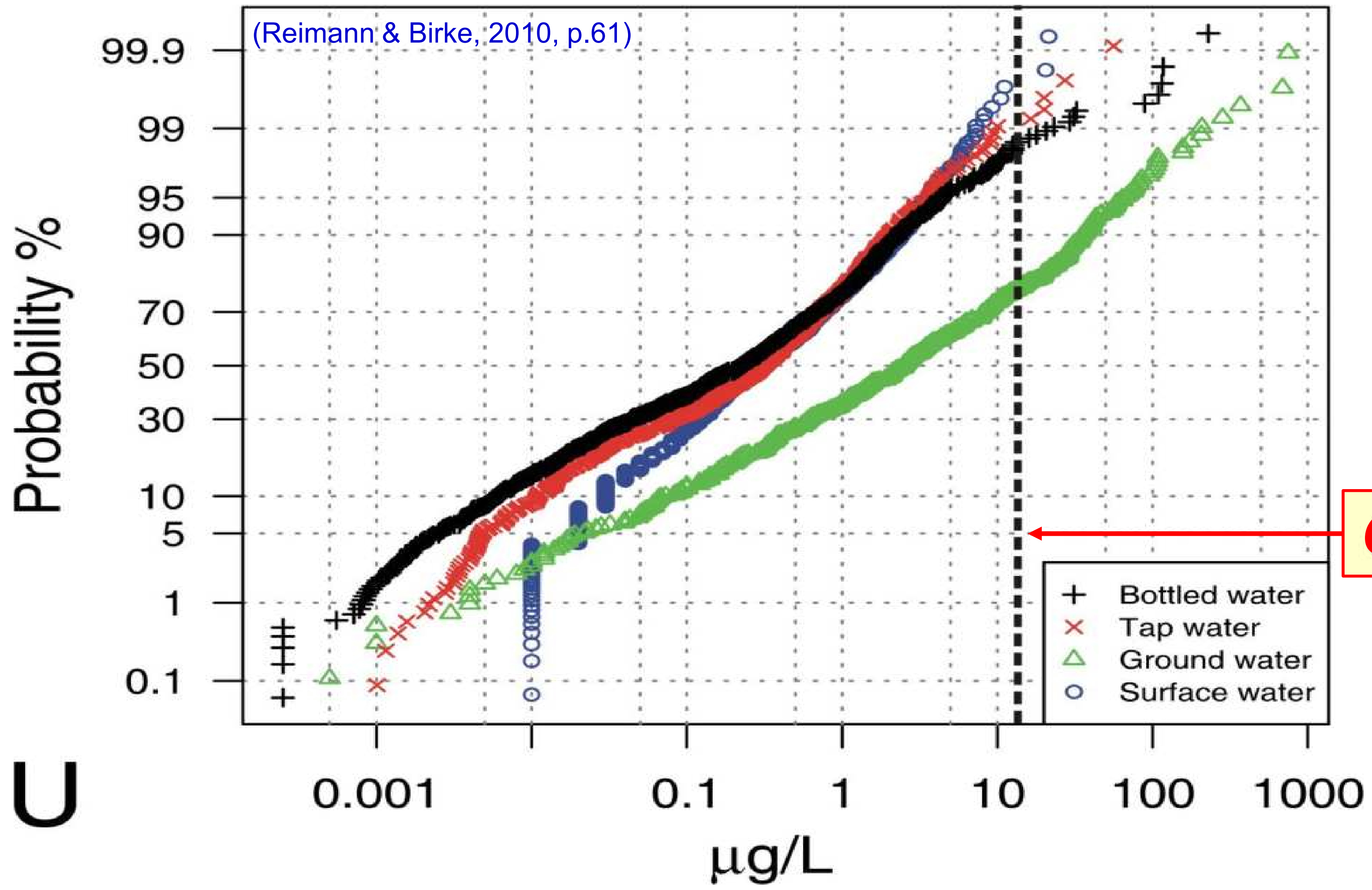
European bottled mineral water (+ black, N=884),
European tap water (x red, N=586),
Norwegian groundwater (Δ green, N=808) [Frengstad *et al.*, 2000],
European stream water (o blue) from the FOREGS project (Salminen *et al.*, 2005)



Distribution of U in samples of bottled mineral water (N=884).

Observe the sudden drop of values at 10 µg U/L.

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



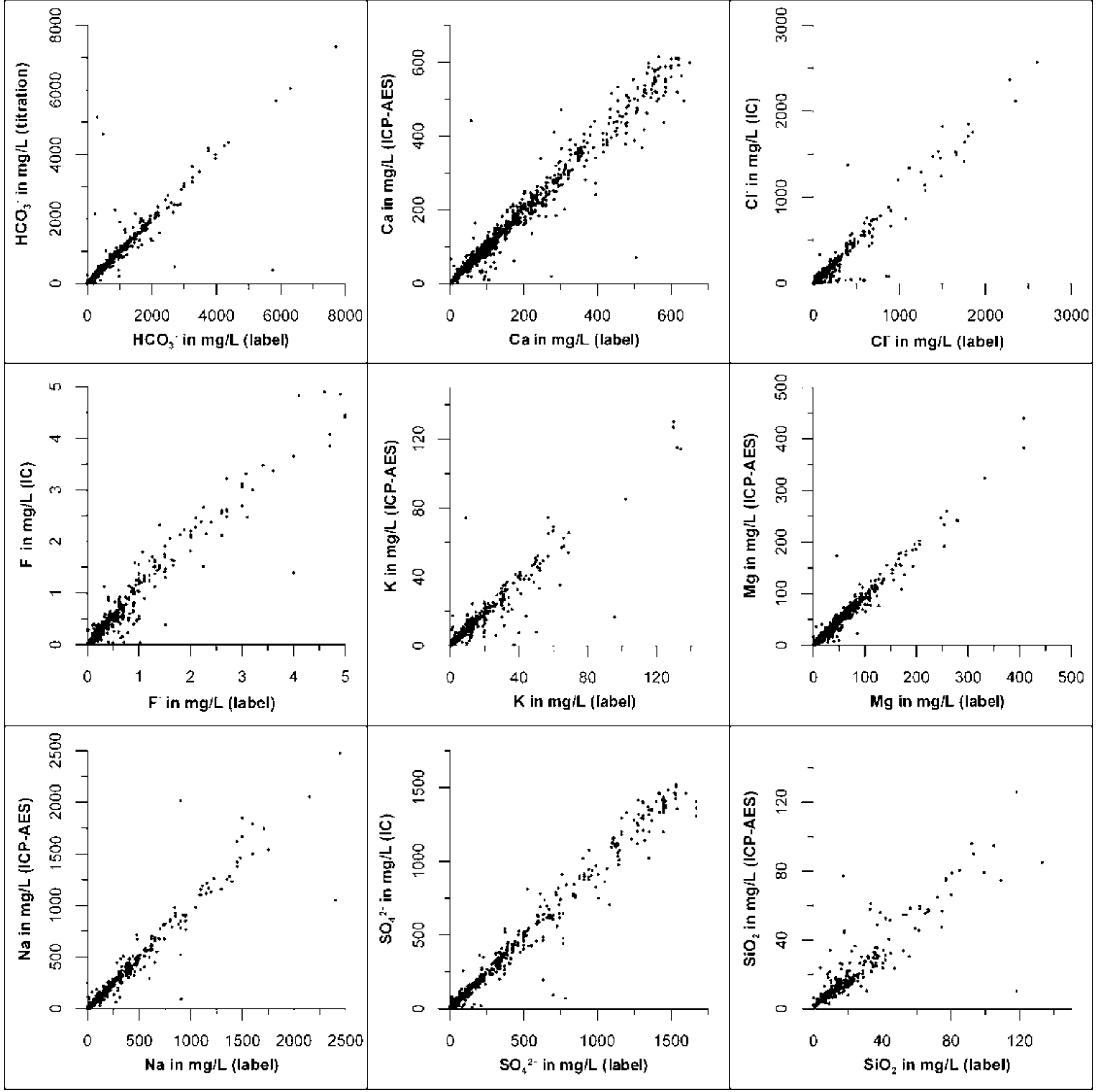
U

Number of water samples exceeding the 15 µg U/L guideline value were:-

12 Bottled mineral water
5 Tap water
100 Norwegian groundwater
2 European stream water

Guideline value at 15 µg U/L

European bottled mineral water (+ black, N=884),
European tap water (x red, N=586),
Norwegian groundwater (Δ green, N=476) [Frengstad *et al*., 2000],
European stream water (o blue, N=808) from the FOREGS project (Salminen *et al*., 2005)



Comparison of analytical data of the EuroGeoSurveys study with those displayed on bottled mineral water labels shows a fairly good linear correlation.

This satisfies the legislative condition of "*stable chemical composition*" (Directives 80/777/EC & 2003/40/EC, 2009/54/EC).

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

Conclusions (1/5)

- **Bottle materials contaminate bottled mineral water. Glass contaminates water with respect to Cu, Pb, Al, Zn, Ti, Hf, Th, La, Pr, Fe, Zn, Nd, Sn, Cr, Tb, Ag, Er, Gd, Bi, Sm, Y, Lu, Yb, Tm, Nb and Cu (also some glass bottles contaminate water with Sb). Green glass contaminates bottled water with Cr (Fe, Zr). Hence, the PET bottle results were used in the statistical data processing and map plotting, since the only problem is contamination of bottled mineral water by Sb.**

- **Consequently, the Sb distribution map was not plotted.**

- **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.**

Conclusions (2/5)

- **For most elements, the bottled mineral water analytical data set provides a realistic picture of their median value and variation in (ground)water at the European scale.**

- **Natural variation is enormous for most elements, usually 3 to 5 and for a few up to 7 orders of magnitude were observed.**

- **When discussing water quality, natural variation must be documented first; the present focus on '*pollution*' ('*contamination*') is misleading given the observed high geochemical background variation.**

- **It may be necessary to study more seriously the problems that are related to the deficiency of elements in groundwater, since water is an important source of elements, such as F, I, Se, and Ba.**

Conclusions (3/5)

Geological characteristics which are visible on the geochemical maps include:

- **Ophiolites (Cr, Ni, V)**
- **Alkaline volcanics, and generally areas of active volcanicity (Al, As, Be, F, K, Mn, Mo, P, Rb, Se, Si, Tl, V)**
- **Hercynian granites (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)**

Thus, geology, or *the rocks that the water is in contact with*, is one of the key factors influencing the observed element concentrations in the bottled mineral water. Other significant factors are precipitation and proximity to the sea.

Conclusions (4/5)

- **Using bottled mineral water as a ‘proxy’ for groundwater geochemistry was more successful than initially anticipated.**

- **‘*Low density sampling and mapping*’, as developed during the last 15-30 years for detecting large-scale geochemical processes at the Earth’s surface, can also be applied to groundwater.**

- **Geochemical mapping at the continental scale permits cost-effective selection of scale and location of monitoring sites.**

- **To obtain a fully harmonised data set at the European scale high-quality measurements in a single laboratory are required, and the installation of a strict quality control procedure.**

Conclusions (5/5)

- **Bottled mineral water standards: The majority of bottled mineral water brands fulfil the requirements of European Union legislation for mineral (and drinking) water. However, for some determinands, a few brands of bottled mineral 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.**

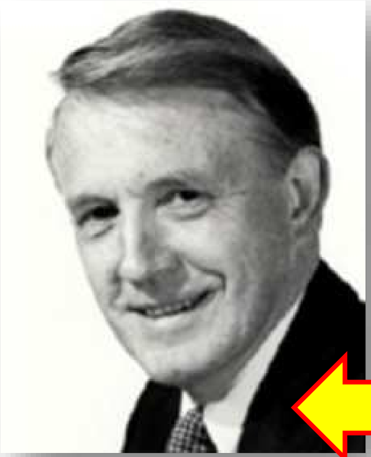
- **The only drawback of this project is the uneven spatial distribution of bottled mineral water installations (boreholes/wells).**

Finally, the new atlas of the geochemistry of bottled mineral water is a valuable addition to the 'Geochemical Atlas of Europe' series.

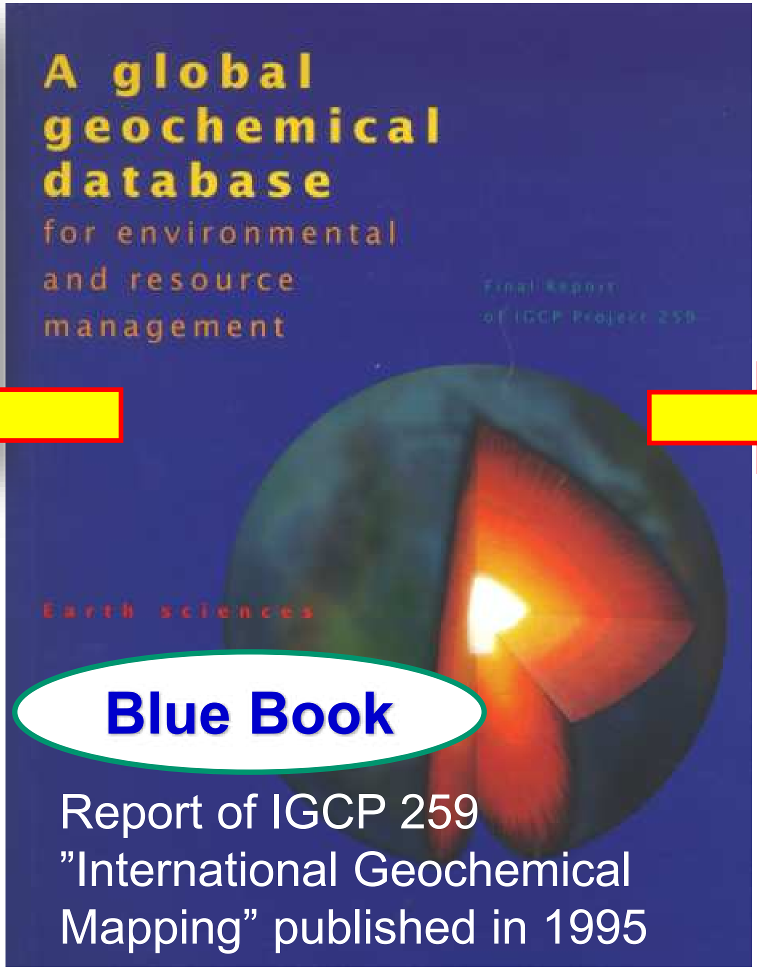
The next few slides are for Young or Early Career Researchers.

However, some of the information may be useful to experienced professionals.

Question: ***Why do we need Harmonised Geochemical Baseline Mapping for the present and future generations, and Why the geochemistry of water and other natural materials are important to our quality of life?***



Arthur G. Darnley
1930-2006
Project leader of
IGCP 259 & 360



Blue Book

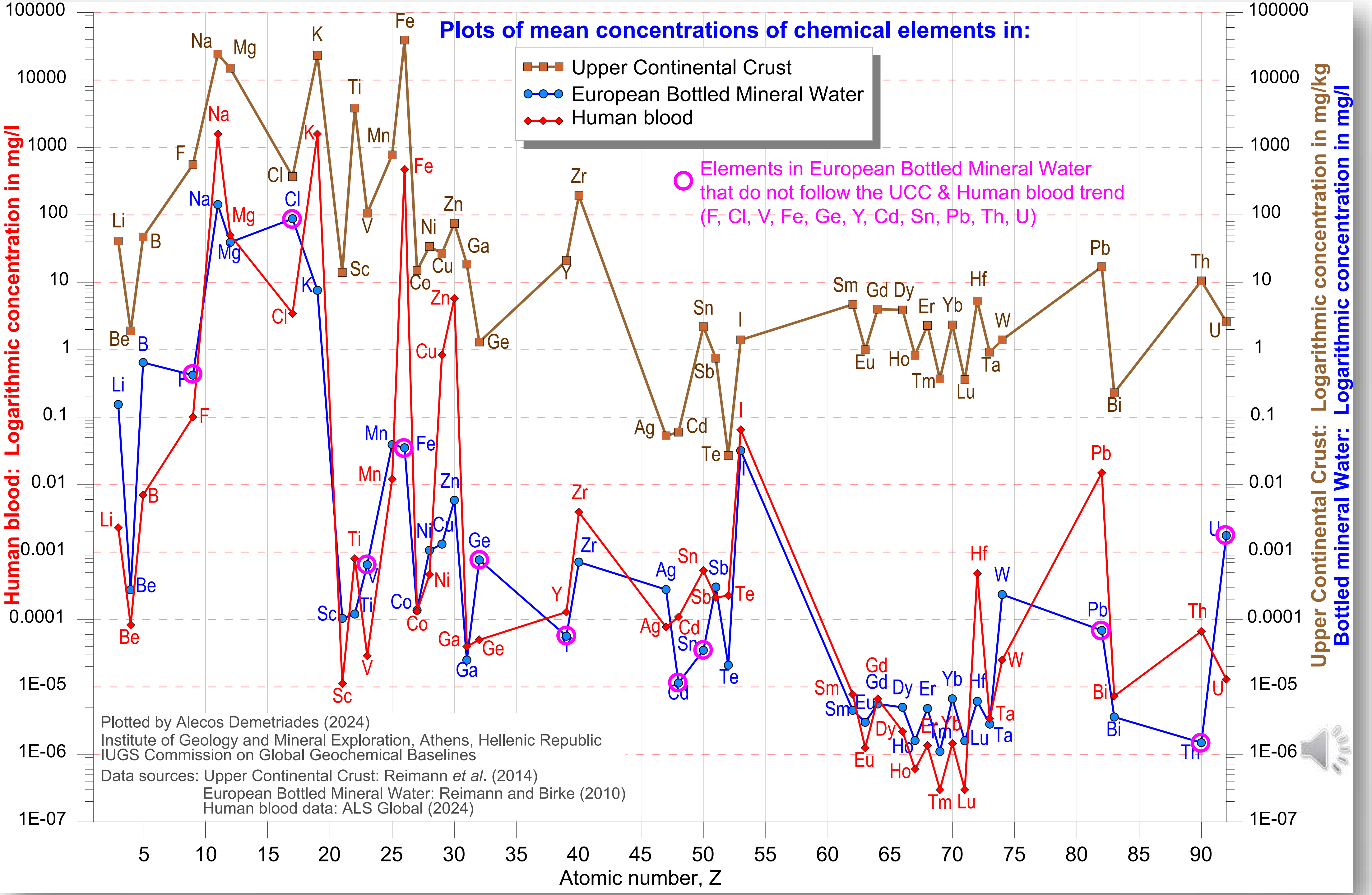
Report of IGCP 259
"International Geochemical
Mapping" published in 1995

The answer is given with the following timeless statements:

"Everything in and on the Earth - mineral, animal and vegetable - is made ….. from naturally occurring chemical 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).

https://www.globalgeochemicalbaselines.eu/datafiles/file/Blue_Book_GGD_IGCP259.pdf



Plots of mean concentrations of chemical elements in:
Upper Continental Crust
European Bottled Mineral Water
Human blood
Elements in European Bottled Mineral Water
that do not follow the UCC & Human blood trend
(F, Cl, V, Fe, Ge, Y, Cd, Sn, Pb, Th, U)
Human blood: Logarithmic concentration in mg/l
Upper Continental Crust: Logarithmic concentration in mg/kg
Bottled mineral Water: Logarithmic concentration in mg/l
Atomic number, Z
100000
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
1E-05
1E-06
1E-07
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
Plotted by Alecos Demetriades (2024)
Institute of Geology and Mineral Exploration, Athens, Hellenic Republic
IUGS Commission on Global Geochemical Baselines
Data sources: Upper Continental Crust: Reimann et al. (2014)
European Bottled Mineral Water: Reimann and Birke (2010)
Human blood data: ALS Global (2024)

WHAT IS A GEOCHEMICAL ATLAS?

Atlas, the famous Titan of Hellenic mythology condemned by Zeus to carry the heavens upon his shoulders for eternity.

https://www.alibaba.com/product-detail/Famous-Roman-Marble-Statue-Nude-Man_60600812917.html?spm=a2700.7724857.0.0.2dbd773a0MiE8u

A ‘Geochemical Atlas’ is a thematic special purpose atlas with maps describing the geographical distribution of chemical elements and other physico-chemical parameters in different natural sample media, such as:-

- **Stream water (surface water),**
- **Groundwater,**
- **Stream sediment,**
- **Overbank or floodplain sediment,**
- **Soil,**
- **Rock,**
- **Plant, *etc*.**

WHY ARE GEOCHEMICAL ATLASES IMPORTANT?

https://greekgodsandgoddesses.net/gods/atlas/

Potter, J.F., 1990. Beneath it all. *The Environmentalist*,**10**(3), 161–162.

According to John F. Potter (1990) geochemical atlases are of great importance, because they

- **Provide data, which can be statistically related to degenerative diseases of plants or animals, and**
- **Reflect variable levels of generated contamination or pollution.**

The importance of natural deficiencies or excesses of localised elements and their possible impacts on agriculture and humankind is particularly relevant.

Hence, Geochemical Atlases should be useful to young and mature members of the Society of Environmental Geochemistry and Health, and not only.

GEOCHEMICAL ATLASES OF EUROPE

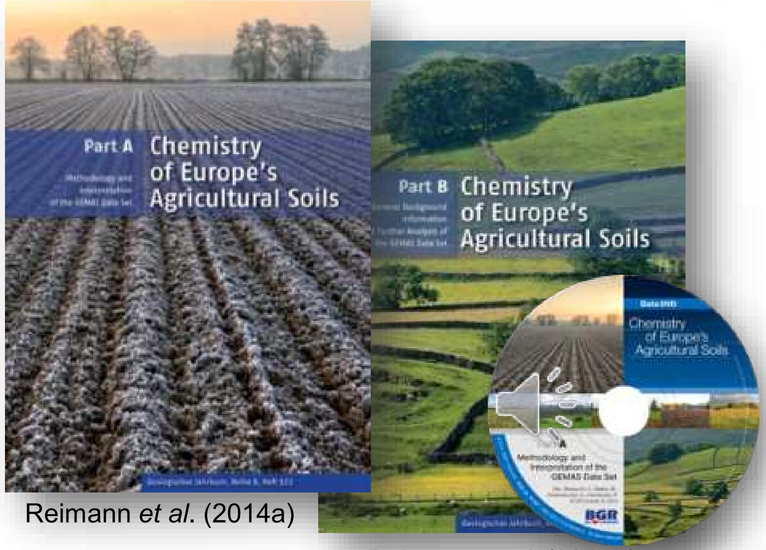
The EuroGeoSurveys Geochemistry Expert Group is dedicated to provide harmonised multi-purpose geochemical data bases,

and has already published the:

- Geochemical Atlas of Europe (2005-6) including data on surface water,
- Atlas of Groundwater Geochemistry of Europe (2010), and
- Atlas of the Geochemistry of agricultural and grazing land soil (GEMAS).

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

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



Reimann *et al.* (2014a)

Reimann *et al.* (2014b)

An important aspect is that all raw data and maps are freely available for downloading either through the Internet or the DVD accompanying the publications. The Geochemical Atlas of Europe provides also the text.

http://www.schweizerbart.de/publications/detail/isbn/9783510968466

Advice to young researchers (1/2)

- **When you design a geochemical project, it is important to verify the generated data by installing your own ‘external’ quality control and assurance programme.** ***As you may have noticed, apart from verifying the quality of the bottled mineral water results, unexpected results were also checked.***

- **It is important to understand that your own ‘external’ quality control and assurance programme is completely different from the quality control procedure that the laboratory has installed to verify the generated analytical results.**

- **Before starting the processing of your project’s analytical data, you should write a quality control report using both your own ‘external’ quality control results and those of the laboratory. You must report all the encountered problems, and solutions given.**

Advice to young researchers (2/2)

- You must study, assimilate, listen, question, and criticise, and when you reach your final conclusion you should be satisfied that you have investigated all possibilities.

- You must be open-minded, and when working in a team you should not be afraid to propose a solution to a problem, even if you think it is far-fetched.

- You must be Professional and follow a Continuous Development Programme in all your working life.

- There must be a balance in everything you do in all aspects of your life.

CLOSING REMARKS (1/2)

Production of harmonised strategic baseline geochemical databases and maps at the national and international levels is only possible if there is standardisation of all procedures of sampling, sample preparation, chemical analysis and data management.

Without harmonisation of methods, and a strict quality control procedure, it is impossible to produce meaningful national and international level geochemical databases for multipurpose use.

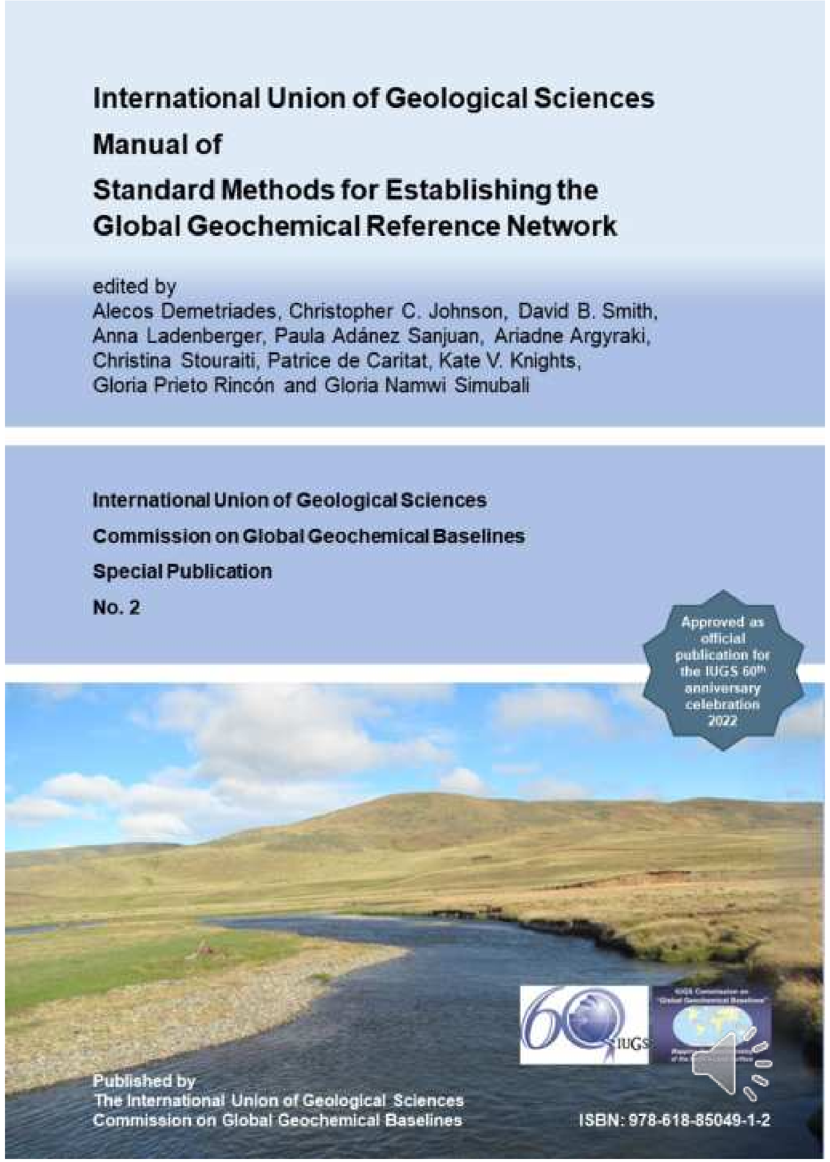
Therefore, it is important for scientists working on the production of national and international geochemical databases to understand the *concept of harmonisation/standardisation of methods*, and to apply it in their work. Otherwise, valuable time, effort and financial resources will be wasted in producing incompatible geochemical data sets both at the national and international levels.

CLOSING REMARKS (2/2)

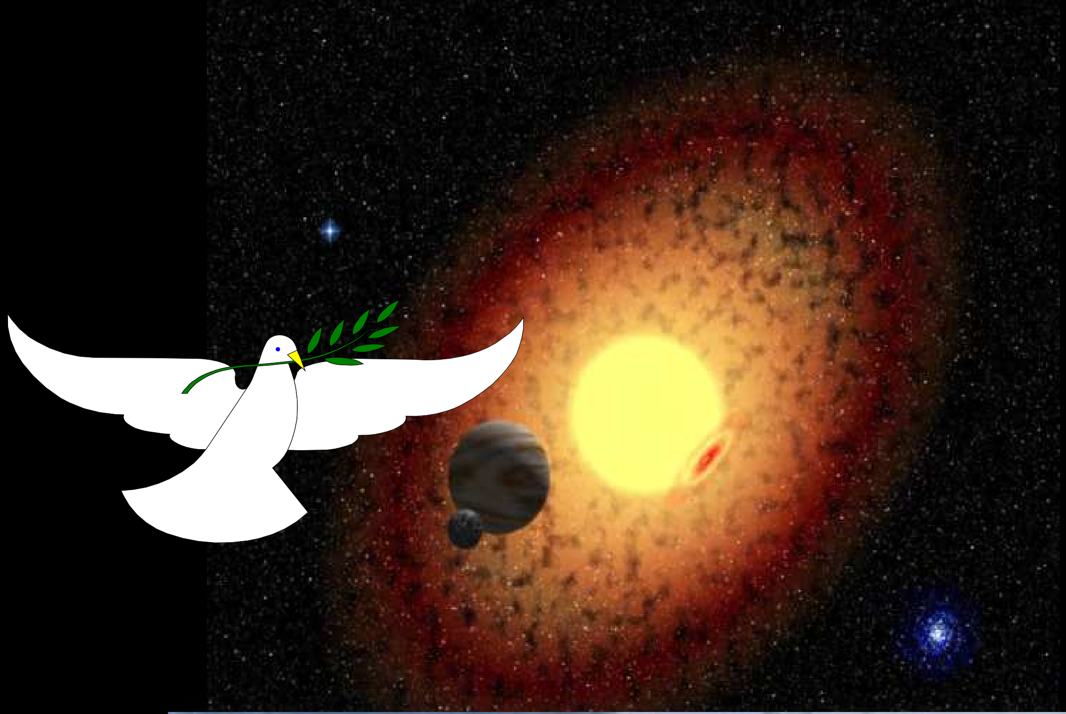
For the production of harmonised baseline geochemical databases and maps consult the IUGS Manual of Standard Methods:

Demetriades, A., Johnson, C.C., Smith, D.B., Ladenberger, A., Adánez Sanjuan, P., Argyraki, A., Stouraiti, C., Caritat, P. de, Knights, K.V., Prieto Rincón, G. & Simubali, G.N. (Editors), 2022. *International Union of Geological Sciences Manual of Standard Methods for Establishing the Global Geochemical Reference Network*. IUGS Commission on Global Geochemical Baselines, Athens, Hellenic Republic, Special Publication, 2, xliv, 515 pages, 375 figures, 35 Tables, 5 Annexes and 1 Appendix, ISBN: 978-618-85049-1-2; https://www.globalgeochemicalbaselines.eu/content/174/iugs-manual-of-standard-methods-for-establishing-the-global-geochemical-reference-network-/ https://doi.org/10.5281/zenodo.7307696.

Also, watch SEGHLive Fellows seminar talk at: https://youtu.be/_qKBpUg2SF4?si=Qq3cG5vepkzmG25G



Geological Surveys are dedicated to provide the present and future generations of humankind with high quality and integrity geochemical data sets, which will be used to improve their living conditions on our home planet Earth.



Thank you for your attention

https://radar.gr/article/olybiakoi-agones-2024-erchontai-allages-stin-teleti-afis-stis-16-apriliou

Questions, Comments and Answers

Question 1 and Comment: *Is there any attempt to compare this water geochemistry with the stream sediment and soil geochemistry rather than bedrock geochemistry?* Geochemistry is affected by the lithology it goes through, that is more related to the weathered sediments.

Answer 1: No attempt has been made to compare the bottled water geochemistry with that of stream sediment and soil. In Europe, the geochemistry of stream sediment and residual soil has been covered by the FOREGS Geochemical Atlas of Europe (http://weppi.gtk.fi/publ/foregsatlas/). Yes, the geochemistry of groundwater is affected by the lithology that the water is in contact with.

Question 2: *Do you plan to measure in the next step organic ingredients in groundwater because in some parts of Poland we have a problem with underground waste dumps, which can be sources of organic or persistent organic pollutants, and very strange chemical compositions. Do you have any plans to expand your analysis for not only inorganic but also organic ingredients?*

Answer 2: There are no plans to analyse organic contaminants in groundwater. Please remember that the determination of the 72 parameters in the bottled mineral water samples was carried out by the German Geological Survey without any charges. We are aware that organic contaminants should be determined in groundwater, but for the moment there are no plans as the cost of repeating the same project and the determination of organic contaminants is very high.

Question 3 - Comment: *The fact that you've used bottled water as a proxy for groundwater geochemistry, one would hope that the bottling companies have actually cleaned up the water from any kind of organic contaminants before it reached the shelves.*

Answer 3: Theoretically the bottling companies should not do any cleaning because the **bottled mineral water** is either natural spring or ground water and bottled at source without any cleaning according to the existing European legislation (see categories). The sources of bottled mineral water are usually far away from any contaminating source. The bottling companies are obliged to submit the analytical results of groundwater to the relevant national authorities before they are given the license to bottle it. The chemical composition of **bottled mineral water** is monitored regularly, and according to European legislation, the chemical composition must be stable.

Question 4 - Comment: *There is no obligation nowadays to check the levels of microplastics and pharmaceuticals and many producers of bottled and tap water because it is expensive do not check the level of other ingredients, and this would be a problem.*

Answer 4: Yes, it would be a problem if all potential contaminants are not checked. Tap water is different because all contaminants including organics should be checked. Next year I will present you the tap water geochemical results we have from European countries.

Question 5 - Comment: *Leaching of elements from bottled materials, does it depend upon the glass and where the glass comes from?*

Answer 5: We have seen the most obvious is the leaching of Cr from green glass bottles. Regarding the source of colourless glass bottles, one will have to do some detective work to find the source of the glass. We have not done this.

Question 5a - Comment: *Where do they come from, What's the commonality, what's the disparities and there's a whole research to be done.*

Answer 5a: Yes, you are quite right we should know the source of the glass material, and Yes, there is room for more research to be done.

Question 6 - Comment: *I like your end part reminding people in term of sample sizes, in terms of keep checking backgrounds, keep checking your references in term of reference materials. Something that is lacking in quite a lot of papers which are submitted for publication. Just those basic answers to good research are missing, and thank you for that particular reminder.*

Answer 6: Usually when I get such papers for review, I reject them immediately. Unfortunately, there are a lot of 'rubbish' papers being published nowadays. Researchers must learn to validate the quality of their results, and they should learn to write up a quality control report.

Question 7 - Comment: *I am actually quite interested in the entirety of this presentation, and going to the early slides in terms of overexploitation and over-abstraction, there is a question if this continues to occur, is there the possibility that whatever inorganics you are seeing in there, can they become over-concentrated? Is that possible or is that a stupid thing to say?*

Answer 7: Remember that the chemical elements in the aquifers are sort of diluted in a large volume of water. So, if there is overexploitation and over-abstraction, Yes, it is possible to cause their overconcentration in the remaining smaller volume of water. I am worried about the Sahara because if they start tapping the groundwater, as they do in Saudi Arabia, then this danger that you are saying, it could happen much faster because the groundwater in these desert areas is not replenished, as is in temperate climates.

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<u>IMPORTANT NOTE</u> for accessing the original PowerPoint file:-

The original PowerPoint presentation can be downloaded from the following pCloud hyperlink:

https://u.pcloud.link/publink/show?code=kZXDB40Z6h5xSQzk2BBRn4zf8d2B5H64xfuV

EGG: European Groundwater Geochemistry

SUMMARY

Alecos Demetriades

With an ever-growing world population and drastic global climatic changes, groundwater will become a valuable resource for our well-being. Clean and safe water is important for our health. According to Ritchie *et al.* (2019) "*One in four people in the world do not have access to safe drinking water. This is a major health risk. Unsafe water is responsible for more than a million deaths each year*."

The EuroGeoSurveys Geochemistry Expert Group (EGS-GEG) carried out a unique and novel project for the assessment of the chemical quality of European groundwater, known by the acronym 'EGG', European Groundwater Geochemistry. It is interesting to report how this project was put together. The European Environmental Agency contacted in 2007 the EGS-GEG whether there was a harmonised geochemical data set for groundwater, similar to the stream water geochemical data set produced during the multi-sample media project of the Geochemical Atlas of Europe (Salminen et al., 2005; De Vos, Tarvainen *et al*., 2006). Of course, the reply was negative. However, there were discussions among the members of EGS-GEG. Collecting representative evenly-spaced groundwater samples at the European scale is not an easy task, and may be prohibitively expensive if done at a high sampling density.

In the attempt to find a cost-effective solution, a colleague, Manfred Birke from the German Geological Survey, came up with the idea that 'bottled mineral water' can be used as a proxy for the geochemistry of groundwater. Though the idea met some resistance, it was in the end decided that it was worth a try, because of the low sampling cost by the EGS-GEG network purchasing 'bottled mineral water' from local markets, and sending them to Germany for analysis.

The atlas ‘Geochemistry of European Bottled Water’ (Reimann and Birke, 2010) includes the results from the detailed analysis of 1785 ‘bottled mineral water’ samples collected from 38 European and neighbouring countries, representing 1247 different sources at 884 locations. The ‘bottled mineral water’ samples were analysed in a single laboratory for 72 determinands by ICP-MS, ICP-OES and IC, including pH, EC, alkalinity, thus producing the first fully harmonised and quality-controlled geochemical data set for European groundwater. The ‘bottled mineral water’ data set, therefore, provides a first impression of variability and the regional distribution of groundwater chemistry at the continental scale.

Many processes affect the hydrochemical fingerprint of groundwater – important factors include: rainfall chemistry, climate, vegetation and soil zone processes, mineral-water interactions, groundwater residence time and the mineralogy and chemistry of the aquifer (and contamination). The influence of geology in determining element concentrations in ‘bottled mineral water’ can be observed for a significant number of elements. Examples include: high values of chromium (Cr) clearly related to the occurrence of ophiolites; beryllium (Be), caesium (Cs), germanium (Ge), potassium (K), lithium (Li) and rubidium (Rb) showing unusually high values in areas underlain by Hercynian granites, while high values of aluminium (Al), arsenic (As), fluorine (F), potassium (K), rubidium (Rb) and silicon (Si) in ‘bottled mineral water’ are related to the occurrence of alkaline volcanic rocks.

A further key observation is that knowledge of geology alone is inadequate to predict the hydrochemistry of ‘bottled mineral water’: natural variation is enormous, usually three to four and for some elements up to seven orders of magnitude. Such variation may reflect, among other factors, groundwater residence time and mixing with deep brackish formation waters. It has also been found that bottled materials can influence ‘bottled mineral water’ chemistry. For antimony (Sb), leaching from the bottle material is so serious that the results for ‘bottled mineral water’ cannot be used as an indication of natural concentrations in groundwater.

Some elements, as observed in the 'bottled mineral water', are not representative of typical, shallow, fresh groundwater; rather, they tend to exhibit unusually high concentrations, typical for 'bottled mineral water': examples are boron (B), beryllium (Be), bromine (Br), caesium (Cs), fluorine (F), germanium (Ge), lithium (Li), rubidium (Rb), tellurium (Te), and zirconium (Zr).

Very few analysed samples (in general less than 1%) returned values exceeding maximum admissible concentrations (MACs) for 'bottled mineral water', as defined by the European Commission.

In conclusion, this unusual project produced interpretable and useful results at the continental scale.

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