

# EGG: European Groundwater Geochemistry

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*A model geochemical study of bottled mineral water in Europe, as a proxy to groundwater, found that wide variations occur in element distribution. Here, bottled mineral water results are compared with surface-, tap- and ground-water survey data, and the role of different geological terrains is considered. In order to produce harmonised hydrogeochemical databases, all samples of each data set were analysed in a single laboratory, following a very strict quality control protocol. Since reliable maps can be obtained from only 1,000 to 2,500 samples evenly distributed across Europe, it is recommended to carry out similar studies for different water sources or types; the resulting harmonised hydrogeochemical databases would provide an excellent resource for European decision makers and scientists.*

*Une étude de modèle géochimique concernant l'eau minérale embouteillée, en Europe, en tant qu'élément représentatif des eaux souterraines, a démontré qu'il existait de grandes variations dans la distribution des éléments chimiques. Les résultats fournis par l'eau minérale en bouteille sont comparés ici avec les données d'étude venant des eaux de surface – au robinet – et des eaux souterraines, en tenant compte du rôle joué par les différents terrains géologiques. Pour obtenir des bases de données hydrogéochimiques comparables (harmonisées), tous les échantillons de chaque lot ont été analysés par un seul laboratoire, suivant une procédure très stricte de contrôle qualité. Puisque les cartes significatives peuvent être obtenues seulement à partir de 1000 à 2500 échantillons, régulièrement distribués à travers l'Europe, il est recommandé d'effectuer des études analogues pour différentes origines de l'eau ou "types"; les bases de données hydrogéochimiques harmonisées constitueraient un excellent outil pour les décideurs et les scientifiques.*

*En representación de las aguas subterráneas, un estudio geoquímico del agua mineral embotellado en Europa, encontró que se producen amplias variaciones en la distribución de los elementos. Aquí los datos del agua mineral embotellado se comparan con los datos de sondeo de aguas superficiales, en la toma de datos del estudio del agua subterránea se considera el papel de los diferentes terrenos geológicos. Para producir bases de datos hidrogeoquímicas armonizadas, todas las muestras de cada conjunto de datos se analizaron en un solo laboratorio, siguiendo un protocolo de control de calidad muy estricto. Dado que mapas fiables se pueden obtener con solamente 1.000 a 2.500 muestras distribuidas de manera uniforme en toda Europa, es recomendado llevar a cabo estudios similares para diferentes fuentes o tipos de agua; las bases de datos hidrogeoquímicas armonizadas obtenidas proporcionarían un excelente recurso para los responsables políticos y científicos europeos.*

For the last 60 years or so, humans have had the capacity to influence groundwater chemistry on both global and countrywide scales. For example, the atmospheric testing of atomic bombs in the late 1950s led to the enrichment of recharging rainfall with tritium, allowing this isotope to be used as a dating tool in groundwater on a global scale (e.g., Carmi and Gat, 2000). As a consequence of the intensification of agriculture across Europe in the 1960s and '70s, with the accompanying unregulated disposal of farm effluents, national legislation was required to prevent nitrate pollution of shallow unconfined groundwater aquifers (e.g., Meinardi *et al.*, 1995).

To monitor groundwater chemistry, and so prevent deterioration in groundwater quality, there is an immediate need to document the current natural variation of the

chemical composition of groundwater in Europe. Future groundwater analyses can then be compared with this and anthropogenic impacts identified. To be of any use to the regulator and the practitioner, such documentation must reflect the diversity of groundwater environments (and use) across Europe, and be able to verify reference values for the variation in (ground)water composition naturally present in aquifers.

The results of the EuroGeoSurvey's Geochemistry Expert Group's project entitled European Groundwater Geochemistry were published as an atlas with the title *Geochemistry of European Bottled Water* (Reimann and Birke, 2010). These data are a useful first step in providing the natural range of variation for over 70 chemical parameters in groundwater, namely Ag, Al, As, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, NH<sub>4</sub><sup>+</sup>, Ni, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, Pb, Pr, Rb, Sb, Sc, Se, Si, Sm, Sn, SO<sub>4</sub><sup>2-</sup>, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, electrical

conductivity, pH and total alkalinity.

This survey has shown that it is possible, by analysing bottled natural mineral water from across Europe, to provide useful guidance on the chemical composition of deep natural groundwater. It also provided important insights about problems related to collection and analytical methodologies and associated costs. More importantly, it showed that by using the analytical results from bottled mineral water samples from just 884 locations, we can gain a good statistical overview of groundwater quality in terms of natural variation at the European scale – quite comparable to the results of general statistical polls.

At the European scale, it is not necessary, therefore, to analyse every single aquifer, as it is possible to get a good impression of water quality by just collecting 1,000–2,500 representative samples across Europe. The validity of the low sample density approach has already been demonstrated by the Geochemical Atlas of Europe (Salminen *et al.*, 2005), and more recently for agricultural

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and grazing land soil in the GEMAS project (Reimann *et al.*, 2014). It is suggested, therefore, to follow the GEMAS approach of one sample site per 2,500 km<sup>2</sup>, resulting in just over 2,000 samples covering Europe. A number of such 'water polls' could thus be carried out at the European scale, for instance for:

- a. springs, providing a chance to get an excellent overview of natural shallow groundwater quality, untouched by human interference via, e.g., well installations;
- b. surface water – a repetition of the FOREGS stream water geochemical survey (Salminen *et al.*, 2005) at double the sample density;
- c. tap water, providing a good idea about what the European population really drinks; recent publications on the geochemistry of tap water prove that this would work (e.g., Banks *et al.*, 2015), and
- d. groundwater from wells, collecting also additional geological information about each well.

## Background

Two key objectives of the EU Water Framework Directive 2000/60/EC are to prevent deterioration in groundwater quality and, if contaminated, to implement measures to reverse the situation in order to bring groundwater quality back to a 'good' status. The successful implementation of these objectives requires (a) knowledge about naturally occurring element concentrations in groundwater, and (b) comparison of groundwater analyses with the mapped natural variation. To date, individual Member States publish their own guidance lists, without considering the natural variation in chemical composition in relation to toxicological and health data. As groundwater, and potable water in general, is very important to the good health status of the human population, maximum admissible determinand concentrations in groundwater must be based on toxicity data, which assess the relationship between chemical elements and compounds and their effect on human health (USEPA, 2011).

However, while the process of setting up threshold or limit values appears quite simple, as they should be based on toxicological and health data, there are a number of points that should be considered for the establishment of the natural variation of

groundwater chemical composition across Europe. As has already been suggested, representative groundwater samples can be collected using a sample density of one site per 2,500 km<sup>2</sup>. The samples should be collected, according to the same specifications, from groundwater wells, which:

- i. have been in operation for many years;
- ii. are located in a wide variety of aquifers, and
- iii. are stable in natural chemical composition.

Finally, the analyses should be carried out in a single laboratory for consistency and repeatability.

By harvesting the groundwater analytical data from such an evenly spaced network of groundwater wells across Europe, it would be possible to establish not only the normal variation in elemental composition of groundwater, but perhaps also – and more importantly – the variation that can occur with individual aquifer types, such as sedimentary, igneous, and metamorphic aquifers. It should be noted, however, that this approach is prone to contamination from well installations, and the degree of contamination can be different from country to country.

## Geochemistry of European Bottled Water

The atlas *Geochemistry of European Bottled Water* (Reimann and Birke, 2010) presents the results from the detailed analysis of 1,785 bottled mineral water samples collected from 38 European countries, representing 1,247 different sources at 884 locations. The bottled mineral water samples were analysed in a single laboratory for more than 70 determinands by ICP-MS, ICP-OES and IC, including pH, alkalinity, etc. (Table 1), thus producing the first harmonised 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.

The maps identify the influence of geology on water composition, as well as other factors (e.g., bottling effects, leaching of elements from bottles). Furthermore, enormous natural variation in concentration (up to 7 orders of magnitude) of many of the analysed chemical elements in groundwater is documented. The bottled water data are plotted against European surface water (Salminen *et al.*, 2005), tap

water (this study; Banks *et al.*, 2015) and Norwegian bedrock groundwater (Frengstad *et al.*, 2000) in cumulative probability plots that highlight the similarities and differences between these different water types (Figure 1); it is worth noting that all samples of each data set were analysed in the same laboratory.

In general, the four data sets shown in Figure 1 are surprisingly comparable for most elements (e.g., Cd, Cl, Cr) with respect to concentration and variation. Cerium shows two distinct trends between the bottled-tap water and the ground-surface water; the Norwegian groundwater is undoubtedly affected by the variable geological terrain and the higher Ce values are due to granitic, granodioritic and gneissic terrains; its similarity with the stream (surface) water leads to the assumption that this trend is also due to the variable geological terrain of Europe. Caesium in bottled mineral water shows a different atypical trend for groundwater, which is most likely due to a higher number of samples sourced from granitic terrains in comparison to other terrain types. Copper seems to display a strong impact of contamination from well installations; this is indicated by the shift towards higher values over the whole concentration range for tap water and Norwegian groundwater. However, bottled mineral water from high production wells most likely shows the 'true' (background) variation of Cu in groundwater, as it is assumed that there is too short a time to 'acquire' a contamination signal from well installations.

## Natural Mineral Water

To obtain and maintain the status of a certified natural mineral water a source must have been sampled for many years prior to recognition, and must remain bacteriologically pure and within set limits for a range of parameters according to European Directives 80/777/EEC and 2003/40/EC.

EU Council Directive 80/777/EEC (Annex 1, p. 6) defines a "natural mineral water" as a water that is "microbiologically wholesome, originating in an underground water table or deposit and emerging from a spring tapped at one or more natural or bore exits". It moreover states, "natural mineral water can be clearly distinguished from ordinary drinking water:

- by its nature, which is characterised by its mineral content, trace elements or other constituents and, where appropriate, by certain effects" and
- "by its original state".

Table 1: Instrumental analytical method, detection limits, precision, number of samples <RDL, % of samples <RDL, and basic statistical parameters of bottled mineral water data set used for mapping (n=884)

Parameter	Method	Unit	IDL*	RDL**	PDL***	N<RDL	%<RDL	P% <sup>(e)</sup>	Percentiles					Max.	MAD <sup>(f)</sup>	Powers <sup>(g)</sup>					
									Min.	5	10	25	50				75	90	95		
Ag	ICP-QMS	µg/l	0.001	0.002	0.002	637	72	13	<0.002	<0.002	<0.002	<0.002	0.002	0.012	0.1	112	0	6			
Al	ICP-QMS	µg/l	0.2	0.5	0.2	158	18	5	<0.5	0.59	1.2	4.2	13	30	966	1.3	4	4			
As	ICP-QMS	µg/l	0.01	0.03	0.001	45	5.1	10	<0.03	0.017	0.041	0.24	0.75	2.8	5.1	90	1.5	4			
B	ICP-QMS	µg/l	0.1	2	0.2	12	1.4	4	<2	4.7	6.6	13	162	730	1618	120000	1.8	6			
Ba	ICP-QMS	µg/l	0.005	0.1	1 <sup>(e)</sup>	0	0	5	0.05	1.2	2.7	10	78	221	390	26800	1.5	7			
Be	ICP-QMS	µg/l	0.001	0.01	0.005	636	72	5	<0.01	<0.01	<0.01	<0.01	0.015	0.1	0.51	64	0	5			
Bi	ICP-QMS	µg/l	0.0005	0.005	0.003	856	97	- <sup>(e)</sup>	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.69	0	3			
Br <sup>-</sup>	IC	µg/l	3	3	- <sup>(e)</sup>	43	4.9	-	<3	3	4	12	35	91	343	1015	21700	1.5	5		
Ca	ICP-OES	mg/l	0.005	0.01	- <sup>(e)</sup>	0	0	-	0.43	3.7	9.1	32	66	115	239	377	611	0.92	4		
Cd	ICP-QMS	µg/l	0.001	0.003	0.002	420	48	29	<0.003	<0.003	<0.003	0.003	0.008	0.02	0.037	1.1	1.1	4	4		
Ce	ICP-QMS	µg/l	0.0005	0.001	0.0001	449	51	13	<0.001	<0.001	<0.001	<0.001	0.007	0.024	0.052	6.2	0	5	5		
Cl <sup>-</sup>	IC	mg/l	0.01	0.01	- <sup>(e)</sup>	0	0	-	0.18	0.82	1.4	4.6	13	41	162	378	3627	1.6	5		
Co	ICP-QMS	µg/l	0.002	0.01	0.002	138	16	5	<0.01	<0.01	<0.01	0.013	0.047	0.12	0.36	16	0.93	5	5		
Cr	ICP-QMS	µg/l	0.01	0.2	0.014	592	67	7	<0.2	<0.2	<0.2	<0.2	0.28	0.76	1.5	27	0	3	3		
Cs	ICP-QMS	µg/l	0.0005	0.002	0.004 <sup>(e)</sup>	59	6.7	3	<0.002	<0.002	0.003	0.007	0.039	0.51	6.9	24	415	2.8	6	6	
Cu	ICP-QMS	µg/l	0.01	0.1	0.029	139	16	2	<0.1	<0.1	<0.1	0.13	0.27	0.61	2.4	4.7	100	1.1	4	4	
Dy	ICP-QMS	µg/l	0.0002	0.001	0.001	362	41	16	<0.001	<0.001	<0.001	<0.001	0.001	0.003	0.01	0.016	0.39	1.3	4	4	
EC	conductometric	µS/cm	-	-	- <sup>(e)</sup>	0	0	-	18	88	181	337	588	1256	2580	3582	26500	0.94	4	4	
Er	ICP-QMS	µg/l	0.0002	0.001	0.0004	468	53	13	<0.001	<0.001	<0.001	<0.001	<0.001	0.003	0.008	0.016	0.77	0	4	4	
Eu	ICP-QMS	µg/l	0.0002	0.001	0.001	473	54	18	<0.001	<0.001	<0.001	<0.001	0.002	0.005	0.008	0.45	0	4	4	4	
F <sup>-</sup>	IC	mg/l	0.003	0.003	-	2	0.23	-	<0.003	0.024	0.039	0.084	0.19	0.43	1.1	1.6	11	1.2	5	5	
Fe	ICP-QMS	µg/l	0.01	0.5	0.08	381	43	4	<0.5	<0.5	<0.5	<0.5	0.69	3.3	15	43	13500	1.5	6	6	
Ga	ICP-QMS	µg/l	0.0005	0.005	0.005	611	69	4	<0.005	<0.005	<0.005	<0.005	0.006	0.013	0.02	3.9	0	4	4	4	
Gd	ICP-QMS	µg/l	0.0002	0.002	0.001	530	60	22	<0.002	<0.002	<0.002	<0.002	0.004	0.009	0.018	0.66	0	3	3	3	
Ge	ICP-QMS	µg/l	0.005	0.03	0.02	461	52	6	<0.03	<0.03	<0.03	<0.03	0.094	0.53	2	110	0	5	5	5	
Hf	ICP-QMS	µg/l	0.0001	0.002	0.001	722	82	28	<0.002	<0.002	<0.002	<0.002	<0.002	0.005	0.008	1.6	0	4	4	4	
Ho	ICP-QMS	µg/l	0.0001	0.001	0.0003	645	73	19	<0.001	<0.001	<0.001	<0.001	0.001	0.003	0.005	0.12	0	4	4	4	
I	ICP-QMS	µg/l	0.01	0.2	0.09	1	0.11	15	<0.2	0.83	1.3	2.4	4.8	11	31	76	4030	1.1	5	5	
K	ICP-OES	mg/l	0.05	0.1	- <sup>(e)</sup>	4	0.45	-	<0.1	0.3	0.5	0.9	2.1	6.5	18	33	558	1.4	5	5	
La	ICP-QMS	µg/l	0.0001	0.001	0.001	264	30	9	<0.001	<0.001	<0.001	<0.001	0.002	0.007	0.021	10	2.1	5	5	5	
Li	ICP-QMS	µg/l	0.01	0.2	0.14	24	2.7	5	<0.2	0.33	0.75	2.6	10	54	298	744	9860	2.3	5	5	
Lu	ICP-QMS	µg/l	0.00005	0.001	0.0002	729	82	16	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	0.004	0.41	0	4	4	
Mg	ICP-OES	mg/l	0.005	0.01	- <sup>(e)</sup>	1	0.11	-	<0.01	0.87	2	5.7	16	32	68	92	4010	1.3	7	7	
Mn	ICP-QMS	µg/l	0.005	0.1	0.111	265	30	2	<0.1	<0.1	<0.1	<0.1	0.54	11	98	249	1870	3.5	6	6	
Mo	ICP-QMS	µg/l	0.001	0.02	0.017	55	6.2	4	<0.02	<0.02	0.031	0.089	0.28	0.82	2.1	4	74	1.6	4	4	
Na	ICP-OES	mg/l	0.02	0.1	- <sup>(e)</sup>	0	0	-	0.4	1.5	2.3	6	16	76	306	620	8160	1.7	5	5	
Nb	ICP-QMS	µg/l	0.001	0.01	0.001	784	89	15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.011	0.025	0.54	0	3	3	3
Nd	ICP-QMS	µg/l	0.0001	0.001	0.001	258	29	18	<0.001	<0.001	<0.001	<0.001	0.002	0.007	0.019	0.041	5.1	2.1	5	5	5
NH <sub>4</sub> <sup>+</sup>	photometric	mg/l	0.005	0.005	- <sup>(e)</sup>	573	65	-	<0.005	<0.005	<0.005	<0.005	<0.005	0.028	0.3	0.89	60	0	5	5	5
Ni	ICP-QMS	µg/l	0.005	0.02	0.01	39	4.4	4	<0.02	0.022	0.029	0.063	0.18	0.64	2	4.3	95	1.7	4	4	4





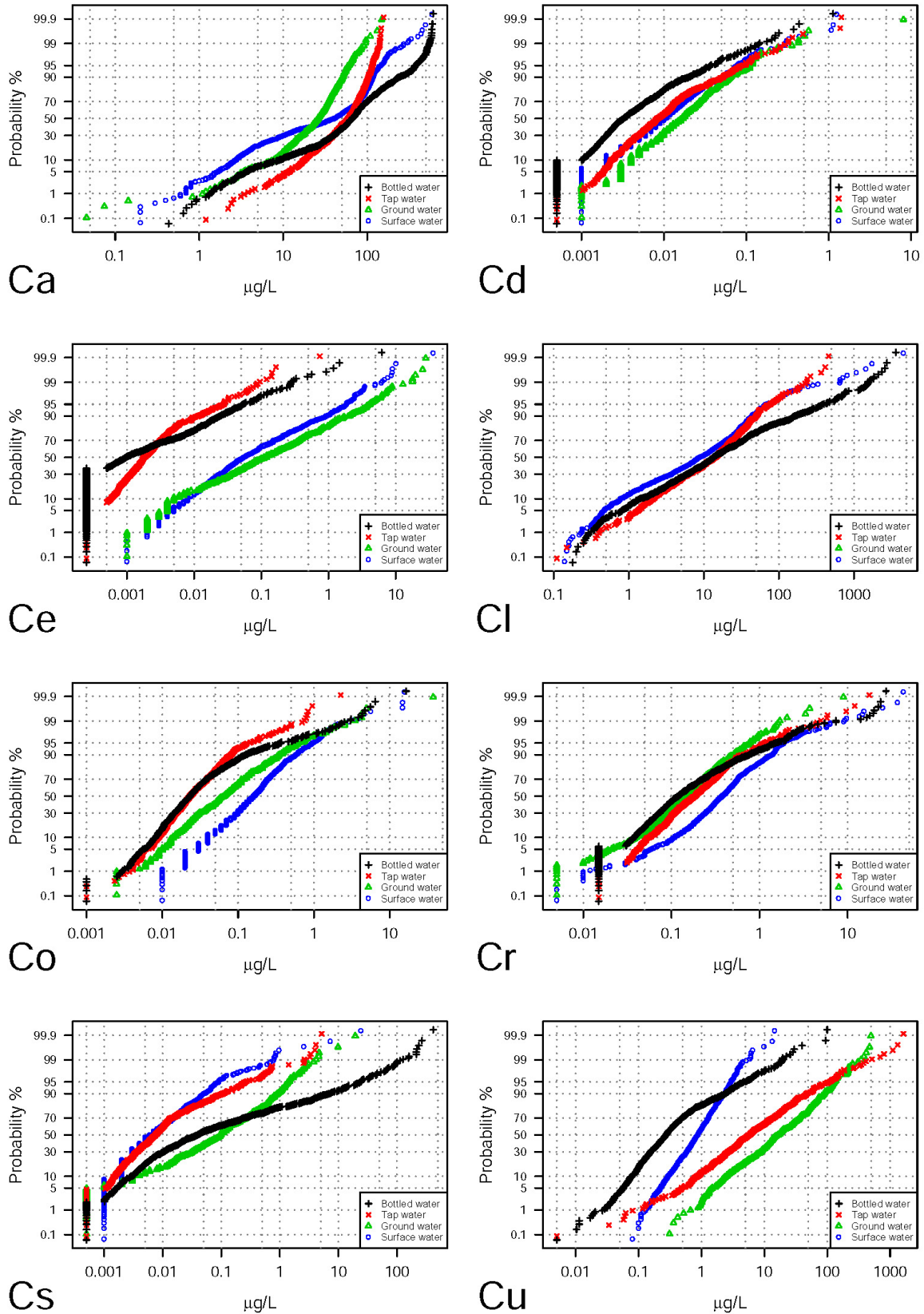


Figure 1: Cumulative probability plots for selected elements in bottled mineral water ( $n=884$ ) data set (black plus). For comparison values for European tap water (red x – this study), European surface water (blue circle – from Salminen et al., 2005) and Norwegian hardrock groundwater (green triangle – from Frenstad et al., 2000) are added to the plots (Source: Reimann and Birke, 2010, Fig. 26, p.55). It is noted that all samples of each data set were analysed in the same laboratory.

Both characteristics having been preserved intact, because of the underground origin of such water, which has been protected from most pollution risks.

The “natural mineral water” at source must be free from pathogenic microorganisms, and its total bacterial content should comply with strict criteria. It must be of such high microbiological quality that no disinfection is required. Its composition and temperature must remain stable within the limits of natural fluctuation and must not vary with flow rate. A natural mineral water source must have been fully characterised in terms of its geology and chemistry and should be protected against pollution.

The mineral water producers usually print the concentration of some of the

major elements on the bottle label. This information provided an ideal opportunity to compare the analytical results produced in this project with those on the labels, which are, in some cases, much older. Mostly, the chemical composition on the labels fits surprisingly well with the produced analytical results (Figure 2). Thus, the condition set by EU Council Directive 80/777/EEC of stable composition within the limits of natural fluctuation is met.

**Analysis and Quality Control**

For the production of a harmonised database of high integrity all samples must be analysed in the same laboratory, over a short period, and under a strict quality con-

trol programme. Experience has shown that without exceptionally strict quality control from sampling to laboratory analysis, data sets will never be comparable (Salminen *et al.*, 2005; Demetriades *et al.*, 2014).

The benefits of using a single laboratory are that one deals with a single point of contact for all laboratory requirements, and that all determinations are made under the same roof, using the same instruments, sample preparation, reagents, and technical staff. Optimal laboratory conditions are thus achieved, enabling good repeatability and reproducibility of analytical results. Finally, one deals only with the evaluation of a single set of quality control results. Therefore, the most cost- and time-effective way of producing harmonised, compatible,

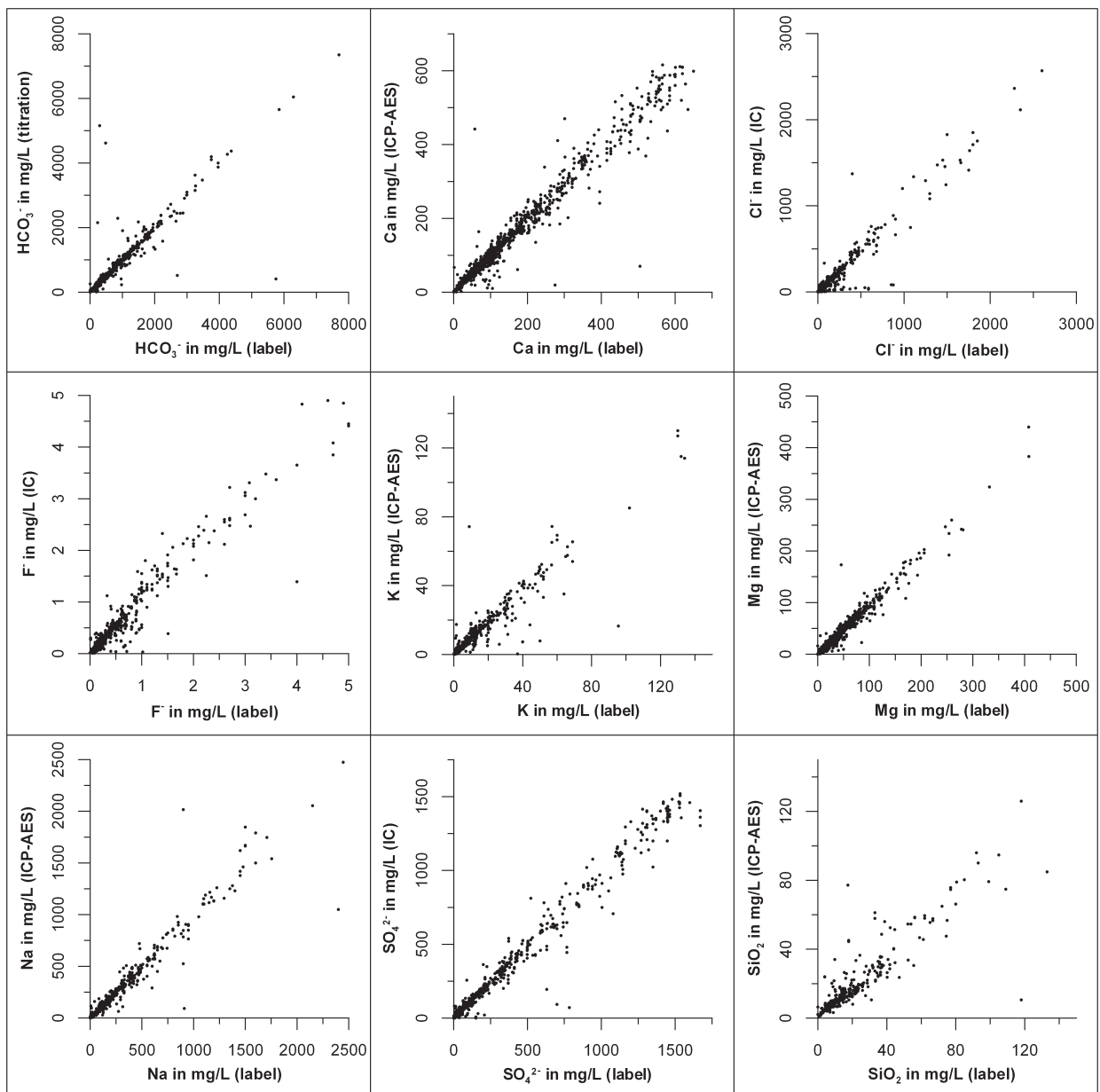


Figure 2: Comparison of the chemical composition displayed on the bottle labels with the measured concentrations of this study (Source: Reimann and Birke, 2010, Fig. 20, p.44).

and reliable analytical results is to collect a manageable number of representative samples, and to use the same laboratory for the analysis of the same suite of determinands.

The 1,785 bottled mineral water samples were all analysed at the chemical laboratory of the Federal Institute for Geosciences and Natural Resources (BGR) in Berlin. Details of sample preparation and the extensive analytical programme are reported in Reimann and Birke (2010) and Birke *et al.* (2010).

### Influence of Geology on Groundwater Chemistry

The output from the sampling of bottled mineral water across Europe has clearly shown the influence that geology has on the composition of the natural mineral water of Europe. Geology is one of the key factors influencing the observed element concentrations for a significant number of elements. Examples include:

- high values of Cr, clearly related to ophiolite complexes (Figure 3);

- Be, Cs, Li showing high values in areas underlain by Hercynian granite masses (Figure 4);
- F, K, Si (Figure 5) related to the occurrence of alkaline rocks, especially near the volcanic centres in Italy, and
- V indicating the presence of active volcanism (Figure 6).

As is quite apparent, geological components are basically the same across the continent, i.e., a limestone or a granite in one country is essentially similar in chemical composition as in other countries. In fact, the background variation of chemical elements in the same rock unit, depending on the degree of weathering, should be quite comparable from one country to the next.

### Discussion

The data presented in the atlas *European Groundwater Geochemistry* (Reimann and Birke, 2010) can be used to gain a first impression of the natural variation of the analysed elements in water at a European scale. Natural variation is enormous, usually spanning three to four and occasionally up to seven orders of magnitude. Several elements for which no potable water standards are defined in Europe (e.g., Be, Bi, Br, Cs, Ga, Ge, I, Li, P, Rb, Sr, Te, Tl, V, Zr) show surprisingly high concentrations in bottled mineral water samples. In terms of health effects, more attention at both ends of the concentration range (deficiency as well as toxicity) may be required for quite a number of elements (e.g., deficiency: I, Se, Zn; toxicity: As, B, Ba, Li, Th, Tl, U, V).

Geology is one of the key factors influencing the observed element concentrations for a significant number of elements. As has already been shown, high values of Cr are clearly related to ophiolite complexes; Be, Cs and Li show high values in areas underlain by Hercynian granite; F, K and Si are related to the occurrence of alkaline rocks, especially near the volcanic centres in Italy, and V indicates the presence of active volcanism. Some elements observed in bottled mineral water are clearly not representative for 'normal' shallow groundwater, but tend to exhibit unusually high concentrations, typical for 'mineral water', e.g., B, Cs, F, Ge, Li, Na, Rb, Te, Tl and Zr.

In terms of water standards, the vast majority of samples fulfil the requirements of the European Union legislation for mineral (and drinking) water. For some elements, a few samples exceed the potable

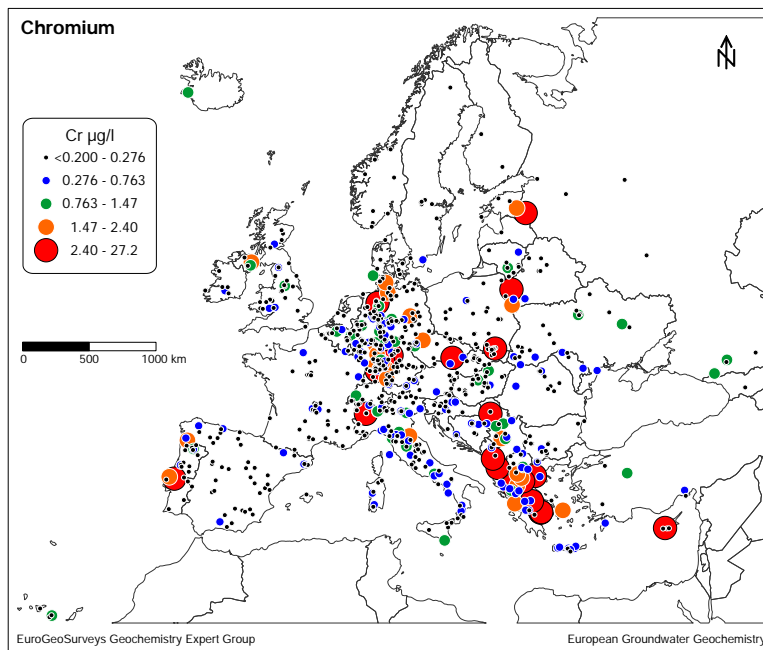


Figure 3: Map of Europe showing the distribution of chromium ( $\mu\text{g/l}$ ) in bottled mineral water ( $N = 884$ ).

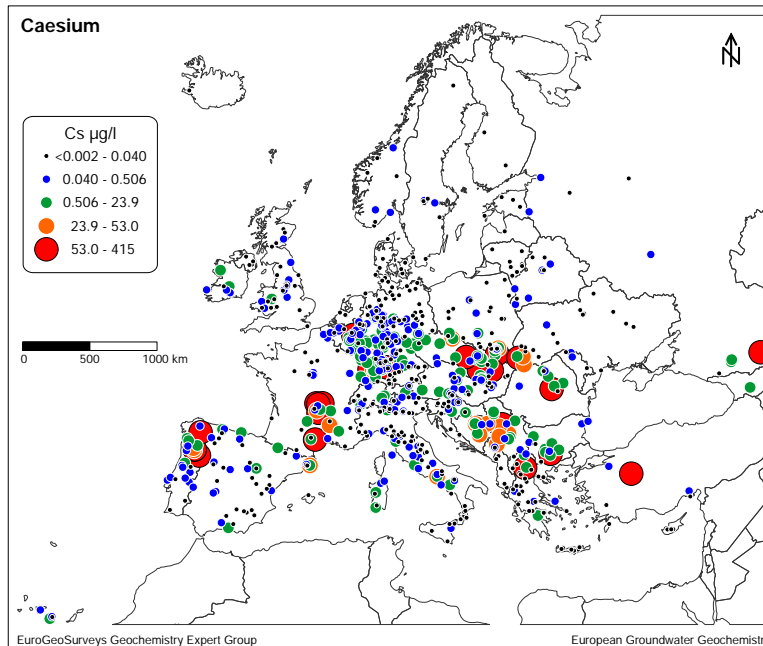


Figure 4: Map of Europe showing the distribution of caesium ( $\mu\text{g/l}$ ) in bottled mineral water ( $N = 884$ ).

water standards, e.g., the maximum values observed for Al, As, Ba, F, Mn, Ni,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , Se and U. It must be noted that the maximum admissible concentration (MAC) for F<sup>-</sup> in mineral water is set very high (5 mg/l instead of the 1.5 mg/l valid for drinking water) in order to avoid too many compliance failures (about 5 % of all mineral water samples report F<sup>-</sup> concentrations above 1.5 mg/l); this practice is questionable in view of the fact that bottled mineral water is increasingly replacing tap water as general drinking water. European tap water, on the other hand, returned considerably higher concentrations of Cu, Pb and Zn than the bottled mineral water – a likely indication of contamination from plumbing and well installations.

With very few exceptions, all values reported in this study are well below the MAC values, as defined by European legislation. There exist, however, a number of elements that have been indicated as having health effects in the international literature, but for which no MAC values are defined in the European Union. Some of these (e.g., Be, I, Li, Th, Tl and U) exhibit a very large natural variation in bottled mineral water.

Overall, it can be concluded that the idea of using bottled water as a first proxy for groundwater quality at the European scale was not as absurd as it might have appeared at first glance. Despite all the potential problems, it has been shown that natural variation in groundwater quality at the European scale is much larger than the impact of any secondary consideration. Thus, on many hydrogeochemical maps, the importance of geology and other natural processes (e.g., climate) affecting the chemical composition of groundwater is clearly visible. In any case, this continental-scale survey provides valuable experience, and should provoke productive proposals for a more systematic investigation of groundwater quality at the European scale, as this database does not cover evenly the whole of Europe.

### Proposal

A continental-scale low-density groundwater survey (e.g., 1 sample site/2,500 km<sup>2</sup>) should be carried out, based on regular low-density grid cells evenly spaced across the entire continent, with all samples analysed at a single laboratory, and under a strict quality control programme. This is a cost-effective survey, as approximately 1,000 to 2,500 samples will be collected, compared to the very elaborate sampling of all groundwater aquifers with hundreds of thousands of samples, and many laboratories involved.

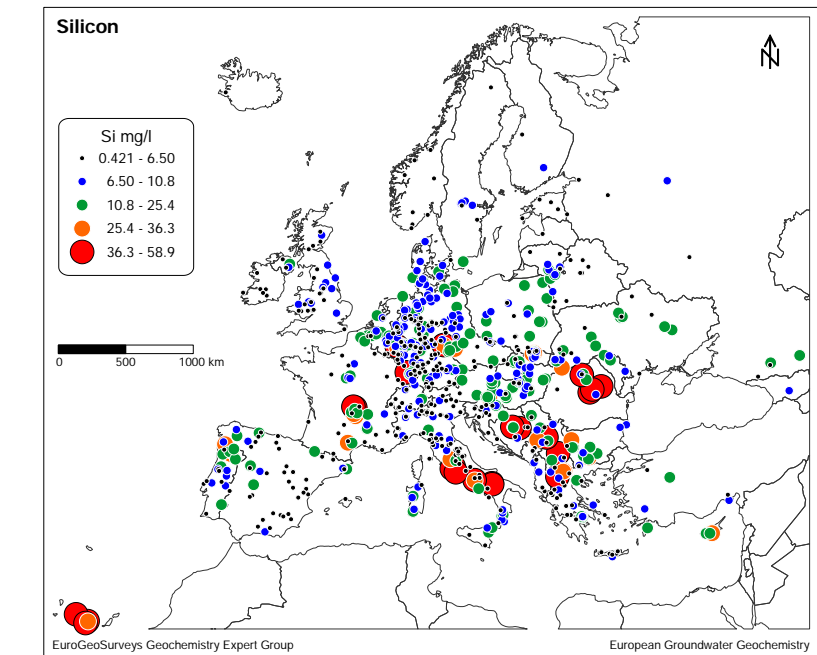


Figure 5: Map of Europe showing the distribution of silicon (mg/l) in bottled mineral water (N = 884).

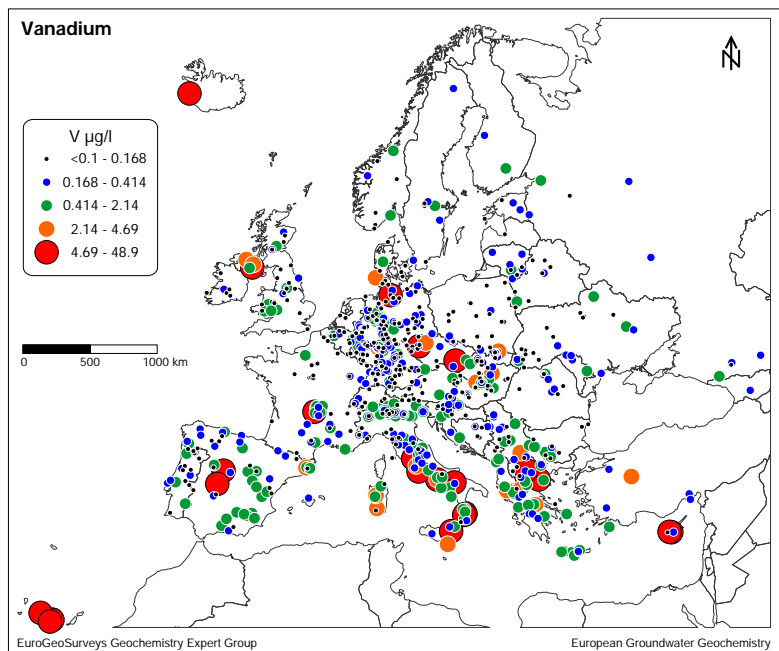


Figure 6: Map of Europe showing the distribution of vanadium (µg/l) in bottled mineral water (N = 884).

Using this affordable low sample density approach, different water surveys, each covering different sources or water types, can easily be carried out, e.g., for natural spring water, surface water, tap water or water at source from water works. Wherever possible, additional information should be collected about the aquifer type, its lithology, and depth of sampling, and on site-site measurements should be made of pH, Eh, electrical conductivity, and alkalinity. The resulting databases would provide an excellent overview of 'normal' concentrations of

chemical elements in different water types and geological settings at the European scale. Such harmonised hydrogeochemical data sets would undoubtedly be very useful for the European legislative process, as well as in a multitude of other applications, e.g., for epidemiological studies.

Whatever the arguments, the first step is to collect harmonised hydrogeochemical data in the proposed systematic way, and to look at the range of concentrations that can occur in 'natural water' at the European scale. The resulting hydrogeochemical



atlases, and associated geological interpretation, will certainly help to identify new risks and risk areas and elements that need attention, with respect to both toxicity and deficiency. Public health authorities and European legislators will have, therefore, the necessary background information for sound decision-making.

Until such systematic and harmonised hydrogeochemical data are available at the European scale, it would be beneficial if the present groundwater geochemical database, which resulted from the analysis of bottled mineral water, were complemented with information about the geological setting and well depth.

### Acknowledgements

The survey of European Groundwater Geochemistry was carried out by the "EGG

Project Team", which comprises (in addition to the three geological survey authors): Stefano Albanese, Madelen Andersson, David Banks, Maria Joao Batista, Alejandro Belan, Liida Bitjukova, Domenico Cicchella, Mar Corral, Anna Degtjarev, Neda Devic, Benedetto De Vivo, Walter De Vos, Enrico Dinelli, Miloslav Duris, Ola Eggen, Peter Filzmoser, Dee Flight, Raymond Flynn, Bjørn Frengstad, Ubul Fügedi, Aivars Gilucis, Mateja Gosar, Virgilija Gregorauskiene, Aleksandra Gulan, Josip Halamić, Edith Haslinger, Peter Hayoz, Gerhard Hobiger, Hazim Hrvatovic, Christophe Innocent, Adriana Ion, Corina Ionesco, Jaana Jarva, Fabian Jähne, Gyoza Jordan, Olga Karnachuk, Lars Kaste, Jaan Kivisilla, Volodymyr Klos, Friedrich Koller, László Kuti, Kaj Lax, Annamaria Lima, Juan Locutura, Hans Lorenz, Carla Lourenço, Peter Malik, Boris I. Malyuk, Robert Maquil, Neven Miosic,

Kujtim Onuzi, Rolf Tore Ottesen, Valter Petersell, Tanja Petrovic, Nikolay Phillipov, Uwe Rauch, Shaun Reeder, Reijo Salminen, Ignace Salpeteur, Natalija Samardzic, Albert Schedl, Ilse Schoeters, Ferid Skopljak, Pauline Smedley, Lech Smietanski, Ajka Šorša, Trajce Stafilov, Marianthi Stefouli, Timo Tarvainen, Maria Titovet, Valeri Trendavilov, Paolo Valera, Maryna Vladymyrova, Børge Johannes Wigum, Milena Zlokolica-Mandic.

The laboratory staff of BGR (Hans Lorenz, Wolfgang Glatte, Bodo Harazim, Fred Flohr, Anna Degtjarev, and Jürgen Rausch) is especially thanked for the analysis of the bottled water samples. The unknown reviewer is thanked for his constructive comments on the initial manuscript, and Robin Lee Nagano (EFG copy editor) for the useful editorial suggestions.

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