



Major and trace elements in German bottled water, their regional distribution, and accordance with national and international standards

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ABSTRACT

The market for mineral water has been growing steadily over the last few years. Germany is the country with the highest number of bottled mineral water brands (908 bottled water samples from 502 wells/brands were analyzed). The per capita consumption of mineral water in Germany in 2003 was 129 L. A wide range of values of one to seven orders of magnitude was determined for 71 elements in the bottled water samples analyzed by ICP-QMS, ICP-AES, IC, titration, photometric, conductometric and potentiometric methods. A comparison of the element concentrations and the legal limits for both bottled and tap water (EU, Germany, US EPA, WHO) shows that only 70% of the 908 mineral water samples fulfill the German and EU drinking water (i.e., tap water) regulations for all parameters (not including pH) for which action levels are defined. Nearly 5% of the bottled water samples not fulfill the German and EU regulations for mineral and table water. Comparison of our results with the current German and European action levels for mineral and table water shows that only 42 of the bottled water samples exceed the limits for one or more of the following elements: arsenic, nitrate, nitrite, manganese, nickel and barium concentrations. Ten of the bottled water samples contain uranium concentrations above the 10 µg/L recommended limit.

A selection of existing water quality classification systems was used in order to characterize the different mineral water types. For example, the relationships among selected variables were examined using Durov, Piper and van Wirdum diagrams. Univariate and multivariate (component analysis) statistical methods were used to analyze the data to characterize the bottled water from the different well regions of Germany. Maps of the element distributions are presented. Most of the elements show a clear regional dependency. The bottled water shows conspicuous geochemical influences by the limestone aquifers of the Muschelkalk (Middle Triassic), the sandstone aquifers of the Bunter and Keuper (Lower and Upper Triassic), the gypsum of the Keuper, and the aquifers in gneiss basement rocks.

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1. Introduction

The first scientific publications on spas and their spring water in Germany appeared in the 18th century (Maurer, 1713; Seip, 1750). Medicinal water (Heilwasser) was sold in Dresden, Leipzig, and Berlin in the early 19th century (Struve, 1824; Minding, 1841). Bottling plants for mineral water were opened in Cologne, Benrath, Naumburg/Saale, Dresden, and Leipzig in the late 19th century (Hirsch, 1871; Evers, 1922; Eisenbach, 2004). The hydrology and hydrogeochemistry of German thermal and medicinal water is documented in numerous publications by Käss (1967, 2000), Käss and Hötzel (1973) and Käss and Käss (2008).

Consumption of bottled water in Germany increased between 1950 and 2007 from 3.8 to 136 L per person per year (Eisenbach, 2004; VDM, 2009). About 11.8 billion liters of bottled water and mineral water

drinks were sold in 2003 by 290 mineral water companies (230 mineral water companies and 60 medicinal water companies) in Germany, which are organized in the Verband Deutscher Mineralbrunnen e. V. (Federation of German Mineral Water Companies, VDM).

In 2005 there were 799 brands of German bottled water recognized by the EU (EU, 2005); at the present time there are more than 800 brands.

In Germany, a distinction is made between Mineralwasser (mineral water), Heilwasser (medicinal water), Quellwasser (spring water), and Tafelwasser (table water). 'Medicinal water' is regulated by the Arzneimittelgesetz (Drug Registration and Administration Act; AMG, 2005); the other classifications are regulated by the Mineral- und Tafelwasserverordnung (Mineral Water and Table Water Ordinance; MTVO, 1984, 2006).

The increasing number of brands of bottled water raises the question of how the water of these brands differs from each other and from regular tap water.

Bottled water is associated with naturalness and perceived by many to taste better, to have fewer impurities, and to confer higher

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social status on the consumer than tap water (Saad et al., 1998). What can and what cannot be considered ‘mineral water’ is laid out in the EU Directive 80/778/EEC.

Groundwater is the source of 76% of the tap water in Germany, 13% is obtained from surface water bodies, and 11% is derived from other sources, e.g., bank filtration (BMFG, Bundesministerium für Gesundheit, UBA, Umweltbundesamtes, 2005).

In accordance with European directives 80/778/EEC and 2003/40/EC ‘natural mineral water’ is defined as “microbiologically wholesome water” from an aquifer tapped via one or more springs or drilled wells. The only treatment allowed prior to bottling is to remove instable contents, such as iron and sulfur oxides and to (re)introduce carbon dioxide. ‘Spring water’ is defined as water from an aquifer tapped via one or more natural or artificially developed springs (MTVO, 2006) and may be bottled only at the site of the spring, the only allowed treatment is that which is allowed for ‘mineral water’. In contrast to ‘mineral water’, ‘spring water’ is not tested for an official ‘seal of quality’ and is not required to have a consistent chemical content.

‘Mineral water’ is obtained from both artesian and pumped wells, some as deep as 800 m. It must have a minimum of mineral content of 150 mg/L (MTVO, 2006). Most countries also recognize some mineral water as having properties favorable to health. In Germany such water is called ‘Heilwasser’ and is legally considered a medicinal product and is subject to the Drug Registration and Administration Act (AMG, Arzneimittelgesetz, 2005).

‘Taking the waters’ (Heilwasser-Trinkkuren) is a traditional medicinal treatment at German health resorts. A therapeutic effect is attributed to certain compounds dissolved in such mineral water. This is the only type of water that is entirely untreated. Iron and sulfur may not be filtered out and no carbon dioxide may be introduced. Clinical tests must have demonstrated that the water contributes to the alleviation or prevention of certain health complaints.

‘Table water’ is prepared from tap water and/or ‘natural mineral water’, natural brine, sea water, mineral salts, and carbon dioxide (MTVO, 1984, 2006). The legal limits for the contents of ‘table water’ are the same as for tap water (TVO, 2001); purification and enrichment with minerals is permitted, in contrast to Mineralwasser (mineral water), Heilwasser (medicinal water), and Quellwasser (spring water). For this reason, ‘table water’ is often prepared from tap water and to avoid being mistaken for ‘natural mineral water’ it may not be labeled with the term ‘natural’, nor given the name of a well (Brunnen) or spring (Quelle).

Tap water is regulated by the Trinkwasserverordnung (Drinking Water Ordinance; TVO, 2001). ‘Drinking water’ is “all water in its original state or which has been treated that is to be used for drinking, cooking, food preparation, the preparation of drinks, or other household purposes (bathing, cleaning).” It is not detrimental to health and is subject to especially high quality standards throughout the EU (EU Directive, 1998/93/EC; TVO, 2001).

The natural variations of chemical elements in groundwater and bottled water in Europe and its health effects have been investigated by Misund and Banks (1994), Misund et al. (1999), Reimann and Banks (2004) and Anke et al. (2009). Other studies have evaluated the quality of bottled and tap water of several countries (Carlé, 1975; Högl, 1980; Gibson et al., 1987; Zötl and Goldbrunner, 1993; Falahee and MacRae, 1995; Reimann et al., 1996; Banks et al., 1998, 1999; Saad et al., 1998; Al Fraij et al., 1999; Arius, 1999; Pip, 2000; Saleh et al., 2001; Vesari et al., 2002; Reimann et al., 2003; Rosborg et al., 2005; Schnug et al., 2005, 2008; Mascha, 2006; Güler, 2007a,b; Raymond-Wish et al., 2007; Baba et al., 2008; Lüpke, 2008; Naddeo et al., 2008; Schmidt, 2008).

The chief aim of the present study, in which 908 samples of German bottled water were analyzed for 71 elements/parameters, was to investigate the geochemical characteristics of bottled water in order to identify the main hydrogeochemical processes and influences controlling the chemical content. A further objective of the study was

to determine the natural variation of the element concentrations in bottled water and tap water, as well as the causes of the regional distribution of these variations. This paper compares and describes several water classification methods and illustrates the differences in the requirements that have to be met by mineral water and tap water. Attempts to differentiate mineral water according to origin and content were made. The action levels established by German and European regulations for selected parameters are compared.

2. Materials and methods

A total of 908 German bottled water samples and 164 tap water samples were analyzed for this study. The bottled water samples were purchased in 2008 at supermarkets throughout Germany; they were from 502 wells at 233 locations. Nine bottled water samples are labeled as Heilwasser (medicinal water, Table 1). Only 12 of the samples had a natural CO₂ content, 781 were artificially carbonated and 115 were not carbonated.

The bottled water was in 530 glass bottles (362 clear glass, 148 green glass, 8 bluish glass and 7 greenish glass), PET (polyethylene terephthalate) bottles, as well as 7 Tetrapacks. Of the glass bottles, 317 had a metal screw cap, 202 had a PE cap, 10 had a crown cap, and one had a ceramic cap.

To compare differences resulting from the bottle materials and from artificial carbonation, 103 brands were purchased and analyzed in both glass and PET bottles, and bottles of both artificially carbonated and non-carbonated water from 85 other brands.

The bottled water was divided into eight groups according to well region (Fig. 1, Table 2). Fig. 1 shows the geographic distribution of the well locations.

The samples were analyzed for 71 chemical parameters in the BGR laboratories (Birke et al., 2010a,b-this issue). Most of the elements were analyzed by inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS) using an Agilent 7500ce instrument. The analyses were conducted in accordance with the German norms DIN 38406-29 (ICP-MS). In addition the samples were analyzed by ICP-AES, while a non-acidified aliquot was used to determine pH, electrical conductivity (EC), to titrate alkalinity and to analyze the anions by ion chromatography (IC). The analytical methods and their accuracy and precision are described in Birke et al. (2010a,b-this issue).

First, the samples were analyzed to determine the extent of leaching of elements from the bottle materials, and to determine differences between carbonated and non-carbonated water, as well as the influence of color was tested (Fig. 2). It was found that Sb was leached from PET bottles in sufficient amounts to completely alter the natural geochemical signature. Significant amounts of the elements Ce, Pb, Al, Zr, Ti, Th and La were leached from the glass bottles. Distinct

Table 1
The analyzed bottled water samples that were labeled as Heilwasser (medicinal water).

Brand	Well name	Well location
Bad Bertricher Heilquelle	Bad Bertricher Heilquelle	Bad Bertrich
Bad Vilbeler Römerbrunnen Heilwasser	Bad Vilbeler Römerbrunnen	Bad Vilbel
Marco Heilquelle	Marco Quelle	Aspach-Rietenau
Natur-Quelle natürliches Heilwasser	Natur-Quelle	Bad Wildungen
Odenwälder Heilquelle	Odenwald Heilquelle	Rothenberg/Odenwald-Finkenbach
Rheinhardt-Quelle natürliches Heilwasser	Rheinhardt-Quelle	Bad Wildungen
St. Gero Heilwasser	St. Gero Quelle	Gerolstein
St. Margareten Heilwasser	St. Margaretenquelle	Löhne
Staatlich Bad Brückenaauer Heilwasser	Sinnberger Heilquelle	Bad Brückenaau

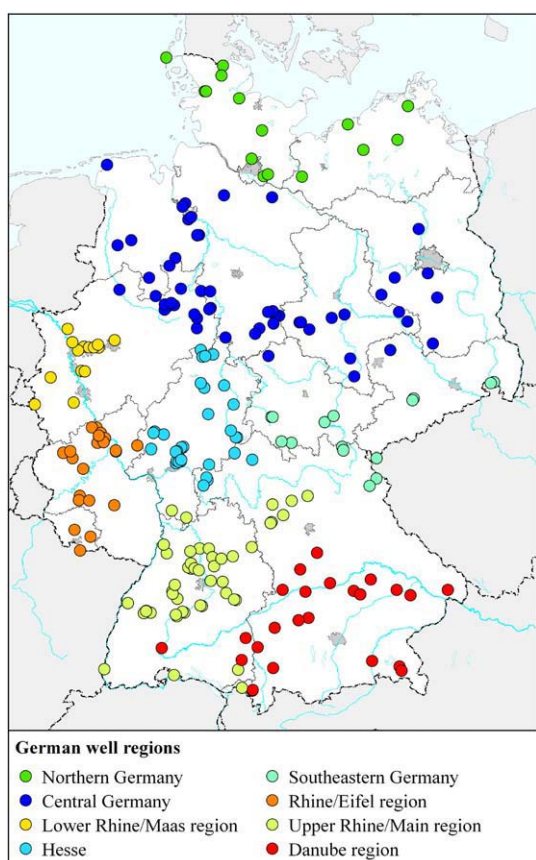


Fig. 1. Distribution of the analyzed bottled water in the German well regions.

differences were also observed in the mineral contents of water in different colored glass bottles: Water in green glass bottles had significantly higher Cr as well as elevated Ag and Th concentrations (Fig. 2).

All samples were analyzed by both ICP-QMS and ICP-AES for the major elements. The results from the two methods are compared for a number of elements in Fig. 3. The fact that nearly all of the results of the two methods agree very well is an indication of the analytical quality. Details of the quality controls used in the project are given in Birke et al. (2010a,b-this issue).

We also plotted the analytical data given on the bottle labels for some elements against our analytical results (Fig. 4). The values on the bottle labels are in overall agreement with our analytical results.

Several water quality classification systems are used in order to characterize the different water types.

SPSS for Windows was used for the univariate and multivariate statistical analyses. Prior to the principal component analysis the data was log-transformed to obtain a set of nearly normal distributed parameters. Values below detection limit were replaced by half of the

detection limit value. The factor scores were calculated by regression method after varimax rotation of the resulting factor matrix.

3. Results and discussion

3.1. Water chemistry and natural variation of elements

To a large extent, the chemical content of bottled water is determined by the composition of the rocks it is abstracted from. Similar types of rock may lead to different types of mineral water. The chemical content depends on the availability of mineralizing agents, such as CO_2 , concentration, redox conditions and the type of adsorption complexes (Voigt, 1972; Siegel, 2002; Merkel and Planer-Friedrich, 2005; Anke et al., 2009).

The natural variation of element concentration in German bottled water is shown in Table 3 and Fig. 5. It can be seen that many of the elements have median values between the detection limit and 2 mg/L. The median value for most of these elements is less than 0.5 mg/L (Ag, Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, Br^- , F^- , NH_4^+ , NO_2^- , and PO_4^{3-}).

The median values for most of the elements in the analyzed German bottled water are above those for EU bottled water (Table 3). The values for EC, B, Ca, Ce, Cs, Fe, K, Li, Mn, Nb, Nd, Ni, Pb, Rb, Ta, Ti, Zn, Zr, Br^- , Cl^- , and SO_4^{2-} are considerably higher than the EU values. Only As, Ga, Sb, Se, U, V, W, and NO_3^- have lower values, some of them significantly lower.

The median values for Ba, Cd, Co, Cr, Cu, Fe, Ga, Ni, Pb, Sc, Se, Sn, Ta, Ti, Tl, Zn and NO_3^- in tap water are significantly higher than those for bottled water (Table 3). The values for Cu (ratio = 78.4), Zn (ratio = 10.9) and Cd (ratio = 2.3) are much higher for tap water than for bottled water; this is probably due to the copper water pipes in the houses where the tap water samples were taken. The considerably higher values for NO_3^- (ratio = 6.7) in tap water may be due to the use of surface water and surface-near groundwater (Birke et al., 2006). The values for Ca, Fe, Ni, Pb, Sc and Tl in tap water are only 1.5–2.0 times higher than those for bottled water. Of note is the 2.7 times higher value for Se.

The differences in concentration of the individual elements range from one to seven orders of magnitude. Ag, Eu, Ga, Sc, Ta, Te and NO_2^- show the least variation (between one and two orders of magnitude; Table 3). Most of the elements show a natural variation in their concentrations in bottled water between three (EC, Bi, Ca, Cd, Ce, Gd, Hf, Ho, K, La, Lu, Nb, Pr, Tb, Th, Tm, Yb, PO_4^{3-} , and Si) and four orders (Al, B, Co, Cr, Dy, Er, Fe, I, Mg, Pb, Rb, Sb, Se, V, W, Br^- , HCO_3^- , and F) of magnitude.

The natural variation in As, Ba, Be, Cu, Ge, Li, Na, Ni, Sn, Sr, Ti, Tl, Y, Zn, Cl^- and NO_3^- concentration in bottled water covers at (least) five orders of magnitude, as shown in the cumulative frequency diagrams (Fig. 5) and in Table 3. Mn, Mo, U, Zr, NH_4^+ and SO_4^{2-} show a large natural variation in their concentrations of six orders of magnitude. Cs shows the largest natural variation. This difference is clearly seen in Table 3.

3.2. Content and hydrogeochemical water types

The more than ten different hydrochemical classification systems discussed by Matthess and Ubell (1983) and Matthess (1994) constitute only the “tip of the iceberg”.

To obtain an insight into the natural diversity in the contents of mineral water all of the German bottled water samples were classified (i) according to medicinal water type (Table 4, Figs. 6–12), (ii) total dissolved solids (TDS) as well as (iii) specific cations and anions or carbon dioxide content. Fig. 6 shows the distribution of the bottled water classified according to TDS as given in EU mineral water directives 80/778/EEC and 2003/40/EC.

The mineral content (TDS) of German bottled water samples ranges from 24.8 to 4120 mg/L with a median of 567 mg/L, with 43.3% classified as having a low mineral concentration (Fig. 6, Table 4). Bottled water with a “low mineral concentration” is mostly from

Table 2
Number of locations, wells and mineral water samples in the German well regions.

Well region	Locations	Wells	Samples
Northern Germany	16	31	70
Central Germany	57	130	287
Lower Rhine/Maas region	14	36	52
Hesse	34	83	142
Southeastern Germany	15	25	48
Rhine/Eifel region	23	61	104
Upper Rhine/Main region	50	100	155
Danube region	24	36	50
Germany	233	502	908

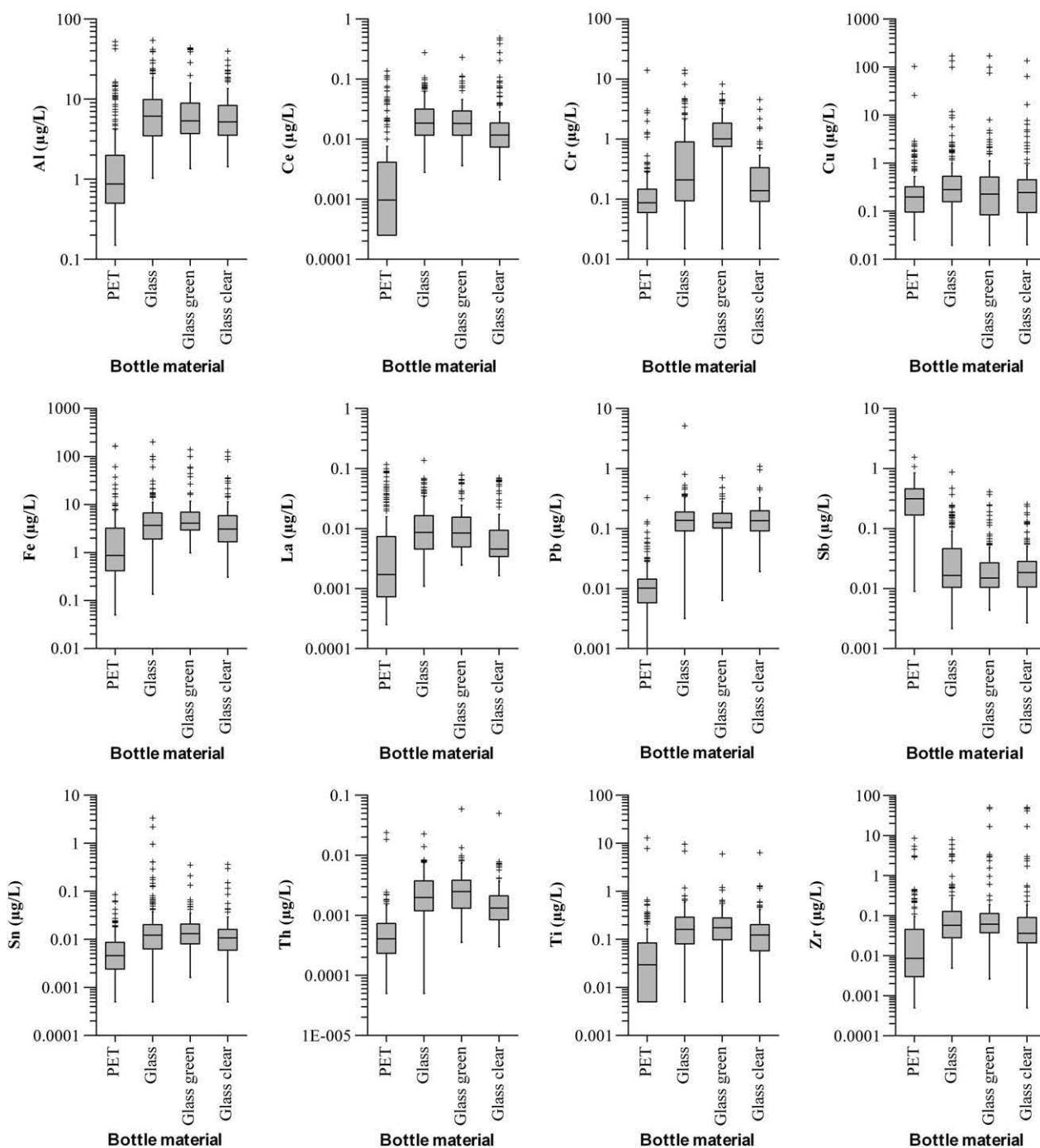


Fig. 2. Boxplot comparison of differences in element concentration in different types of bottle material.

northern Germany (57 bottles), Hesse (48 bottles), the northern part of central Germany (150 bottles), southeastern Germany (36 brands), and the Danube region (43 bottles) (Figs. 1 and 6, Table 4). Bottled water from the Upper Rhine/Main and Hesse regions mostly have an “intermediate mineral concentration” (41.4% of the samples). Bottled water with a “high mineral concentration” (14.4% of the samples) is mostly from the Upper Rhine/Main and the Rhine/Eifel regions (Figs. 1 and 6, Table 4). Only 5 of the 908 bottled water samples (0.6%) had a “very low mineral concentration”, mainly in the Upper Rhine/Main region (Table 4).

According to the EU classification (Table 4), which was largely adopted from the German Mineral- und Tafelwasser-Verordnung (Mineral Water and Table Water Ordinance; MTVO, 1984, 2006), 28.6% of the analyzed bottled water may be classified as “containing

calcium”, 24.0% as “containing sulfate”, 20.8% as “containing magnesium”, 15.1% as “containing bicarbonate”, 13.2% as “containing sodium” and 9.7% as “containing chloride”.

The classes “very low mineral concentration” and “low mineral concentration” consist almost entirely of bottled water that can be designated as “suitable for low sodium diets” (Figs. 6 and 9). Of the analyzed mineral water samples, 49.6% were “suitable for low sodium diets”.

Mineral water with a high sodium concentration ($\text{Na} > 200 \text{ mg/L}$; MTVO, 2006) is more frequently found in the Upper Rhine/Main region, in Hesse and in the Lower Rhine/Maas region than in the other parts of the country. Sodium-bearing mineral water can help persons with blood pressure that is too low (Ebert, 2004); it can also be used to treat acidic stomach problems (Käss and Käss, 2008).

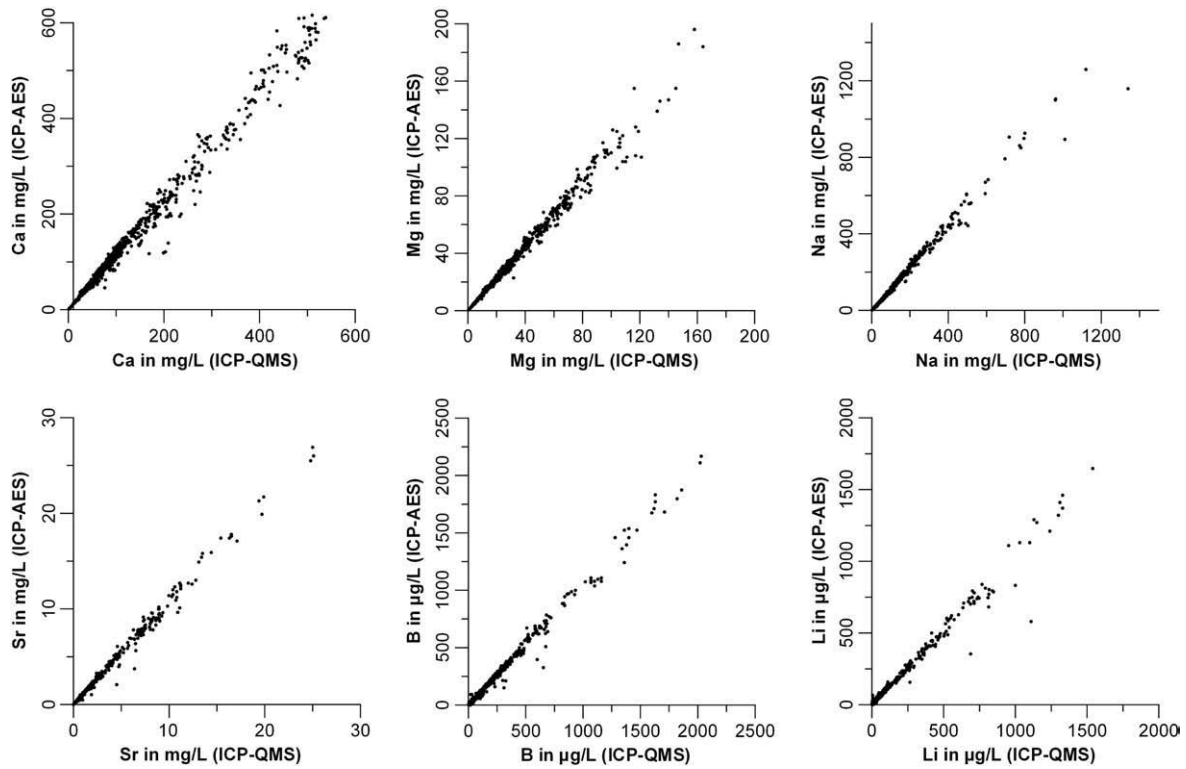


Fig. 3. Comparison of the analytical results of the ICP-QMS and ICP-AES methods.

A high bicarbonate content (>600 mg/L) is characteristic of bottled water from the western part of the Rhine/Eifel region, from Hesse, the Upper Rhine/Main region, as well as west of the Weser River in central Germany (Fig. 7). This distribution correlates in general with the

distribution of sulfate and magnesium-bearing mineral water (Figs. 7 and 9). Bicarbonate is physiologically important as it regulates the acid/base balance in blood; for this purpose it is produced by the body from CO₂ without any additional intake from food.

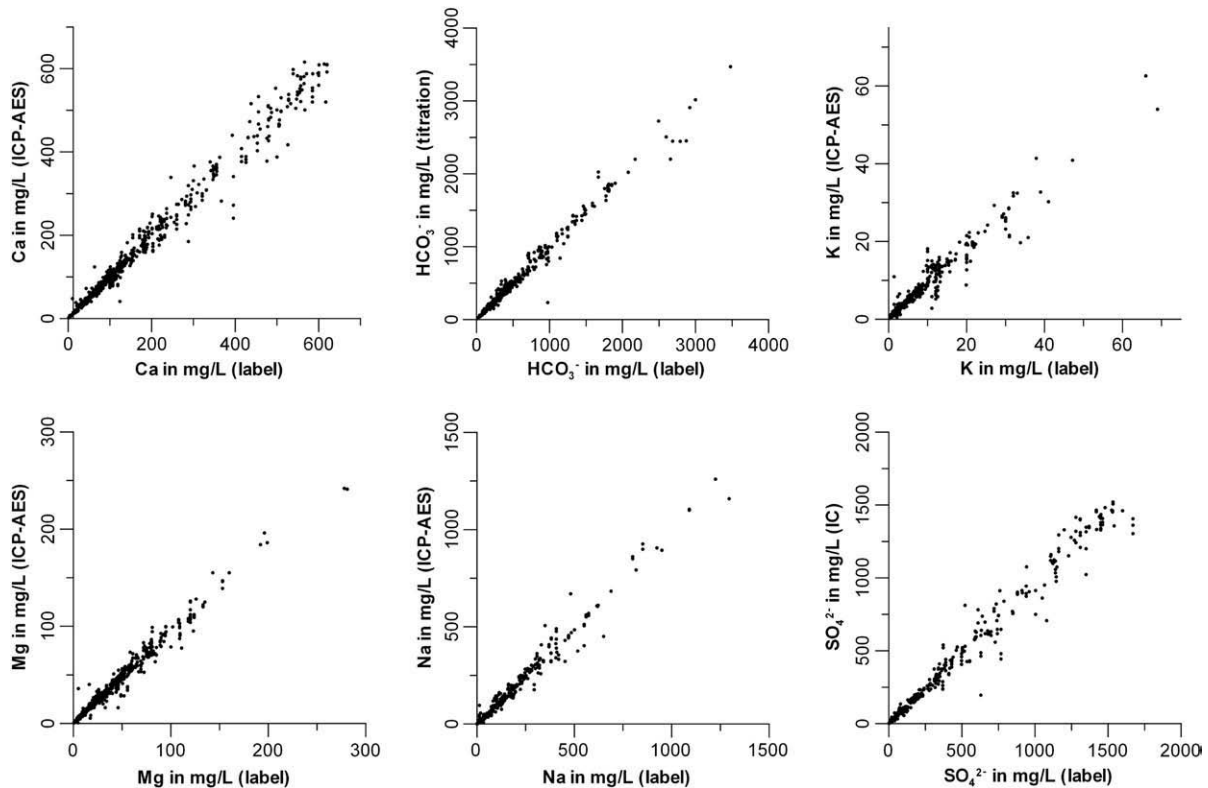


Fig. 4. Comparison of the analytical results with the data given on the bottle labels.

Table 3

Statistical parameters for the elements in the analyzed German bottled water (N = 908).

Element	Unit	DL	Number below DL	Minimum	Q5	Q25	Median	Median of European bottled water ¹⁾ (N = 1785)	Median of European tap water ¹⁾ (N = 579)	Median of German tap water (N = 164)	Q75	Q95	Maximum	Order of magnitude variation	Percent above action level ²⁾
pH		–	–	3.80	4.65	5.00	5.20	5.60	7.67	7.92	5.50	7.18	8.10	1	92.3% ³⁾
EC	µS/cm	–	–	38.1	226	485	872	668	365	391	1700	2840	6340	3	10.0% ⁴⁾
TDS	mg/L	–	–	24.8	147	315	567	434	237	254	1110	1850	4120	3	–
Ag	µg/L	0.001	498	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.00202	0.00478	0.0934	2	–
Al	µg/L	0.3	32	<0.3	0.353	1.03	3.78	1.95	2.47	1.98	7.52	21.3	281	4	0.11% ³⁾
As	µg/L	0.01	2	<0.01	0.0287	0.0586	0.190	0.214	0.190	0.163	0.616	3.74	17.2	5	0.99%
B	µg/L	0.1	0	2.16	7.75	20.3	64.0	47.6	15.5	17.0	183	670	2610	4	2.97% ³⁾
Ba	µg/L	0.1	0	0.130	3.79	15.7	31.8	30.6	30.1	40.4	64.4	196	1490	5	0.11%
Be	µg/L	0.001	155	<0.001	<0.001	0.00140	0.00321	0.00272	0.00275	0.00239	0.0152	0.188	7.30	5	–
Bi	µg/L	0.0005	320	<0.0005	<0.0005	<0.0005	0.000704	0.00067	0.000560	<0.0005	0.00121	0.00337	0.692	3	–
Ca	mg/L	0.01	0	1.40	15.2	54.9	90.8	76.3	59.5	63.1	176	507	616	3	–
Cd	µg/L	0.001	99	<0.001	<0.001	0.00170	0.00324	0.00324	0.00829	0.00750	0.00700	0.0353	0.439	3	0%
Ce	µg/L	0.0005	128	<0.0005	<0.0005	0.00124	0.00972	0.00229	0.00180	0.00155	0.0203	0.0727	0.559	3	–
Co	µg/L	0.002	4	<0.002	0.00565	0.0127	0.0229	0.0232	0.0231	0.02580	0.0449	0.305	6.60	4	–
Cr	µg/L	0.03	51	<0.03	<0.03	0.0680	0.121	0.123	0.185	0.177	0.272	1.99	12.4	4	0%
Cs	µg/L	0.001	3	<0.001	0.00295	0.0109	0.0600	0.0428	0.00750	0.00890	0.951	14.7	119	7	–
Cu	µg/L	0.01	0	0.0128	0.0414	0.109	0.231	0.251	5.65	18.1	0.426	2.31	170	5	0%
Dy	µg/L	0.0001	3	<0.0001	0.000251	0.000662	0.00128	0.00120	0.00104	0.000960	0.00255	0.0126	0.131	4	–
Er	µg/L	0.0001	9	<0.0001	0.000218	0.000565	0.00113	0.000990	0.000870	0.000910	0.00238	0.0147	0.104	4	–
Eu	µg/L	0.0001	65	<0.0001	<0.0001	0.000554	0.00103	0.000960	0.00202	0.00360	0.00180	0.00481	0.0287	2	–
Fe	µg/L	0.1	0	0.109	0.292	0.835	1.96	1.26	3.21	3.89	4.58	17.6	166	4	0% ⁴⁾
Ga	µg/L	0.0005	499	<0.0005	<0.0005	<0.0005	<0.0005	0.00199	0.0727	0.00299	0.00390	0.0113	0.0610	2	–
Gd	µg/L	0.0002	8	<0.0002	0.000436	0.00101	0.00181	0.00163	0.00196	0.00218	0.00331	0.00906	0.127	3	–
Ge	µg/L	0.005	58	<0.005	<0.005	0.0126	0.0316	0.0294	0.0109	0.0130	0.0881	0.492	11.1	5	–
Hf	µg/L	0.0005	309	<0.0005	<0.0005	<0.0005	0.000778	0.000650	0.000800	0.000860	0.00165	0.0103	0.283	3	–
Hg	ng/L	5	908	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	1	0%
Ho	µg/L	0.0001	21	<0.0001	0.000158	0.000385	0.000661	0.000540	0.000380	0.000415	0.00119	0.00443	0.0318	3	–
I	µg/L	0.2	0	0.253	1.42	2.86	4.78	4.76	3.23	3.99	9.58	22.3	766	4	–
K	mg/L	0.1	0	0.100	0.800	1.62	3.30	2.50	1.60	2.15	7.70	19.1	92.5	3	–
La	µg/L	0.0005	49	<0.0005	<0.0005	0.00199	0.00494	0.00336	0.00230	0.00205	0.0114	0.0545	0.229	3	–
Li	µg/L	0.1	0	0.510	2.15	7.70	29.0	14.9	2.65	4.45	84.8	525	2790	5	–
Lu	µg/L	0.00005	56	<0.00005	<0.00005	0.000136	0.000251	0.000230	0.000240	0.000250	0.000550	0.00374	0.0520	3	–
Mg	mg/L	0.01	0	0.558	3.18	8.84	21.9	18.9	9.61	7.90	44.2	98.7	242	4	–
Mn	µg/L	0.1	78	<0.1	<0.1	0.331	1.50	0.808	0.544	0.543	18.0	195	1160	6	0.88%
Mo	µg/L	0.001	1	<0.001	0.0141	0.0907	0.276	0.275	0.233	0.119	0.646	2.84	12.0	6	–
Na	mg/L	0.1	0	0.500	4.24	9.90	20.4	17.8	9.47	11.4	108	383	1260	5	13.2% ⁴⁾

Nb	µg/L	0.001	34	<0.001	0.00112	0.00249	0.00459	0.00232	0.00251	0.00294	0.0105	0.0729	0.878	3	–
Nd	µg/L	0.0002	11	<0.0002	0.000587	0.00177	0.00405	0.00288	0.00223	0.00179	0.00925	0.0363	0.320	3	–
Ni	µg/L	0.01	1	<0.01	0.0279	0.0839	0.251	0.204	0.381	0.486	0.901	7.78	26.4	5	0.55%
Pb	µg/L	0.002	7	<0.002	0.00358	0.0104	0.0870	0.0229	0.118	0.160	0.159	0.298	5.13	4	0%
Pr	µg/L	0.00005	25	<0.00005	0.0000852	0.000390	0.00100	0.000640	0.000540	0.000390	0.00233	0.00883	0.0590	3	–
Rb	µg/L	0.001	0	0.102	0.448	1.28	3.44	2.69	0.909	1.30	10.7	55.3	410	4	–
Sb	µg/L	0.002	0	0.00215	0.00619	0.0133	0.0383	0.217	0.0673	0.0300	0.272	0.604	2.35	4	0%
Sc	µg/L	0.01	1	<0.01	0.0350	0.0562	0.0752	0.0720	0.0614	0.125	0.114	0.227	0.597	2	–
Se	µg/L	0.01	142	<0.01	<0.01	0.0138	0.0249	0.0364	0.115	0.0672	0.116	0.865	4.97	4	0%
Sm	µg/L	0.0002	18	<0.0002	0.000362	0.000912	0.00162	0.00141	0.00146	0.00167	0.00288	0.00741	0.0993	2	–
Sn	µg/L	0.001	46	<0.001	<0.001	0.00360	0.00713	0.00684	0.00865	0.0106	0.0137	0.0429	3.33	5	–
Sr	mg/L	0.001	0	0.00600	0.0640	0.199	0.536	0.406	0.177	0.207	1.84	9.05	26.9	5	–
Ta	µg/L	0.001	241	<0.001	<0.001	<0.001	0.00166	<0.001	0.00177	0.00225	0.00329	0.00718	0.0374	2	–
Tb	µg/L	0.00005	66	<0.00005	<0.00005	0.000114	0.000219	0.000190	0.000190	0.000170	0.000431	0.00156	0.0194	3	–
Te	µg/L	0.005	255	<0.005	<0.005	<0.005	0.00954	0.00798	0.00998	0.00975	0.0218	0.0694	0.207	2	–
Th	µg/L	0.0001	24	<0.0001	0.000140	0.000405	0.00105	0.000620	0.000770	0.000860	0.00232	0.00612	0.0591	3	–
Ti	µg/L	0.01	164	<0.01	<0.01	0.0303	0.0840	0.0520	0.0867	0.114	0.192	0.514	12.9	5	–
Tl	µg/L	0.0005	63	<0.0005	<0.0005	0.00122	0.00309	0.00365	0.00368	0.00742	0.00966	0.124	1.18	5	–
Tm	µg/L	0.00005	51	<0.00005	<0.00005	0.000115	0.000216	0.000190	0.000200	0.000180	0.000410	0.00236	0.0241	3	–
U	µg/L	0.0005	11	<0.0005	0.00172	0.0177	0.172	0.209	0.307	0.0845	0.921	4.75	16.0	6	1.10% ³⁾
V	µg/L	0.01	8	<0.01	0.0333	0.0759	0.130	0.146	0.174	0.0829	0.244	0.919	5.33	4	–
W	µg/L	0.002	27	<0.002	0.00313	0.00843	0.0154	0.0189	0.0113	0.0127	0.0286	0.144	6.53	4	–
Y	µg/L	0.0005	0	0.000603	0.00253	0.00773	0.0170	0.0140	0.00985	0.0105	0.0360	0.160	1.37	5	–
Yb	µg/L	0.0002	24	<0.0002	0.000319	0.000668	0.00128	0.00111	0.00110	0.00130	0.00291	0.0178	0.222	3	–
Zn	µg/L	0.05	4	<0.05	0.107	0.540	1.76	1.20	23.5	19.1	5.14	16.0	293	5	–
Zr	µg/L	0.001	10	<0.001	0.00194	0.00761	0.0306	0.0149	0.00945	0.0118	0.0849	1.49	50.5	6	–
Br [–]	mg/L	0.003	5	<0.003	0.00900	0.0240	0.0470	0.0390	0.0110	0.0210	0.115	0.508	3.15	4	–
HCO ₃ ^{2–}	mg/L	2	0	3.80	84.2	204	333	305	191	152	439	1430	3470	4	–
Cl [–]	mg/L	0.01	0	0.430	2.94	12.0	29.2	18.6	14.1	20.4	79.2	313	1470	5	7.49% ⁴⁾
F [–]	mg/L	0.003	0	0.00700	0.0640	0.142	0.242	0.211	0.0870	0.105	0.458	1.19	3.48	4	0%
NH ₄ ⁺	mg/L	0.005	540	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.0357	0.545	11.9	6	6.06% ⁴⁾
NO ₂	mg/L	0.005	781	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.0245	0.456	2	1.21%
NO ₃	mg/L	0.01	17	<0.01	0.0100	0.131	0.740	1.08	3.88	4.95	3.45	13.0	53.8	5	0.11%
PO ₄ ^{3–}	mg/L	0.02	34	<0.02	0.0200	0.120	0.160	0.140	0.0300	0.0600	0.220	0.395	1.75	3	–
SO ₄ ^{2–}	mg/L	0.01	0	0.0300	4.97	22.6	57.3	30.2	26.9	37.8	190	1270	2210	6	22.0% ⁴⁾
Si	mg/L	0.05	0	0.935	3.37	5.24	6.68	6.64	4.30	5.70	9.20	16.8	40.4	3	–

¹⁾EGS, 2010, ²⁾German action levels for bottled water (MTVO, 1984, 2006); ³⁾German action levels for tap water (TVO, 2001); ⁴⁾EU Directive, 1998/83/EC Drinking water.

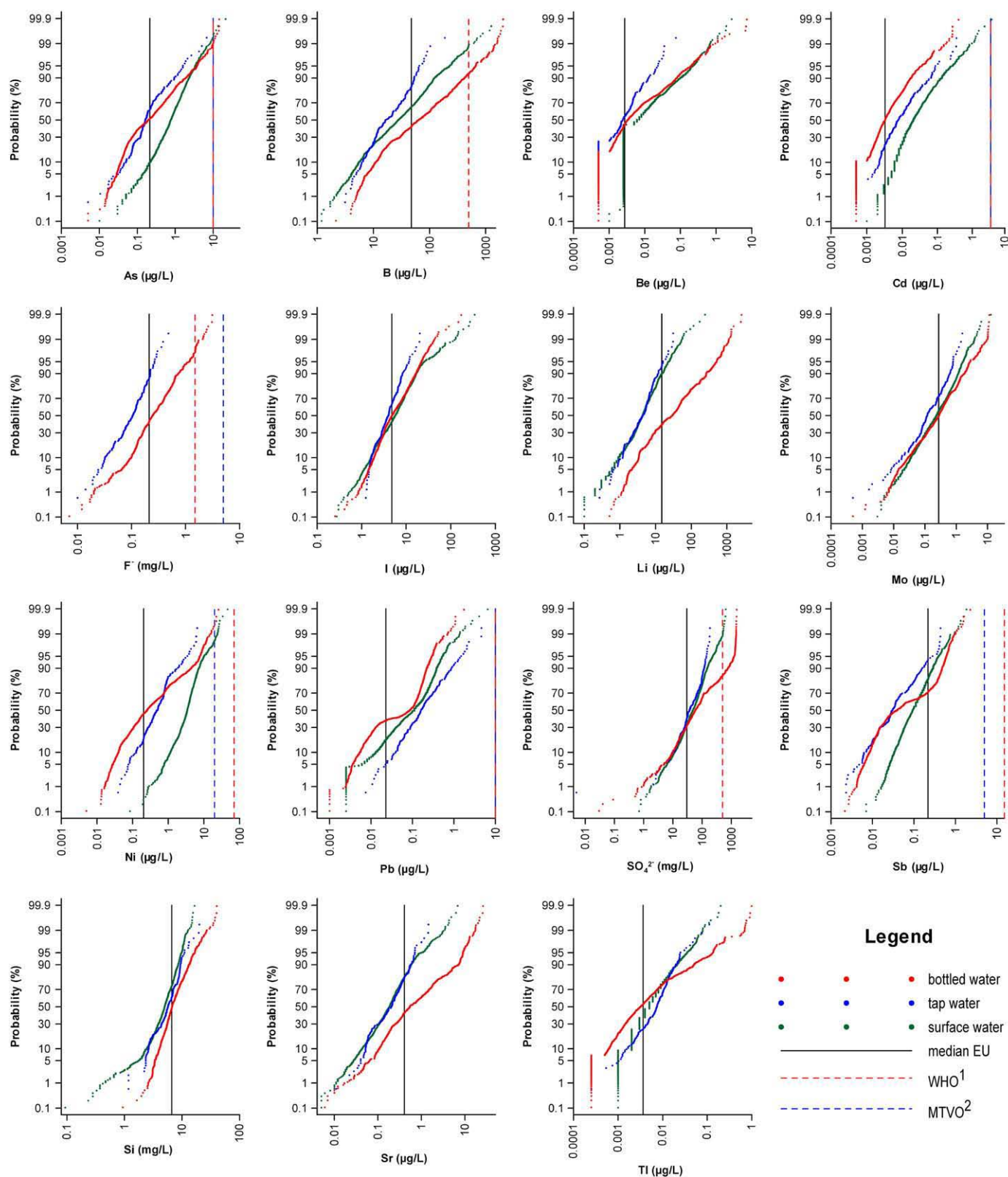


Fig. 5. Comparison of selected elements in German bottled water with tap water and surface water (cumulative frequency diagrams). ¹WHO Guideline value for drinking water (WHO, 1996, 2006); ²German action levels for bottled water (MTVO, 1984, 2006).

The distribution of potassium-bearing (>150 mg/L) mineral water corresponds in general with the distribution of sulfate-bearing (>200 mg/L) mineral water (Fig. 7).

The distribution of fluoride-bearing mineral water is shown in Fig. 9. Fluoride-bearing water is defined as water containing a fluoride

concentration >1 mg/L (MTVO, 1984, 2006). Fluoride concentration must be given on the label only when it is above 1.5 mg F⁻/L; the following text must be used: "Contains more than 1.5 mg/L fluoride. It is not suitable for regular consumption by babies or children under 7 years old."

Table 4

Compliance of the bottled water samples with the EU mineral water directives (80/778/EEC and 2003/40/EC) and the German mineral water regulations (MTVO, 2006).

Mineral water type	Criterion	Percentage of German bottled water
Very low mineral concentration	TDS ≤ 50 mg/L	0.60
Low mineral concentration	50 mg/L < TDS ≤ 500 mg/L	43.3
Intermediate mineral concentration	500 mg/L < TDS ≤ 1500 mg/L	41.7
High mineral concentration	TDS > 1500 mg/L	14.4
Containing bicarbonate	bicarbonate > 600 mg/L	15.1
Containing sulfate	sulfate > 200 mg/L	24.0
Containing chloride	chloride > 200 mg/L	9.69
Containing calcium	calcium > 150 mg/L	28.6
Containing magnesium	magnesium > 50 mg/L	20.8
Containing fluoride	fluoride > 1 mg/L	5.95
Containing sodium	sodium > 200 mg/L	13.2
Suitable for low sodium diets	sodium < 20 mg/L	49.6

TDS = total dissolved solids.

Only brands of mineral water from the Upper Rhine/Main region have a fluoride concentration high enough that it must be declared (Table 5, Fig. 9). Fluoride concentrations in bottled water from the Upper Rhine/Main region (Figs. 1 and 9) are comparable to the levels in the rock of the aquifers and also correlate with mineral deposits, e.g., fluoride veins extending up to the Bunter (Lower Triassic) in the Black Forest, the Spessart region, and in the Hessian Basin. EU law allows a maximum admissible fluoride concentration (MAC) of 5.0 mg/L in bottled water. However, a fluoride concentration above 1.5 mg/L can lead to fluorosis (accumulation of fluoride in teeth and bones). Skeletal fluorosis develops after long-term consumption of water with a high fluoride concentration (>4 mg/L). WHO (1996, 2006) suggests a MAC of 1.5 mg F⁻/L in tap water. Fluorine has been avoided in medical practice for a number of years, as its side effects on metabolism, mind, and neurovegetative system are greater than its benefits (Ebert, 2004). Beginning in 2008, mineral water may be sold only when the fluoride concentration is less than 5.0 mg/L (MTVO, 1984, 2006; EU directive, 2003/40/EC).

Permissible advertising of mineral water as “suitable for the preparation of baby food” must be based on the concentrations of As, F, Mn, Na, NO₃⁻, NO₂⁻, SO₄²⁻ and U (MTVO, 1984, 2006). Of the 233 well localities in Germany, bottled water from only 77 localities is suitable for preparing baby food (Fig. 10). Most of the “suitable” mineral water brands are from the Danube region and Schleswig-Holstein. Bottled water was suitable from only a few localities in the well regions Upper Rhine/Main region, Central Germany, Rhine/Eifel region, Lower Rhine/Maas region, Hesse, and southeast Germany. Of the 908 analyzed bottled water samples, only 295 fulfilled the conditions for the preparation of baby food.

The Stuyfzand water classification is based on chloride concentration (Stuyfzand, 1986, 1993). Of the eight types of the Stuyfzand classification, only six were observed among the analyzed samples (Table 6): “very oligohaline” (9.14%), “oligohaline” (41.5%), “fresh” (34.6%), “fresh-brackish” (9.69%), and “brackish” (4.85%), followed by “brackish-salt” with only two well locations (0.22%). In the well regions Central Germany, Lower Rhine/Maas region, Hesse and part of the Upper Rhine/Main region, fresh-brackish and brackish water types occur only in a few wells (Fig. 1).

“Oligohaline” and “fresh” type water is found mainly in northern and central Germany, as well as in the Upper Rhine/Main region and in southeast Germany. The main areas of distribution are the Lower Rhine/Maas region, the Rhine/Eifel region, Hesse and the Upper Rhine/Main region (Fig. 11). With only a few exceptions, the “very oligohaline” type is found only in the Danube region in the areas of Tertiary sediments (Fig. 13). In northern Germany, the “oligohaline”

type predominates in Schleswig-Holstein, whereas the fresh type predominates in Mecklenburg-Vorpommern.

The main contents of mineral water are also the main constituents of animal bodily fluids and cells, which have characteristic and constant concentrations of electrolytes (Lang, 1974). The analyzed bottled water samples were also classified on the basis of all of the analyzed ions that are present at ≥20 meq-% (referred to here as the “German classification system”). For each sample, the cations were ordered in decreasing concentration and then the anions, which is then the water type name (Grünhut, 1911; Carlé, 1975; Deutscher Bäderverband, 1991; Fresenius and Kussmaul, 1995). A total of 19 water types were determined for the German well localities (Fig. 12) and a total of 23 types of German bottled water brands (resulting from carbonation). The frequency of the bottled water samples and of the well localities is given for each water type in Table 7.

Most German bottled water (47.1%) can be characterized as Ca-HCO₃⁻ according to the “German classification system” (Table 7, Fig. 12). A total of 35.4% can be classified as one of the types Ca-SO₄²⁻, Na-HCO₃⁻ or Na-Cl⁻ (Table 7).

Calcium-bicarbonate is the main water type in northern Germany (Mecklenburg-Vorpommern und Schleswig-Holstein) and the foreland of the Alps. This water type often occurs in Hesse, as well as at single occurrences in the other well regions. The Upper Rhine/Main region is characterized by a large number of calcium-sulfate localities (15.45%). Sodium-bicarbonate water type is mainly found in the Rhine/Eifel region (9.44%) and sodium-chloride water type occurs in 6.44% of the well localities (Fig. 12). Only three of the samples (0.33%) were of the calcium-chloride water type (Table 7), which is seldom found in near-surface aquifers.

Calcium-sulfate water type occurs mainly in areas of Keuper (Upper Triassic) sediments; sodium-bicarbonate water type is often found in the areas of Devonian deposits in the Rhine/Eifel well region (Figs. 12

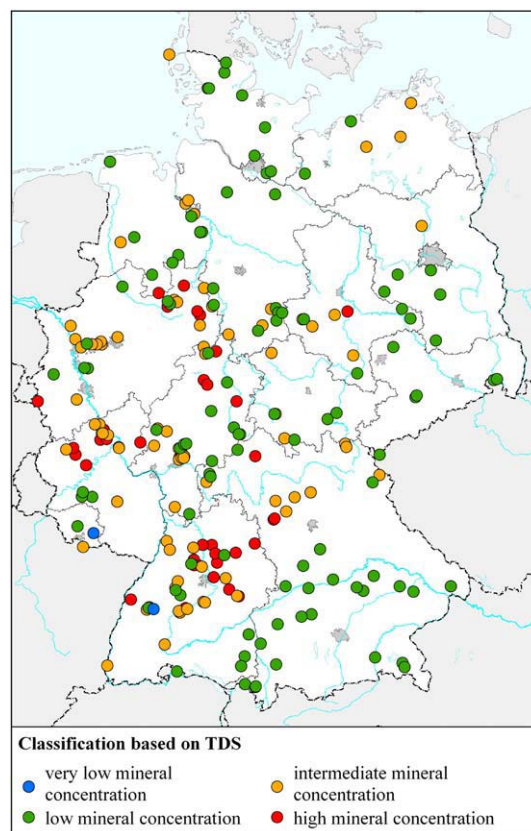


Fig. 6. Classification and distribution of bottled water based on total dissolved solids (TDS).

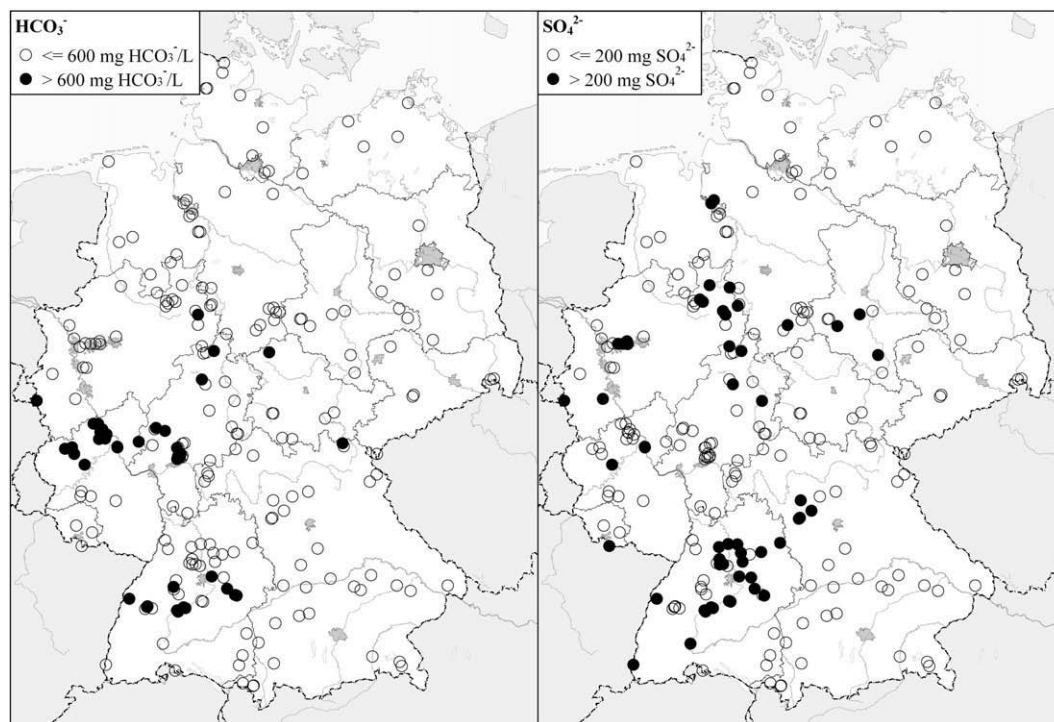


Fig. 7. Classification and distribution of bottled water based on bicarbonate and sulphate concentrations.

and 13). The calcium-magnesium-bicarbonate water type represents a transition from the calcium-sulfate type to the sodium-bicarbonate type. In order to obtain a significant concentration of the low-solubility alkaline earth carbonates, the concentration of hydrogen carbonate must be relatively high and free CO_2 must be present. Calcium-bicarbonate water types with a relatively high concentration must thus almost always have a rather high CO_2 concentration ($>250 \text{ mg/L}$).

The type of bottled water is a parameter which provides information on the possible use of the waterPiper diagrams (Piper, 1932, 1944; Furtak and Langguth, 1967) and Durov diagrams (Durov, 1948; Al-Bassam et al., 1997) provide a more precise picture of the diversity in the content of German bottled water (Figs. 14–16).

A Piper diagram is a graphical representation of the chemical content of water samples. The cations and anions are shown on separate ternary graphs, which are then projected onto a diamond graph (Figs. 14 and 15). The different water types occur in different parts of the diamond graph (Furtak and Langguth, 1967). There are three main groups: alkaline earth water, alkaline earth water with elevated alkali concentration, and alkaline water. It can be seen that most of the analyzed bottled water samples fall in subgroups 'a' (mainly bicarbonate) and 'c' (mainly sulfate) of the alkaline earth group, as well as in subgroup 'd' (mainly bicarbonate) of the alkaline earth water with elevated alkali content group. Only a small number of the analyzed samples fall into the mixed type subgroups.

The samples are plotted in Fig. 14 according to well region. In the Danube region, most of the samples plot in the subgroup 'a' area (alkaline earth water, mainly bicarbonate); in Hesse the subgroups 'a' and 'd' predominate (alkaline earth water with elevated alkali content group, mainly bicarbonate); in central Germany, all subgroups are present ('a'–'g'); in northern Germany, only subgroup 'a' is present; in the Upper Rhine/Main region, subgroups 'a' and 'c' predominate (alkaline water, mainly sulfate); in the Rhine/Eifel region, subgroups d and f predominate (alkaline water, mainly bicarbonate); in southeastern Germany and the Lower Rhine/Maas region, most of the samples plot in the subgroup 'b' area (alkaline earth water, bicarbonate-sulfate).

In Fig. 15, the samples are plotted according to bedrock geology. It can be seen that in Pleistocene and Tertiary areas, the samples plot in

subgroups 'a' and 'd'; in areas of Cretaceous deposits nearly all of the samples plot in subgroup 'a'. In areas of Paleozoic and Precambrian deposits, subgroups 'd' and 'f' predominate, some in subgroup 'a'.

In a Durov diagram (Fig. 16), the major cations (Na, K, Mg, and Ca) are plotted in the ternary graph on the left (in meq), the major anions (Cl^- , SO_4^{2-} , HCO_3^-) are plotted on the upper ternary graph. These two graphs are then projected onto a square graph in the middle. It can be seen that most of the samples plot in the Ca-HCO_3^- corner of the cation graph. A

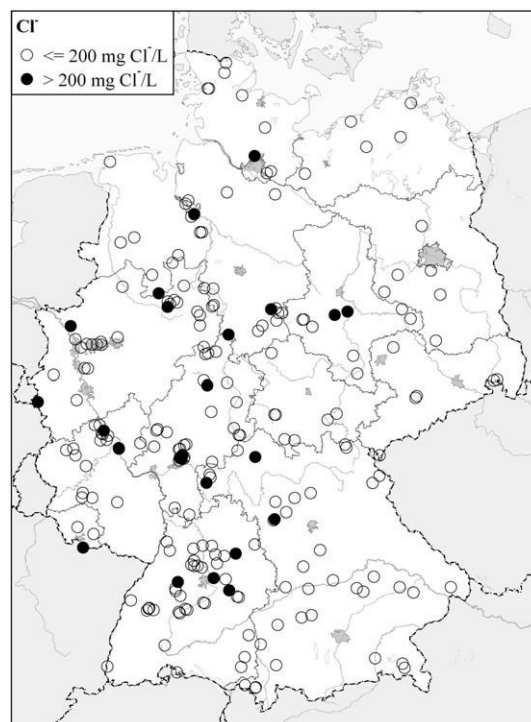


Fig. 8. Classification and distribution of bottled water based on chloride concentration.

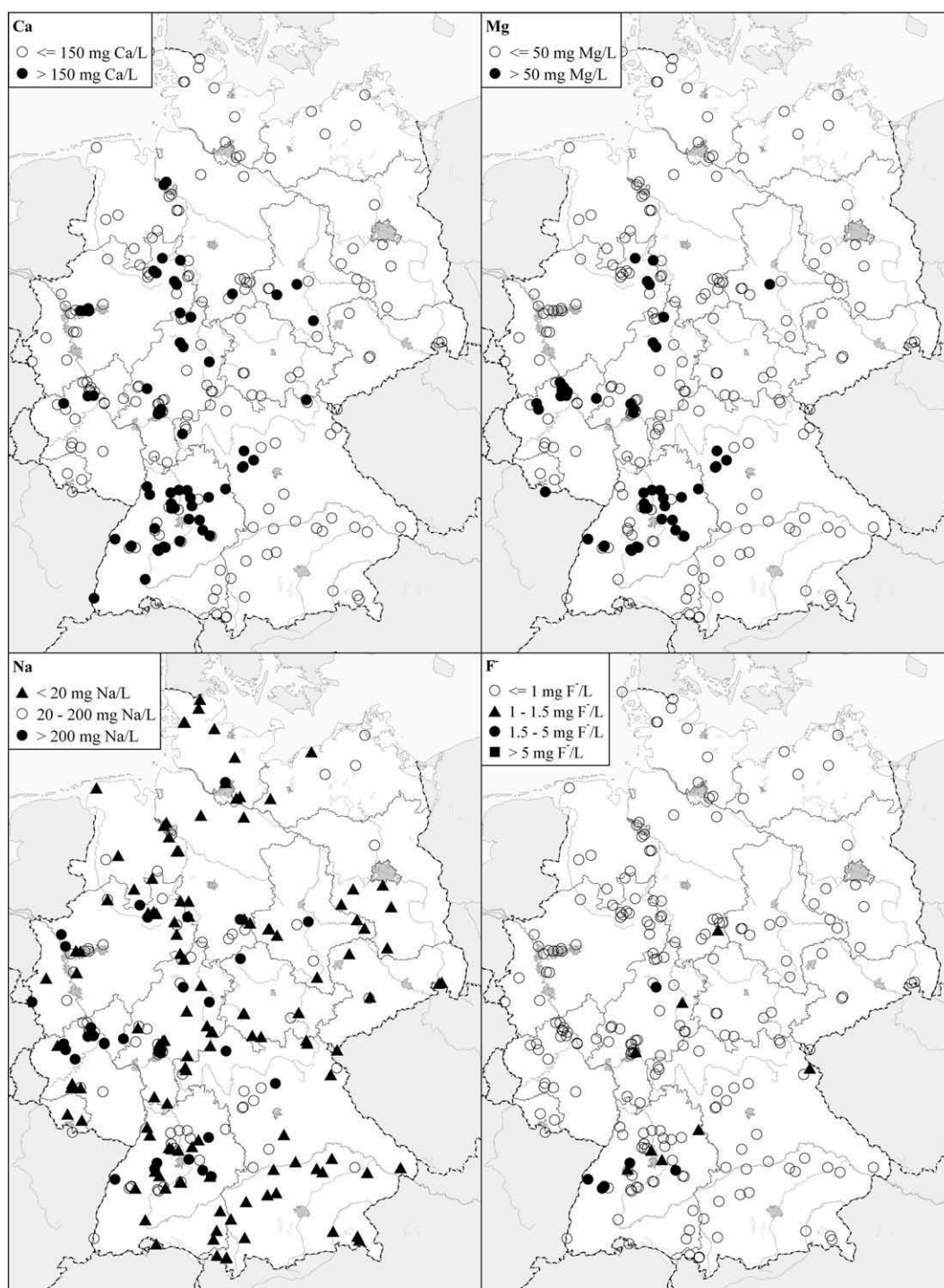


Fig. 9. Classification and distribution of bottled water based on calcium, magnesium, sodium and fluoride concentrations.

few samples have a predominant Na + K cation content. The large variety of types of bottled water is evident in the central graph. It can be seen that few samples plot in the lower left (Na–Cl[−] water type). Ca–HCO₃[−] type water with a low concentration plot in the top right.

In a van Wirdum diagram (van Wirdum, 1991, 1980) the ion ratio (IR) is plotted versus the electrical conductivity (EC), where IR (in %) = $(0.5 \cdot \text{Ca}^{2+}) / (0.5 \cdot \text{Ca}^{2+} + \text{Cl}^{-}) \cdot 100$ with concentrations expressed in meq/L. The EC can be seen as a measure of the salinity, the IR as a measure of the prevalence of calcium among the cations. This prevalence is a result of geochemical processes that occurred within the aquifer. Based on the position in the van Wirdum diagram (Figs. 17 and 18), the bottled water samples can be classified as atmocline (rainwater),

lithocline (calcium-rich fresh water), thalassocline (seawater) or anything in between. The van Wirdum diagram shows that the samples are rather equally distributed among the three reference water types from the hydrological cycle. However, most cluster around lithocline water. There are also bottled water samples (especially from southeastern and central Germany) that plot near the atmocline type (Fig. 17). Moreover, the content of a few of the samples (only two) from the Lower Rhine/Maas region (Figs. 1 and 17) have a composition similar to that of seawater.

The samples are plotted in Fig. 18 the van Wirdum diagram according to their Stuyfzand classification. As expected, the oligohaline and very oligohaline bottled water samples (Fig. 18, Table 6) plot in the zone of lithocline water, and the fresh-brackish, the brackish

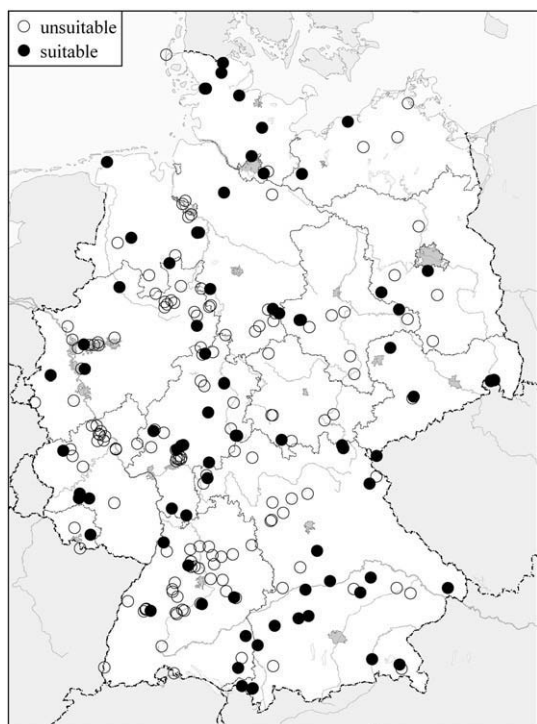


Fig. 10. Distribution of bottled water suitable for the preparation of baby food. Criteria: As <5 µg/L, F⁻ <0.7 mg/L, Mn <50 µg/L, Na <20 mg/L, U <2 µg/L, NO₂⁻ <0.02 mg/L, NO₃⁻ <10 mg/L, SO₄²⁻ <240 mg/L (MTVO, 2006).

and the brackish-salt classes in the area between the atmocline and thalassocline water types. Most of the brackish water samples plot midway between the atmocline and thalassocline zones. Most of the fresh water type samples (Table 6, Fig. 18) plot between atmocline and lithocline zones.

3.3. Comparison with national and international standards

In many countries there are regulations governing the bottling and sale of mineral water. Only in the last 20 years has it been recognized that more stringent legislation is needed for maximum admissible concentration (MAC) values (action levels) for certain parameters. In different countries, different public authorities are charged with protecting public health by setting action levels for tap water and mineral water.

The daily intake of elements via bottled water depends greatly on how much is consumed. Consumption of bottled mineral water is common in some countries, e.g., in Italy and Germany. For some people, bottled water is their major source of drinking water.

The present German and international limits for tap water and bottled water are shown in Tables 8 and 9. Values for organic contaminants are not given in the table because analyses were not carried for these parameters. Many elements are essential for a healthy existence and a certain daily minimum supply of these elements is needed to sustain life. The question is whether all these elements can have an effect on health at the recommended concentrations. It is generally recognized that in addition to the major elements (e.g., Ca, K, Mg, Na, P and S) there are a number of elements (e.g., Co, Cr, Cu, Fe, I, Mn, Mo, Se, V and Zn) that are essential for many life functions (Oehlmann and Markert, 1997; Eisenbrand and Metzler, 2001; Ebert, 2004). To complicate matters, many elements can be both beneficial and toxic. For each element, a different range of optimum concentrations exists. Tap water and bottled water are both an important source of the daily intake of many

of these elements. It is assumed that water contains such low values of most of the toxic elements that the daily intake via bottled and tap water is a minor part of the intake. There are exceptions, however, for example, uranium, for which bottled and tap water is the main source of intake (Schnug et al., 2008), whereas intake of this element via foodstuffs is rather insignificant (Schnug and Schnug, 2004, only 2–4 µg U per day). Moreover, because they are usually present in water in ionic form, trace elements have a greater bioavailability (more easily resorbed) in water than in solid foods.

Trace metals may occur naturally in groundwater in very small amounts and may include As, Ba, Cd, Cr, Pb, Hg, F, Se, Ag and Zn. In low concentrations, these are harmless and in some cases even beneficial to health. Intake above the tap and bottled water action levels may have serious health effects. Elevated levels of either essential or nonessential elements can cause morphological abnormalities, reduced growth, increased mortality and mutagenic effects in humans (Edmunds and Smedley, 1996; Ebert, 2004). The importance and problems associated with the setting of action levels for tap water have been extensively discussed (Misund et al., 1999; Reimann and Banks, 2004). To avoid potential health risks from elevated concentrations of trace elements in tap water and bottled mineral water, Germany has passed regulations for maximum allowable levels of these elements in tap and bottled water. International standards have also been set by WHO, EPA and the EU. German and international action levels or guideline values (WHO) for trace elements are compared in Table 8.

There are action levels for elements which are essential and nontoxic, but there are no action levels or guidelines for elements for which no biological role is known or which are extremely toxic, e.g., Ag, Br, Mo, Cr (IV), and U (Table 8). It can be seen that there are often large differences in the action levels given for different countries (e.g., Pb and Al).

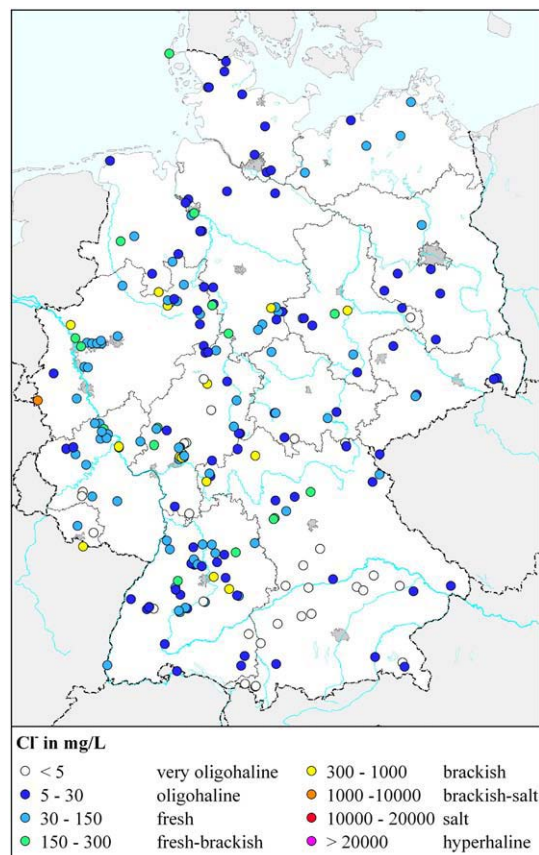


Fig. 11. Distribution of bottled water based on chloride concentration (see Table 8).

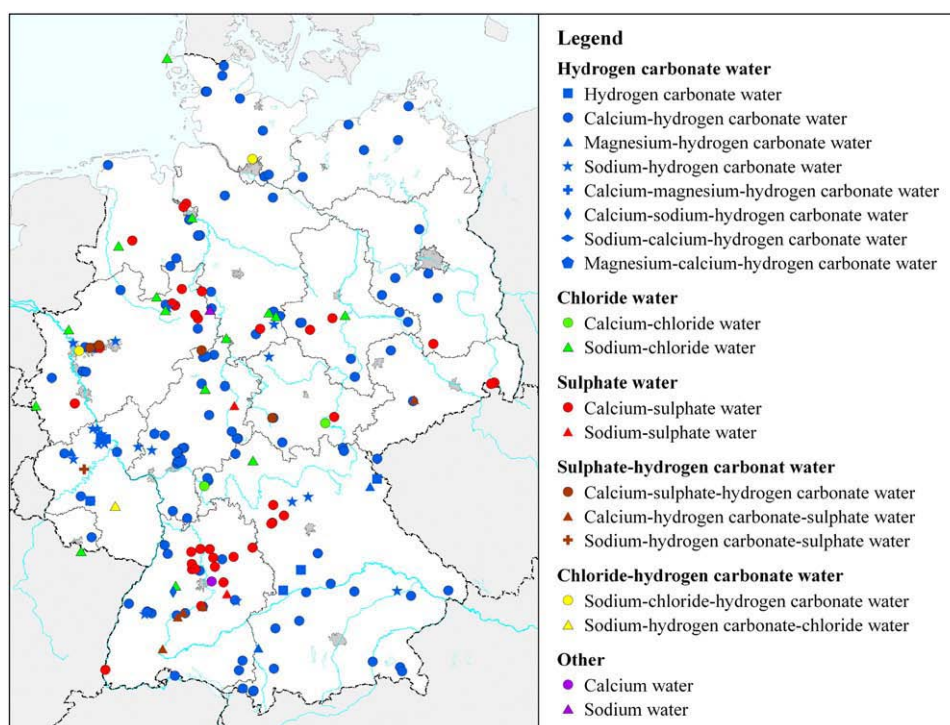


Fig. 12. Classification of water type based on all components with a concentration greater than 20 meq-%.

Standards have often been established with the misconception that bottled water and tap water does not show a large variation in element concentration if there is no contamination. Element concentrations in German bottled water (908 brands) are compared in Table 9 with the more restrictive action levels and WHO guideline concentrations that are given in Table 8. The results of this comparison are shown in Table 9, which shows the number of samples above the action levels for each element. The applicable regulation as well as the well region of bottled water is also indicated.

Only 42 of the 908 bottled samples do not pass the German mineral water standards (MTVO, 1984, 2006) and 267 brands do not pass the German standards for tap water (TVO, 2001), whereby deviations from the action levels for pH and electrical conductivity (EC) were not taken into consideration.

Of the 908 samples, 838 had pH values <6.5 owing to their CO₂ concentration; 91 had EC values above the action level of the “Drinking Water Ordinance” (TVO, 2001) of 2500 µS/cm. Only one sample exceeded the action levels for Al (TVO, 2001), and this was also the case for the MTVO levels for Ba and NO₃⁻ (MTVO, 1984, 2006). Only about 1% of the samples exceeded the action levels for As, Mn, and Ni. Ten samples exceeded the Umweltbundesamt (UBA; German Federal Environmental Agency) guideline value of 10 µg/L for uranium, nevertheless, 127 samples had uranium concentrations above 2 µg/L (the upper limit for baby food) (Birke et al., 2010a,b-this issue). There are no obligatory action levels anywhere in the world for uranium concentration in tap or bottled water, and uranium concentrations vary extremely (Fig. 5). The US Environmental Protection Agency (EPA) has proposed an action level of 30 µg U/L

Table 5
Fluoride concentrations in the analyzed bottled water.

Brand	Well name	Well location	F ⁻ in mg/L	n
Bad Liebenzeller	Bad Liebenzeller	Bad Liebenzell	1.38–1.55	2
Kimi Mineralwasser	Kimi-Quelle	Heilbronn am Neckar	1.40–1.51	2
Peterstaler	Peterstaler Mineralquelle	Bad Peterstal-Griesbach	1.49–1.58	6
Kristallperle	Brunnen 4	Heilbronn am Neckar	1.51	1
Europel	Emil-Heinrich-Quelle	Bad Peterstal-Griesbach	1.51	1
Zwestener Löwensprudel	Zwestener Löwensprudel	Bad Zwesten	1.54–1.63	2
Schwarzwaldspudel	Schwarzwaldspudel	Bad Peterstal-Griesbach	1.61	1
Eichenzeller St. Maria-Brunnen	St. Maria-Brunnen	Eichenzell-Lütter	1.70	1
Kellerwald-Quelle 1	Kellerwald-Quelle 1	Bad Zwesten	1.72–1.73	2
Napoleon Mineralbrunnen Apart	Napoleon Mineralbrunnen Apart	Schierling	2.08	1
Stauferquelle	Stauferquelle	Göppingen	2.12	1
Laurentius Quirli	Quirli	Bad Peterstal-Griesbach	2.15–2.38	2
Paracelsusquelle	Paracelsusquelle II	Bad Liebenzell	2.23	1
Kisslegger	Otto-Quelle	Kiplegg	2.46	1
Freyersbacher Mineralwasser	Freyersbacher Mineralquelle	Bad Peterstal-Griesbach	2.62	1
Überkingen	Überkingen Mineralquelle	Bad Überkingen	3.06–3.12	2
Labertaler Sebastiani-Brunnen	Labertaler Sebastiani-Brunnen	Schierling	3.48	1

Table 6
Classification of well locations based on chloride concentration.

Main type	Cl ⁻ in mg/L	Percentage	Code
Very oligohaline	<5	9.14	G
Oligohaline	5–30	41.5	g
Fresh	305–150	34.6	F
Fresh-brackish	150–300	9.69	f
Brackish	300–1000	4.85	B
Brackish-salt	1000–10,000	0.22	b
Salt	10,000–20,000	0.00	S
Hyperhaline	>20000	0.00	H

in the USA (US EPA, 2003, 2009, Table 8), and a guideline limit of 15 µg U/L has been proposed by WHO (2006).

The parameters with the highest number of samples above the German and EU action levels are SO₄²⁻, Cl⁻, Mn and Na:

For sulfate, 133 of the 908 samples exceeded the 500 mg/L action level for German tap water (TVO, 2001). Sulfate concentration was given on the label of about 88% (800) of the samples.

For chloride, 68 of the samples exceed the action level for tap water (EU directive, 1998/83/EC). Chloride concentration was given on the label of about 91% (827) of the samples.

For sodium, 120 of the samples exceeded the EU action level of 200 mg/L. Sodium concentration was given on the labels of nearly all of samples (900 samples).

For manganese, 110 of the samples exceeded the action level of 50 µg/L of for German tap water (TVO, 2001) and only 8 samples exceeded the 500 µg/L allowed for mineral water (MTVO, 2006).

In the last column of Table 9 the well regions are shown in which concentrations of the respective parameter exceeded the action levels given in Table 8. It is shown that of eight German well regions not one of them passes all the German tap water standards. Only 16 analyzed brands from northern Germany pass all the German mineral water standards (MTVO, 2006) (Tables 8 and 9; Fig. 1).

Table 7
The analyzed bottled water classified according to the “German classification system”.

Water type	Bottle samples (N = 908)		Well locations (N = 233)	
	n	%	n	%
Hydrogen carbonate	17	1.87	6	2.58
Calcium-chloride	3	0.33	2	0.86
Calcium-hydrogen carbonate-sulfate	27	2.97	5	2.15
Calcium-hydrogen carbonate	428	47.1	117	50.2
Calcium-magnesium-hydrogen carbonate-sulfate	1	0.11		
Calcium-magnesium-hydrogen carbonate	37	4.07	9	3.86
Calcium-sodium-chloride	2	0.22		
Calcium-sodium-hydrogen carbonate	2	0.22	1	0.43
Calcium-sulfate-hydrogen carbonate	10	1.10	4	1.72
Calcium-sulfate	167	18.4	36	15.5
Calcium	9	0.99	1	0.43
Magnesium-hydrogen carbonate	15	1.65	4	1.72
Magnesium-calcium-hydrogen carbonate	9	0.99	3	1.29
Sodium-chloride-hydrogen carbonate	6	0.66	2	0.86
Sodium-chloride	49	5.40	15	6.44
Sodium-hydrogen carbonate-chloride	7	0.77	1	0.43
Sodium-hydrogen carbonate-sulfate	1	0.11	1	0.43
Sodium-hydrogen carbonate	105	11.6	22	9.44
Sodium-calcium-hydrogen carbonate	2	0.22	1	0.43
Sodium-sulfate-hydrogen carbonate	2	0.22		
Sodium-sulfate	4	0.44	2	0.86
Sodium	4	0.44	1	0.43
Sulfate	1	0.11		

For boron, concentrations ranged from 2.16 µg/L to 2610 µg/L. Bottled water had much higher B concentrations than tap water (Fig. 5), and was up to 2.5 times the action level for tap water (Table 8). Nonetheless, no limit has been set for B in bottled water to date. In 72 of the samples the B concentration exceeds the WHO guideline value of 500 µg/L, and in 27 of the samples it exceeds the German action level of 1000 µg/L for tap water. The maximum B concentration in the bottled water samples was ten times the maximum value determined for the

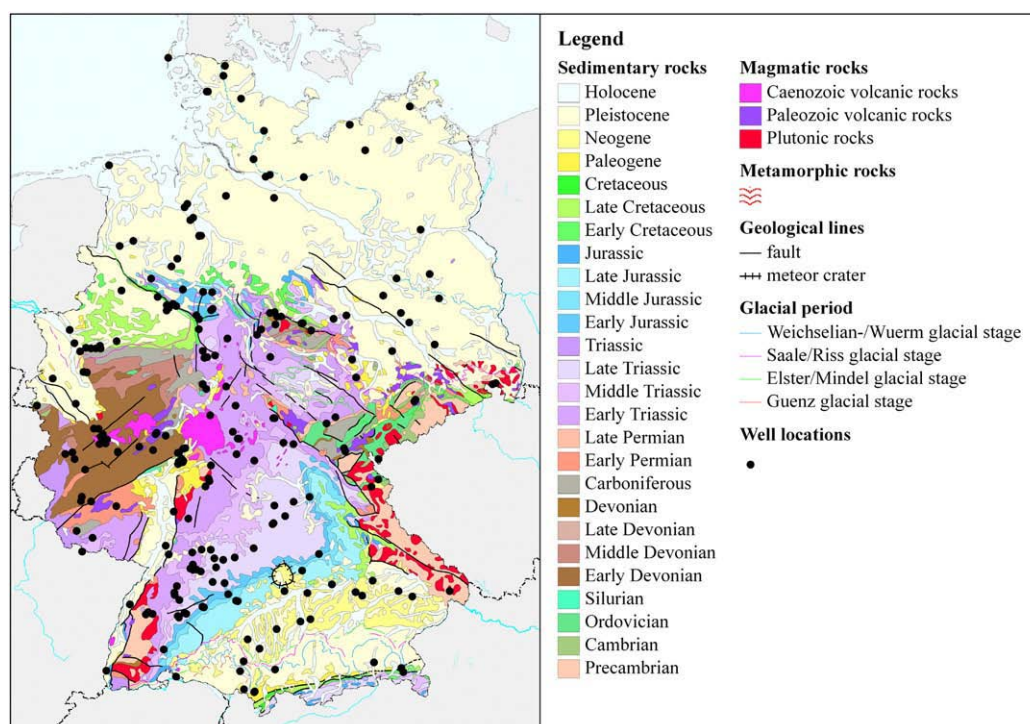


Fig. 13. Geological map of Germany (BGR, 2004) and well localities.

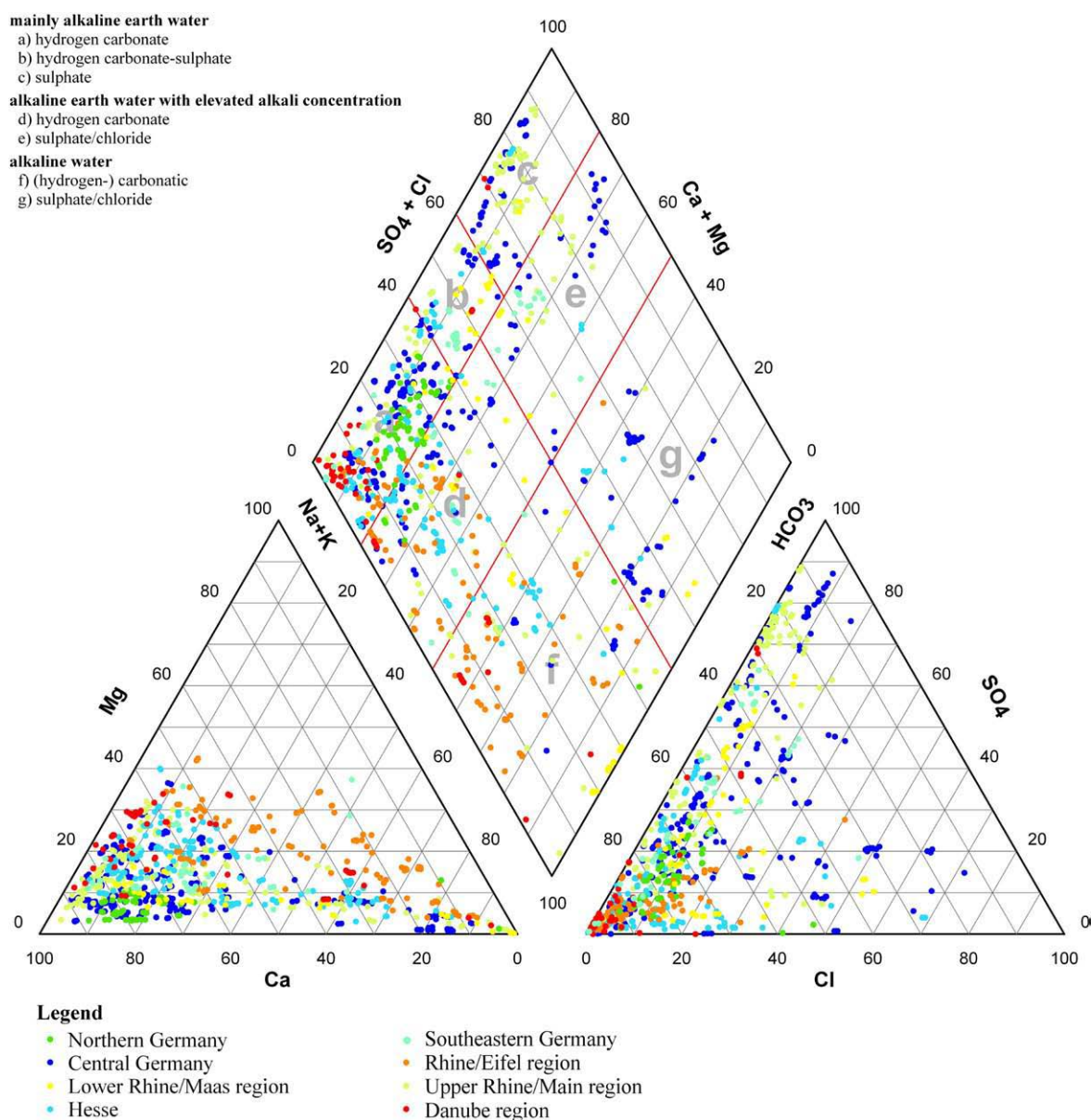


Fig. 14. Piper diagram of the German bottled water based on well region.

tap water samples. The German action level for borate in tap water is 30,000 µg/L (5500 µg B/L) (TVO, 2001).

3.4. Regional distribution of selected elements

The major element contents and the distribution of water types are discussed in Section 3.2. Cumulative frequency diagrams of selected elements in the analyzed German “tap water”, “surface water” (Birke et al., 2006) and “bottled water” are shown in Fig. 5. The median values for European bottled water (EGS, 2010), the WHO guideline values (1996, 2006) and the German action levels for bottled water (MTVO, 2006) are also plotted for reference. Maps showing the distribution of element concentrations in the bottled water samples are included here only for selected elements of interest.

The pH of the analyzed bottled water ranged from 3.80 to 8.10, and from 6.84 to 8.63 in tap water (Table 3). According to the German and EU “drinking water” standards, the pH should be in the range of 6.5 to 9.5. There is no standard for mineral water. About 92% of the bottled

water samples reported here have a pH lower than 6.5 (many of these are carbonated). Carbonated and non-carbonated bottled water of the same brands (N = 132) are shown in Fig. 19. The bottled water with the lowest pH (3.8) is from a well in Pleistocene rock and is mineral-poor water (Bad Liebenwerda Mineralwasser, and Ambassador, the latter is carbonated). The large range of pH values was mainly due to the addition of carbon dioxide, which lowered the pH by up to two units (Fig. 19). Carbon dioxide is used in Germany as a conservative for mineral water. This acid, however, lowers the intestinal flora needed for digestion and nutrient absorption and can lead to an overacidification of the body. It not only lowers the pH but also lowers the ability to form aqueous colloids that are important for the metabolism of the body (Green and Green, 1987).

The electrical conductivity (EC) ranged between 38.1 and 6340 µS/cm in the analyzed bottled water and between 60 and 878 in tap water; 10% of the 908 bottled water samples exceeded the German and EU action level of 2500 µS/cm for tap water (Table 3). For mineral water no limit is defined.

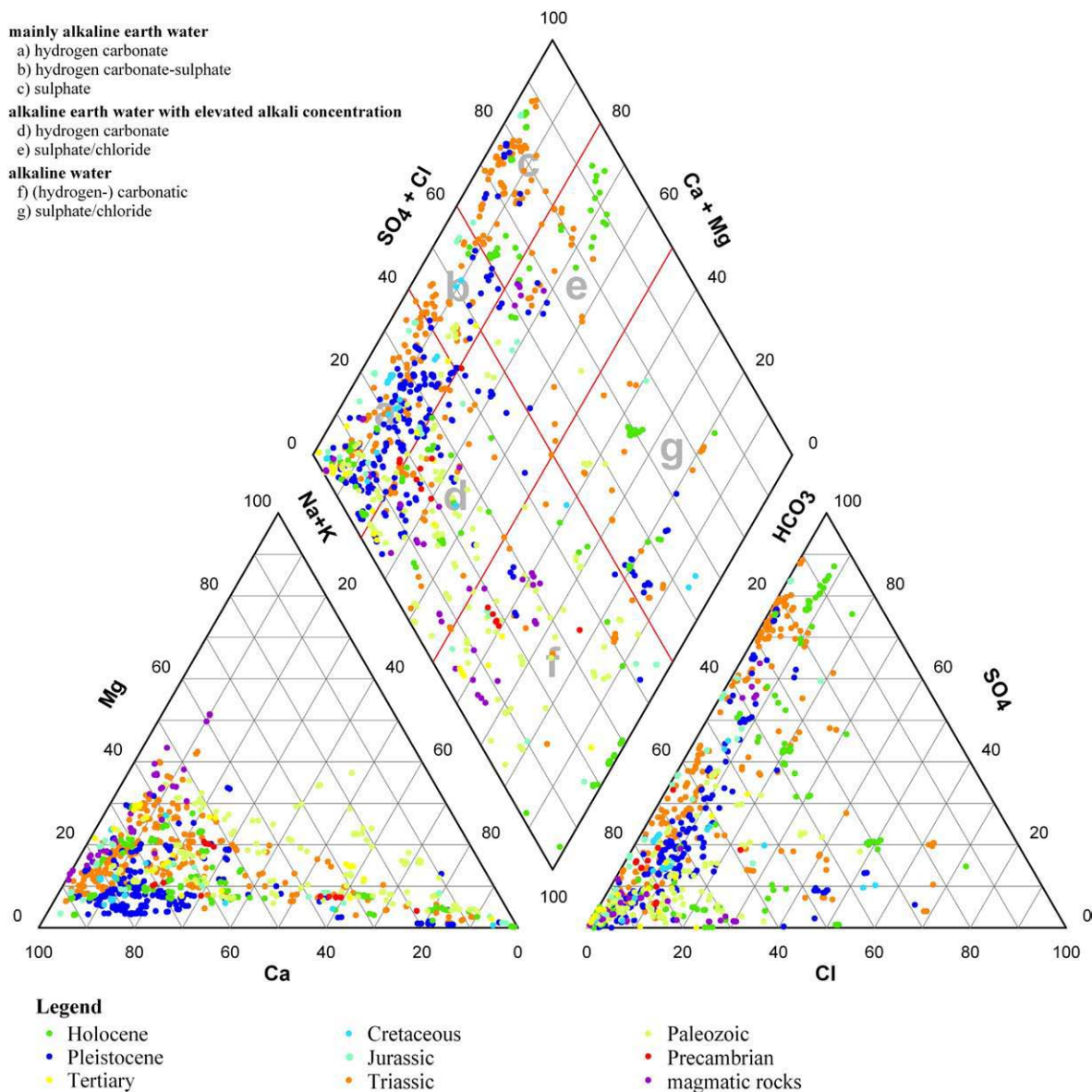


Fig. 15. Piper diagram of the German bottled water based on geology.

The natural variation of EC in German bottled water spans three orders of magnitude. The median value for German bottled water is more than twice as high as that for the tap water (Table 3).

Most of the bottled water from southwestern Germany had a high EC value.

The highest EC values ($\geq 2500 \mu\text{S}/\text{cm}$) were for samples from the medicinal springs at Stuttgart, in the Upper Rhine/Main and the Rhine/Eifel regions (Figs. 20 and 21). In the Upper Rhine/Main region, the Bunter sediments and the Upper and Middle Muschelkalk (Middle Triassic) are strongly leached. In the Paleozoic areas of the Rhine/Eifel well region, as well as in the areas of Devonian limestone in the western Eifel, the high EC values result from saline water. Saline groundwater is also the reason for the elevated, anomalous EC values south of Magdeburg (Fig. 21).

Silicon is present almost exclusively as unionized orthosilicic acid $[\text{Si}(\text{OH})_4]$ (Krauskopf, 1956). The dissolved silicic acid is derived either from the weathering or decomposition of silicates, the dissolving of amorphous silicic acid, or by extreme temperatures (Michel, 1997). The normal concentration of silicic acid in water is between 1 and 30 mg/L, formation water from oil wells

has concentrations between 30 and 95 mg SiO_2/L (Krejci-Graf, 1963, 1978). The highest concentrations are in thermal water in volcanic rock ($\geq 300 \text{ mg SiO}_2/\text{L}$). Silicon gives stability to bones, elasticity of connective tissue, tautness of the skin, and is also enriched in hair and fingernails and toenails (D'Haese et al., 2004).

The Si concentration in the analyzed German bottled water lies between 0.94 and 40.5 mg/L, in the tap water between 1.17 and 20.1 mg/L. The variation in Si concentration covers only three orders of magnitude. A relatively low median value of 4.98 mg Si/L has been determined for surface water in Germany (Birke et al., 2006). The map of the distribution of Si in bottled water (Fig. 22) shows two regional features: High values ($> 17 \text{ mg Si/L}$) occur in Tertiary volcanic rocks in the Rhine/Eifel well region, in the Oberlausitzer Bergland (Oppacher Mineralwasser), in the crystalline basement rocks (strongly decomposed gneiss) of the Black Forest region (Freyersbacher Mineralwasser), in the Fichtel Mts. and in the Franconian Forest. Noticeable are also the elevated Si concentrations ($> 12.0 \text{ mg/L}$) in the areas affected by the Weichsel ice sheet in northern and northeastern Germany (Fig. 22). Owing to the multitude of industrial applications of silicon (glass,

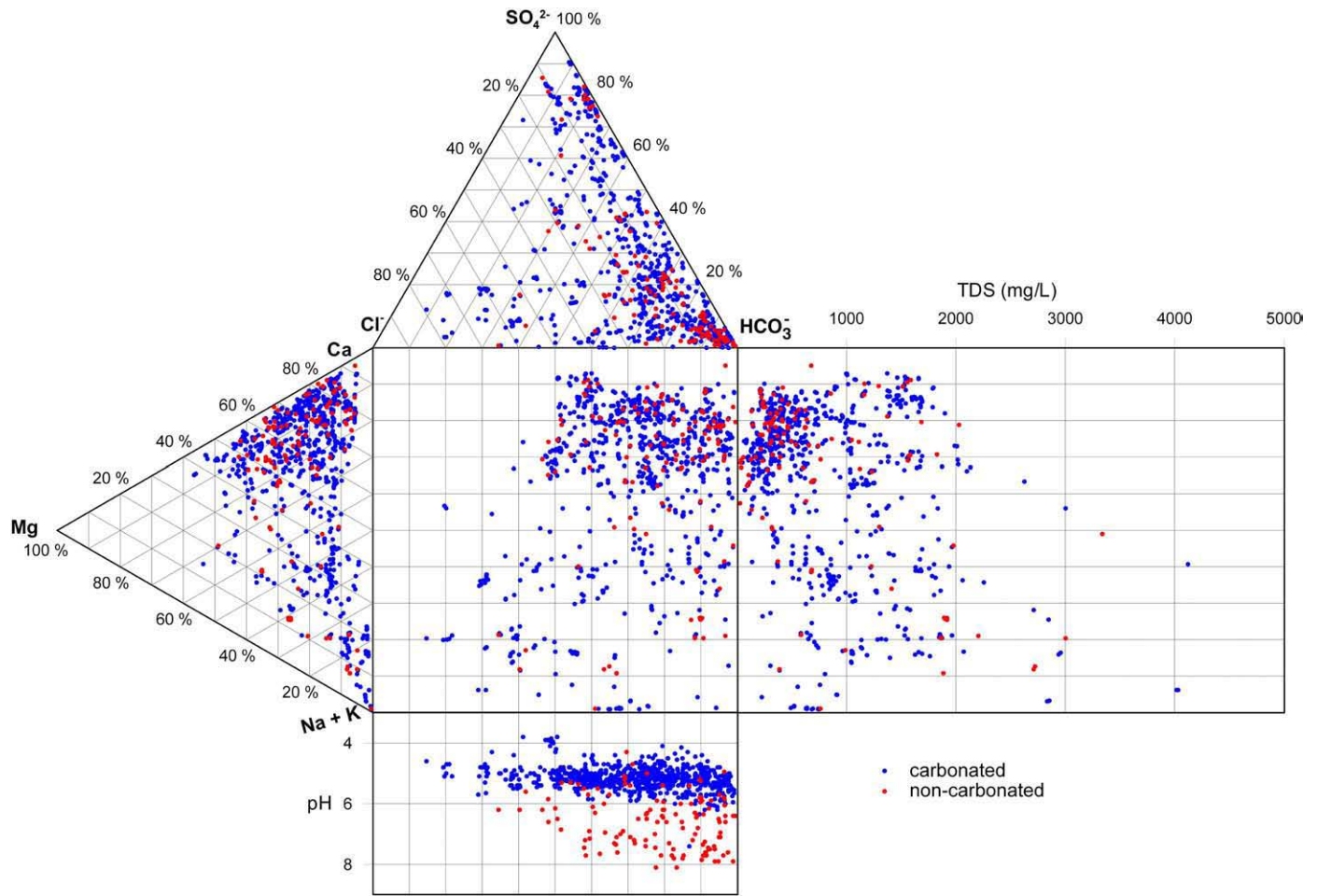


Fig. 16. Durov diagram of the German bottled water based on milliequivalent fractions of the major cations and anions.

cement, ceramics, and electronics), anthropogenic influences for locally elevated concentrations cannot be excluded (e.g., in the Ruhr District).

Boron is normally present in groundwater in concentrations of only a few 0.01–0.1 mg/L. Elevated concentrations can indicate anthropogenic contamination owing to the multitude of uses of

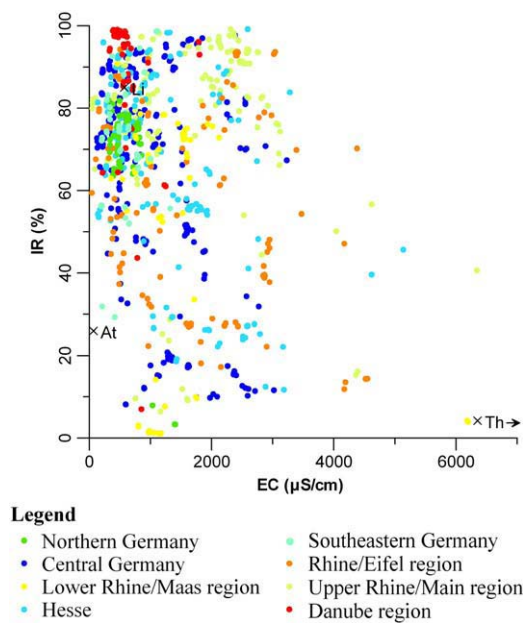


Fig. 17. Van Wirdum diagram for German bottled water based on well region. (At – atmocline, Li – lithocline, Th – thalassocline groundwater).

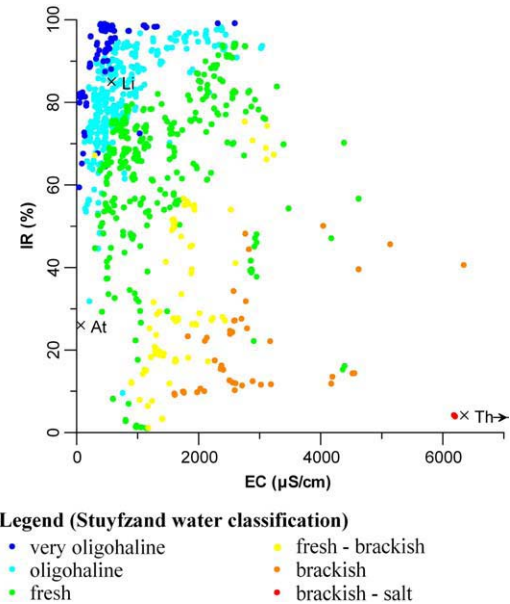


Fig. 18. Comparison of the van Wirdum diagram with the Stuyfzand water classification for the German bottled water samples (At – atmocline, Li – lithocline, Th – thalassocline groundwater).

Table 8

National and international action levels for element concentrations for bottled and tap water.

Parameter	German action levels for bottled water ¹⁾ (MTVO, 1984, 2006)	German action levels for tap water (TVO, 2001)	EU Directive, 2003/40/EC Mineral water	EU Directive, 1998/83/EC Drinking water	US EPA National Primary Drinking Water Standard Regulations (2003)	WHO (1996, 2006) Guideline values for drinking water	Russian MPC ²⁾ for drinking water (2006)
EC ($\mu\text{S}/\text{cm}$)	–	2500 ³⁾	–	2500 ³⁾	–	–	1000
pH	–	6.5–9.5 ³⁾	–	6.5–9.5 ³⁾	6.5–8.5 ⁴⁾	–	6.0–9.0
Al ($\mu\text{g}/\text{L}$)	–	200 ³⁾	–	200 ³⁾	50–200 ⁴⁾	200 ⁵⁾	500
As ($\mu\text{g}/\text{L}$)	10	10	10	10	10	10	50
B ($\mu\text{g}/\text{L}$)	30,000 ⁶⁾	1000	– ⁷⁾	1000	–	500	500
Ba ($\mu\text{g}/\text{L}$)	1000	–	1000	–	2000	700	–
Cd ($\mu\text{g}/\text{L}$)	3	5	3	5	5	3	1
Cl [–] (mg/L)	–	–	–	250 ³⁾	250 ⁴⁾	250 ⁸⁾	–
Cr ($\mu\text{g}/\text{L}$)	50	50	50	50	100	50	50
Cu ($\mu\text{g}/\text{L}$)	1000	2000	1000	2000	1300	2000	1000
F [–] (mg/L)	5 ⁹⁾	1.5	5 ⁹⁾	1.5	4	1.5	1.5
Fe ($\mu\text{g}/\text{L}$)	–	200 ³⁾	–	200 ³⁾	300 ⁴⁾	–	300
Hg ($\mu\text{g}/\text{L}$)	1	1	1	1	2	6	0.5
Mn ($\mu\text{g}/\text{L}$)	500	50 ³⁾	500	50 ³⁾	50 ⁴⁾	400	100
Na (mg/L)	–	–	–	200 ³⁾	–	200 ⁸⁾	–
NH ₄ ⁺ (mg/L)	–	–	–	0.5 ³⁾	–	–	1.0
Ni ($\mu\text{g}/\text{L}$)	20	20	20	20	–	70	100
NO ₂ [–] (mg/L)	0.1	0.5	0.1	0.5	1 ¹⁰⁾	3 ¹¹⁾	0.75
NO ₃ [–] (mg/L)	50	50	50	50	10 ¹²⁾	50	10
Pb ($\mu\text{g}/\text{L}$)	10	25 ¹³⁾	10	25 ¹³⁾	15	10	30
Sb ($\mu\text{g}/\text{L}$)	5 ¹⁴⁾	5	5 ¹⁴⁾	5	6	20	–
Se ($\mu\text{g}/\text{L}$)	10	10	10	10	50	10	–
SO ₄ ^{2–} (mg/L)	–	500 ³⁾	–	250 ³⁾	250 ⁴⁾	500 ⁸⁾	500
U ($\mu\text{g}/\text{L}$)	2 ¹⁵⁾ , 10 ¹⁶⁾	10 ¹⁶⁾	–	–	30	15	–
Zn ($\mu\text{g}/\text{L}$)	–	–	–	–	5000	3000 ⁸⁾	30

¹⁾ valid only for “natural mineral water”; the values for “spring water”, and table water are given in Appendix 2 of the German Drinking Water Regulations; ²⁾ maximum permissible concentration; ³⁾ indicator parameter; ⁴⁾ secondary standard; ⁵⁾ large water treatment facilities; ⁶⁾ borate; ⁷⁾ not yet decided; ⁸⁾ guideline value, not legally binding; ⁹⁾ highest value for fluoride; for values above 1.5 mg/L the label must contain a warning and the actual value; ¹⁰⁾ measured as nitrogen, approximately 3 mg/L when measured as NO₂[–]; ¹¹⁾ for “short-term exposure”, 0.2 mg/L for “long-term exposure”; ¹²⁾ measured as nitrogen, approximately 45 mg/L when measured as NO₃[–]; ¹³⁾ 10 $\mu\text{g}/\text{L}$ from 2013; ¹⁴⁾ This value is the limit at the time of bottling; there is a “migration limit” of 40 μg Sb/L to take into account potential migration from PET plastic bottles; ¹⁵⁾ legal limit for preparation of baby food; ¹⁶⁾ guideline value proposed by UBA for uranium – not legally binding.

boron compounds in industry and household (glass production, detergents, bleaches, wood preservatives, fertilizers, herbicides, astringents, antiseptics, neutron absorbers in nuclear reactors). However, B concentrations of up to 100 mg/L are known to be present in mineral and thermal water as the very soluble orthoboric acid (H₃BO₃) (Senften, 1971). The highest known B concentrations are in highly saline formation water from oil wells (up to 310 mg/L; Michel, 1997). Boron in the form of H₃BO₃ is an essential trace element for plants, but is of no importance for animal life. For humans the main source of boron intake is wine. It is spread throughout the body and is excreted through the kidneys (Ebert, 2004).

Concentrations of boron in mineral and ‘medicinal’ water above 10 mg/L are very seldom observed. In the analyzed bottled water they vary between 2.16 $\mu\text{g}/\text{L}$ and 2610 $\mu\text{g}/\text{L}$, in tap water between 3.13 and 253 $\mu\text{g}/\text{L}$ (Table 3). The median for bottled water (64.0 μg B/L) is four times higher than that for tap water. A median value of 27.6 $\mu\text{g}/\text{L}$ has been determined for surface water (Birke et al., 2006). Of the 908 bottled water samples, 27 had boron concentrations above the German and EU action levels of 1000 μg B/L for tap water (Tables 8 and 9). The German action level of 30,000 $\mu\text{g}/\text{L}$ borate (5500 μg B/L) for mineral water is not exceeded, however (Table 9). The cumulative frequency diagrams (Fig. 5) show that the bottled water samples are clearly more enriched in B than tap or surface water. The variation of B concentration in bottled water covers four orders of magnitude.

Elevated B concentrations are observed in the Upper Rhine/Main well region (>600 μg B/L, Figs. 1 and 23), as well as in areas of Triassic sediments (Keuper) and crystalline basement (Black Forest). Elevated geogenic concentrations in Keuper sediments (up to 220 μg B/L) have been observed by other authors (Abke et al., 1997). The median value in the analyzed bottled water (Table 3) is double the median value determined by Schleyer and Kerndorff (1992) for groundwater in unconsolidated sediments. The highest B concentrations (>2000 $\mu\text{g}/\text{L}$) are observed in the Upper Rhine/Main (at Bad Überkingen) well region

(Adelheidsquelle and Überkingen). Elevated concentrations also occur in the Lower Rhine/Maas and Rhine/Eifel well regions (Fig. 23).

The mean B/Cl ratio in the bottled water samples was 0.002 (0.00002–0.03). In sea water and surface water the ratio is about 0.0002, in volcanogenic thermal water it is 0.1 (White, 1957a, b).

Owing to the very low solubility of beryllium compounds, it is present in groundwater only in extremely low concentrations of less than 0.001 $\mu\text{g}/\text{L}$ (Hem, 1992). Their solubility, however, increases with decreasing pH. A median value of <0.5 μg Be/L (<0.5 to 3.7 μg Be/L) has been determined for surface water in Germany (Birke et al., 2006). In brines it is present mainly in complexes with concentrations of 0.02–0.2 μg Be/L (Collins, 1975). In groundwater at depth, it has been observed in concentrations as high as 200 μg Be/L. Beryllium is present in coal smoke, which is deposited in wet and dry particulate matter. The leaching of coal ashes in landfills can be a source of input into groundwater.

Unfortunately, beryllium is one of the most toxic metals known. Although it is not toxic by ingestion, Be inhalation can cause an acute tracheobronchitis/pneumonia at high concentrations, and even at very low concentrations a chronic hypersensitivity granulomatosis may develop. Beryllium can also cause toxic and hypersensitive reactions in the skin (Rossmann, 2000).

Beryllium concentration in the analyzed bottled water samples ranges between <0.001 $\mu\text{g}/\text{L}$ and 7.30 $\mu\text{g}/\text{L}$, in the tap water samples from 0.001 $\mu\text{g}/\text{L}$ to 0.2 $\mu\text{g}/\text{L}$. The tap water samples from other parts of Europe also show a very low median value similar to those from Germany (Table 3). There are no defined water standards for Be in mineral and tap water in the EU or in Germany. The limit in Russia (Fiedler and Rösler, 1993), Serbia and Ukraine is 0.2 μg Be/L for tap water; in the US, the EPA has set a limit of 4.0 μg Be/L. There is little indication that beryllium in tap water poses a health threat. The Be concentration in bottled water has a range of five orders of magnitude. According to the cumulative frequency diagram (Fig. 5), four bottled water samples had values above the

Table 9

Comparison of element concentrations in German bottled water with the national and international action levels.

Parameter	Unit	Mean	Max	Action levels	Water standards	Above action level		Well regions ¹
						No. of samples	% of samples	
pH		5.38	3.8 ² /8.1	≥6.5/≤8.5	US-EPA ^a	838 ³ /0 ⁴	92.3 ³ /0 ⁴	NDL, MDL, URM, HES, SOD, REF, ORM, DON
EC	μS/cm	1187	6340	6.5–9.5	TVO ^b , EU98 ^c	838 ³ /0 ⁵	92.3 ³ /0 ⁵	NDL, MDL, URM, HES, SOD, REF, ORM, DON
Al	μg/L	6.65	281	200	TVO ^b , EU98 ^c	91	10.0	MDL, URM, HES, ORM, REF
As	μg/L	0.771	17.2	10	MTVO ^e , TVO ^b , EU03 ^f , EU98 ^c , WHO ^d , US-EPA ^a	1	0.11	URM
B	μg/L	169	2610	500	WHO ^d	9	0.99	MDL, URM, SOD, REF, ORM
Ba	μg/L	59.9	1490	1000	TVO ^b , EU98 ^c	72	7.93	MDL, URM, HES, REF, ORM, DON
Cd	μg/L	0.0102	0.439	3	WHO ^d	27	2.97	URM, HES, REF, ORM
Cl ⁻	mg/L	75.6	1474	250	WHO ^d	1	0.11	REF
Cr	μg/L	0.412	12.4	50	MTVO ^e , EU03 ^f	1	0.11	REF
Cu	μg/L	1.28	170	1000	MTVO ^e , EU03 ^f	0	0	-
F ⁻	mg/L	0.371	3.48	1.5	EU98 ^c , WHO ^d	0	0	-
Fe	μg/L	5.25	166	200	EU98 ^c , US-EPA ^a	68	7.49	NDL, MDL, URM, HES, REF, ORM
Hg	ng/L	<5	<5	1000	MTVO ^e , TVO ^b , EU03 ^f , EU98 ^c	0	0	-
Mn	μg/L	32.6	1160	50	TVO ^b , EU98 ^c , US-EPA ^a	0	0	-
Na	mg/L	87.6	1260	500	MTVO ^e , EU03 ^f	110	12.1	NDL, MDL, URM, HES, SOD, REF, ORM
NH ₄ ⁺	mg/L	0.178	11.9	200	EU98 ^c , WHO ^d	8	0.88	MDL, HES
Ni	μg/L	1.37	26.4	20	EU98 ^c	120	13.2	NDL, MDL, URM, HES, REF, ORM
NO ₂ ⁻	mg/L	0.00717	0.456	0.1	MTVO ^e , TVO ^b , EU03 ^f , EU98 ^c	55	6.06	NDL, MDL, URM, HES, REF, ORM, DON
NO ₃ ⁻	mg/L	3.12	53.8	10	EU98 ^c , EU03 ^f	5	0.55	REF
Pb	μg/L	0.112	5.13	10	MTVO ^e , TVO ^b , EU03 ^f , EU98 ^c , WHO ^d	11	1.21	MDL, REF, ORM, DON
Sb	μg/L	0.166	2.35	5	WHO ^d	73	8.04	MDL, HES, SOD, ORM, DON
Se	μg/L	0.182	4.97	10	MTVO ^e , TVO ^b , EU03 ^f , EU98 ^c , WHO ^d	1	0.11	DON
SO ₄ ²⁻	mg/L	220	2210	250	EU98 ^c , US-EPA ^a	0	0	-
U	μg/L	0.938	16.0	2	TVO ^b , WHO ^d	0	0	-
Zn	μg/L	4.77	293	10	MTVO ^e	200	22.0	MDL, URM, HES, REF, ORM, DON
				3000	TVO ^b	133	14.6	MDL, URM, HES, REF, ORM, DON
					WHO ^d	127	14.0	MDL, HES, SOD, REF, ORM, DON
						10	1.10	MDL, HES, SOD, ORM
						0	0	-

¹NDL = Northern Germany, MDL = Central Germany, URM = Lower Rhine/Maas region, HES = Hesse, SOD = Southeastern Germany, REF = Rhine/Eifel region, ORM = Upper Rhine/Main region, DON = Danube region; ²minimum; ³below 6.5; ⁴above 8.5; ⁵above 9.5.

^aUS-EPA National Primary Drinking water Standard Regulations (2003); ^bGerman action levels for tap water (TVO, 2001); ^cEU Directive, 1998/83/EC Drinking water; ^dWHO (1996, 2006) Guideline values for drinking water; ^eGerman action levels for mineral water (MTVO, 1984, 2006); ^fEU Directive, 2003/40/EC Mineral water.

US EPA limit. About 20% of all samples had values below the detection limit (Table 3).

The map of the distribution of Be (Fig. 24) shows that anomalous concentrations (>1 μg Be/L) have a similar distribution to that of crystalline basement rocks (samples from the Black Forest region and the Fichtel Mts.) Elevated concentrations (>0.25 μg Be/L) are also

present in the Rhine/Eifel region and in Hesse (Fig. 1). Very low Be concentrations (<0.0063 μg/L) are characteristic of northern and central Germany and the region south of the Danube River (Fig. 24).

The highest concentrations of lithium are in saline fossil water. Groundwater that has come in contact with acid crystalline rocks during

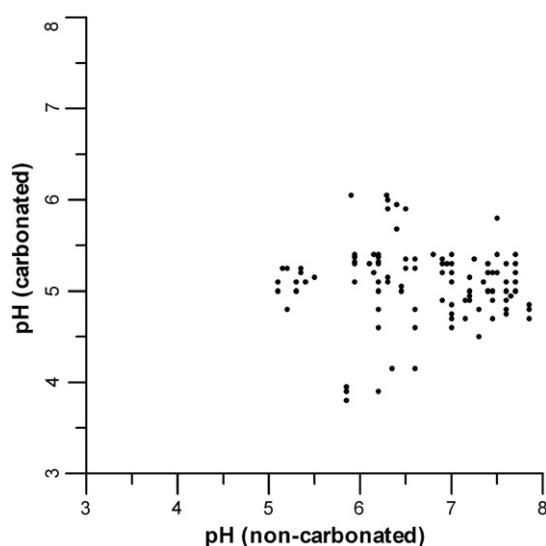


Fig. 19. Comparison of pH values in carbonated and non-carbonated bottled water of the same brands (N = 132).

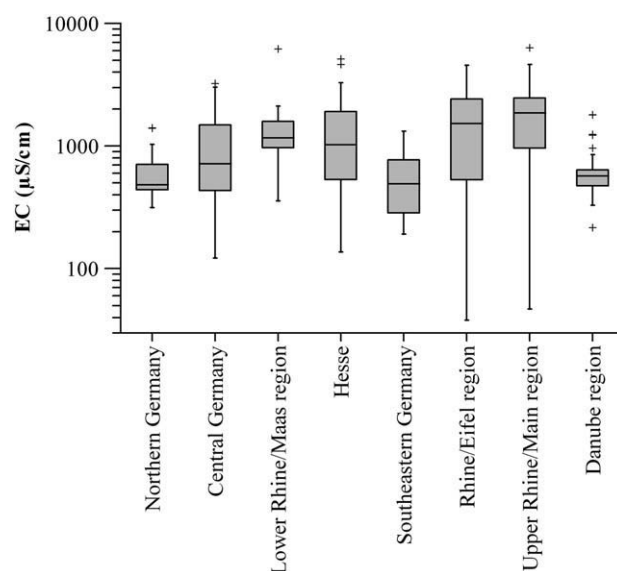


Fig. 20. Boxplot comparison of electrical conductivity (EC) in the German well regions.

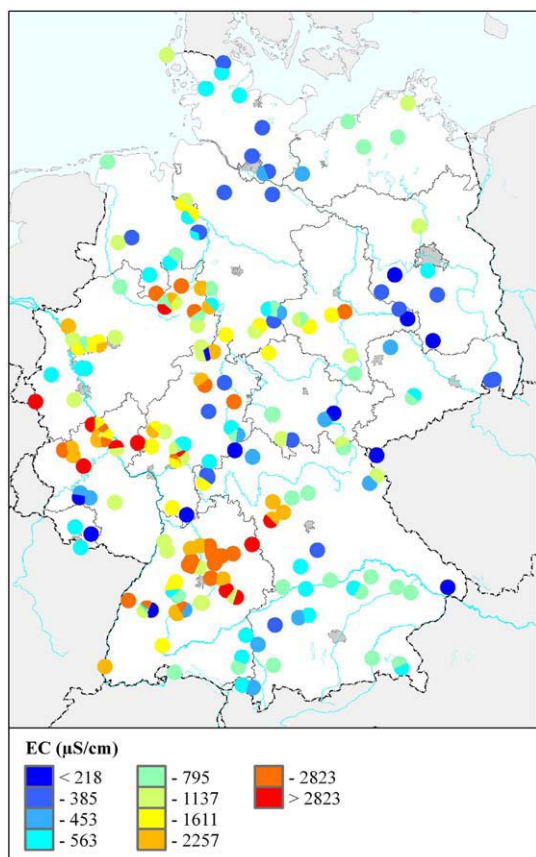


Fig. 21. Distribution of the median electrical conductivity (EC) in German bottled water.

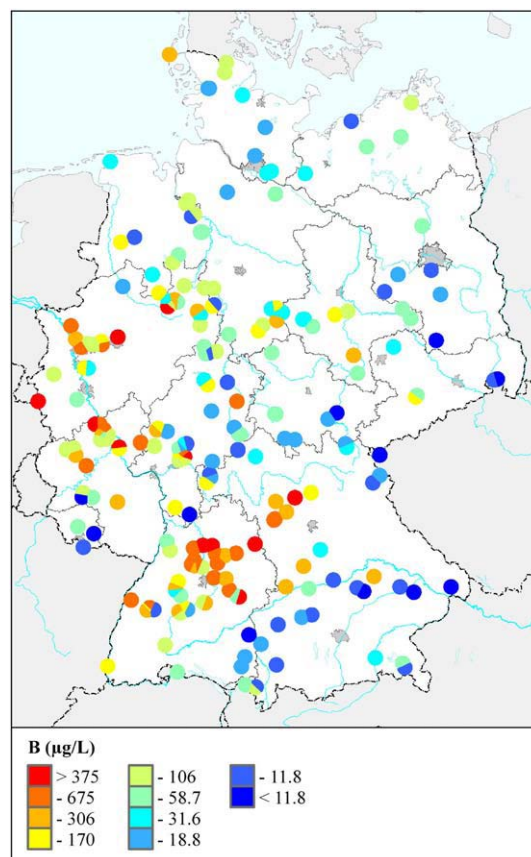


Fig. 23. Distribution of the median boron concentration in German bottled water.

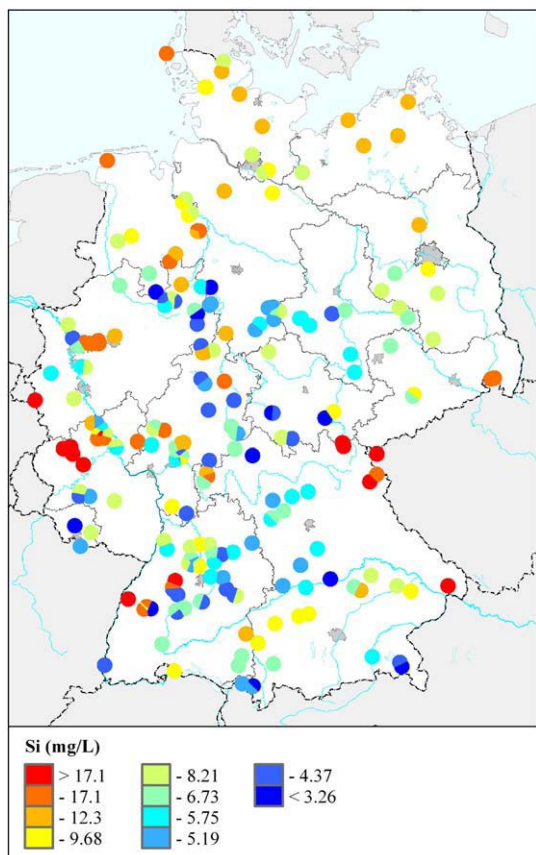


Fig. 22. Distribution of the median Si concentration in German bottled water.

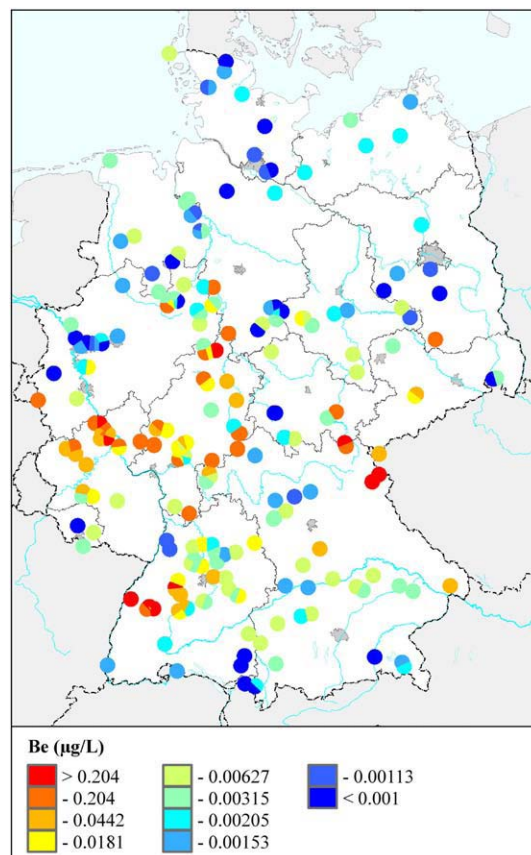


Fig. 24. Distribution of the median Be concentration in German bottled water.

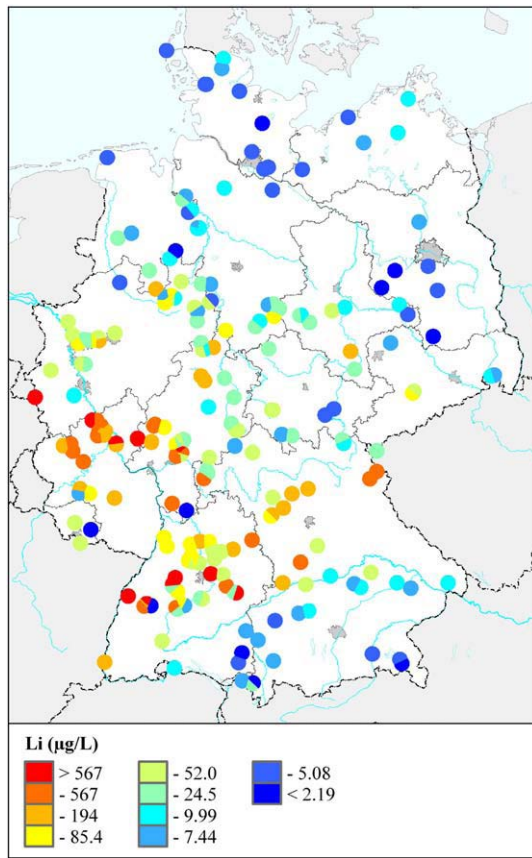


Fig. 25. Distribution of the median Li concentration in German bottled water.

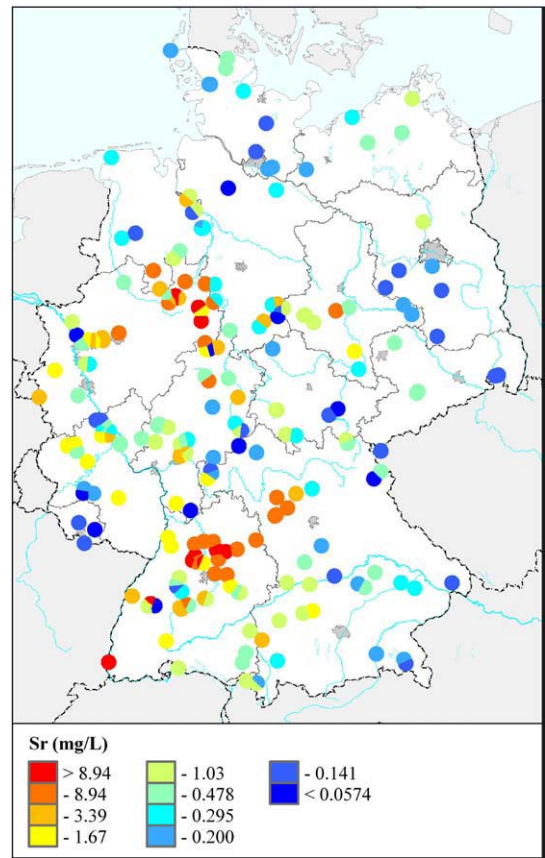


Fig. 27. Distribution of the median Sr concentration in German bottled water.

its migration can be enriched with Li. Elevated Li concentrations in mineral water in basement rocks can be due to the decomposition of mica. Geochemically, Li behaves similar to Na. Owing to its weaker binding than Na during ion exchange, lithium is preferentially leached during the weathering of silicate rocks. Groundwater normally has a Li concentration of 0.001–0.5 mg/L, thermal water can have concentrations between 0.01 mg/L and 27 mg Li/L (Wedepohl, 1978). Sea water has a mean concentration of 0.17 mg Li/L (Faure, 1991; Hem, 1992). In surface water bodies in Germany the mean concentration is 7.83 µg Li/L

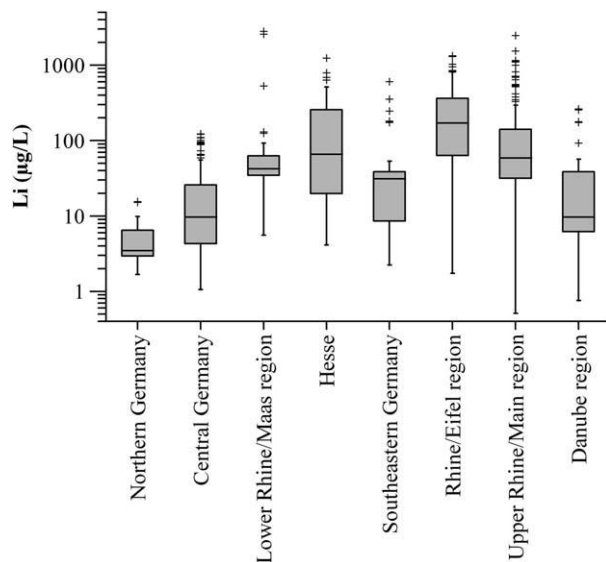


Fig. 26. Boxplot comparison of Li concentrations in the German well regions.

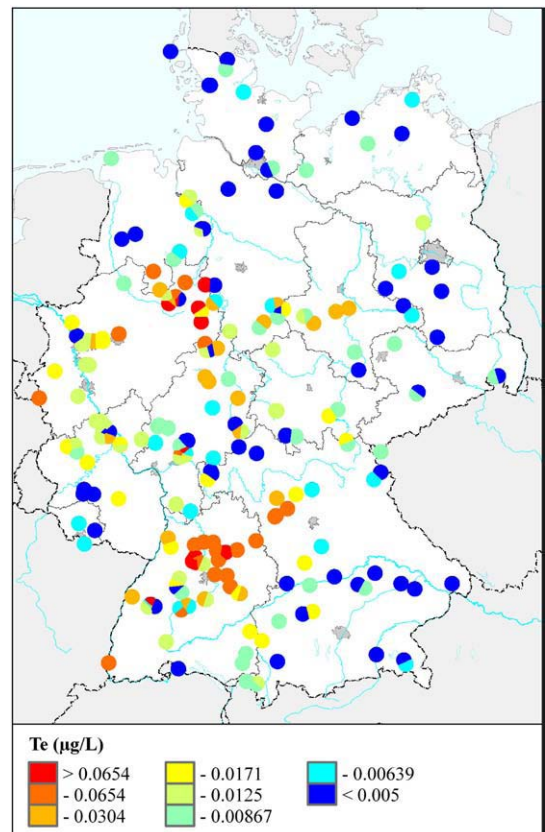


Fig. 28. Distribution of the median Te concentration in German bottled water.

Table 10

Principal component analysis results for the analyzed bottled water.

Factor	Source	Eigenvalue	Pct of var	Element and factor loading
1	Geogenic	8.514	12.2	Gd (0.947), Tb (0.938), Sm (0.933), Dy (0.888), Nd (0.885), Y (0.857), Pr (0.830), Ho (0.771), La (0.647), Er (0.593), Tm (0.415), Al (0.398), Ce (0.357), I (0.356)
2	Geogenic	6.917	9.88	Rb (0.897), Li (0.891), Cs (0.880), Ge (0.817), Na (0.771), Cl ⁻ (0.759), K (0.727), Br ⁻ (0.642), EC (0.599), B (0.548), Al (0.498), HCO ₃ ⁻ (0.4), F ⁻ (0.315)
3	Geogenic	4.552	6.5	SO ₄ ²⁻ (0.899), Ca (0.886), Sr (0.834), Te (0.826), EC (0.616), Mg (0.567), ta (0.508), Mo (0.364), B (0.325)
4	Geogenic	4.118	5.88	Lu (0.943), Yb (0.93), Tm (0.883), Er (0.777), Ho (0.575), Dy (0.404), Y (0.329)
5	Geogenic	3.141	4.49	HCO ₃ ⁻ (0.654), Mg (0.641), Ni (0.587), Sc (0.534), Nb (0.522), SiO ₂ (0.454), Ti (0.427), K (0.385), Mn (0.327)
6	Geogenic	2.612	3.73	Th (0.849), Ti (0.705), Fe (0.636), V (0.466), Cr (0.404), Ce (0.385), Pr (0.311)
7	Geogenic	2.603	3.72	Zr (0.937), Hf (0.932), Sc (0.423), HCO ₃ ⁻ (0.415)
8	Complex	2.129	3.04	Co (0.74), Cd (0.717), Ni (0.498), Zn (0.491)
9	Complex	2.078	2.97	Ba (0.950), Eu (0.905)
10	Anthropogenic	2.046	2.92	NO ₃ ⁻ (0.703), Se (0.694), Cu (0.649), U (0.545)
11	Geogenic	1.924	2.75	Be (0.825), Bi (0.734), SiO ₂ (0.33)
12	Geogenic	1.838	2.63	I (0.672), Zn (0.582), PO ₄ ³⁻ (0.562), Br ⁻ (0.397)
13	Complex	1.561	2.23	Sb (-0.671), Pb (0.654), Ag (0.322)
14	Complex	1.467	2.1	NO ₂ ⁻ (0.651), As (0.645), Mo (0.408)
15	Complex	1.437	2.05	NH ₄ ⁺ (0.611), Ag (-0.414), Ti (-0.363), Ga (0.321)
16	Geogenic	1.411	2.02	F ⁻ (0.664), Ce (0.38)
17	Geogenic	1.332	1.9	pH (0.696), SiO ₂ (-0.387)
18	Geogenic	1.314	1.88	Sn (0.662), W (0.629), Ga (0.383)

and the median is 4.30 µg Li/L (Birke et al., 2006). Both tap water and bottled water in Germany have median values that are 1.7 times higher than the median values for tap water and bottled water in other European countries (Table 3). The median for bottled water is 7 times higher than the value for surface water. Lithium concentration in bottled water varies between 0.51 µg/L and 2790 µg/L, in tap water from 0.27 to 74.9 µg/L. In the cumulative frequency diagrams for bottled water, tap water, and surface water (Fig. 5), the highest Li concentrations are clearly in the bottled water. The diagrams show a range of five orders of magnitude in the bottled water from Germany and three orders of magnitude for tap water.

In northern, northeastern, southeastern and southern Germany (south of the Danube River) Li concentrations in bottled water are generally >10 µg/L. These regions are also characterized by acid soils (Salminen, 2005; De Vos and Tarvainen, 2006). The highest values (>25 µg Li/L) are in bottled water from areas of slightly acid or neutral soils south of the Main River and west of the Fulda River (Upper Rhine/Main well region, Rhine/Eifel region and southwest Hesse; Figs. 1, 25 and 26). The same distribution pattern was found by Arnhold (1989) and Anke et al. (1991, 1995) in German tap water. The EU has not defined a water standard for Li. Thus, bottled water, tap water, and the various beverages may contribute very significantly to the Li intake and, therefore, must be taken into consideration when the Li balance is determined in humans. Lithium is a biologically active element. It is used in psychiatric therapy for bipolar disorder or manic-depressive disorder (Ebert, 2004), lithium as a drug does not lose its efficacy, and does not induce addiction or dependence. The

possible beneficial medical effects of concentrations in the range of 50–100 µg Li/L have recently been discussed in the literature (Schäfer, 2004; Ohgami et al., 2009).

Strontium is often enriched in calcium-sulfate water (up to 12 mg/L) and in brines (22–290 mg/L in Thuringia). Extremely high Sr concentrations are observed in formation water from oil wells (e.g., Bad Langensalza–1400 µg/L, Matthess, 1994). Sr concentrations between 66 and 2300 µg/L have been measured in mine water and groundwater in the Ore Mts. (Merkel and Sperling, 1998). Strontium is used in some industries (electronics, pyrotechnics, nuclear medicine, radiation measurement instruments, pharmacy and batteries).

Sr concentration can vary considerably in rivers, springs and wells. Concentrations of 0.19 to 3.2 mg Sr/L have been found in Canadian tap water (Skoryna, 1981); Flaten (1984) found only 1.5 to 570 µg Sr/L in Norwegian tap water samples. Our analyses of German bottled water yielded values between 0.006 and 26.9 mg Sr/L, confirming the concentration range of 0.036–24.5 mg/L obtained by Jaritz et al. (1997). The variation in Sr concentration in German bottled water spans five orders of magnitude, in tap water four orders of magnitude. The median Sr concentration (0.54 mg Sr/L) in the analyzed bottled water is 2.6 times higher than that for tap water, whereas the median for tap water is about the same as for surface water.

Strontium can be toxic when consumed in too high amounts, causing bone calcification disturbances (Glover, 1972). Acute Sr toxicity resembles a typical intestinal flu (Ebert, 2004). A Ca/Sr ratio <100 in drinking water in the Arkhangelsk region of Russia is said to have caused a high incidence of osteoporosis (increased fragility of bones) (Yudakin and Malov, 2008). The German bottled water samples had Ca/Sr ratios of 4.7 to 2830 (median: 154), the tap

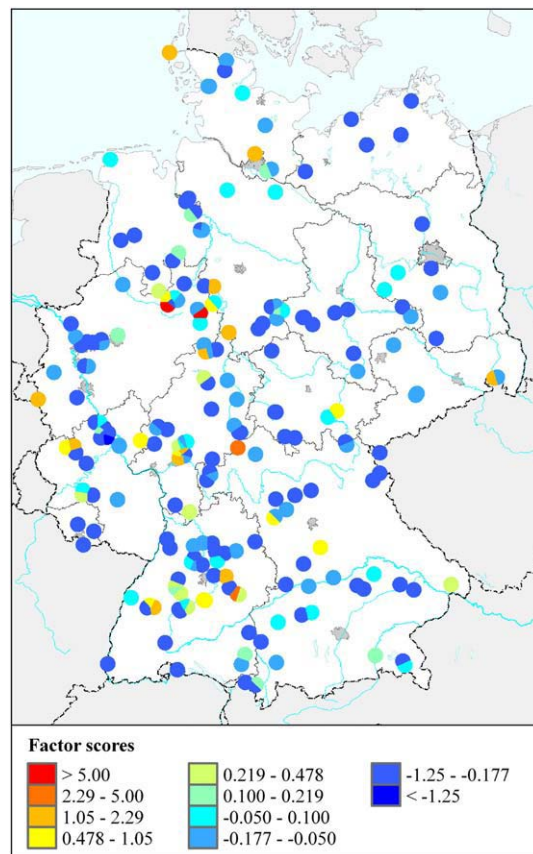


Fig. 29. Geochemical map of the factor scores for the factor 1: Gd–Tb–Sm–Dy–Nd–Y–Pr–Ho–La–Er–Tm–(Al–Ce) in German bottled water.

Table 11

Communalities of geochemical elements and parameters resulting from principal component analysis of the analyzed bottled water.

Parameter	Communality	Parameter	Communality
pH	0.5970	Nd	0.9496
EC	0.9299	Ni	0.6767
Ag	0.4433	Pb	0.5401
Al	0.5839	Pr	0.9384
As	0.5554	Rb	0.8830
B	0.6689	Sb	0.5659
Ba	0.9423	Sc	0.7829
Be	0.7345	Se	0.5780
Bi	0.5812	Sm	0.9544
Ca	0.8475	Sn	0.5383
Cd	0.6602	Sr	0.7208
Ce	0.6220	Ta	0.4040
Co	0.6285	Tb	0.9579
Cr	0.3139	Te	0.7081
Cs	0.8568	Th	0.8136
Cu	0.5570	Ti	0.5586
Dy	0.9695	Tl	0.5338
Er	0.9872	Tm	0.9814
Eu	0.9479	U	0.6659
Fe	0.5253	V	0.5841
Ga	0.6154	W	0.5664
Gd	0.9613	Y	0.9286
Ge	0.7775	Yb	0.9707
Hf	0.9444	Zn	0.6639
Ho	0.9517	Zr	0.9483
I	0.7704	Br ⁻	0.7074
K	0.7634	HCO ₃ ⁻	0.8818
La	0.8434	Cl ⁻	0.7707
Li	0.9072	F ⁻	0.6759
Lu	0.9599	NH ₄ ⁺	0.4101
Mg	0.8183	NO ₂ ⁻	0.6731
Mn	0.5340	NO ₃ ⁻	0.6166
Mo	0.5642	PO ₄ ³⁻	0.6385
Na	0.8567	SO ₄ ²⁻	0.8474
Nb	0.4764	SiO ₂	0.6651

water sample ratios were 24.3 to 1762 (median: 355). The lowest ratios occur in southern Germany, Weser Mts., and the Ruhr District.

There is no defined standard for Sr in water in Germany; Russia and Ukraine have a limit of 7 mg Sr/L for bottled and tap water, and Bosnia and Herzegovina has a limit of 2 mg Sr/L for tap water. Of the 908 analyzed German bottled water samples, 91 (10%) had a concentration above the Russian limit.

Three areas (Fig. 27) can be discerned with a high frequency of elevated, anomalous Sr concentrations (>3.31 mg/L): the Weser Mts., Swabia (Keuper/Liassic areas), western Frankonia (Keuper/Liassic area), and the central Black Forest. The anomalous Sr concentrations (13 mg/L) south of Steinensadt on the Upper Rhine (Fig. 27) were in a calcium-sulfate water. This is probably due to the thermal water occurrences of Tertiary brine that are known in this area (Carlé, 1975). The very high concentrations of 15.0–26.9 mg Sr/L in the Weser Mts. are from the gypsum or limestone Bunter, Muschelkalk, and Keuper. In this highly faulted area (intersection of NW–SE and NNW–SSE fault zones), saline water can ascend from the Zechstein (Upper Permian) or Bunter (Figs. 13 and 27). Most the bottled water with elevated Sr concentrations is of the calcium-sulfate type (Fig. 12). The ionic composition of the bottled water from eastern Westphalia indicates the influence of gypsum in the Keuper and rock salt in the Upper Bunter. The bottled water with elevated Sr concentrations in the area of Stuttgart in Baden-Württemberg is also of the calcium-sulfate type, again showing the influence of the gypsum in the Keuper. This is also the case for the bottled water from northwest of Nürnberg. The elevated Sr concentrations in the central Black Forest are from the highly fractured crystalline basement.

The areas of distribution of elevated and anomalous tellurium concentrations are nearly the same as those for strontium (Fig. 28).

This is probably due to Te enrichment in the same deep formation water as Sr. The chemical properties of Te resemble those of selenium and sulfur, although it is more metallic than these elements. Tellurium is used in iron and steel products, catalyzers, and electronic components. It forms water-soluble tellurites and tellurates. It often replaces sulfur in sulfides. It occurs in traces in coal. The most common signs of toxicity after occupational exposure to tellurium are a sharp garlic odor of the breath and a metallic taste in the mouth (Kobayashi, 2004).

The Te concentrations in bottled water varies between <0.005 µg/L and 0.21 µg/L, while in the tap water between <0.005 µg/L and 0.025 µg/L. The maximum Te concentration measured in surface water in Germany is 0.073 µg/L. Other authors have observed values between 0.00017 µg Te/L and 0.073 µg Te/L in surface water (Sugimura and Suzuki, 1981; Lee and Edmond, 1985), and between 0.00051 µg Te/L and 0.0033 µg Te/L in rain water (Andreae, 1984). The median value for German and European tap water is slightly higher than the median for European bottled water. In German bottled water the natural variation in Te concentration spans only two orders of magnitude.

No country has a standard for Te in tap water. Germany has a concentration limit of 100 µg Te/m³ for Te in dust, the Occupational Safety and Health Administration (OSHA) of the US has also set a permissible exposure of 100 µg Te/m³ for dust (Kobayashi, 2004).

The distribution pattern for sulfate in bottled water is nearly the same as for strontium and tellurium. The elevated and anomalous sulfate concentrations are also in the Keuper/Liassic areas of Swabia and Frankonia (Upper Rhine/Main well region) and in the Weser Mts. (Fig. 1). Sulfate-rich water results in most cases by the leaching of gypsum and anhydrite. Sulfate concentrations in the analyzed bottled water lie between 0.03 mg/L and 2210 mg/L, in tap water samples between <0.01 mg/L and 267 mg/L, and in German surface water

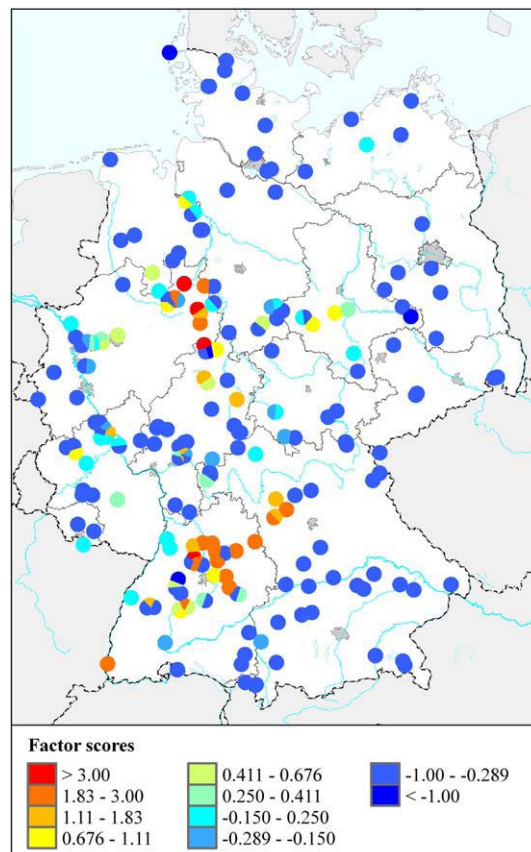


Fig. 30. Geochemical map of the factor scores for the factor 3: SO₄-Ca-Sr-Te-EC-Mg-Ta-(Mo-B) in German bottled water.

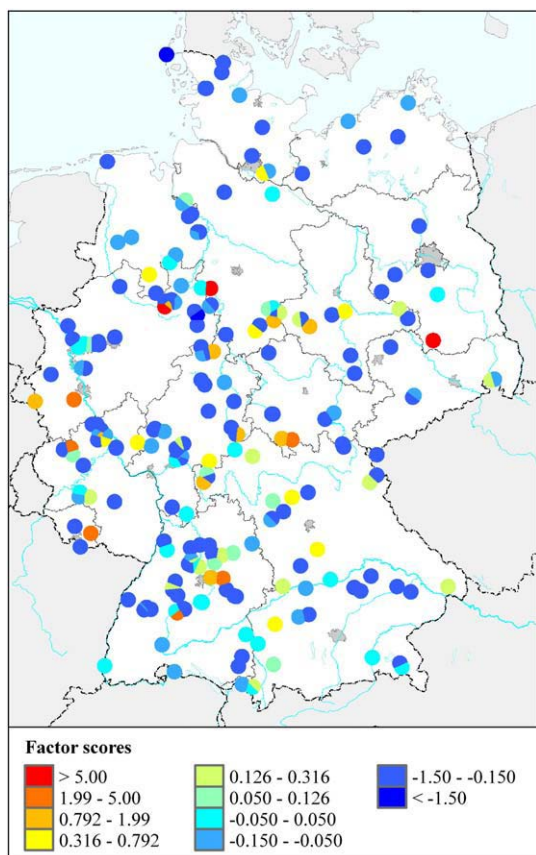


Fig. 31. Geochemical map of the factor scores for the factor 8: Co–Cd–Ni–Zn in German bottled water.

between 0.7 mg/L and 1500 mg/L. The highest median value was for German bottled water (57.3 mg SO_4^{2-} /L). The variation in sulfate concentration in bottled water spans six orders of magnitude.

For SO_4^{2-} the EU has defined a guideline value of 250 mg/L in drinking water (EU Directive, 1998/83/EC), while no limit value is defined for mineral water.

Sulfate has no nutritive value for humans. Concentrations above 1000 mg/L can have a laxative effect. Concentrations above 700 mg/L give the water a bitter taste. The action level for sulfate and its concentrations in bottle and tap water is discussed in Section 3.3.

3.5. Results of the principal component analysis (factor analysis)

A principal component analysis (R-mode) was carried out to investigate the correlation between the 70 measured inorganic parameters. Mercury was not included in the analysis because this element was not detected in the bottled water samples. The method (PCA) reveals the complex multivariate relationships among variables, that is not normally shown by simple correlation analysis. At the introductory stage of the interpretation of the German bottled water data, principal component analysis (factor analysis) was applied as an exploratory technique for getting an insight into the structure (composition, distribution, migration and different caused influences) of the 70 determined elements. The idea is to explore the various assemblages of the parameters and associations between them, the various patterns of areal distribution of factor scores, and then to use the results in geochemical interpretation of the element distribution in German bottled water. The requirement for normality was answered by logarithm transformation of the data. Values below detection limit were replaced by half of the detection limit values.

For the calculation the “Dimension Reduction” module of SPSS software package was used. The factors were extracted as principal components and then rotated according to the Varimax method. The criterion for factor extraction was an eigenvalue greater than 1. The extraction yielded eighteen factors, accounting for 72.8% of the total variance in the data. The factor loading values of the principal components are given in Table 10, together with the eigenvalues and percentage of variance. Classification of the factors permits the examination of the complex causes of element distributions and their influences on element enrichment and migration. The factors are named according to the various causes and geochemical aspects of the element loadings and their distribution patterns. They can be divided into several general causes: geogenic, anthropogenic and complex.

The general distribution patterns are discussed below only for a few selected factors. The results of the factor analysis of the data for German bottled water by and large show considerable similarity to the results for bottled water from other European countries and with the results for surface water in Germany and other European countries (Pirc et al., 2006; Birke et al., 2008).

Factor 1 is responsible for the largest part of the total variance in the data for both German and EU bottled water, as well as in the data for German surface water. It is characterized by high factor loading values for the rare earth elements (REE). Interestingly, the same factor 1 with high factor loading values for the REE + U was also obtained for whole blood and blood plasma in the human biomonitoring research of Dobler et al. (2007, see Table 4 in Birke et al., 2010-this issue). Factor 1 Gd–Tb–Sm–Dy–Nd–Y–Pr–Ho–La–Er–Tm–(Al–Ce–I) accounts for about 12% of the total variance within the data for German bottled water. In this factor Gd, Tb, Sm, Dy, Nd, Y, Pr, and Ho have very high factor loadings (>0.70), La and Er have high loadings (>0.5) and Tm, Al, and Ce have moderate loadings (>0.3). The factor 1 distribution for bottled water reflects the geological influence of the aquifers on the groundwater in the different regions (Weser Mts., around Stuttgart, in Hesse, around Aachen, and south of Fulda; Fig. 29). The high anomalous factor scores >1.0 are caused by the Triassic sediments and especially the Cenozoic volcanic rocks (Swabian Jura, Weser Mts., Eifel region). Saline water from the Zechstein or Bunter is present in highly fractured regions (e.g., in the Weser Mts.). The influence of the crystalline basement is probable only in the Black Forest region. The REE are very similar in geochemical behavior. A few of the REE had concentrations below the detection limits. The influence of these elements on the factor, however, is not important considering the high total number of loaded elements. The REE have the highest communalities (>0.90) in the calculated data (Table 11).

The similarity in the distribution patterns of strontium, tellurium, sulfate, and electrical conductivity (Section 3.4) is reflected in the distribution patterns of bottled water samples with high scores for factor 3 SO_4^{2-} –Ca–Sr–Te–EC–Mg–Ta–(Mo–B). This factor has very high factor loadings (>0.82) for SO_4^{2-} , Ca, Sr, and Te; high factor loadings (>0.5) for EC, Mg and Ta; and moderate loadings (>0.3) for B (Table 10). The elements with high factor loadings in factor 3 for bottle water are nearly the same as those with high factor loadings in factor 6 for surface water in Germany (Birke et al., 2008) and in factor 2 for surface water in Europe (Pirc et al., 2006). In surface water this factor is a result of geogenic and anthropogenic influences. The distribution of bottled water samples with high factor scores in factor 3 includes several of the same areas in the distribution of surface water with high factor scores in factor 6 (Weser Mts. and the Swabian Jura). There are high factor scores (>1.11) for bottled water from the well regions Weser Mts., Swabian Jura region, and the western part of the Frankonian Jura, which indicate gypsum and limestone sediments of the Bunter, Muschelkalk, Keuper. These geogenic influences can also be seen in the factors for surface water. The factor 3 scores are very low (<0) in all of the other regions. This factor explains 6.50% of the total variance (Table 10). The high factor loading value (0.62) for EC results from the high concentration of the major ions. Especially

calcium-sulfate water has a high factor 3 score (Figs. 12 and 30). The influence of deep saline water is also seen in the regional distribution of high factor 3 scores (e.g., brine ascending from the Zechstein along the fault along the north side of the Harz Mts.).

The distribution pattern of factor 10 NO_3^- –Se–Cu–U points mostly to anthropogenic influences (Table 10). The factors associated with uranium in German bottled water are discussed in Birke et al. (2010a, b-this issue) in this issue.

Factor 8 Co–Cd–Ni–Zn (Fig. 31) accounts for 3.04% of the total variance and is associated principally with chalcophile elements (Co, Cd, and Zn). The high Co, Cd and moderate Ni and Zn factor loadings suggest the influence of several causes. High values for this factor indicates the presence of certain types of rocks, old mining districts and dispersed mineralization and anthropogenic influences (e.g., old mining districts and smelting plants). In the results of the preliminary component analysis for German surface water (Birke et al., 2008) these elements divided into two factors Zn–Cd–(Tl) and Ni–Co–(Rb), which supports the assumption of several influences for the bottled water samples.

The elevated factor scores along the faults at the edge of the Harz Mts. (Fig. 31) indicate the influence of sulfidic vein mineralization and deep saline water (leachate from the Zechstein). Mineralization and anthropogenic influences (mining and smelting) are indicated by the elevated factor scores in the area of the Aachen-Stolberger coal mining district in the Lower Rhine/Maas region (Figs 1 and 31). Mineralization (e.g., nickeline and erythrite, as well as barite in the Kupferschiefer) can be the cause of the elevated factor scores observed in the Spessart region. The aquifer is in gneiss. Lithological influences are responsible for the anomalous factor scores in the Weser Mts. (Gipskeuper, Bunter) and the Swabian Jura (Muschelkalk, Bunter, as well as Keuper sandstone). Sulfide mineralization layers are also known in the Muschelkalk and Keuper (e.g., the galena layer in the Gipskeuper, Walther and Dill, 1995).

4. Conclusions

A wide range of concentrations was found for most of the 71 elements analyzed in the bottled water and tap water samples. For most elements the difference between lowest and highest measured concentration is three or four orders of magnitude. The smallest range was for pH (one order of magnitude), the largest range was for Cs (seven orders of magnitude). This result made it evident that little is known about the natural variation of element concentration in water from different sources with no apparent sources of pollution. Nearly half (43.3%) of the analyzed bottled water from Germany may be classified as having a “low mineral content”, about one-seventh (14.4%) as having a “high mineral content” (especially the water from the Upper Rhine/Main and the Rhine/Eifel regions).

Comparison of our results with the current German and European action levels for mineral and table water shows that 4.63% (42 samples) of all bottled water samples exceed the limits for one or more of the following elements: arsenic (9 samples), nitrate (1 sample), nitrite (11 samples), manganese (8 samples), nickel (1 sample) and barium (1 sample). Moreover, ten of the samples have uranium concentrations above $10 \mu\text{g/L}$, and 127 samples yielded $>2.0 \mu\text{g U/L}$.

The standard for fluoride in tap water (1.5 mg/L) was exceeded in 25 of the bottled water samples (3%). It is common medical knowledge that fluoride levels higher than 1.5 mg/L may cause dental fluorosis.

Water with a potassium concentration greater than 12 mg/L is not suitable for regular drinking because it may cause kidney stress and possibly kidney failure (Lau and Luk, 2002). Potassium concentrations in groundwater are commonly low, partly because of the high degree of stability of potassium-bearing aluminosilicate minerals. The

potassium concentration of bottled and tap water is significantly influenced by its geological origin. In Germany the K concentration in bottled and tap water ranges between 0.10 mg K/L and 92.5 mg K/L . The median value in bottled water is 3.30 mg K/L , and in tap water 2.15 mg K/L . Anke et al. (2003) observed an mean concentration of 12.0 mg K/L in tap water in Germany.

About 50% of German bottled water can be classified as “suitable for low sodium diets” ($<20 \text{ mg/L}$). Persons with hypertension are advised not to drink water with sodium concentration more than 20 mg/L (Allen et al., 1991; Ebert, 2004; Anke, 2004). Excessive sodium intake has long been known to cause certain types of heart and circulatory problems. The effect of blood pressure strongly depends on the anion: with chloride there is a very strong increase, with bicarbonate the effect can be a decrease in blood pressure. The WHO guideline value of 200 mg Na/L is exceeded by 120 of the bottled water samples (13%). The median for tap water is 11.4 mg Na/L (up to 204 mg Na/L), for bottled water 20.4 mg Na/L (up to 1260 mg Na/L).

Of the 908 analyzed bottled water samples, 295 samples fulfilled the requirements for being labeled as “suitable for the preparation of baby food”.

The bottled water samples could be classified into 23 different water types on the basis of the sum total of the cations and anions that contribute at least 20 meq-% to the ionic content. Most of the samples were of the calcium-bicarbonate type.

The comparison of element concentrations in the bottled water with the current German mineral water regulations shows that only 42 of the 908 bottled water samples do not pass the action levels. There are no action levels or guidelines for elements for which there is no known biological role or which are extremely toxic (e.g., Ag, Br, Mo, Cr (VI), and U). There is a need for recommendations of maximum values, and sometimes also for minimum values for essential toxic elements.

Mapping of the element concentrations in the bottled water samples reveals patterns of regional distribution uncovering sources of these concentrations, for example, lithology, e.g., dispersed mineralization, marine, anthropogenic. In coastal areas, groundwater can show a marine influence on Cl^- , Br^- , Na, and I concentrations. Some of the element associations in the bottled water point to the influence of the overlying soil, others indicate anthropogenic influences (such as old mining activity or industrial emissions) superimposed on geogenic influences. The distribution of most of the bottled water samples indicates a predominant lithological influence by Triassic sediments (Muschelkalk, Bunter, Gipskeuper) and crystalline basement (gneiss), as well as Zechstein salt beds. Factor analysis (principal component analysis) clarified the complex multivariate relationships among the elements and parameters. Most of the extracted factors with their high loading of element associations have geological sources.

The influence of the various bottle materials and colors was also tested. It was found that significant amounts of certain elements (e.g., Pb, Al, Zr, and La) can be leached from the glass bottles, and Sb can be leached from PET bottles. The data shows clearly that bottled water sold in PET bottles is contaminated by the toxic element antimony.

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