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Concentrations of inorganic elements in bottled waters on the Swedish market

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Abstract

This study presents the concentrations of about 50 metals and ions in 33 different brands of bottled waters on the Swedish market. Ten of the brands showed calcium (Ca) concentrations ≤10 mg L^{-1} and magnesium (Mg) levels <3 mg L^{-1}, implying very soft waters. Three of these waters had in addition low concentrations of sodium (Na; <7 mg L^{-1}), potassium (K; <3 mg L^{-1}) and bicarbonate (HCO_3; ≤31 mg L^{-1}). These brands were collected from barren districts. Nine of the brands were collected from limestone regions. They showed increased Ca-levels exceeding 50 mg L^{-1} with a maximum of 289 mg L^{-1}. Corresponding Mg-levels were also raised in two brands exceeding 90 mg L^{-1}. Two soft and carbonated waters were supplemented with Na_2CO_3 and NaCl, resulting in high concentrations of Na (644 and 648 mg L^{-1}) and chloride (Cl; 204 and 219 mg L^{-1}). Such waters may make a substantial contribution to the daily intake of NaCl in high water consumers. The storage of carbonated drinking water in aluminum (Al) cans increased the Al-concentration to about 70 μg L^{-1}. *Conclusion:* As there was a large variation in the material as regards concentrations of macro-elements such as Ca, Mg, Na, K and Cl. Supplementation with salts, e.g., Na_2CO_3, K_2CO_3 and NaCl, can lead to increased concentrations of Na, K and Cl, as well as decreased ratios of Ca/Na and larger ratios of Na/K. Water with high concentrations of e.g., Ca and Mg, may make a substantial contribution to the daily intake of these elements in high water consumers. Al cans are less suited for storage of carbonated waters, as the lowered pH-values may dissolve Al. The levels of potentially toxic metals in the studied brands were generally low.

Introduction

During the 18th and 19th centuries, health effects from drinking water that was taken from certain wells were discussed and tested among, e.g. groups of wealthy people. They spent some time now and then in so-called health resorts, drinking their special health-bringing water as well as bottled synthetic or imported water. Well water with elevated concentrations of carbonic acid, iron, sulfur and different kinds of salts, as well as water with radioactivity from uranium and nuclei in its decay chain, were regarded as health bringing by some groups. More recently, especially during the last decades of the 20th century, a growing interest has been focused on bottled water. Health effects of water intake have been discussed as well as the importance of maintaining the water balance, e.g. in connection with sports activities. In 10 years, from 1992 to 2001, the consumption of bottled water in Sweden increased from 92 million liters up to 161 million liters.

The water sources for bottled drinking water are usually bore-holes and they differ in content due to the composition of the bedrock of the well. Waters originating from limestone areas are rich in minerals, while waters from barren districts, where hard weathered gneiss and granite are dominant, have very low concentrations of e.g. calcium, magnesium and bicarbonate (Aastrup *et al.* 1995). If the water originates from an acid area, it may have decreased concentrations of essential metals such as calcium, chromium, selenium and potassium as well as increased concentrations of potentially toxic metals like cadmium, mercury, lead and aluminum (Rosborg *et al.* 2003a).

In Sweden, the National Swedish Food Administration (NSFA) controls and regulates the production and marketing of bottled waters. Before selling the product on the market, it must be analyzed by an accredited laboratory and judged as suitable. In addition, the unit for production and packing is inspected and the program for self-control is checked. The labeling of the product is restricted by rules and permission is given by the municipal environmental protection administration (NSFA 1989).

Guideline values regarding drinking water quality have been presented by WHO (1993, 1998). In Sweden, similar guideline values have been presented by NSFA in several regulations (NSFA 1989; NSFA 2001). To be labeled as a natural mineral water, the product must be free from chemicals and microbiological pollutants. The well water must show well defined and stable element concentrations. The production must also be stable from a geohydrological viewpoint. Also, the water should be bottled at the place where the spring is located (NSFA 1989).

Generally, the range of salt concentrations in natural mineral waters may vary considerably. In some bottled waters salts like $NaHCO_3$, $KHCO_3$, Na_2CO_3, K_2CO_3, NaCl and Na_2SO_4 have been supplemented. The NSFA is recommending consumers, especially children, to avoid high intakes of salt in food and drinking water. Children, aged 7 years or less, are recommended to avoid water with fluoride concentrations higher than 1.3 mg L^{-1}.

Bottled waters flavored with lemon, lime, etc. are not presented in this study, since the added substances mainly affect the concentration of total organic carbon (TOC) and the pH. Generally, these products have about the same concentrations of metals and ions as the original and unflavored waters.

The aim of the present study was to make a survey of the composition of minerals and elements in some of the most frequently occurring bottled waters on the Swedish market. The question was whether there would be a large variation between different brands and how the levels determined were related to standards presented by the NSFA, WHO and other organizations.

Materials and methods

Forty-eight different bottled waters found on the Swedish market were selected for this study for the determination of the concentrations of about 50 metals and ions. Most of the bottled waters were of Swedish origin, but some were collected from other European countries. One brand was taken from Africa. Only 33 of the waters are presented in this paper, since some of them were bottled from the same well, only differing by e.g. taste additives like lemon, which did not influence the metal concentrations of the water.

After thawing and adjusting the bottled water to room temperature, pH (Radiometer PHM 84, glass-electrode) and conductivity (Radiometer CMD92, 20 °C) were measured, with an accuracy of 0.01 for both parameters. The original samples as well as standards were acidified by adding nitric acid (HNO_3) to 1%. Aluminum (Al, 396.152 nm), calcium (Ca, 317.933 nm), copper (Cu, 324.754 nm), iron (Fe, 238.204 nm), potassium (K, 766.491 nm), magnesium (Mg, 279.079 nm), manganese (Mn, 257.610 nm), sodium (Na, 589.592 nm) and zinc (Zn, 213.856 nm) in the water samples were analyzed by ICP OES (Inductively coupled plasma optical emission spectroscopy; Perkin–Elmer, Optima, 3000 DV). The analyses of silver (Ag 107), arsenic (As 75), boron (B 10), barium (Ba 137), beryllium (Be 9), bismuth (Bi 209), bromine (Br 79), cadmium (Cd 111), cerium (Ce 140), cobalt (Co 59), chromium (Cr 52), cesium (Cs 133), mercury (Hg 202), iodine (I 127), lithium (Li 7), molybdenum (Mo 98), nickel (Ni 58), phosphorus (P 31), lead (Pb 208), rubidium (Rb 85), antimony (Sb 120), scandium (Sc 45), selenium (Se 82), silicon (Si 28), tin (Sn 120), strontium (Sr 88), titanium (Ti 48), uranium (U 238), vanadium (V 51), wolfram (W 184) and zirconium (Zr 90), which were down to the ng L^{-1}

range, were made by ICP-MS (inductively coupled plasma mass-spectrometry; Perkin–Elmer, ELAN-6000). Atomic spectroscopy standards from Perkin–Elmer, Spex, AccuStandard and Merck were used. The ICP OES instrument was calibrated using a mixed multi-component standard at three different concentrations within a factor of 50, and calibration was controlled with independent standards. The ICP-MS instrument was calibrated against three mixed standards. One was Merck's ICP multi-element standard VI, the others were prepared from single element standards. As quality control some of the elements were also analyzed using other isotopes. Irrespective of the isotope analyzed, the analysis gives the total concentration of the element, as the isotope ratios in the standards should correspond closely to the normal ratios in earth. Running standard concentrations were 10 μg L^{-1} for most elements, 1 μg L^{-1} for mercury and 100 μg L^{-1} for arsenic and boron. Rhodium was used as internal standard, added to all samples and standard solutions. The sample flow into the instrument was 1 ml min^{-1}. Plastic vessels were used. The tubes were rinsed in distilled water for 1 min between each analysis. Three replicate analyses were performed. Internal quality control with retest of standards was undertaken after every 20 analyses. If the deviation was more than 5% from previous analyses, all of these 20 samples were re-analyzed (Nihlgård, personal communication, 2002).

Ammonium-nitrogen (NH_4–N) and nitrate-nitrogen (NO_3–N) were analyzed using colorimetric methods on a FIA-instrument. Chloride (Cl), sulfate–sulfur (SO_4-S) and fluoride (F) were analyzed using ion chromatography, bicarbonate (HCO_3) with HCl titration or by total inorganic carbon (TIC) analysis and TOC on a Shimadzu TOC-500 instrument. All analyses were made at the Department of Plant Ecology, Lund University, whose laboratory has taken part in the ITM (Institute of Applied Environmental Research testing programe). The results have consistently been within ± 10% of the average values presented by the participating laboratories.

In this report the charges of elements and ions are not presented, but all elements in the bottled waters are considered to be present as ions. The concentrations of bismuth, cerium, dysprosium, erbium, europium, gallium, gadolinium, germanium, hafnium, holmium, lanthanum, lutetium, nobelium, neodymium and samarium were < 1 μg L^{-1}, and these elements are therefore not further commented on in this article. The concentration of HCO_3 was very unstable immediately after the bottle had been opened, especially if the bottled water was carbonated. Therefore, this concentration was calculated from the difference between the sum of specific ion conductivity for anions minus cations, and not separately analyzed.

Detection limits were set as three times the standard of the blanks, and the precision was calculated as the standard deviation of the lowest standard. The coefficient of variation was below 5%.

Results

Median values and ranges of elements and ions in the 33 bottled waters are presented in Table 1, as well as the detection limits and precision of the analyses. In Table 2, concentrations of elements and ions of special interest are shown for each brand. In Table 3, the NSFA and WHO guideline values for drinking water quality are presented.

pH

The pH-values ranged from 4.4 to 8.3, with a median of 5.8 (Table 1). The lowest values were detected in carbonated waters (No. 8, 11, 18, 21, 23, 24, 25, 30 and 33, Table 2). In some cases the pH-value presented on the label of the bottle was not in accordance with the analyzed value, but rather seemed to be the value observed in the raw water. Addition of carbon dioxide may depress the pH-value by up to two pH-units.

Soft bottled waters

The median concentrations of calcium (Ca) and magnesium (Mg) were 24 mg L^{-1} and 3.2 mg L^{-1}, respectively (Table 1). Ten of the brands analyzed showed Ca-values below or equal to 10 mg L^{-1} and Mg-levels below 3 mg L^{-1}, indicating very soft waters. In addition, three of these bottled waters (No. 4, 10 and 12, Table 2) also had low concentrations of sodium (Na; < 7 mg L^{-1}), potassium (K; < 3 mg L^{-1}) and bicarbonate (HCO_3; ≤31 mg L^{-1}). One of them (No. 10) came from a barren, but not acidified district in Norway,

Table 1. Median values, ranges, detection limits and precision of concentrations of elements and ions in 33 bottled waters on the Swedish market.

Variable	Median, mg L^{-1}	Range, mg L^{-1}	Detection limit, μg L^{-1}	Precision, μg L^{-1} (±)	Number of samples
pH	5.79 (no unit)	4.42–8.29			33
Conductivity	55,50 (ms M^{-1})	6.14–527			33
Na	24.7	0.98–648	5.0	10	33
K	3.23	0.54–268	6.0	24	33
Ca	23.8	2.47–289	6.0	12	33
Mg	3.23	0.37–96.6	5.0	10	33
Al	0.036	< det.lim.–0.10	0.3	0.6	33
NH_4–N	< det.lim.	< det.lim.–0.68	7.0	14	33
Cl	15.8	0.59–219	170	300	33
SO_4–S	4.33	0.95–174	100	200	33
NO_3–N	< det.lim.	< det.lim.–1.25	60	150	33
F	0.68	< det.lim.–3.05	190	190	33
Fe	0.002	< det.lim.–0.084	10	10	33
HCO_3	188	12–1743	600	1000	33
Si	4	0.4–15.8	15	150	33
Na/K	5.35	0.7–99.6			33
Ca/Mg	4.68	2.07–27.8			33
	μg/L^{-1}	μg/L^{-1}			
Ag	< det.lim.	< det.lim.–1.3	0.05	0.5	33
As	0.3	< det.lim.–13.0	1.0	4	33
B	15.9	< det.lim.–851	1	10	33
Ba	27.1	6.8–63.4	1	5	13
Be	0.02	< det.lim.–0.35	0.02	0.05	33
Br	51.6	10.8–335	14	30	33
Cd	0.01	< det.lim.–0.06	0.01	0.02	33
Co	0.06	0.01–0.60	0.01	0.02	33
Cr	3.42	< det.lim.–92.9	0.01	0.02	33
Cs	0.02	< det.lim.–32.5	0.002	0.006	33
Cu	1.53	< det.lim.–22.3	0.01	0.001	33
Hg	0.002	< det.lim.–0.434	0.02	0.04	33
I	79.6	< det.lim.–613	26	30	17
Li	3.59	0.19–237	0.09	0.2	33
Mn	1	< det.lim.–78.9	0.15	1.5	29
Mo	0.41	0.01–23.4	0.01	0.05	33
Ni	0.42	< det.lim.–7.52	0.01	0.1	33
P	16	< det.lim.–718	0.50	5.0	29
Pb	0.06	< det.lim.–2.34	0.001	0.01	33
Rb	1.89	0.07–49.3	0.002	0.004	33
Sb	0.32	0.01–0.80	0.005	0.025	16
Sc	1.71	0.40–8.54	0.03	0.015	16
Se	0.25	< det.lim.–3.11	0.06	0.06	33
Sn	< det.lim.	< det.lim.–1.02	0.04	0.2	20
Sr	63	19.6–2120	0.001	0.01	33
Ti	1.02	0.25–12.1	0.01	0.04	33
U	0.11	< det.lim.–72.0	0.003	0.015	33
V	0.39	< det.lim.–68.2	0.01	0.025	33

Table 1. Continued.

Variable	Median, ms M^{-1}	Range, mg L^{-1}	Detection limit, μg L^{-1}	Precision, $\mu g\ L^{-1}$ (±)	Number of samples
W	0.06	0.03–2.00	0.003	0.015	16
Zn	3.38	< det.lim.–331	0.01	0.1	33
Zr	0.18	0.02–5.25	0.01	0.05	16

and had pH 7.2. Another brand (No. 12) originated from a region in Africa where the geology was dominated by volcanic bedrock giving an increased pH (7.6), although the concentrations of elements such as Ca, Mg and HCO_3 were very low. In addition conductivity was low in these three waters, for all < 10 mS m^{-1} none of them was carbonated.

Hard bottled waters

The concentrations of Ca and Mg ranged from 2.5 to 289 mg L^{-1}, and from 0.4 to 97 mg L^{-1}, respectively, in this study (Table 1). Nine of the bottled waters had Ca concentrations exceeding 50 mg L^{-1}, with Mg-levels ranging from 3 to 97 mg L^{-1}. They were all from limestone areas.

One of the bottled waters from the latter group (No. 17, Table 2) showed increased concentrations of Ca (287 mg L^{-1}), Mg (97 mg L^{-1}), chromium (Cr), Na and HCO_3. Other elements with raised concentrations in this brand were aluminum (Al), arsenic (As), beryllium (Be), boron (B), lead (Pb), manganese (Mn), nickel (Ni), silica (Si), strontium (Sr) and sulfate–sulfur (SO_4-S). A second bottle (No. 11, Table 2) also showed increased concentrations of Ca (289 mg L^{-1}), Mg (93 mg L^{-1}), SO_4–S, Sr and Ti. This water was carbonated, giving a low pH of 5.0. Both these two waters had their origin in limestone springs.

Bottled waters with addition of salts

The concentration ranges of Na, K and Cl in our study were 1–648 mg L^{-1}, 0.5–268 mg L^{-1} and 0.6–219 mg L^{-1}, respectively (Table 1). Two soft and carbonated waters had been supplemented with CO_2, Na_2CO_3 and NaCl in order to improve the taste of the water (personal communication with the producer 2002). They showed increased concentrations of Na (644 and 648 mg L^{-1}; No. 22 and 28, Table 2) and Cl (204 and 219 mg L^{-1}), also resulting in raised conductivity (315 and 312 mS m^{-1}; median in the total material 56 mS m^{-1}). These two brands also had increased concentrations of HCO_3 and Cr, while the levels of the remaining elements and ions were below or at the same magnitude as the median values found in the total material. The concentrations of Ca and Mg were low in these two bottled waters, indicating very soft waters.

Element ratios

The median Na/K ratio in the total material was 5.4 (range 0.7–100, Table 1). Two bottled waters with increased concentrations of Na and K (No. 2 and 27, Table 2) had Na/K ratios < 1, while five other brands showed high Na/K ratios (54–100; No. 9, 19, 20, 22 and 28, Table 2).

The median ratio of Ca/Na in this study was 1.4 (range 0.01–12.5). Fifteen waters had ratios below 1, and six below 0.1. The latter consisted of very soft waters or waters supplemented with Na-salts. The median ratio of Ca/Mg was 4.7 (range 2.1–28, Table 1). In three brands the ratio exceeded 20.

Other elements

The Fe concentrations were very low in all brands, ranging from below the detection limit of 10 μg L^{-1} in 29 samples to 0.08 mg L^{-1} (median 0.002 mg L^{-1}, Table 1). The Mn concentrations were also very low (median 1 μg L^{-1}, range 0–79 μg L^{-1}). Only one brand (No. 17) exceeded the upper threshold limit value of 50 μg L^{-1}, recommended for domestic waters (NSFA 2001). The F concentrations ranged from below the detection limit of 190 μg L^{-1} to 3.1 mg L^{-1} in the bottled waters with a median of 0.68 mg L^{-1} (Table 1). Twenty waters showed concentrations below 0.8 mg L^{-1}, the concentration recommended for protection against caries (NSFA 1989). Three waters (No. 2, 17 and 20; concentrations 1.5–3.1 mg L^{-1}) exceeded the threshold limit value

Table 2. Concentrations of elements and ions of special interest in 33 bottled waters on the Swedish market.

Detection limit Nr	pH	Conductivity mS m^{-1}	SO_4-S, (0.1) mg L^{-1}	NO_3-N, (0.06) mg L^{-1}	Cl^-, (0.02) mg L^{-1}	F^-, (0.04) mg L^{-1}	HCO_3^-, (0.600) mg L^{-1}	Na, (0.005) mg L^{-1}	K, (0.006) mg L^{-1}	Ca, (0.006) mg L^{-1}	Mg, (0.005) mg L^{-1}	Na/K	Ca/Mg
1	7.16	19.8	2.3	0.14	15.7	< 0.04	85.4	11.7	2.4	16.3	7.88	4.88	2.07
2	5.86	173	8	0.18	30.8	1.53	939	216	232	23.8	2.63	0.93	9.05
3	5.42	83	5.6	< 0.06	18.7	1.03	438	112	96.1	15.1	6.01	1.17	2.51
4	6.18	8.3	5.1	1.2	4.7	< 0.04	12	1.98	2.64	7.78	2.51	0.75	3.10
5	5.05	66.3	2.5	< 0.06	36.7	0.7	275	88	56.3	4.58	1.82	1.56	2.52
6	7.76	24.6	4.3	< 0.06	9.3	0.25	122	7.44	2.46	41.5	4.16	3.03	9.98
7	7.27	49.5	4.1	0.69	6.8	0.12	305	6.51	1.22	79.9	23.4	5.34	3.41
8	4.92	41.4	12.2	< 0.06	20.2	1.07	165	86	5.05	2.91	1.13	17.0	2.58
9	5.53	128	6.1	0.7	167	1.34	390	218	3.14	28.9	3.94	69.4	7.34
10	7.23	6.1	1	0.01	0.6	< 0.04	31	0.98	0.54	10.3	0.37	1.81	27.8
11	4.98	175	174	< 0.06	27.3	< 0.04	69	23.3	4.06	289	92.5	5.74	3.12
12	7.64	7.7	2.6	0.32	2.2	0.11	26	6.98	1.42	5.3	1.77	4.91	2.99
13	7.92	21.9	3.85	0.11	11.5	0.17	104	8.25	0.89	36.9	2.89	9.29	12.8
14	5.24	54.7	8.8	0.13	31.8	0.93	276	42.9	5.5	54.9	9.72	7.80	5.65
15	5.55	95.5	3.1	< 0.06	31.3	0.74	546	127	53.9	32.3	13.9	2.35	2.32
16	6.56	34.1	2.3	< 0.06	8.9	0.06	188	5.24	3.15	65.7	4.22	1.66	15.6
17	5.95	242	145	< 0.06	35	1.63	1100	130	20.6	287	96.6	6.31	2.97
18	4.88	36.5	8.5	< 0.06	11.6	0.63	153	13.5	1.42	59.1	2.87	9.54	20.6
19	5.47	76.5	0.9	< 0.06	15.4	1.33	492	175	3.23	3.13	0.62	54.0	5.08
20	5.55	73.7	2.5	< 0.06	15.8	3.05	470	190	2.12	2.47	0.53	89.6	4.68
21	4.42	12.8	2.9	0.06	2.4	0.68	40	3.53	0.96	11.2	2.23	3.68	5.01
22	6.02	315	3.8	< 0.06	204	1.29	1480	644	6.46	19.7	3.09	99.6	6.38
23	4.94	36.1	18.3	< 0.06	23.8	0.74	96	18.7	1.43	48.4	2.38	13.0	20.3
24	4.89	38	14.8	0.99	4.7	1.22	159	11.4	3.97	49.9	9.38	2.88	5.32
25	4.99	53	14.6	< 0.06	36.7	1.26	165	25.9	6.98	60.5	6.87	3.71	8.80
26	7.5	55.5	13.4	0.71	26.4	0.11	183	24.7	4.31	78.8	19.3	5.73	4.09
27	5.79	179	7.3	1.25	84.3	1.32	854	188	268	23.8	6.83	0.70	3.48
28	6.01	312	3.6	< 0.06	219	1.24	1100	648	6.99	19.7	3.23	92.7	6.11
29	7.38	55.1	40.3	< 0.06	3.6	< 0.04	1470	8.08	6.03	90.6	19.4	1.34	4.67
30	4.59	171	3.04	0.84	13.7	0.24	1740	17.8	0.71	5.83	2.24	25.2	2.60
31	8.29	238	5.77	0.13	21.1	0.27	85	42.4	1.65	9.14	1.63	25.7	5.60
32	7.85	527	1.25	< 0.06	12.2	0.38	342	91.5	7.57	30.9	7.78	12.1	3.97
33	4.48	106	1.86	0.25	1.19	0.03	1430	4.88	1.14	6.85	2	4.28	3.43

Table 3. The National Swedish Food Agency regulation for bottled waters (NSFA 2001) and the WHO guideline values for drinking water quality (WHO 1996).

	NSFA	NSFA	WHO	WHO
	Unsuitable	Suitable with annotation	Guideline value	Guideline value
Conductivity		> 250 mS m^{-1}		
NH_4		> 0.50 μg L^{-1}		
Fe		> 0.2 mg L^{-1}		
Ca		> 100 mg L^{-1}		
Mg		> 30 mg L^{-1}		
Na		> 100 mg L^{-1}		
Cl		> 100 mg L^{-1}		
F	> 1.5 mg L^{-1}		1.5 mg L^{-1}	
Cd	> 5 μg L^{-1}		3 μg L^{-1}	
Cu	> 2 mg L^{-1}	> 0.20 mg L^{-1}	2 mg L^{-1}	
Cr	> 50 μg L^{-1}		50 μg L^{-1}	
Hg	> 1 μg L^{-1}		1 μg L^{-1}	
Ni	> 20 μg L^{-1}		20 μg L^{-1}	
NO_3	> 50 mg L^{-1}	> 20 mg L^{-1}	50 mg L^{-1}	
NO_2	> 0.50 mg L^{-1}	> 0.10 mg L^{-1}	3 mg L^{-1} (acute)	0.2 mg L^{-1} (chronic)
SO_4		> 100 mg L^{-1}		
pH	> 10.5	pH < 7; pH > 9.0; pH < 4.5 (in noncarbonated bottled w.)		
Se	> 10 μg L^{-1}		10 μg L^{-1}	
U			2 μg L^{-1}	

presented as unsuitable for children (1.5 mg L^{-1}, NSFA 2001). Al concentrations were usually very low in the bottled waters. Two waters of a similar brand differed considerably in Al concentrations (17 and 72 μg L^{-1}; No. 19 and 20). The second one was stored in an Al can, while the first one was kept in a plastic bottle. One bottled water (No. 24) showed a clearly increased concentration of uranium (72 μg L^{-1}) as compared to the other brands (median 0.1 μg L^{-1}). This water also had the highest or among the highest levels of Hg, Cd and Co in the total material.

Discussion

Bottled water probably represents a minor part of the daily intake of drinking water for most people. For some individuals, however, drinking a lot of a special brand of bottled water, this intake may be of interest from a chemical as well as from a nutritional point of view. In some countries the habit of drinking mineral water is widespread, e.g. in Italy, where approximately 90% of the population regularly consume bottled water (Costi *et al.* 1999). In the future this consumption can be foreseen to increase in most countries.

pH and HCO_3

The large range of pH values was mainly due to the addition of CO_2, which lowered the pH values. When pH of the water was below 5, it was with high probability carbonated. When a bottled water is opened for the first time, HCO_3^- turns into CO_2, which is emitted, and then pH rises, but very slowly. The determination of HCO_3^- was therefore considered of minor interest in carbonated waters. In natural waters, which are not carbonated, the concentration of HCO_3^- is dependant on the pH-value. At pH-levels below 5, all HCO_3^- have combined with H^+ to form H_2CO_3, and CO_2 may be emitted. At pH-values exceeding 8, most of the bicarbonate is in the form of CO_3^{2-}, while the concentration of HCO_3^- is highest at pH 7–8.

From the days of health visits to spas, bicarbonate has been known to neutralize acids and to relieve symptoms in subjects with indigestion, constipation, irritable colon syndrome and gastric ulcers (Grossi and Scalabrino 1997). During the reaction with acids in the stomach CO_2 is emitted, which increases the volume of the stomach, and may be pain relieving. A significant cholecystokinetic effect of mineral water as compared with tap water intake has been reported (Grossi *et al.* 1996).

Contemporary net-acid producing diets may cause a low-grade systemic metabolic acidosis in otherwise healthy adult subjects (Frassetto *et al.* 2001). The degree of acidosis increases with age due to the normally occurring age-related decrease in renal function. Neutralization of the diet net acid load by dietary supplements such as $KHCO_3$ can improve the calcium and phosphorus balances, reduce the bone resorption rate and improve the nitrogen balance, without the need of restricting dietary NaCl intake (Frassetto *et al.* 2001). Thus HCO_3 in bottled waters may have an impact on human health.

Hard versus soft waters

According to the Swedish Environmental Protection Agency (SEPA 1999) the range of Ca in natural Swedish ground water is normally from 1 to 100 mg L^{-1}. This variation of Ca concentrations obviously depended on the original well water and the composition of the bedrock. According to WHO (1996), a concentration of $CaCO_3$ above 200 mg L^{-1} (80 mg Ca L^{-1}), can result in calcium deposition in pipelines. Concentrations of Ca in water exceeding 100 mg L^{-1} are considered unsuitable for technical reasons by the National Swedish Food Agency (NSFA 2001). In our study, two of the 33 brands had Ca-levels by far exceeding this level (No. 11 and 17). One of them originated from Central Europe, where the limestone is more dolomitic with higher concentrations of Mg than in Sweden.

The range of Mg in Swedish ground waters is between 0.5 and 10 mg L^{-1} (SEPA 1999). In Sweden, the limestone is dominated by Ca, giving low concentrations of Mg as compared to dolomitic limestone. In our study, six brands showed Mg-levels exceeding 10 mg L^{-1} (Table 2). All were located in limestone areas. Two of these brands (No. 11 and 17) had concentrations higher than 90 mg L^{-1}, clearly exceeding the NSFA technical guideline value for Mg of 30 mg L^{-1} (NSFA 2001).

Both Ca and Mg in drinking water may affect the body Ca and Mg status in high consumers of water (Rubenowitz *et al.* 1998; Rosborg *et al.* 2003b). Several studies suggest that magnesium and calcium in drinking water are protective factors for death from cardiovascular diseases (Rylander *et al.* 1991), e.g. acute myocardial infarction (Rubenowitz *et al.* 1999; Rubenowitz *et al.* 2000). Similarly, a significant protective effect of calcium and magnesium intake from drinking water on the risk of cerebrovascular diseases has been reported (Sakamoto *et al.* 1997; Yang 1998a). In accordance, increased Ca concentrations in drinking water have shown a protective effect versus cognitive impairment in the elderly (Jacqmin *et al.* 1994).

A significant protective effect of Mg intake from drinking water on the risk of dying from diabetes mellitus has been reported in studies from e.g. Taiwan and Europe (Yang *et al.* 1999a; Zhao *et al.* 2001).

A significant negative relationship between drinking water hardness and rectal cancer mortality has been observed in a case–control study in Taiwan (Yang *et al.* 1999b). In a similar study an approximately 40% excess risk of mortality from esophageal cancer was found in relation to the use of soft water (Yang *et al.* 1999c). Also, magnesium intake from drinking water has shown a significant protective effect versus colon cancer mortality (Yang *et al.* 1998b), prostate cancer development (Yang *et al.* 2000a) and death from breast cancer (Yang *et al.* 2000b). In a Japanese study (Sakamoto *et al.* 1997), the mortality rate of stomach cancer correlated negatively to the Ca/Mg ratio of well water. A significantly higher rate of stomach cancer was observed in a district with a Ca/Mg ratio of 1.5 in well water. A main finding by the authors was relatively higher Mg levels as compared to Ca concentrations in drinking water. In our study, clearly higher Ca/Mg ratios were observed (median 4.7, range 2.1–27.8, Tables 1 and 2). In natural Swedish waters this ratio is normally from 1 to 10 (SEPA 1999).

A life-long regular daily calcium intake of highly bioavailable calcium in water may be of importance for maintaining the calcium balance and for improving the spinal bone mass, especially in post-menopausal women (Costi *et al.* 1999). A short-term clinical trial with calcium mineral water supplementation for one year has shown an increase of the bone mass density in post-menopausal women (Cepollaro *et al.* 1996).

The bioavailability of Ca in the GI-tract depends on the concentration of ionized Ca in the small intestine, which is influenced by the water and food composition and on the action of gastric and enteric-digestive enzymes (Nellans 1990). A higher total daily intake usually carries a higher total quantity of bioavailable calcium. Calcium intake through water may be favorable for subjects needing a diet rich in calcium, but poor in calories and lipids (Costi *et al.* 1999; Cepollaro *et al.* 1996). The RDI (Recommended Daily Intake) for Ca is 800 mg, Mg : 280 mg for women aged 31–60 years (NSFA 1997). Thus the contribution from bottled water, 2 Liter's consumption d^{-1}, ranges from $<1\%$ to 72%, $<1\%$ to 69% for women between 31 and 60 years old.

The uptake of trace elements like Ca and Hg from drinking water consumed between meals may be more efficient than if consumed in combination with food. Intake from water is usually in the form of ions, which may be readily absorbed from the GI-tract compared to organic and complex bound metals in food.

Addition of salt

A daily consumption of 1 L of the two bottled waters with the highest concentration of Na following salt supplementation (No. 22 and 28, Table 2) would contribute about one third of the recommended daily intake of Na in Sweden (2 g; NSFA 1997). An increased Na intake may lead to hypertension and amplify the effect of arterial pressure on both the left ventricle and the kidney (Du *et al.* 2002). Therefore, it is important to persuade salt, soft drink and food manufacturers to reduce the unnecessarily high salt content of some processed foods (MacGregor 2001).

In natural water the Na/K ratio is usually between 1 and 10 (SEPA 1999). In our study five brands showed ratios clearly exceeding these levels (ratio 54–100; No. 9, 19, 20, 22 and 28, Table 2). A significant positive correlation has been observed between the Na/K ratio and systolic as well as diastolic blood pressure (Xie *et al.* 2001; Liu *et al.* 2001; Njelekela *et al.* 2001). If a ratio of 1 is considered optimal, the achievement of that goal is estimated to reduce the systolic and diastolic blood pressures by 6 and 3 mm Hg, respectively, in a normotensive population (Xie *et al.* 2001).

Single elements

Aluminum

Al cans may increase the concentrations of Al, especially in carbonated waters, which was evident when comparing two waters of a similar brand (No. 19 and 20). In this case, the storage in an Al can, increased the Al concentration from 17 to 72 µg L^{-1}, as compared to storage in a plastic bottle. Accordingly, Al cans are less suited for storage of carbonated mineral water.

Copper, iron and selenium

The concentrations of copper and iron in the bottled waters were generally low, with median values of 1.5 and 2 µg L^{-1}, respectively. The highest levels observed were 22 and 84 µg L^{-1}, respectively (Table 1). These concentrations are far below the water guideline values presented by NSFA (2001); Cu: >2 mg L^{-1} – unsuitable; >0.2 mg L^{-1} – suitable with annotation; Fe: >0.2 mg L^{-1} – suitable with annotation, and WHO (1996); Cu: 2 mg L^{-1}. Also, the selenium concentrations in the material were low (median 0.3 μg L^{-1}; maximum 3.1 µg L^{-1}) as compared to the NSFA water guideline value of >10 μg L^{-1} (unsuitable; NSFA 2001).

Uranium

The uranium concentrations in the total material were generally low (median 0.1 µg L^{-1}). One of the brands, however, showed a considerably higher level (72 µg L^{-1}) than the others. This brand (No. 24) also showed the highest or among the highest concentrations of Hg, Cd and Co in the material. The daily intake of uranium in food and water varies from approximately 1–5 µg U d^{-1} in uncontaminated areas and up to 13–18 µg d^{-1} or higher in uranium mining regions (Taylor and Taylor 1997). In a recent study (Kurttio *et al.* 2002), uranium concentrations in drinking water and urine were measured in subjects who had used drilled wells for drinking water (median water concentration 28 µg L^{-1}; maximum level 1920 µg L^{-1}). The uranium exposure was found to be weakly associated with altered function of the proximal tubules of the kidney. As no clear threshold was found, the authors conclude that even low uranium levels in drinking water may cause nephrotoxic effects. A drinking water guideline value of 2–30 μg L^{-1}, was suggested.

Suggested future perspectives

Based on existing knowledge, and the fact that bottled water constitutes an increasing market in the world and may affect health conditions, we can see the need for more strict recommendations for element concentrations in water, not only for technical reasons. There is a need for recommendations of maximum values, and sometimes also for minimum values. For macro elements like Ca, Mg, Na and K this seems less complicated, as well as for certain micro elements, e.g. F and Cu, while many elements may be recommended to vary within their dominating natural ranges. For health recommendations and/or discussions about possible adverse health effects in high water consumers, the dose (drinking volume × concentration) must also be considered.

Conclusions

- A large variation in the concentrations of especially macro-elements such as Ca, Mg, Na, K and Cl was found in bottled waters on the Swedish market.
- The addition of salts like Na_2CO_3, K_2CO_3 and NaCl may cause increased concentrations of Na, K and Cl, as well as a raised Na/K ratio and a depressed Ca/Na ratio.
- Intake of bottled water with high concentrations of essential elements such as Ca and Mg, may contribute a substantial part of the daily intake of these metals in high water consumers.
- Al cans should be considered less suitable for the storage of carbonated waters, as the lowered pH values may dissolve Al into the water.
- The concentrations of heavy metals in the material were generally low. One of the brands, however, showed a U level that may affect the proximal tubules function of the kidney.
- It seems very likely that the variation in concentation of several important mineral elemtns in boiled water may have a long-term impact on human health.
- Extremely high concentrations of Na bottled waters can be harmful for high consumers.
- Ca from bottled waters can contribute to all from negligible to almost the whole Recommended Daily Intake of Ca: < 1–72% and Mg: < 1–69%, constumption: 2 Liter d^{-1}.

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