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Trace and ultratrace metals in bottled waters: Survey of sources worldwide and comparison with refillable metal bottles

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ABSTRACT

Bottled waters from diverse natural and industrial sources are becoming increasingly popular worldwide. Several potentially harmful trace metals (Ag, Be, Li, Ge, Sb, Sc, Te, Th, U) are not monitored regularly in such waters. As a consequence, there is extremely limited data on the abundance and potential health impacts of many potentially toxic trace elements. Containers used for the storage of bottled waters might also increase trace metal levels above threshold limits established for human consumption by the EPA or WHO. Applying strict clean room techniques and sector field ICP–MS, 23 elements were determined in 132 brands of bottled water from 28 countries. In addition, leaching experiments with high purity water and various popular metal bottles investigated the release of trace metals from these containers. The threshold limits for elements such as Al, Be, Mn and U in drinking water were clearly exceeded in some waters. Several bottled waters had Li concentrations in the low mg/L range, a level which is comparable to blood plasma levels of patients treated against manic depression with Li-containing drugs. The rate of release of trace metals from metal bottles assessed after 13 days was generally low, with one exception: Substantial amounts of both Sb and Tl were released from a commercially available pewter pocket flask, exceeding international guidelines 5- and 11-fold, respectively. Trace metal levels of most bottled waters are below guideline levels currently considered harmful for human health. The few exceptions that exist, however, clearly reveal that health concerns are likely to manifest through prolonged use of such waters. The investigated coated aluminium and stainless steel bottles are harmless with respect to leaching of trace metals into drinking water. Pocket flasks, in turn, should be selected with great care to avoid contamination of beverages with harmful amounts of potentially toxic trace metals such as Sb and Tl.

1. Introduction

Drinking water of good quality is essential for human health and development. Pollutants such as pesticides, fertilizers, bacteria, toxic metals and other potentially harmful—not yet identified—environmental contaminants, may deteriorate the quality of drinking water in many regions of the world.

With growing concern about the quality of municipal water, e.g. Pb and Cu contamination through the plumbing system (Gulson et al., 1994, 1997; Pizarro et al., 1999, 2001, 2007;

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Zietz et al., 2001, 2003), bottled waters are becoming increasingly popular worldwide. Italy ranks as the country with the greatest annual production (10 billion L/year) and consumption (151 L/per capita/year) (Versari et al., 2002). While tap water intended for human consumption is controlled regularly for an extensive array of potential contaminants by certified authorities, bottled waters undergo less comprehensive testing, and less frequently. Moreover, the legal guidelines established to regulate the quality of tap water generally do not apply to bottled waters. The potential risks from exposure to potentially harmful contaminants from drinking bottled water, therefore, are rather difficult to assess.

In addition to the uncertain chemical composition of natural spring waters from diverse geological terrains, recent studies revealed that most bottled waters are contaminated with either antimony (Sb) or lead (Pb) leaching from polyethylene terephthalate (PET) and glass bottles, respectively (Shotyk et al., 2006; Shotyk and Krachler, 2007a,b). Although the measured concentrations of Sb and Pb due to leaching from the containers are generally well below the drinking water guidelines, the concentrations increase with duration of storage. By far most bottled waters are sold in PET containers with antimony trioxide employed as the catalyst in the manufacture of this polymer.

With the growing awareness of the environmental impacts of water bottling and transportation, reusable water bottles are becoming increasingly popular. One of the more popular brands in this category is aluminium but with a proprietary, non-toxic liner. A second type of popular bottle is simply made of stainless steel. We know of no published studies of trace metal contamination as a result of leaching from such containers.

Applying clean lab techniques that have been developed for the reliable determination of trace elements in Arctic ice and snow, the major goals of this study include the quantitative evaluation of trace and ultra-trace metals in bottled waters from diverse sources and regions. Specifically we have measured 23 trace elements in 132 brands of bottled water from 28 countries. The results clearly show that there is legitimate cause for concern regarding some trace elements in some of the brands of bottled water. In addition, leaching experiments in clean lab conditions using high purity water documented the release of trace elements from the reusable bottles. All obtained values are compared to international standards for drinking water and, whenever these threshold limits are exceeded, potential health concerns are further discussed.

2. Materials and methods

2.1. Bottles waters

One hundred and thirty-two brands of bottled water were purchased in Australia, Belgium, Brazil, Canada, Czech Republic, Denmark, Dominican Republic, England, Finland, France, Germany, Hong Kong, Iceland, Israel, Italy, Japan, Kenya, Mexico, The Netherlands, Peru, Poland, Slovenia, Spain, Sweden, Switzerland, Trinidad, the U.S., and Yugoslavia. All waters were bottled in plastic (mainly PET) unless otherwise stated.

The reusable bottles included two brands of stainless steel bottles and one brand of aluminium bottle with proprietary internal coating. Three bottles of each brand was used in the experiments. In addition, one stainless steel and one pewter pocket hip flask were also tested. Although pewter in the past was a Sn–Pb alloy, the pewter hip flask was bought new (2007) and consists of a Cu–Sb alloy. These metal bottles were cleaned thoroughly using a detergent, followed by extensive rinsing with high purity water. All bottles were subsequently filled with high-purity water under clean room conditions and left in a U.S. class 100 clean bench for 13 days. The same high purity water was filled into three acid-cleaned 15 mL polyethylene (PE) tubes (Falcon, Becton Dickinson) and leached for the same period to serve as a control sample.

2.2. Laboratories and instrumentation

Clean lab procedures developed earlier for the reliable analysis of Arctic snow and ice, were applied throughout this study (Krachler et al., 2005a). All sample handling and the preparation of all standards were performed in clean rooms under laminar flow clean air benches of at least class 100 to minimize the potential risk of contamination. All PFA vials in contact with the samples were thoroughly cleaned using HNO_3 baths of increasing purity.

All ICP–MS measurements were carried out using an Element 2 ICP–SMS (Thermo Fisher Scientific, Bremen, Germany) equipped with a guard electrode to eliminate secondary discharge in the plasma and to enhance overall sensitivity. A micro volume autosampler (ASX 100, Cetac Technologies, Omaha, NE, USA) and a sample introduction kit comprising a microflow PFA nebulizer connected either to a PEEK micro cyclone spray chamber or a tandem spray chamber arrangement and a sapphire injector tube were employed for the quantification of trace elements in the water samples. The low flow PFA nebulizer was always operated in the self-aspirating mode to reduce the risk of contamination by the peristaltic pump tubing. Further details of the entire analytical protocol can be found elsewhere (Krachler et al., 2005a,b).

2.3. Trace element analysis

For ICP–MS analysis, all bottled waters were diluted 1+4 with 1% HNO_3 to reduce the high concentrations of alkaline and earth alkaline elements, to avoid clogging of the cones, to add the internal standard element, i.e. Rh, and to reduce the amount of dissolved CO_2 in the samples, thus avoiding deterioration of the ICP–SMS measurements (Shotyk et al., 2006; Shotyk and Krachler, 2007a,b).

A 2-mL aliquot from the water leached in each of the metal bottles for 13 days was subsampled, acidified to 1% HNO_3 using doubly subboiled nitric acid and analysed as is (Krachler et al., 2005a).

2.4. Reagents and standards

For the preparation of all solutions, high-purity water (18.2 MΩ cm) from a MilliQ-Element system designed for inorganic ultra trace analysis (Millipore, Milford, MA, USA) was used. Nitric acid (65%, analytical-reagent grade, Merck, Darmstadt, Germany) was further purified by double sub-boiling distillation (MLS GmbH, Leutkirch, Germany). Both the water purification

system and the sub-boiling distillation unit were operated in clean rooms.

Calibration solutions of all investigated elements were prepared daily by appropriate dilution of 10 mg l^{-1} and 1000 mg l^{-1} stock standard solutions (Merck) with 0.14 mol l^{-1} high-purity nitric acid.

2.5. *Quality control*

The riverine water reference material SLRS-4 from the National Research Council Canada, Ottawa, Canada was analyzed at regular intervals during sample analysis to assess the accuracy of the trace element analyses of the investigated water samples. For most elements considered in this study, certified concentrations in this reference material are available. The experimental concentrations determined in this study agreed well with these certified values (Krachler et al., 2005a).

3. Results

3.1. *Bottled waters*

The summary statistics of the elements determined in the 132 brands of bottled water from 28 countries are detailed in Table 1 together with corresponding guidelines issued by the World Health Organisation (WHO, 2004) and the U.S. Environmental Protection Agency (EPA, 2003).

For several elements a concentration range of only a few hundred (Al, Cd, Cr, Cu, Pb, Sc, and Te) to a few thousand (Co, Fe, Mo, Sb, and Tl) times was established. Minimum and maximum concentrations of all other elements considered in this survey varied between ~10^4 and ~10^6 times (Table 1). By far the greatest range in concentrations was found for Be.

Among the major element cations, Ca, Mg, and Sr varied between ~15 000 times between minimum and maximum concentrations, whereas Na showed a spread of ~50 000 times.

While the maximum concentrations of most elements were well below existing guideline values, concentrations of Al, Be, Mn, and U in several bottled waters exceeded these threshold limits (Table 1). It should be noted, that to date, no guideline values exist for other potential harmful elements that have been determined in this study such as Ge, Li, Te and Th.

3.2. *Metal bottles*

A summary of the concentrations of 16 selected elements from the leaching experiments is given in Table 2.

In general, all elemental concentrations are far below any threshold levels reported for drinking water except for three

Table 1 – Summary statistics of trace (μg/L) and major (mg/L) element data in 132 brands of bottled water from 28 countries

Element	Min	Max	Median	Spread	Guidelines WHO[a]	EPA[b]
Major elements (mg/L)						
Ca	0.03	508	62.8	16,500		
Mg	0.007	96.1	13.4	14,200		
Na	0.03	1370	9.17	51,100		
Sr	0.001	10.7	0.17	17,400		
Trace elements (μg/L)						
Ag	0.0004	2.20	0.002	5200		100
Al	0.19	108	1.60	560		50–200
Ba	0.02	557	21.0	32,000	700	2000
Be	0.00004	31.0	0.005	801,000		4
Cd	0.0006	0.265	0.008	470	3	5
Co	0.0009	2.99	0.024	3370		1300
Cr	0.006	1.72	0.082	307	50	
Cu	0.025	19.0	0.17	770	2000	1000
Fe	0.070	104	0.75	1480		300
Ge	<0.001	119	0.015	119,000		
Li	0.057	5460	4.80	96,200		
Mn	0.025	310	0.15	125,000	400	50
Mo	0.006	12.4	0.30	2090	70	
Pb*	<0.001	0.76	0.009	760	10	15
Rb	0.005	840	0.87	162,000		
Sb#	0.001	2.57	0.33	1850	20	6
Sc	0.0005	0.36	0.002	690		
Te	0.0006	0.18	0.004	280		
Tl	0.00004	0.30	0.002	7840		2
Th	0.00002	0.26	0.0002	11,550		
U	0.0002	27.5	0.23	147,700	15	30
V	0.0006	93.1	0.126	164,700		
Zn	0.043	442	0.64	10,270		5000

*This study does not include glass bottles which may leach Pb (Shotyk and Krachler, 2007b).
#Natural value perhaps 1% of this value, due to leaching of Sb from PET containers (Shotyk and Krachler, 2007a).
[a] Refers to drinking water.
[b] Refers to drinking and ground water.

Table 2 – Concentrations (mean ± standard deviation, ng/L) of selected trace elements in high purity water leaching in various containers for 13 days (N = 3, except for pocket flasks 1+2 where N = 1)

Element	Control [a]	Aluminium	Stainless steel A	Stainless steel B	Pocket pewter	Pocket stainless
Ag	0.6±0.0	0.7±0.1	2.0±0.1	1.7±0.2	182	53
As	4.1±0.9	4.2±0.1	9.4±0.9	17.1±9.5	16.9	48.2
Ba	6.7±2.5	92±56	1380±205	1500±590	4000	17,700
Cd	0.1±0.0	0.4±0.1	6.2±2.0	3.1±1.3	89	248
Co	0.1±0.0	2.5±1.4	131±39	40±9	145	917
Cr	0.6±0.1	1.2±0.9	1440±190	880±210	49	3420
Cu	0.7±0.4	6.1±2.3	35±4	194±190	51,400	12,670
Fe [b]	0.07±0.01	0.11±0.03	80.9±1.5	30.4±18.9	0.40	555
Mn	0.7±0.3	37±24	1340±70	5070±430	2000	14,170
Pb	1.8±0.9	4.5±2.4	8.3±4.1	24±8	1140	120
Rb	0.5±0.2	12±8	5.8±1.0	15±3	15	78
Sb	0.3±0.1	3.0±2.7	6.2±0.7	34±6	24,350	5000
Sr [b]	7.4±1.8	87±60	250±67	438±83	1750	9100
Tl	0.01±0.00	0.5±0.3	0.2±0.0	1.6±1.2	22,000	8.2
V	0.2±0.0	2.2±1.3	10.3±2.0	71±38	0.8	20
Zn [b]	0.01±0.01	2.4±2.4	11.5±2.8	8.7±2.6	176	271

[a] High purity water in PE tubes.
[b] Concentrations in μg/L.

elements. The antimony concentrations in both pocket flasks (24.4 μg/L and 5.0 μg/L) are either at the upper limit set by the European Commission (EC) or largely exceed the EC (5 μg/L) and EPA (6 μg/L) guideline levels (Table 2). The EPA guideline level of 300 μg/L for iron is exceeded by the stainless steel pocket flask (555 μg/L) by a factor of nearly two. Of considerably greater concern, however, is the fact that the Tl concentration in the pewter pocket flask (22 μg/L) exceeds the EPA maximum contaminant level for drinking water (2 μg/L) by more than an order of magnitude.

The aluminium bottle released the least of the trace elements, while much higher concentrations were found in the stainless steel bottles. The two brands of stainless steel bottles show consistent differences which must reflect small differences in the qualities of the steel used (Table 2).

4. Discussion

Several elements considered in this study have been already determined in some bottled waters (Allen et al., 1989; Misund et al., 1999; Rosborg et al., 2005; Fiket et al., 2007). In contrast to these earlier studies, however, the clean room procedures developed for analyzing Arctic ice and snow in our lab and applied here, allow the reliable determination of these elements well below the part per trillion (ng/L) concentration range. As such, actual concentration values rather than values<LOD (limit of detection), are reported for almost all elements in Table 1. Specifically, for elements whose median concentrations are <10 ng/L (Ag, Be, Cd, Pb, Sc, Te, Th, Tl), we present the first robust data set. Trace elements such as Cu and Zn which are relatively abundant, not extremely toxic, and have been determined in other studies are not discussed in detail, but the corresponding concentration data is reported for the sake of completeness.

In addition, the present investigation includes a worldwide survey (28 countries) of trace element concentrations of bottled waters (132 brands) and thus is not limited to a specific geographical region. Therefore the data presented here provides an estimate of the range in concentrations of selected trace elements in bottled waters around the globe.

In the following we focus on these elements for which only limited or no data are available or whose maximum concentrations in bottled waters was found to exceed guideline levels set by WHO or EPA, respectively.

Beryllium: By far the largest spread between lowest and highest concentrations (~10^6) was found for Be (median: 5 ng/L). Both the lowest and the highest Be concentration (0.04 ng/L and 31 μg/L in bottled waters from Hongkong and France, respectively) are beyond the range of values reported previously (Allen et al., 1989; Misund et al., 1999; Rosborg et al., 2005). While the median Be concentration of all bottled waters (5 ng/L) is far below the guideline value set by EPA (2003), one of each bottled waters from France (31 μg/L), Germany (8.1 μg/L) and Yugoslavia (11 μg/L) exceeded the EPA threshold level of 4 μg/L. Applying the much stricter Russian guideline level of 0.2 μg/L (Kirjukhin et al., 1993), however, only two additional bottled waters exceed this limit. Most tap waters around the world have <0.1 μg/L Be (Vaessen and Szteke, 2000), while certain geological settings might increase groundwater Be levels in Norway up to 6.6 μg/L (Frengstad et al., 2000). Beryllium concentrations in rainfall and UK rivers are on the order of 0.05 μg/L, while potential leaching of Be from the bedrock increase Be in groundwaters by approximately 2–3 times (Neal, 2003). Anomalous and short-lived Be concentrations of up to 29 μg/L in river water was linked to drought conditions and sewage/industrially related discharges (Neal, 2003). It is important to note that aquatic organism such as fish are negatively impacted by Be levels higher than approximately 1 μg/L (Neal, 2003).

According to the EPA (2003) elevated Be concentrations in groundwaters potentially reflect exposure to various contamination sources such as discharges from metal refineries, coal-burning factories, electrical, aerospace, and defence industries. Regular consumption of such water might lead to intestinal lesions (EPA, 2003). In fact, Be is listed as a Class A EPA carcinogen and one of the most toxic elements in the

periodic table (Taylot et al., 2003). As Be is related to Mg, an essential element for human nutrition, it can mimic Mg and displace it from certain key enzymes which then malfunction (Emsley, 2001). Given the available data, it is not clear whether the elevated Be concentrations are natural and a reflection of the geology of the source areas, or anthropogenic and a result of contamination due to local impacts (metallurgy, aerospace, defence industries).

Germanium: Similar to actual Be concentrations, the range of Ge concentrations (~120000 times) in the investigated bottled waters exceeds that of previous investigations (Misund et al., 1999). While most waters contained far less than 1 μg/L Ge, bottled waters from France (12 μg/L), Germany (3.0 μg/L), Slovenia (1.7 μg/L), Yugoslavia (6.6 μg/L) and four out of the eleven tested Japanese waters (1.1 μg/L, 5.5 μg/L, 5.8 μg/L, 8.9 μg/L) had distinctly higher Ge concentrations. Germanium concentrations in the Japanese waters may include a contribution from leaching of Ge from the PET bottles: Japanese PET production employs Ti as a catalyst which requires Ge to adjust the colour; up to 80 mg/kg of Ge may be found in such PET bottles (Thiele, 2006). In contrast, the other bottled waters with elevated Ge concentrations are either from natural (geological) or anthropogenic contributions in the source area.

So far, no guideline levels for Ge in drinking water exist, and its health impacts are under debate (Emsley, 2001). No biological role of Ge has been established yet, although it acts to stimulate the metabolism (Emsley, 2001). Almost three decades ago claims began that Ge could be beneficial to health, although this has never been demonstrated scientifically. Since 1989 the sale of expensive organic Ge food supplements is forbidden in the UK, while still being considered to be a helpful micro-nutrient in the USA (Emsley, 2001).

Lithium: Lithium concentrations in the investigated waters varied over five orders of magnitude, reflecting the geology of the source region (Table 1). The highest concentration of 5.5 mg/L Li was found in a bottled water from France that also contained the highest Be concentration of all investigated waters. The bottled waters containing the greatest Be concentrations (in excess of the EPA threshold level of 4 μg/L Be) also had the highest Li concentrations (Germany (1.4 mg/L), Yugoslavia (1.3 mg/L) pointing to a natural source of both elements. Although no guideline level for Li in drinking water exists, it is worth mentioning that the Li blood plasma level of patients treated with Li-containing drugs against manic depression is adjusted to 3.5 to 8 mg/L (Emsley, 2001). A blood plasma level of 10 mg/L is considered as mild Li poisoning, while levels exceeding 20 mg/L may cause death. While similar maximum Li concentrations of 5.1 mg/L (Allen et al., 1989), 3.1 mg/L (Misund et al., 1999) and 3.2 mg/L (Fiket et al., 2007) have been determined in bottled waters, a Li value of as high as 8.71 mg/L has been reported for a spring in the Baden–Baden area, Germany (LaMoreaux and Tanner, 2001). Regular consumption of such waters might increase the body Li burden to levels of concern for health. As a consequence, such a Li intake exceeds the lower level of the therapeutic dose range (300–2700 mg Li/day) recommended when treating depressive bipolar affective disorders (Linakis and Eisenmesser, 2001). It is important to stress that a narrow margin exists between the therapeutic effects of Li and adverse effects caused by excess Li and that individuals being treated with Li could risk overdose when drinking such waters (Dabeka et al., 2002).

Manganese: Even though the Mn median value of 0.15 μg/L is far below the EPA guideline value of 50 μg/L, four bottled waters from Germany (two with 93 μg/L, 290 μg/L 310 μg/L) and one from Slovenia (240 μg/L) distinctly exceeded this concentration (Table 1). Although generally considered an aesthetic parameter because high levels of Mn (and also Fe) cause an undesirable taste and odour to the water, Mn may also cause neurotoxic effects and hyperactive behaviours (Bouchard et al., 2007; Dabeka et al., 2002), especially in infants. Therefore, for safety reasons, the Canadian Paediatric Society does not recommend bottled water for infant consumption (Joint Working Group, 1998).

Scandium: The Sc concentrations in all investigated bottled waters are rather constant. They vary between 0.5 ng/L and 360 ng/L and are reported here only because no such data exists in the entire literature. Scandium has no known biological role and is considered not toxic, therefore it can serve as a useful reference element against which others may be compared. Although there have been suggestions that some of its compounds might be carcinogenic, there are no commercial uses of this element and global production amounts to only 45 kg/a (Emsley, 2001).

Silver: Even though Ag concentrations varied ~55000 times, the maximum value of 2.2 μg/L in the investigated bottled waters is far below the health-based guideline value for silver (100 μg/L). Silver concentrations higher than 5 μg/L are only occasionally found in ground water, surface water or drinking water (Misund et al., 1999; WHO, 2004). Levels in drinking water treated with Ag for disinfection may be above 50 μg/L (WHO, 2004). Where Ag salts are used to maintain the bacterial quality of drinking water, levels of up to 100 μg/L can be tolerated without risk to health (WHO, 2004).

The only obvious sign of Ag overload is argyria, a condition in which skin and hair are heavily discoloured by silver in the tissues. Daily consumption of drinking water containing high levels of Ag (up to 100 μg/L) gives a total dose over 70 years of half the human NOAEL (No Observed Adverse Effect Level) of 10 g and can be tolerated without risk to health (WHO, 2004).

Tellurium: The spread of Te concentrations (280-fold) was the smallest observed among all elements investigated (Table 1). The highest Te concentration found in the bottled waters is 0.18 μg/L and is unlikely to be of any health concern. The element has no known biological function and concentrations are only reported here for the sake of completeness.

Thorium: The median Th concentration (0.2 ng/L) is the lowest of all the elements studied (Table 1). Even though Th concentrations did not exceed 0.26 μg/L (bottled water from Kenya), the concentration differences among all bottled waters exceeded four orders of magnitude. A survey of 56 bottled waters across Europe (Misund et al., 1999) reported a median Th concentration of 0.031 μg/L (minimum 0.001 μg/L, maximum 2.06 μg/L) which is ca. 150× greater than the median reported here. Reliable data on Th concentrations in bottled water are scarce, mainly because the element could not be detected in many previous studies due to the extremely low concentrations found in uncontaminated waters.

The extremely low LOD (0.003 ng/L) of our ICP–SMS approach allows the assessment of the release of Th from

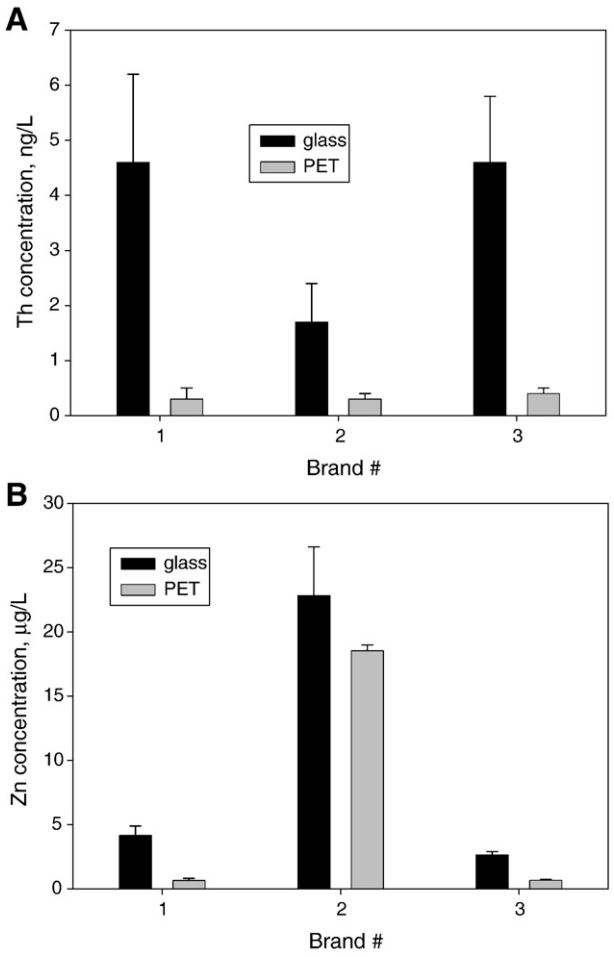

Fig. 1 – Comparison of Th (A) and Zn (B) concentrations in three brands of bottled water from Germany bottled in glass and PET containers after a storage period of 6 months at room temperature. Average and standard deviations of displayed concentrations reflect data from six individual bottles each. Note the extremely low Th concentrations (<0.5 ng/L) in all three brands of water bottled in PET and ~10-times higher concentrations in corresponding glass bottles.

glass bottles (Fig. 1A). While the three randomly selected brands of German water bottled in PET had Th levels <0.5 ng/L, ~10-times greater Th concentrations were found in the corresponding glass bottles after a storage period of six months at room temperature (Fig. 1A). The leaching of Th from the glass bottles, however, is so limited, that health concerns are unlikely to occur. However, this finding raises the question of the validity of trace metal measurements in bottled waters which do not consider the possible importance of leaching from the containers, such as that of Misund et al. (1999).

There is no biological role for Th and it is radioactive in all of its forms. As Th compounds are very insoluble, 99.98% of the ingested Th passes through the body unabsorbed. Among the 0.02% which is absorbed, three-quarters deposits in the skeleton and is likely to increase the risk of cancer (Emsley, 2001).

Uranium: Minimum and maximum concentrations of U varied ~150 000-times in the investigated bottled waters yielding a median of 0.23 µg/L. While the majority of waters possessed U concentrations below the present WHO (WHO, 2004) threshold limit of 15 µg/L, one bottled water from Finland (27.5 µg/L) exceeds this value and one water from Spain (15.1 µg/L) reaches this value. It should be noted, however, that the WHO guideline limit of 15 µg/L is a provisional value, as there is evidence of a hazard, but the available information on health effects are limited. A guideline value of 2 µg/L was recommended by WHO in 1998 (WHO, 1998). A Croatian study reported maximum U concentrations of 1.53 µg/L (Fiket et al., 2007) in bottled water, while a survey of 56 European bottled waters revealed a maximum value of 9.45 µg/L (Misund et al., 1999). In a German study U concentrations as high as 10.6 µg/L were reported (Schnug et al., 2005). The highest U concentration (72 µg/L), however, was reported from a survey of bottled waters available on the Swedish market (Rosborg et al., 2005).

Drinking water U concentrations of up to 14 mg/L have been reported in granitic bedrock near Helsinki, Finland (Asikainen and Kahlos, 1979). In Scandinavia, in general, the lithogenic setting is characterized by an abundance of uranium bearing minerals, the chemical weathering of which leads to highly elevated U concentrations in groundwater (Frengstad et al., 2000).

Even though the radiation hazard of U generally overrides other toxicity considerations, U compounds are chemically poisonous and may cause irreversible kidney damage and increased risk of cancer (Emsley, 2001; Auvinen et al., 2002; EPA, 2003). Although there exists no hard evidence for acute health risks of U in bottled water, the coincidence of increasing consumption of bottled waters and with increased numbers of kidney cancers attracts attention (Schnug et al., 2005). A recent study strongly suggested that uranium is an endocrine-disrupting chemical and populations exposed to environmental uranium (also through drinking water with U below the EPA guideline limit of 30 µg/L) should be followed for increased risk of fertility problems and reproductive cancers (Raymond-Whish et al., 2007).

Influence of bottle material of trace element levels: The Sb values in bottled waters reported here are predominantly caused by leaching of the element from the PET bottles and do not reflect the natural abundance of Sb in the source waters (Shotyk et al., 2006; Shotyk and Krachler, 2007a). Based on our extensive Sb measurements in groundwater samples from artesian flows in a calcareous terrain, the natural abundance of Sb in such waters is on the order of 2 ng/L (Shotyk et al., 2005), i.e. more than two orders of magnitude lower than the mean value reported here. In previous studies of trace metals in bottled waters (Misund et al., 1999; Dabeka et al., 2002; Rosborg et al., 2005; Fiket et al., 2007), no consideration was given of the possible importance of the bottles themselves. Given the extremely low abundance of many trace elements in natural waters, this factor must be duly considered.

Leaching of Pb from glass bottles into bottled water has been documented previously (Shotyk and Krachler, 2007b). As no glass bottles were considered as part of this study, the Pb data in Table 1 are valid, i.e. there is no leaching of Pb from PET. Other studies have reported far higher Pb concentrations in bottled water (Pip, 2000) than observed here but these

results are questionable for a number of reasons which are listed elsewhere (Shotyk and Krachler, 2007b). The median value shown here, in turn, is comparable to the "natural" abundance of Pb which we have reported for groundwater samples from artesian flows in a calcareous terrain (Shotyk and Krachler, 2007b).

As mentioned above glass bottles leach Pb, Th (Fig. 1A) but also Zn (Fig. 1B). Even though the rate of release of these trace metals is low and do not necessarily possess a health concern, this effect has to be considered for a sound understanding of "natural" levels of these elements in uncontaminated waters, when bottled waters are employed as "samples" (Misund et al., 1999; Dabeka et al., 2002; Rosborg et al., 2005; Fiket et al., 2007).

4.1. *Metal bottles*

Among the metal bottles investigated, the specially coated aluminium bottle showed the least leaching over 13 days (Table 2). Much higher trace metal concentrations were found in the water filled into the stainless steel bottles. The two brands of stainless steel bottles revealed a considerably different leaching behaviour, with distinctly higher concentrations of Co, Cr and Fe in the Brand A bottles and considerably higher concentrations of As, Mn, Pb and Sb in the Brand B bottles (Table 2). These different trace metal leaching rates indicate different sources, quality and/or manufacturing of the raw materials employed. It is important to note, however, that all trace metal concentrations determined in both the aluminium and stainless steel bottles are far below any threshold levels and therefore are of no health concern with respect to trace metals leaching into drinking water.

Although there is clearly some leaching of potentially toxic trace elements from each brand of stainless steel bottle, these data should be put into perspective. First, it is important to emphasize that the concentrations of the most toxic of these elements (e.g. Cd, Pb, Tl), even after 13 days of leaching by deionized water, are then still comparable to the median concentrations found in the bottled waters (c.f. Tables 1 and 2). Second, most users of these bottles will probably rinse the bottle and change the water daily, thus the leaching time during normal use will be considerably less. Third, users of these bottles will generally be filling them with tap water which, on the one hand is less corrosive than deionized water; at the same time, as this water is exposed to a number of metals and alloys in the municipal water supply system, will contain higher "background" concentrations of most of these metals.

In contrast to the bottles referred to above, high purity water leached much higher amounts of trace metals from both pocket flasks (Table 2). Besides the high Fe concentration of 555 μg/L in the stainless steel pocket flask—exceeding the EPA guideline of 300 μg/L—the Sb concentration in both flasks (5 μg/L and 24.4 μg/L) are at or above actual threshold levels. The elevated Sb concentration, found in the pewter flask (an alloy of Cu and Sb) was not surprising, but the elevated Sb concentrations in the stainless steel flask was unexpected. By far most critical is the extremely high thallium concentration of 22 μg/L in the water of the pewter pocket flask. Not only the threshold value was exceeded 11-fold, but thallium is very toxic: It is a known insidious poison because it mimics the essential element potassium by resembling it in size and ionic charge (Emsley, 2001). The elevated Sb and Tl values of this pocket flask are certainly a health concern to individuals using such containers regularly. The leaching study was carried out with high purity water, but the lower pH of alcoholic beverages such as wine (pH ~ 3–4) or whisky (pH ~ 4–5) and the abundance of organic ligands might even accelerate the release of these two but also other metals from such pocket flasks.

5. Conclusions

This study demonstrates the tremendous variability of trace metal concentrations in 132 brands of bottled waters worldwide providing a robust data set of the concentration ranges of 23 trace elements. While the majority of elemental concentration levels found in bottled waters are below national and international guideline values, a few exceptions (Al, Be, Mn, U) exist, representing 15 brands from nine countries. Other trace elements such as Li, for example, are not yet regulated by threshold limits. Possible regulation of this element should perhaps be considered because some bottled waters had Li concentrations in the low mg/L range which is comparable to blood plasma levels of patients treated with Li-containing drugs against manic depression.

It is important to note, however, that several trace elements considered here such as Be, Li, Ge, Th, U, etc. are also not monitored regularly by municipal water suppliers. In other words, the consumer cannot make a decision on the use of bottled water or tap water with respect to the Be or Li levels in the water, for example, because this data is usually not available.

Even though substantial differences in the release of trace elements from metal containers to the bottled water are evident, both coated aluminium and stainless steel bottles release elements at rates which can be considered negligible for the customer. Pocket flasks, in turn, should be considered with great caution, because they might contaminate beverages with substantial amounts of Sb (from stainless steel) or Sb and Tl (from pewter), to the extent that they quickly exceed present guideline levels for drinking water.

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