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Lead in Bottled Waters: Contamination from Glass and Comparison with Pristine Groundwater

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Using clean lab methods and protocols developed for measuring lead (Pb) in polar snow and ice, we report the abundance of Pb in 125 brands of bottled water from 28 countries. Comparison of six samples of each of three brands of water available in both glass and polyethyelene terephthalate (PET(E)) showed that the waters bottled in glass contained approximately 57, 30, and 26 times more Pb due to leaching from the containers. Excluding the bottled waters in glass, the median Pb concentration in all bottled waters was found to be 8.5 ng/L (n = 185), with a range from <1 to 761 ng/L Pb. Our study includes 25 brands of bottled water from Canada, and the median Pb concentration in these samples was 15.9 ng/L (n = 25), with a range from 2.1 to 268 ng/L. For comparison with the bottled waters, pristine groundwater from six artesian flows in southern Ontario, Canada, where some of the bottled waters originate, yielded a median concentration of 5.1 ng/L Pb (n = 18). The median Pb concentrations reported here for bottled waters from Canada are 32–588 times less than those presented in recently published studies. In fact, all of the waters tested were well below the maximum allowable concentration established by the EU, Health Canada, and the WHO for Pb in drinking water (10 μg/L).

Introduction

Lead (Pb) is a potentially toxic trace metal whose geochemical cycle has been profoundly affected by human activities. The environmental geochemistry of Pb has probably stimulated more scientific interest than all other metallic elements combined (*1*). Pioneering studies of Pb in polar snow and ice (*2*, *3*) not only provided unambiguous evidence of global atmospheric Pb contamination but helped to develop clean lab methods and procedures that allowed Pb to be measured reliably in the nanogram per liter concentration range. Using these analytical methodologies, concentrations of total dissolved Pb as low as 15 ng/L were reported in remote streamwaters of the Sierra Nevada watershed (*4*) that established, probably for the first time, reliable information about the natural abundance of Pb in freshwaters. More recently, measurements of water samples from Lake Superior reported Pb in the range of 0.3–8 ng/L (*5*). Any studies of Pb in pristine natural waters, therefore, require detection limits in the nanogram per liter concentration range. Measuring Pb reliably at these concentrations requires not only tremendous analytical sensitivity, but extreme care must be taken to avoid sample contamination (*6*–*10*).

Given the ongoing interest in human Pb exposure from food and beverages, and the dramatic recent increase in popularity of bottled waters, several recent studies have reported Pb concentrations in waters being sold commercially. In her study of 40 brands of domestic and imported bottled waters purchased in Canada, Pip (*11*) reported a median Pb concentration of 5 μg/L; this value is 50% of the maximum allowable concentration (MAC) established by the EU, Health Canada, and the WHO for Pb in drinking water (10 μg/L). In fact, in three of the brands studied, the Pb concentration exceeded the MAC for drinking water. In another study of bottled water from Canada, Dabeka et al. (*12*) measured Pb concentrations in bottled mineral waters (n = 42), spring waters (n = 102), distilled waters (n = 25), soda waters (n = 19), and tap waters (n = 11). In each category, however, the reported median Pb concentration was 0.27 μg/L, which is below the stated limit of detection (0.34 μg/L). Compounding the uncertainty created by the gap between the median concentration and the detection limit (*12*), this reported median concentration is more than a factor of 10 less than that reported earlier by Pip (*11*). In contrast to these studies, a study of 56 brands of bottled water in Europe found Pb concentrations ranging from <0.002 to 0.51 μg/L, with a median concentration of 0.01 μg/L (i.e., 10 ng/L (*13*)). Given (i) the proximity of the median Pb concentration reported by Pip (*11*) to the MAC, (ii) the discrepancy between the median concentrations of Pb reported by Pip (*11*) versus those by Dabeka et al. (*12*), and (iii) the extremely low abundance of Pb in pristine natural waters (*4*, *5*), a closer look at Pb in bottled waters is warranted.

Following our recent study of the natural abundance of antimony (Sb) in pristine groundwaters from southern Ontario, Canada (*14*), it became clear that waters bottled in polyethylene terephthalate (PET(E)) containers are contaminated with Sb leaching from the bottles (*15*). The extent of Sb contamination of waters bottled in PET(E) increases with duration of storage (*16*). Given the occurrence of extremely low concentrations of Pb in some natural waters, any study of Pb in bottled waters must also consider the possibility of contamination from the containers.

Experimental Procedures

Bottled Waters. One hundred and twenty-five 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, Spain, Trinidad, the U.S., and Yugoslavia. Twenty-five of the brands were purchased in Canada and include both natural waters as well as bottled tap water. With respect to the bottled tap water, these products are sold commercially by drinks manufacturers, after treatment by reverse osmosis and deionization. The bottled waters from Europe were all natural waters. All bottled waters had been purchased commercially from retail outlets except for the natural water from Canada bottled in polypropylene (PP); this water was provided by an airline. Three of the brands from Germany were purchased both in glass bottles as well as in PET(E).

Pristine Groundwaters. Water samples were collected in triplicate from natural artesian flows near Elmvale, Ontario (44°35′00″ N, 79°51′57.0″ W) in Springwater and Tiny Townships, Ontario, Canada (Figure S1A, Supporting Information). Eight flows were sampled on April 12 and 13, 2006,

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along a transect of approximately 20 km, from Wyevale to Anten Mills (Figure S1B, Supporting Information). Wearing appropriate clean lab clothing and employing polyethylene gloves, samples were collected directly into acid-cleaned, 100 mL low density polyethylene (LDPE) bottles to which high purity HNO_3 (100 μL) had already been added. This acid is produced in-house, purified twice by sub-boiling distillation, and has an average Pb concentration of 800 pg/L. Addition of 100 μL of this acid to 100 mL of water from these artesian flows is sufficient to reduce the pH to 1.7, which is sufficient to stabilize the trace metals until the samples could be measured (*14*). The contribution of Pb to the sample from this acid is approximately 0.8 pg/L. To minimize the risks of contamination, none of the water samples were filtered. Water samples were collected in triplicate, each packed into three ziplock plastic bags and kept refrigerated until they could be transported to the laboratory in Germany for analyses. For transport, they were placed into an insulated plastic box containing freezer packs and shipped airfreight; the samples were still cool when they arrived at the lab.

All of the flows run continuously. At six of the flows, the water runs only through steel pipes, and no pumps or valves are employed in the delivery system. In contrast, at two of the sites, the water flows continuously but could only be sampled from faucets. A time series undertaken at one of these sites in July of 2005 showed that the first sample contained elevated concentrations of Pb (5 μg/L) as well as Cu, Zn, and Sb, presumably because of the leaching of metals from the brass tap. Allowing the water to run for 120 min yielded Pb concentrations ≤20 ng/L. However, the Pb/Sc ratio of the water samples collected from the two flows employing faucets containing brass valves was approximately 5–10 times greater than the average Pb/Sc of the sites without faucets (1.9 ± 1.2, n = 18). We assume, therefore, that the samples from these two sites were contaminated with trace amounts of Pb leaching from the brass, despite the flushing time employed, and these samples are not considered further.

Household Tap Water from a Faucet versus PET(E) Bottles. A natural artesian flow between Bammental and Heidelberg, in Germany, was sampled on May 30, 2006, using the procedures described previously for pristine groundwaters from Canada. On the same day, tap water was sampled in triplicate from a household in Bammental, after allowing the faucet to run for 60 min. Tap water from this same village had been bottled commercially in PET(E) in December of 2005. Three bottles of the tap water in PET(E) were measured along with the other bottled waters, as described previously.

Analytical Procedures. For Pb analyses, comparable analytical procedures and clean room techniques that have been previously developed for the reliable determination of Pb in polar ice and water samples were applied in this study (*17–20*). To this end, clean benches of U.S. class 100 and a sector field inductively coupled plasma mass spectrometer (ICP-SMS, Element2, Thermo Scientific, Bremen, Germany), operated under clean room conditions, were used throughout. Samples were fed into the mass spectrometer via a microvolume autosampler (ASX 100, Cetac Technologies, Omaha, NE), a low volume PFA nebulizer (Elemental Scientific Inc., Omaha, NE) pumped at ~100 μL/min, a tandem spray chamber arrangement (*20*), a sapphire injector tube, and Ni cones. The mass spectrometer was operated in the low resolution mode monitoring ^{103}Rh and ^{208}Pb, in addition to a suite of other elements. Bottled waters were diluted 1+4 with 1% high purity HNO_3 to reduce the high concentrations of alkali and earth alkaline elements, to avoid clogging of the cones, and to reduce the amount of dissolved CO_2 in the samples, thus avoiding deterioration of the ICP-SMS measurements (*16*). For the analysis of ice samples and pristine groundwaters (*17–19*), the Ar dimer measured at m/z 80 in the medium resolution mode ($m/\Delta m$ 4000) was used as an internal standard element to correct for instrumental drifts. Here, however, Rh was employed for the same purpose, at a concentration of 1 μg/L. The detection limit for Pb (1 ng/L) allowed the reliable quantification of this element in all but two samples out of 185. To ensure the quality of the obtained results, a riverine water reference material (SLRS-4, National Research Council Canada) was analyzed at regular intervals. The experimental value of 88 ± 5 ng/L (n = 25) was in excellent agreement with the certified Pb concentration of 86 ± 7 ng/L.

TABLE 1. Comparison of Pb Concentrations (ng/L) in Three Brands of Water from Germany, Bottled in Glass[a] versus PET(E)

brand	glass (May 2006)	PET(E) (November 2005)	ratio glass/PET(E)
A	227 ± 111 (n = 6)	4.0 ± 1.6 (n = 5)	56.8
B	261 ± 43 (n = 6)	8.7 ± 3.3 (n = 6)	30
C	154 ± 66 (n = 6)	5.9 ± 3.7 (n = 6)	26.1

[a] Lead concentrations were measured in nine of the glass bottles using nondestructive XRF spectrometry (*26*). Except for one bottle with 3 mg/kg Pb, the bottles contained 114–267 mg/kg Pb.

Results and Discussion

Contamination of Bottled Waters with Pb Leaching from Glass. Three brands of bottled water from Germany yielded significantly higher concentrations of Pb when purchased in glass bottles versus PET(E) (Table 1). The water samples had first been measured as soon as possible after purchase, in November of 2005, then again after storage for 6 months at room temperature in a class 10 000 clean laboratory, in May of 2006. Comparison of the Pb concentrations before and after 6 months of storage shows that the Pb concentrations have increased markedly (Figure 1). These results show clearly that the Pb concentrations in waters bottled in glass do not reflect the natural abundance of Pb in the source waters. Moreover, these findings suggest that Pb concentrations in bottled waters stored in glass are primarily a reflection of the duration of storage in those containers. In one previous study of Pb in bottled waters, eight of 40 brands tested were in glass bottles (*12*), but the possible importance of contamination from the container was not considered. Despite the leaching phenomenon that has been documented here, the greatest Pb concentration found in water from a glass bottle (417 ng/L) is well below the maximum allowable concentration for Pb in drinking water set by the EU, Health Canada, and the WHO (10 μg/L).

Abundance of Pb in Bottled Waters. Analyses of replicate bottles of 18 brands of water from Australia, Belgium, Brazil, France, Germany, Israel, Mexico, and the U.S. showed that the Pb concentration measurements were generally reproducible (Figure 2A). Using the average concentration obtained from each of these brands combined with the measurements of Pb in single bottles of other brands, the median abundance of Pb in 98 brands of bottled waters from 26 countries was found to be 8.4 ng/L (n = 98), with a range from <1 to 761 ng/L Pb (Figure 2B). The Pb concentrations shown in Figure 2 all correspond to waters purchased in plastic bottles, and we assume that leaching from the containers themselves is very low. The median Pb concentration reported here is comparable to that reported by Misund et al. (*13*) for 56 brands of European bottled waters (10 ng/L).

To allow a comparison of the bottled waters with pristine groundwaters, the abundance of Pb in 25 brands of bottled water from Canada is shown separately (Figure 3). Analyses of replicate bottles of five brands of water from Canada showed that the Pb concentration measurements were generally reproducible (Figure 3A). Using the average con-

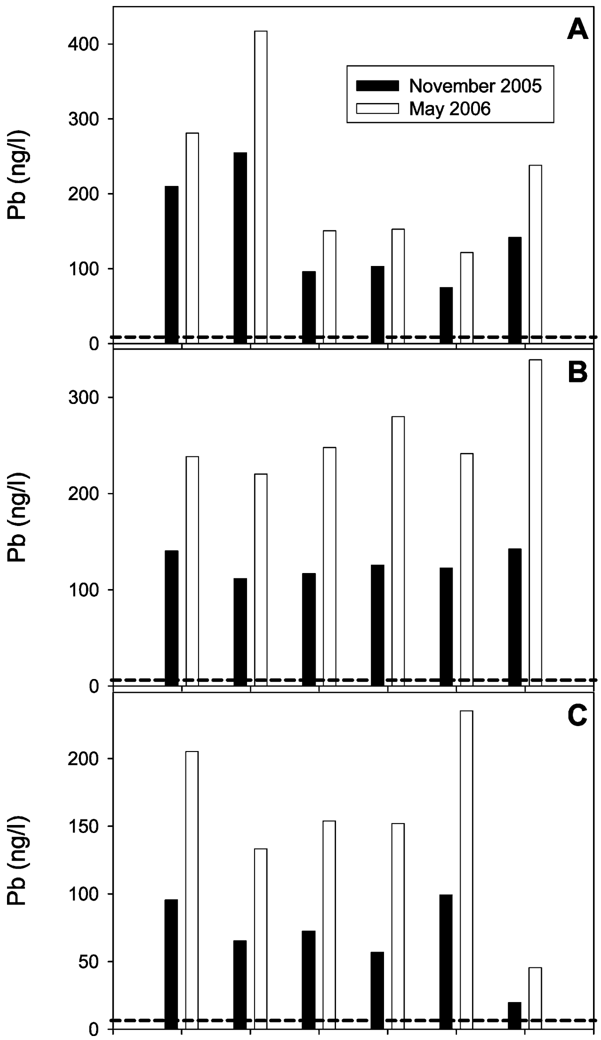

FIGURE 1. Lead concentrations (ng/L) in three brands (A−C) of water from Germany, purchased in glass bottles. Six bottles of each brand were purchased in November 2005 and analyzed immediately (solid bars). The bottles were then stored in their original containers, at room temperature and ambient lighting, in a Class 10 000 clean lab for 6 months. The samples were then remeasured in May 2006 (open bars). The horizontal dashed line represents the Pb concentrations in these same brands of bottled waters but in PET(E) containers (from Table 1).

centration obtained from each of these brands combined with the measurements of Pb in single bottles of other brands, the median abundance of Pb in 25 brands of bottled waters from Canada was found to be 15.9 ng/L (n = 26), with a range from 2.1 to 268 ng/L Pb (Figure 3B).

For comparison with the median Pb concentration in the bottled waters from Canada (15.9 ng/L), pristine groundwater from six artesian flows in southern Ontario, Canada yielded a median Pb concentration of 5.1 ng/L Pb (n = 18). The comparison is relevant because 20 out of 25 of the bottled waters from Canada tested in this study originated from southern Ontario. Although these median concentrations are similar, some of the bottled waters consistently yield tens of nanograms per liter Pb, while others may contain several hundred nanograms per liter (Table S1, Supporting Information). The higher Pb concentrations found in some bottled natural waters as compared to the pristine groundwaters described here certainly may reflect the geological, mineralogical, and geochemical differences between different source areas. However, the bottled tap waters (i.e., those waters sold commercially after reverse osmosis and deionization) either contain only a few nanograms per liter Pb, or they may have tens of nanograms per liter Pb (Table S1, Supporting Information). In these cases, the variations in Pb concentrations may reflect differences in the efficiencies of removal of this element from the tap water used to manufacture these products or a small but significant contamination of the water during processing or packaging.

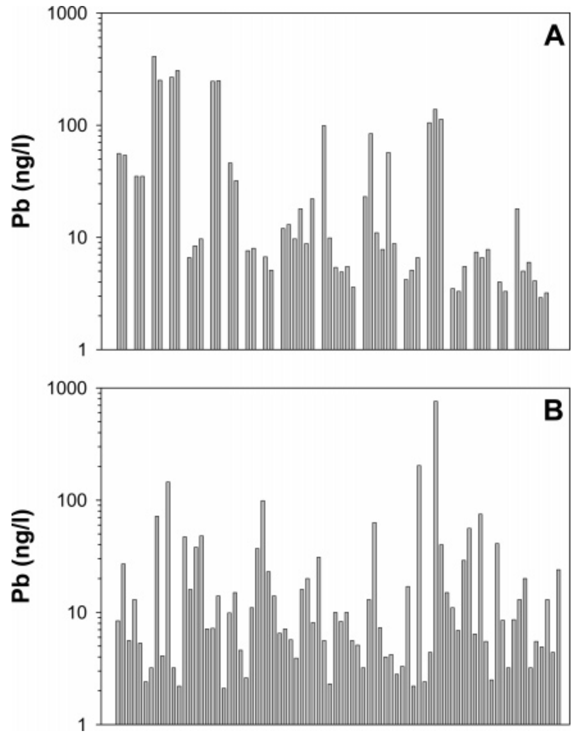

FIGURE 2. (A) Lead concentrations (ng/L) in 18 brands of bottled water, purchased as replicate samples, in plastic bottles. The brands represented here are from the following countries: Australia, Belgium, Brazil, France, Germany, Israel, Mexico, and the U.S. All of the bottles are PET(E) except for one brand sold in a bioplastic (BP). The average Pb concentrations for each of these brands are included in panel B. (B) Lead concentrations (ng/L) in 98 brands of bottled water. In addition to the countries listed above, the samples include brands from the Czech Republic, Denmark, Dominican Republic, England, Finland, Hong Kong, Iceland, Italy, Japan, Kenya, The Netherlands, Peru, Poland, Slovenia, Spain, Trinidad, and Yugoslavia. Except for one brand of water from the U.S. in bioplastic (noted above), all of these waters were purchased in PET(E) containers. The median Pb concentration of all brands presented here is 8.4 ng/L (n = 98), with a range from <1 to 761 ng/L Pb. Two brands of bottled water yielded <1 ng/L Pb and are not shown.

Comparison with Previous Studies of Pb in Bottled Waters. The median Pb concentrations reported here contrast with the median Pb concentrations reported in some previous studies of bottled waters (*11*, *12*). In her study of 40 brands of domestic and imported bottled water from Canada, Pip (*11*) reported a mean concentration of 5 μg/L Pb but did not provide relevant quality control information. Using anodic stripping voltammetry (ASV), only three samples were found to be under the limit of detection, which was 0.1 μg/L Pb. Note that this limit of detection is more than 6 times above the median Pb concentration reported here and shows that ASV is not a suitable analytical method for measuring Pb in bottled waters. Given that the median Pb concentration found for all of the bottled waters considered in our study is 588 times less than the median reported by Pip (*11*), we urge caution when interpreting previously published Pb concentrations.

The Pb concentrations reported for bottled waters from Canada by Dabeka et al. (*12*) also warrant scrutiny. They

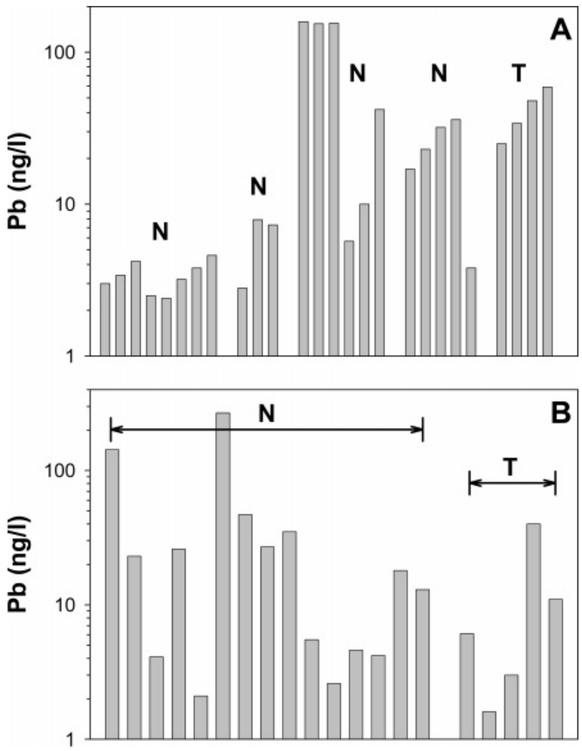

FIGURE 3. (A) Lead concentrations (ng/L) in five brands of bottled water from Canada, purchased as replicate samples, in plastic containers. These results include both bottled natural waters (N) as well as bottled tap water (T). All of the bottles are PET(E) except for one brand that is packaged in polypropylene (PP). The average Pb concentrations for each of these brands are included in panel B. (B) Lead concentrations (ng/L) in single bottles of 25 brands of bottled water in PET(E) bottles. These results include both bottled natural waters (N) as well as bottled tap water (T). The median Pb concentration of all Canadian brands tested is 15.9 ng/L ($n = 26$), with a range from 2.1 to 268 ng/L.

measured Pb concentrations in mineral waters ($n = 42$), spring waters ($n = 102$), distilled waters ($n = 25$), soda waters ($n = 19$), and tap waters ($n = 11$). In each category, however, the median Pb concentration was 0.27 μg/L, which is below the stated limit of detection (0.34 μg/L) that they obtained using an early generation quadrupole ICP-MS. Although the median Pb concentrations reported by Dabeka et al. (*12*) are 19 times less than that reported by Pip (*11*), they are still approximately 30 times greater than the median Pb concentration reported here. Given that the detection limit for Pb obtained by Dabeka et al. (*12*) is approximately 30 times greater than the median Pb concentration reported here, the results by Dabeka et al. (*12*) also must be reviewed with caution.

The proximity of Pb concentrations in previously published studies (*11*, *12*) to MAC values for drinking water leads logically to health concerns about Pb in bottled water. Any investigation of the possible health implications of Pb in bottled water, however, must begin with reliable analytical data for this element. Given the extremely low concentrations of Pb in some bottled waters (<1 ng/L), reliable measurements of Pb in these types of samples require extreme precautions to be taken to guard against contamination in the laboratory environment and the most sensitive analytical methods available.

Lead in Pristine Groundwaters. Lead concentrations in groundwater samples from six artesian flows ranged from 0.9 to 18.0 ng/L (Table 2). The Pb concentration data presented here are consistent with the measured values for this element (Shotyk and Krachler, unpublished data) obtained during 2004 ($n = 4$) and 2005 ($n = 27$). To help put these values into perspective, the median Pb concentration in the groundwaters (5.1 ng/L, $n = 18$) is not significantly different from the average Pb concentration (5.1 ± 1.4 ng/L, $n = 5$) reported for ancient arctic ice from Devon Island, Canada dating from 4000 to 6000 years old (*21*). Moreover, during the past 3 years of sampling and analysis, five of the groundwater samples obtained from three of these artesian flows yielded Pb concentrations ≤1 ng/L, which are significantly lower than the average values from the cleanest layers of ancient, arctic ice (*21*). Although it has been known for decades that measurements of Pb in dilute natural waters require extreme precautions to guard against contamination (*2*−*4*), it is important that we are aware of the need for these precautions. Our findings suggest that reliable measurements of Pb in pristine groundwaters, where Pb concentrations are sometimes below 1 ng/L, require the comprehensive procedures, protocols, and analytical methods developed for polar snow and ice, with detection limits on the order of 0.1 ng/L or less. The performance characteristics described here can only be achieved following strict clean laboratory procedures and by making use of the most sensitive instrumental techniques such as ICP-SMS.

TABLE 2. Concentrations of Pb (ng/L) in Natural, Artesian Flows (Single Measurements of Triplicate Samples)[a]

groundwater samples	Pb (ng/L)
Parnell	7.0 ± 3.9
Pigeon	5.3 ± 2.7
Temolder	10.1 ± 5.6
Belluz	3.8 ± 1.8
County Rd. 27	3.3 ± 2.1
Burgsma	7.0 ± 9.6
median ($n = 18$)	5.1

[a] Water samples from two other sites are not included for reasons given in the text.

Lead in Bottled Waters versus Tap Water. The spring water sampled between Heidelberg and Bammental yielded an average of 50 ± 3 ng/L Pb ($n = 3$). For comparison, the tap water in Bammental that had been bottled commercially in PET(E) yielded an average of 119 ± 17 ng/L ($n = 3$), and the tap water from a household in Bammental, after flushing for 1 h, was 223 ± 4 ng/L Pb ($n = 3$). The difference between the tap water bottled in PET(E) and that obtained from a household faucet may reflect Pb contributions from any number of sources in the water supply system, including steel and copper pipes, lead solder, and brass valves (*22*−*24*). These measured concentrations, however, are not only well below the drinking water standards for Pb cited earlier but often less than the Pb concentrations found in bottled waters in glass containers (Figure 1). Moreover, the tap water collected from a household in Bammental, Germany (223 ± 4 ng/L Pb, $n = 3$) contains less Pb than some brands of bottled natural waters in PET(E) containers from Australia, Brazil, and Canada (Table S1, Supporting Information). With respect to these bottled natural waters that contain up to 761 ng/L Pb, there is insufficient information available to determine how much of this Pb can attributed to the original source water and how much is due to processing, handling, and packaging.

Bottled Water: Quo Vadis? Drinking bottled water is currently very fashionable in many countries, and its popularity is growing rapidly. Bottled water is being successfully promoted by a wellness industry that extols the virtues of drinking copious amounts of water each day, but the demand for bottled water is also fuelled by concerns from consumers about the safety of tap water (*25*). Consumers, however, often pay very little attention to either the source of the water or the type of container and may not even appreciate the difference between bottled natural waters and bottled tap water. Regardless of the source of the water or the type of container, the consumer may be of the impression that the water being purchased is pure and unadulterated. The reality, however, may be somewhat different: bottled waters in glass are contaminated to a measurable extent with Pb (Figure 1) whereas those in PET(E) containers are contaminated with Sb (*14*, *15*). In both cases, the source of the contamination is the bottle itself, and the extent of contamination increases with duration of storage in the container. The contamination is readily apparent in most cases, when the analytical methods and procedures described here are employed, primarily because the natural abundance of Pb and Sb in pristine freshwaters is, in general, extremely low; these inherent, natural concentrations, therefore, are soon dwarfed by the supply of these elements contributed by leaching from the containers. Even though freshwater extracted from ancient layers of alpine and arctic glaciers may initially have extremely low concentrations (e.g., 1 ng/L or less) of Pb and Sb when they are in their pristine, natural condition, this will certainly change when the waters are collected, processed, packaged in either glass or PET(E), and stored. Excluding the bottled waters in glass, the median Pb concentration in all bottled waters reported here (8.5 ng/L, $n = 185$) is well below the median Pb concentration recently reported for Pb in tap water from the city of Columbus, OH of 0.49 μg/L (*24*). However, some of the bottled natural waters in PET(E), and all of the bottled waters in glass, yielded Pb concentrations that are within the range found in tap water (*24*).

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Supporting Information Available

Figure S1 ((A) Location of Springwater and Tiny Townships, Simcoe County, Ontario, Canada and (B) approximate location of sampling sites. The hatched area corresponds to the Elmvale Clay Plain, which is an area of groundwater discharge. Stippled areas are part of the Simcoe Uplands and represent an area of groundwater recharge. The solid triangle shows the approximate locations of the natural, artesian flows that were sampled in April 2006); Table S1 (Concentrations of Pb in all investigated bottled waters). This material is available free of charge via the Internet at http://pubs.acs.org.

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