



January 15, 2018

Protecting Water

Ministry of Municipal Affairs
Provincial Planning Policy Branch
777 Bay Street, 13th Floor
Toronto, ON M5G 2E5

Dear Ministry staff,

I am pleased that the Government of Ontario is taking an important step to help protect the water resources of the Province. I would like to offer my organization's comments on this proposal (EBR # 013-1661).

I represent the Elmvale Foundation, a federally registered charity for environmental education. The Elmvale Foundation is helping to change the way we think about water. As a non-profit, science-based organization dedicated to environmental research and education, we help to educate people of all ages and from all walks of life about the importance of our water resources: we generate awareness about current issues of water security, promote conservation, watershed protection, and environmental stewardship. The Foundation achieves its goals by hosting community events (primarily the annual Elmvale Water Festival), supporting water-based research at all levels, and providing global access to this information via our website (www.elmvale.org). We helped to create the Elmvale Water Kiosk (www.elmvalewater.org) which provides shelter to the public when they are filling their water bottles at the artesian spring on the east side of County Road 27, just north on Elmvale.

I wish to draw your attention to an important area which has been left out of your study area map: the Simcoe Uplands which includes the Oro Moraine. The location of the Simcoe Uplands is shown in the map attached which was taken from Chapman and Putnam "The Physiography of Southern Ontario". The Simcoe Uplands represent the recharge area for the important artesian spring waters of Springwater, Tiny and Tay Townships in Simcoe County.

The quality of the waters in these artesian springs has been documented in international, peer-reviewed scientific journals (copies enclosed). I have been testing these spring waters on and off for more than 25 years, first at my laboratory at the University of Berne (Switzerland), then the University of Heidelberg (Germany), and now at the University of Alberta. Using metal-free, ultraclean research facilities at each of these universities, I have shown that these spring waters contain lower concentrations of trace metals such as lead (Pb) than ancient arctic ice (which I have also tested). These are arguably the cleanest natural waters on Earth. I have no





doubt about their unique quality and inherent value. These artesian spring waters have supported the inhabitants of the region for millennia, and every effort should be made to protect them for future generations.

The Elmvale Foundation is strongly in support of expanding the Green Belt and creating a Blue Belt of groundwater protection. Our rural landscapes are much more than just aesthetic jewels where city dwellers can go to find peace: they include unique natural ecosystems found nowhere else in the country and the best farmlands of our nation, currently being managed in an effort to enable food production in perpetuity. Moreover, our forest and agricultural soils act as natural, integrated water filtration systems, maintaining the quality of surface and groundwaters for countless life forms, including our own. Stewarded by First Nations peoples for millennia, these landscapes represent the most important inheritance for future generations.

An expanded Greenbelt, and the creation of a Blue Belt, will benefit all Ontarians. I strongly recommend this expansion includes the Simcoe Uplands.

Sincerely,

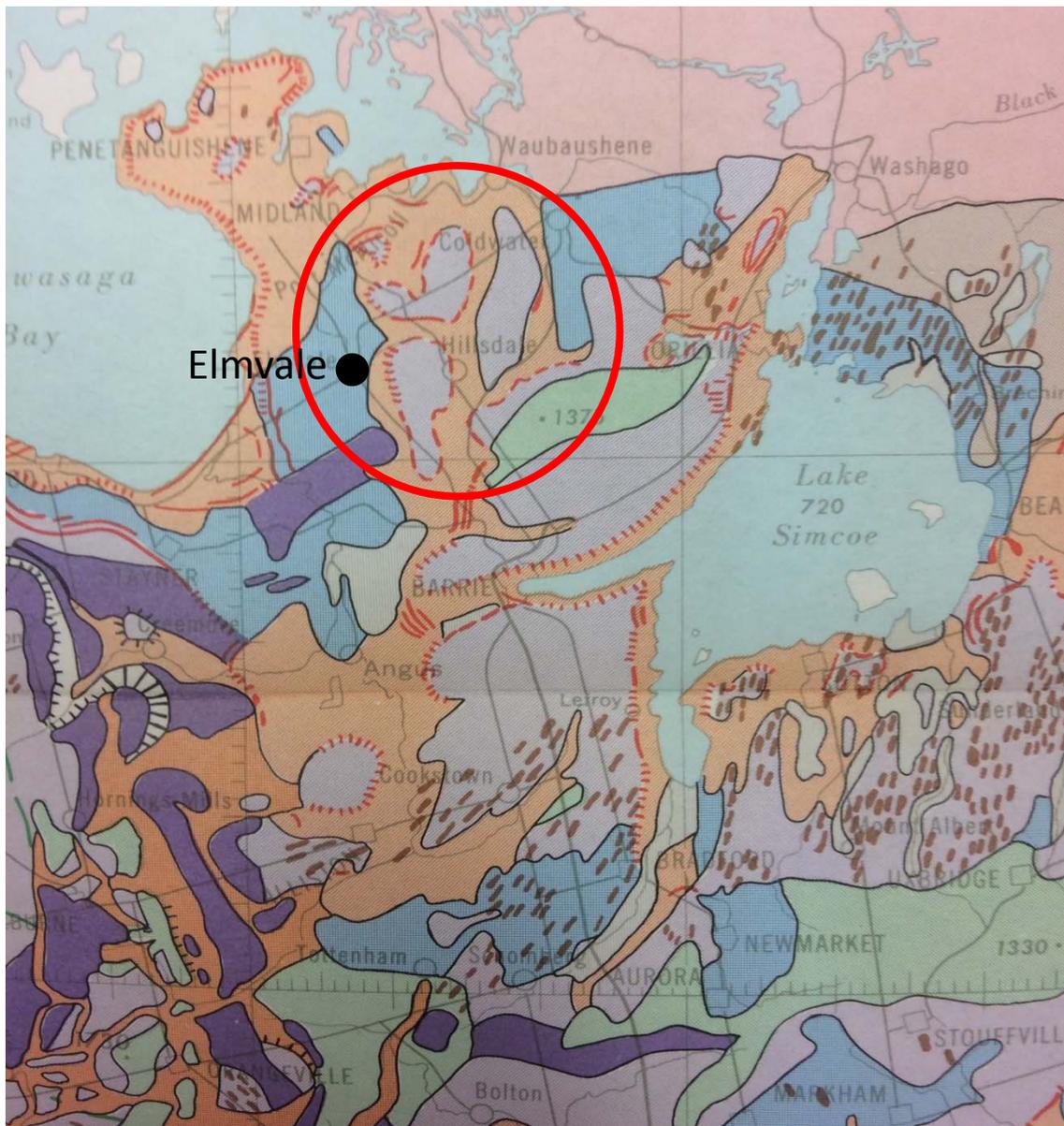
William Shotyk, Ph.D. , Dr. rer. nat. habil., P.Ag.,
President, Elmvale Foundation
and
Bocock Chair for Agriculture and the Environment, University of Alberta

Enclosures:

1. Map showing the approximate location of the Simcoe Uplands.
2. Shotyk, W., Krachler, M., Aeschbach-Hertig, W., Hillier, S. and Zheng, J. (2010) Trace elements in recent groundwater of an artesian flow system and comparison with snow: enrichments, depletions, and chemical evolution of the water. *Journal of Environmental Monitoring* 12:208-217.
3. Shotyk, W. and Krachler, M. (2009) Determination of trace element concentrations in natural freshwaters: how low is “low”, and how low do we have to go? *Journal of Environmental Monitoring* 11:1747 – 1753.



Location of Simcoe Uplands Groundwater Recharge Zone



L. J. Chapman and D. F. Putnam, *The Physiography of Southern Ontario*, University of Toronto Press, Toronto, 2nd ed., 1966.

Trace elements in recent groundwater of an artesian flow system and comparison with snow: enrichments, depletions, and chemical evolution of the water†

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Received 15th May 2009, Accepted 14th August 2009

First published as an Advance Article on the web 14th September 2009

DOI: 10.1039/b909723f

Snow samples collected from hand-dug pits at two sites in Simcoe County, Ontario, Canada were analysed for major and trace elements using the clean lab methods established for polar ice. Potentially toxic, chalcophile elements are highly enriched in snow, relative to their natural abundance in crustal rocks, with enrichment factor (EF) values (calculated using Sc) in the range 107 to 1081 for Ag, As, Bi, Cd, Cu, Mo, Pb, Sb, Te, and Zn. Relative to M/Sc ratios in snow, water samples collected at two artesian flows in this area are significantly *depleted* in Ag, Al, Be, Bi, Cd, Cr, Cu, Ni, Pb, Sb, Tl, V, and Zn at both sites, and in Co, Th and Tl at one of the sites. The removal from the waters of these elements is presumably due to such processes as physical retention (filtration) of metal-bearing atmospheric aerosols by organic and mineral soil components as well as adsorption and surface complexation of ionic species onto organic, metal oxyhydroxide and clay mineral surfaces. In the case of Pb, the removal processes are so effective that apparently “natural” ratios of Pb to Sc are found in the groundwaters. Tritium measurements show that the groundwater at one of the sites is modern (ie not more than 30 years old) meaning that the inputs of Pb and other trace elements to the groundwaters may originally have been much higher than they are today; the M/Sc ratios measured in the groundwaters today, therefore, represent a conservative estimate of the extent of metal removal along the flow path. Lithogenic elements significantly *enriched* in the groundwaters at both sites include Ba, Ca, Li, Mg, Mn, Na, Rb, S, Si, Sr, and Ti. The abundance of these elements can largely be explained in terms of weathering of the dominant silicate (plagioclase, potassium feldspar, amphibole and biotite) and carbonate minerals (calcite, dolomite and ankerite) in the soils and sediments of the watershed. Arsenic, Mo, Te, and especially U are also highly *enriched* in the groundwaters, due to chemical weathering: these could easily be explained if there are small amounts of sulfides (As, Mo, Te) and apatite (U) in the soils of the source area. Elements *neither* significantly enriched nor depleted at *both* sites include Fe, Ga, Ge, and P.

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† Part of a themed issue dealing with water and water related issues.

Introduction

The importance of human impacts on the environmental geochemical cycles of potentially toxic trace metals such as Pb has stimulated interest in the use of arctic ice as archives of global change.^{1–4} Measuring trace metals reliably at the concentrations found in polar snow and ice requires not only tremendous analytical sensitivity, but extreme care must be taken to avoid sample contamination.⁵ However, with the latest advances in

Environmental impact

Using the clean lab methods developed for arctic ice, snow samples collected from hand-dug pits at two sites in Simcoe County, Ontario, Canada were found to be highly enriched in potentially toxic, chalcophile elements such as Ag, As, Bi, Cd, Cu, Mo, Pb, Sb, Te, and Zn. Relative to snow, water samples collected at two artesian flows in this area are significantly depleted in Ag, Al, Be, Bi, Cd, Cr, Cu, Ni, Pb, Sb, Tl, V, and Zn. The differences between the enrichments in snow *versus* groundwater is probably a testimony to the remarkable natural filtration ability of the forest soils of the recharge area. Tritium measurements show that the groundwater at one of the sites is modern (ie not more than 30 years old) meaning that metal removal along the flow path is not only efficient, but also rapid.

clean lab methods and inductively coupled plasma sector field mass spectrometry (ICP-SMS), it has become possible to measure not only the concentrations of Pb and most other elements of contemporary environmental relevance,^{6,7} but also Pb isotope ratios,^{8–10} in arctic snow and ice.

An understanding of the significance of metals such as Pb in the environment requires not only quantitative information about the chronology and intensity of their deposition from the atmosphere to the biosphere, but also their subsequent release to the hydrosphere.¹¹ Biological availability of metals in the environment depends on bioaccessibility, and this is largely dictated by their abundance and chemical speciation in natural waters. With atmospheric contamination by trace metals recognised as a global phenomenon,¹² there is increasing interest in trying to determine the extent to which metals contaminating our soils will eventually leak into lakes and streams,^{13–17} as well as groundwaters.^{18,19} As the quantity of available drinking water supplies comes under growing pressures, the quality of these resources will come under even greater scrutiny.²⁰ Accurate descriptions of the quality of water resources can only be obtained using accurate analytical data. Because the concentrations of many trace metals in freshwaters are extremely low, once again clean lab methods and procedures are of paramount importance.^{21,22}

With the growing concern for the quality of drinking water worldwide, it is important to be able to characterize the chemical composition of surface waters and groundwaters, in their natural condition, prior to any intervention by man, and to understand the processes regulating them. Once this has been accomplished, this chemical information can serve as a reference level, against which any impacts in future may be measured. An opportunity for such a study has recently arisen in Tiny Township, Ontario, Canada where a landfill is being constructed by the County of Simcoe, known locally as Site 41.²³ This region of southern Ontario is an area of abundant, naturally flowing artesian springs, and the plan is to construct the landfill in an area of groundwater discharge. Using the clean lab methods and protocols successfully developed for polar snow and ice,^{6,7,9,10,24,25} we recently determined the natural abundances of Sb and Pb in these groundwaters:^{26,27} these values provided a reference level which helped to document the contamination of bottled waters because of Sb leaching from PET^{28,29} and Pb leaching from glass.²⁷

Here, in addition to Sb and Pb, other potentially toxic trace elements are considered, namely Ag, As, Bi, Cd, Co, Cr, Cu, Mo, Ni, Te, Tl, V, and Zn. To help understand natural inputs to the groundwaters from chemical weathering of minerals in the soils and sediments, lithogenic elements (Al, Ba, Be, Ca, Fe, Ga, Ge, Li, Mg, Mn, Na, P, Rb, S, Sc, Si, Sr, Th, Ti, and U) were included for comparison. The main goals of the study were to determine the extent to which potentially toxic trace elements are enriched in contemporary snow due to anthropogenic inputs, and to quantify the extent to which these elements are subsequently enriched or depleted, as the meteoric fluids migrate through the soils and sediments of the watershed.

Materials and methods

Water samples were collected from two natural artesian flows in Simcoe County, Ontario, Canada, near Elmvale (44° 35' 00" N,

79° 51' 57.0" W): the Old Johnson Farm is *ca.* 1.5 km N of Elmvale, in Springwater Township, and the Parnell Farm *ca.* 4.5 km N of Elmvale, in Tiny Township (Fig. 1a); the Parnell Farm is adjacent to Site 41. This region contains an abundance of groundwater under artesian conditions, and these represent an important source of water to the Wye River, ultimately flowing into Georgian Bay of Lake Huron, one of the Great Lakes. Eleven samples were collected at the Johnson Farm and twelve samples collected at the Parnell Farm, on 5.10.07, using the clean lab methods and procedures described earlier.²⁶ The data obtained from the current set of measurements are consistent with the values obtained when water samples were collected from these and other flows in the area, during 2004, 2005, and 2006. To date, however, only a summary of the data for Sb²⁶ and Pb²⁷ has been published.

Part of the St. Lawrence Platform, this region of southern Ontario is underlain by Ordovician limestones and dolostones.³⁰ The dominant physiographic zones are the Simcoe Lowlands and the Simcoe Uplands.³¹ Once part of glacial Lake Algonquin, the surficial deposits of the Lowlands (2816 km²) consist of a clay plain made up of glacial drift which covers the bedrock to depths of more than 100 m. The Elmvale Clay Plain (Fig. 1b) is a typical

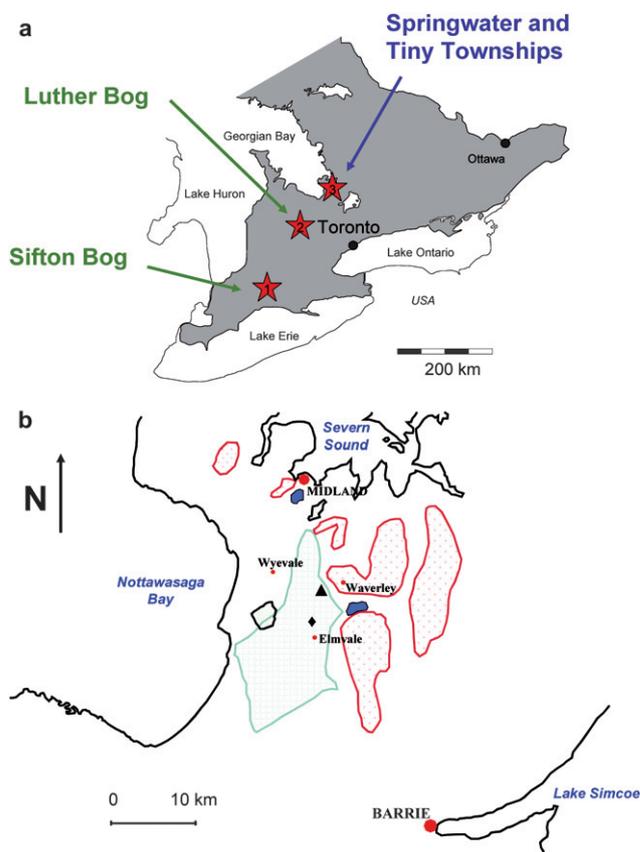


Fig. 1 a) Location of Springwater Township, Ontario, Canada as well as Luther Bog and Sifton Bog. b) Approximate location of sampling sites. The light blue hatched area corresponds to the Elmvale Clay Plain which is an area of groundwater discharge. The stippled red areas are part of the Simcoe Uplands and represent an area of groundwater recharge. The solid triangle (\blacktriangle) shows the approximate location of the Parnell Farm, and the diamond (\blacklozenge) the location of the Johnson Farm.

feature of the lowlands.³¹ This is an area of groundwater discharge: the water in the sand aquifer below the clays is under pressure, giving rise to upward gradients and many natural flows and springs.

In contrast, the Uplands (1024 km²) represent the recharge area (Fig. 1b). The uplands are characterised by a rolling topography, up to 70 m higher than the clay plain below, with a series of broad curved ridges separated by steep-sided, flat-floored valleys. The uplands are encircled by numerous shorelines, indicating that they were islands in glacial Lake Algonquin.³¹ The till in the uplands consists mainly of materials derived from Precambrian bedrock which characterizes the Canadian Shield found further to the north. Containing boulders, gravel and sand, these materials are highly permeable, and streams are rare. Here the soils are not only well drained, but they contain less carbonate and are moderately acidic.

A general description of the chemical characteristics of the waters from these aquifers was provided by the County of Simcoe. Water samples from the aquifer at Site 41 which had been collected between 1999 and 2002 from boreholes at the site, yielded the following average values: pH 8.0, 182 mg/l carbonate alkalinity, major element cations and anions (mg/l): Ca 47.6, Mg 17.6, Sr 5.0, Na 6.4, K 3.6, SO₄²⁻ 17.9, Cl⁻ 1.2, DOC 1.1.³²

The climate of the region can be summarised using the data available for the cities of Barrie and Midland (Fig. 1b). During 1971–2000, Midland had an average annual temperature of 6.8 °C and 1067.1 mm of precipitation (321.9 mm as snow). For Barrie, the corresponding values are 6.7 °C and 938.5 mm of precipitation (238.4 mm as snow).

Sample collection

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 HNO₃ (100 µl) had already been added. This acid is produced in-house and purified twice by sub-boiling distillation. Addition of 100 µl of this acid to 100 ml of water from the Johnson Farm reduced the pH to 1.7 which is sufficient to stabilise the trace metals until the samples could be measured.²⁶ The contribution of trace metals to the samples from this acid is negligible for each element considered here.⁶ To minimise the risks of contamination, none of the water samples were filtered.

Both of the flows run continuously. At Parnell, the water flows continuously through a steel pipe and no pumps or valves are employed in the water delivery system. In contrast, the flow at the Johnson farm runs continuously, but was sampled from an outdoor faucet. The original faucet was brass and a time series for Pb yielded elevated Pb/Sc ratios regardless of the duration of flushing.²⁷ The small but detectable contribution of Pb from the brass faucet was eliminated simply by replacing it with one made of stainless steel in May of 2007; a second time series for Pb, after installing the stainless steel faucet, confirmed that the problem of contamination from the valve had been eliminated (unpublished data).

Water samples were 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.

To provide an estimate of contemporary atmospheric inputs of trace metals to the groundwaters, snow was sampled as follows: two snow pits were dug by hand using a Ti shovel, at two sites on the Old Johnson Farm (E and W of the Wye River), on 27.2.2007 and 28.2.2007 and at one site on the Parnell Farm on 28.2.2007. In each pit, samples were collected from three depths (*ca.* 0–10, 10–20, and 20–30 cm) and each depth treated as an individual sample. For comparison with the data obtained from these snow pits, data from two additional snow pits are included: snow was collected on 18.3.2005 from the Luther Bog north of Guelph, Ontario, and on 14.3.2005 from the Sifton Bog in the City of London, Ontario. All snow samples were packed in insulated boxes using dry ice, and shipped airfreight; the samples were still frozen when they arrived at the lab in Germany.

In the lab, snow samples which had been packed into ziplock polyethylene bags were melted in acid-cleaned Teflon beakers in a Class 10, metal-free, laminar flow clean air cabinet. The samples were acidified with 1% HNO₃ (100 µl added per 10 ml of water) which had been distilled twice in a high purity quartz still. The acidified solutions were transferred to acid-cleaned polypropylene tubes until they were analyzed.

Determination of trace metals in groundwaters using ICP-SMS

All cleaning procedures and sample manipulations were carried out in a clean lab using clean benches of at least U.S. class 100 with the operator wearing PE gloves. The 100 ml LDPE bottles and screw caps used for the collection of waters were initially rinsed five times with high-purity water (18.2 MΩ cm) supplied from a MilliQ-Element system (Millipore, MA, USA). Thereafter, the bottles were filled with 10% nitric acid for at least 3 weeks. This acid had been prepared in-house and was distilled twice by sub-boiling, using a commercial instrument made of high purity quartz (MLS, Leutkirch, Germany). Similarly, the screw caps were submerged into 10% HNO₃ and left in the clean bench for 3 weeks, before both the bottles and the caps were again rinsed with high-purity water and filled with 1% HNO₃ for another week. Subsequently, the bottles and caps were rinsed again five times with high-purity water and dried in the clean bench overnight, before adding 100 µl high purity HNO₃ to the bottles and sealing the bottles with the screw cap. For practical reasons and to reduce the risk of contamination during sampling, the acid was added to each bottle in the lab. Bottles containing acid were then packed individually in plastic bags, and sealed for transport to the field.

Selected major and trace elements (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sc, Si, Sr, Te, Th, Ti, Tl, U, V, Zn) were determined in the waters using inductively coupled plasma-sector field mass spectrometry (ICP-SMS) applying ultra clean techniques as previously adapted for the determination of trace elements in polar ice.^{6,7} To this end, a high efficiency, desolvating sample introduction system (APEX Q; ESI, Omaha, NE, USA) including a low flow PFA nebulizer (ESI) operated in the self-aspirating mode was employed. The ICP-SMS was operated in a Class 1000 clean room, while the microvolume autosampler (ASX-100,

Cetec, Omaha, NE, USA) and the Apex were hosted in a class 100 clean bench. Details about instrument settings, acquisition and evaluation parameters are given elsewhere.^{6,7}

For quality control purposes, SLRS-4, a certified, standard reference material (river water) was analyzed with every sample batch. The measured values are in good agreement with the certified and information values for this reference material.^{6,7}

Concentrations of tritium in the waters

Tritium concentrations measured in a water sample from the Johnson Farm in 2006 yielded 0 tritium units (TU) but two samples collected in 2007 showed 1.83 ± 0.95 and 0.56 ± 0.87 , respectively. Thus, there may be a small amount of “post bomb” water in this flow, but most of the water is older than *ca.* 1950. In contrast, two samples from the Parnell Flow collected in 2006 yielded 9.52 ± 0.88 and 9.97 ± 0.9 TU, respectively: this water, therefore, is modern; certainly younger than 50 years, and probably less than 30 years, although dating with tritium alone is not possible. The tritium measurements summarized here are consistent with the data obtained at three other artesian flows in the region (unpublished data).

Mineral identification

At Site 41, adjacent to the artesian flow on the Parnell farm property, a bulk sediment sample had been collected approximately 2.5 m below the soil surface and provided to us for study. The sample was dried at 105 °C, wet ground and spray dried³³ to produce a random powder. An X-ray powder diffraction (XRPD) pattern was recorded from 2–75° 2 θ using Cobalt K α radiation. Quantitative analysis was done by a normalised full pattern reference intensity ratio (RIR) method.³⁴ The uncertainty in the estimated concentration of the minerals, using a 95% confidence level, is given by $\pm X^{0.35}$, where X = concentration in wt.%, *e.g.* 30 wt.% ± 3.3 .³⁵

Clay fractions of <2 μm were obtained by timed sedimentation, prepared as oriented mounts using the filter peel transfer technique and scanned from 2–45° 2 θ in the air-dried state, after glycolation, and after heating to 300 °C for one hour. Clay minerals identified were quantified using a mineral intensity factor approach based on calculated XRPD patterns.³⁵ For clay minerals present in amounts >10wt.%, uncertainty is estimated as better than $\pm 5\text{wt.}\%$ at the 95% confidence level.

Results and discussion

Abundance of elements in snow and groundwater

The measured concentrations of major and trace elements in the groundwater and snow samples are given in Table 1. With respect to the data obtained from the three snow pits taken in Springwater and Tiny Townships, the results are presented as an average of all 9 samples (Table 1). A snow pit dug at the Johnson farm in February of 2009 showed similar values to those given in Table 1. Comparable concentrations for virtually all elements are seen in the snow pits collected two years earlier in two peat bogs in southern Ontario (Table 1). Moreover, snow pit samples collected at these two peat bogs, as well as three other peatlands in southern and central Ontario (Tiny Marsh, Wye Marsh and

Spruce Bog, Algonquin Park), during February and March of 2009 (data not shown) are similar to the data given for the Luther and Sifton bogs (Table 1). Thus, for the elements of interest, the snow samples collected from the Johnson and Parnell farms provide a reasonable first estimate of the contemporary atmospheric inputs to the groundwater recharge area.

For most of the trace elements of environmental interest, concentrations in snow collected at all sites were much higher than in groundwater, namely Ag, Bi, Cd, Co, Cu, Ni, Pb, Sb, Tl, V and Zn (Table 1). In the case of Pb, for example, the concentrations in snow are at least 100x greater than in the groundwaters. For a few trace elements (As, Mo, Te and U), however, concentrations in groundwater are much greater than in snow (Table 1). As expected, lithogenic elements, namely Ba, Ca, Li, Mg, Na, Rb, Si, Sr, and Ti, are more abundant in groundwater compared to snow, due to chemical weathering. In contrast to these groups of elements, Fe, Ga and Ge revealed comparable concentrations in snow and groundwater.

Enrichments and depletions of elements in groundwater, compared to snow

It is worthwhile to quantify the magnitude of the changes between snow and groundwater, using a common denominator, to better understand the chemical evolution of the fluids. Scandium is commonly used as a reference element for quantifying the extent of trace element enrichment in atmospheric aerosols because there are effectively no industrial uses of Sc and therefore no anthropogenic emissions. In addition, Sc behaves conservatively during chemical weathering in soil profiles, and has no preference for a specific mineral phase.³⁶ Scandium has already been determined in these groundwaters, and used as a reference element for Sb and Pb.^{26,27} Relative to the average M/Sc ratios in all snow samples collected from Simcoe County (Table 1), water samples collected at the two artesian flows in this area are significantly *depleted* in Ag, Al, Bi, Cd, Cr, Cu, Ni, Pb, Sb, Tl, V, and Zn at both sites (Fig. 2a,b).

Lithogenic elements significantly *enriched* in the groundwater at both sites includes Ba, Ca, Li, Mg, Mn, Na, Rb, S, Si, Sr, and Ti (Fig. 2a,b). The abundance of these elements can largely be explained in terms of weathering of the dominant silicate and carbonate minerals in the soils and sediments of the discharge area (see below). Arsenic, Mo, Te, and U are also highly *enriched* in the groundwaters (Fig. 2a,b), with U being especially affected. Three or four elements show slight enrichments at both sites, namely Fe, Ga, Ge, and P.

Beryllium and Co are slightly depleted in the waters from the Johnson flow, but slightly enriched at the Parnell flow: because the changes are not consistent, they are not considered further. Similarly, Th is significantly depleted at Parnell, but slightly enriched at Johnson, and is not considered further.

Enrichments of trace elements in snow due to human activities

The groundwaters are supplied with water from rain and snow in the recharge area, and to some extent the quality of rain and snow may affect the quality of the groundwater. To help understand the extent to which human activities have affected the quality of atmospheric water supplied to the aquifer, it is

Table 1 Summary of groundwater *versus* snow^a

	Average Groundwater, Johnson (n = 11)		Average Groundwater, Parnell (n = 12)		Average Snow (Johnson n = 6, Parnell n = 3)		Average Snow, Luther Bog (n = 3)		Average Snow, Sifton Bog (n = 3)	
		std. dev		std. dev		std. dev.		std. dev.		std. dev.
Ag	0.95	0.19	0.47	0.08	2.77	0.96	2.6	1.5	2.1	0.4
Al (ppb)	3.5	1.1	0.46	0.10	16	6	33	40	20	4
As	1591	73	244	38	71	22	68	72	66	14
Ba (ppb)	100	3	110	18	0.88	0.45	1.3	1.6	1.7	0.6
Be	0.55	0.06	0.56	0.11	1.4	0.5	2.9	3.5	2.3	0.7
Bi	0.13	0.10	0.83	0.17	7.6	3.0	9.7	7.9	9.7	4.0
Ca (ppm)	27	1	51	8	0.45	0.26	0.73	0.75	1.4	0.6
Cd	4.9	0.9	2.3	0.5	35	27	10	8	17	7
Co	8.6	0.9	16.6	2.7	18	9	21.5	20.8	31.6	17.1
Cr	7.7	3.9	4.6	2.2	116	39	142	141	142	53
Cu	64	77	17	9	852	584	455	482	696	96
Fe (ppb)	12	1	159	26	15	6	41	51	29	5
Ga	8.0	0.6	4.2	0.8	8.4	2.2	19	22	14	5
Ge	4.0	0.3	5.9	1.0	3.8	1.1	8.5	9.8	5.9	1.9
Li	3443	121	3537	574	47	24	45	35	52	13
Mg (ppm)	19	1	16	3	0.09	0.04	0.19	0.17	0.23	0.11
Mn (ppb)	7.9	0.4	7.4	1.2	1.8	1.0	3.0	3.3	3.9	1.1
Mo	673	108	453	122	75	26	102	72	124	33
Na (ppm)	9.4	0.5	3.1	0.5	0.70	0.43	0.12	0.07	0.89	0.30
Ni	48	12	26	5	336	261	130	101	159	62
P (ppb)	10	0.6	4.0	1.0	5.8	3.3	9.5	11.0	10.4	1.9
Pb	5.9	3.6	3.4	1.9	672	264	747	726	798	396
Rb	299	9	930	156	56	21	63	58	76	11
S (ppm)	8.6	0.5	15.4	2.7	0.58	0.36	0.32	0.24	0.56	0.20
Sb	1.4	0.2	2.2	0.4	31	18	50	55	66	29
Sc	1.3	0.5	0.8	0.1	2.3	0.9	6.8	7.4	4.7	1.7
Si (ppm)	17	1	8.9	1.6	0.03	0.02	0.10	0.14	0.04	0.01
Sr (ppb)	1207	41	122	20	1.4	0.7	1.1	1.0	2.2	0.9
Te	12	2	2.6	0.8	1.8	0.7	0.80	0.29	0.92	0.33
Th	2.0	0.9	0.07	0.02	1.8	0.7	5.5	6.5	3.1	0.9
Ti (ppb)	6.7	0.8	14	3	0.17	0.07	0.26	0.27	0.42	0.18
Tl	0.67	0.29	0.43	0.06	2.5	1.4	2.5	2.6	3.5	1.6
U	843	28	1299	221	4.0	2.3	9.4	12.2	7.3	2.3
V	25	3	9.1	1.7	172	105	233	288	314	135
Zn (ppb)	0.37	0.10	0.55	0.14	6.6	2.6	4.7	0.5	5.8	1.3

^a All concentrations in ng/L (ppt) unless otherwise indicated.

worthwhile to try to quantify the absolute magnitude of trace element enrichments in snow. The abundance of trace elements in the Upper Continental Crust has been used successfully as a first step to quantify trace element enrichments in continental peat bogs^{37–40} as well as polar snow and ice.^{10,25,41} Using the UCC to provide a baseline, and employing Sc as reference element, it becomes clear that Ag, As, Bi, Cd, Cu, Mo, Ni, Pb, Sb, Te, Tl, V and Zn are all significantly enriched in the snow samples (Table 2). Studies have shown significant natural enrichments of Ag and Cd in atmospheric aerosols, relative to crustal rocks,^{37,39,41} such that the enrichment factors reported here for the snow pits most likely overestimate the extent of anthropogenic enrichments of Ag and Cd. However, for the other elements the crustal abundance has been shown using continental bogs and arctic ice to provide a reasonable reference point for atmospheric aerosols. Specifically, the M/Sc ratios of Mo, Ni, Tl and V in aerosols from the mid-Holocene, obtained from continental bogs^{37–40} and polar ice,^{10,25} are virtually identical to crustal values. In the case of Pb and Sb, the background M/Sc ratios obtained from continental bogs³⁷ and polar ice^{10,25} are within a factor of 2 of the crustal values. Thus, the profound (10 to 1000 x) enrichments of Ag, As, Bi, Cd, Cu, Mo, Ni, Pb, Sb, Te,

Tl, V and Zn in contemporary snow are assumed to mainly be a reflection of human activities in northeastern North America.

Although As, Mo, and Te are significantly enriched in snow (Table 2), the M/Sc ratios for each of these elements in groundwater is far greater than in snow. There are no industrial activities in the groundwater recharge area, so the additional enrichment of As, Mo and Te in the groundwaters, relative to atmospheric inputs, along with the profound enrichment of U, reveals a chemically reactive natural source of these elements.

Enrichment factors for trace elements in snow and groundwater

The absolute value of the enrichment factor, using Sc as reference element, and calculated relative to the M/Sc ratios in the UCC, is shown in Fig. 3. Although As, Mo, Te and U are clearly enriched in snow, the EF for these elements in groundwater is far greater (Fig. 3). In contrast to the elements enriched in groundwater, relative to snow, the following elements show significantly lower enrichments in groundwater: Ag, Bi, Cd, Cr, Cu, Ni, Pb, Sb, Tl, V, and Zn (Fig. 3). We note that Cr and Pb are particularly well removed from groundwater such that the M/Sc ratios approach

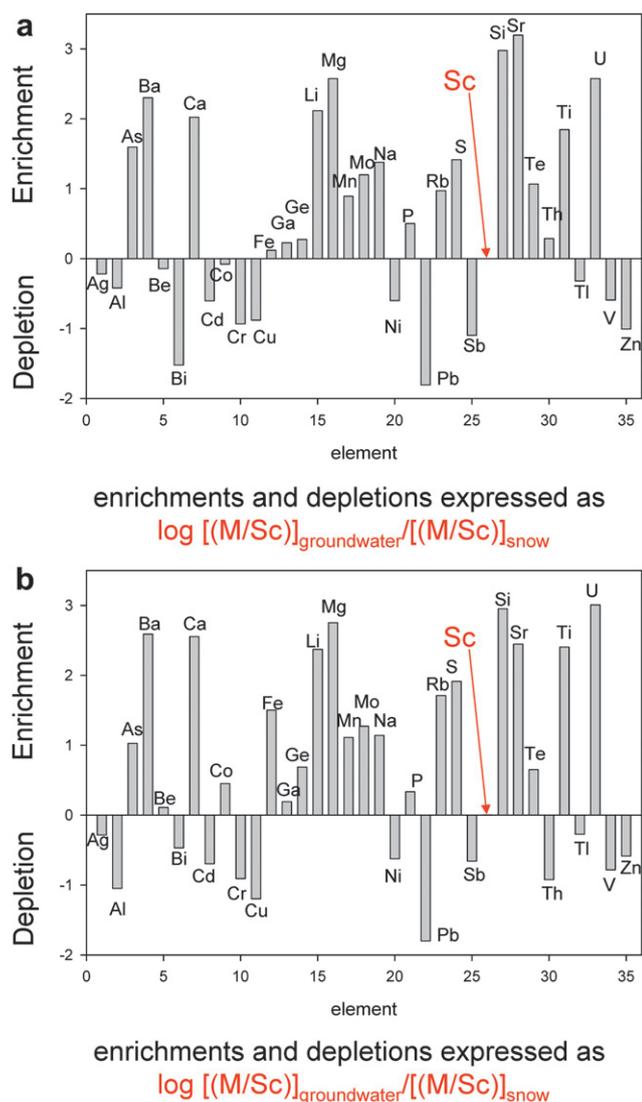


Fig. 2 a) Enrichments and depletions of elements in groundwater, relative to snow, in the samples from Johnson Farm. b) Parnell Farm.

the proportions typical of crustal rocks, ie they appear to reflect “natural” values.

Processes supplying major and trace elements to groundwater

As shown in the cartoon (Fig. 4), meteoric waters must percolate through approximately 100 m of coarse-grained glacial debris before they reach the shallow aquifers which are so common in the Elmvale area. The glacial debris is derived from the Canadian Shield, having been transported during the last ice age. We assume that these materials were ultimately derived from granites and their metamorphic equivalents, and therefore consist mainly of quartz, plagioclase and potassium feldspar, biotite and hornblende. In the acidic, organic-rich forest soils currently found in the recharge area and developed from these parent materials, chemical weathering will be dominated by the reaction of plagioclase feldspar, biotite, hornblende, and potassium feldspar.⁴² In the weathering zone of the recharge area, therefore,

reactions between these minerals and meteoric fluids will contribute Na, K, Mg, Ca and Si to the solutions, in addition to the trace elements which can substitute for them, namely Li, Be, Rb, Sr, and Ba (Table 3). In the soil solutions, therefore, all of these elements will become enriched, relative to precipitation, and the meteoric waters will acquire these solutes as they percolate through the column of glacial material.

In the Elmvale Clay Plain which is made up of glacial lake sediments (Fig. 4), the dominant primary minerals in bulk samples include not only the silicate minerals noted above, but also calcite, dolomite/ankerite, and a number of phyllosilicates including hydrobiotite, illite, and chlorite (Table 3). Once the fluids have migrated down through the glacial debris of the Simcoe Uplands, chemical weathering of the carbonate minerals will elevate the pH to 8.0 (the measured pH of the groundwaters), generate considerable carbonate alkalinity, and contribute considerably more Ca, Mg, Sr, Ba and Mn to solution (Table 3).

Processes removing trace elements from groundwater

As shown in the cartoon (Fig. 4), meteoric waters must percolate through the forest soils of the recharge area, and a column of glacial till approximately 100 m thick, prior to reaching the aquifer. During this migration, there is considerable potential for trace metals to be removed from rain and melting snow, as metal-bearing aerosol particles are physically removed by “filtration” provided by above- and below-ground plant matter, soil humus, and mineral particles. In addition to the obvious physical removal processes, there are many chemically reactive surfaces in the soil zone which can remove ionic species from solution by adsorption and surface complexation, namely the humic acids created during the decomposition of plant and animal matter, as well as the metal (Al, Fe, Mn) oxyhydroxides and phyllosilicate (clay) minerals created during chemical weathering.

In addition to the potential for trace element removal in the soils and glacial debris from which they are derived, the clay fraction (<2 µm) of the glacial lake sediments (Simcoe Lowlands) includes illite (56%), vermiculite (36%) and chlorite (8%). In contrast to the feldspars which dominate the soil profiles but have cation exchange capacities (CEC) on the order of only 1–2 meq/100 g, the clay minerals have far higher CECs, with typical values for illite and chlorite in the range 10 to 40 meq/100 g, and vermiculite on the order of 100 to 150 or more. The abundance of these clay minerals with their much large surface areas and high CECs, combined with the elevated pH values (pH 8.0) of the groundwater provides optimal circumstances for additional removal of trace metals such as Ag, Bi, Cd, Cr, Cu, Ni, Pb, Sb, Tl, V, and Zn. The processes which have led to the removal of trace elements from the groundwaters can only be speculated using the existing data. More detailed studies of the soil profiles and the glacial tills are needed to begin to understand the mechanisms of trace element removal along the groundwater flowpath. Regardless of the mechanisms of trace metal removal, the extremely low concentrations of many trace metals, relative to their abundance in contemporary snow, suggests that the removal process is very effective.

Table 2 Enrichment factors for trace elements in snow and groundwater^a

	Average Snow (Johnson n = 6, Parnell n = 3)	M/Sc, snow	UCC (ppm, Wedepohl 1995)	M/Sc UCC (Wedepohl, 1995)	M EF snow/UCC	M EF groundwater Johnson/UCC	M EF groundwater Parnell/UCC
Ag	2.8	1.2	0.055	0.01	152	92	79
Al (ppb)	16	6915	77440	11063	0.6	0.2	0.1
As	71	31	2	0.29	107	4219	1138
Ba (ppb)	0.88	377	668	95	4.0	793	1537
Be	1.4	0.6	3.1	0.44	1.3	0.9	1.7
Bi	7.6	3.3	0.123	0.02	185	5.6	63
Ca (ppm)	0.45	191262	29450	4207	45	4778	16290
Cd	35	15	0.102	0.01	1028	256	207
Co	18	7.8	11.6	1.7	4.7	3.9	13
Cr	116	50	35	5.0	10	1.2	1.2
Cu	852	366	14.3	2.0	179	24	11
Fe (ppb)	15	6648	30890	4413	1.5	2.0	48
Ga	8.4	3.6	14	2.0	1.8	3.0	2.8
Ge	3.8	1.6	1.4	0.20	8.1	15	39
Li	47	20	22	3.1	6.4	830	1501
Mg (ppm)	0.09	38351	13510	1930	20	7470	11228
Mn (ppb)	1.8	764	527	75	10	79	131
Mo	75	32	1.4	0.20	161	2551	3017
Na (ppm)	0.70	298370	25670	3667	81	1941	1124
Ni	336	144	18.6	2.7	54	14	13
P (ppb)	5.8	2478	665	95	26	83	57
Pb	672	288	17	2.4	119	1.9	1.9
Rb	56	24	110	16	1.5	14	79
S (ppm)	0.58	249780	953	136	1835	47721	150486
Sb	31	13	0.31	0.04	299	24	66
Sc	2.3	1.0	7	1.0	1.0	1.0	1.0
Si (ppm)	0.03	13242	303480	43354	0.3	290	274
Sr (ppb)	1.4	580	316	45	13	20264	3592
Te	1.8	0.8	0.005	0.001	1082	12625	4848
Th	1.8	0.8	10.3	1.5	0.5	1.0	0.1
Ti (ppb)	0.17	72	3117	445	0.2	11	41
Tl	2.5	1.1	0.75	0.11	9.9	4.8	5.3
U	4.0	1.7	2.5	0.36	4.8	1788	4850
V	172	74	53	7.6	9.7	2.5	1.6
Zn (ppb)	6.6	2823	52	7.4	380	37	99

^a All concentrations in ng/L (ppt) unless otherwise indicated.

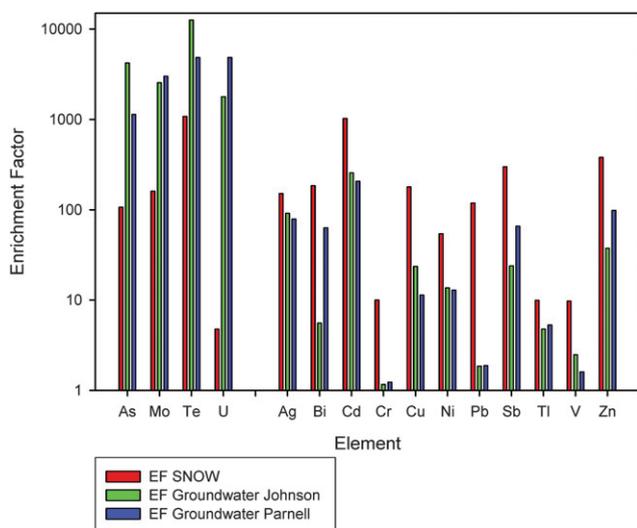


Fig. 3 Enrichment Factor, relative to Upper Continental Crust,⁵⁰ of trace metals in snow and groundwater. As, Mo, Te and U are more enriched in groundwater compared to snow, but the opposite is true for the other elements.

Reproducibility of the trace metal analyses of the groundwaters

The two artesian flows sampled at the Johnson and Parnell farms show some significant differences (Table 1). At the flow on the Johnson farm, for example, the concentrations of As, Cu, Sr and V are much greater, but the Fe and Rb concentrations much lower, than at Parnell. In fact, the data from 2005 and 2006 (unpublished) shows very similar and remarkably reproducible differences between the two sites. Arsenic concentrations in the groundwaters from the Johnson farm in 2005, for example, were $1.70 \pm 0.47 \mu\text{g/l}$ ($n = 14$, three sampling campaigns) compared to Parnell which was $0.22 \pm 0.10 \mu\text{g/l}$ ($n = 6$, one sampling campaign). Water samples collected from the Johnson farm on 13.2.09 and from the Parnell flow on 12.2.09 yielded 1.77 ± 0.02 ($n = 3$) and 0.31 ± 0.05 ($n = 6$), respectively. Also in 2005, the Ag, Cr, Cu, Mo, Sr and V concentrations in the waters from the Johnson flow were approximately double those of the Parnell flow, but Rb concentrations one-half, and Fe concentrations were one-quarter those at Parnell; similar differences were found in 2007 (Table 1). Thus, the concentration differences seen between the Johnson and Parnell flows for the sampling campaigns shown in Table 1 are also seen for the same elements

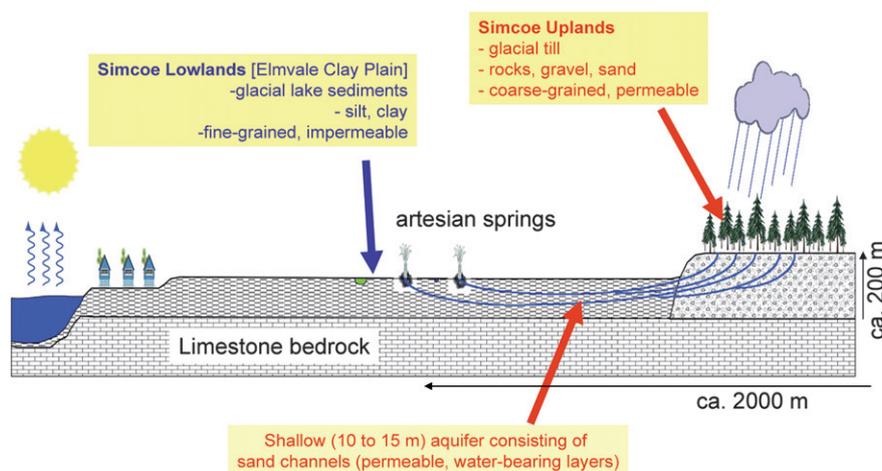


Fig. 4 Cartoon of geological cross section.

Table 3 Mineralogical composition of the sediments, mineral abundances, and estimated contribution to the chemical composition of the groundwaters^a

Name	Formula	Abundance	Solutes
Quartz	SiO ₂	14.6%	—
Plagioclase Feldspar (Albite)	NaAlSi ₃ O ₈	21.1%	Si, Na, Ca, Sr, Ba (Pb)
Potassium Feldspar (Microcline)	KAlSi ₃ O ₈	10.0%	Si, K, Rb, Li, Ba (Pb)
Hornblende	Na _{0.9} K _{0.4} Ca _{1.6} Mg _{2.9} Fe _{1.4} Ti _{0.5} Al _{2.4} Si ₆ O ₂₄	6.5%	Na, K, Ca, Mg, Si, Fe, Ti (Cr, V)
Hydrobiotite	Mg _{2.3} Fe ³⁺ _{0.6} K _{0.3} Ca _{0.1} Si _{2.8} Al _{1.2} O ₁₀ (OH) _{1.8} F _{0.2} ·3(H ₂ O)	8.3%	K, Mg, Ca, Fe, Si
Illite	K _{0.6} (H ₃ O) _{0.4} Al _{1.3} Mg _{0.3} Fe ²⁺ _{0.1} Si _{3.5} O ₁₀ (OH) ₂ ·(H ₂ O)	5.8%	K, Mg, Fe, Si
Chlorite	(Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·(Mg,Fe) ₃ (OH) ₆	1.4%	Mg, Fe, Si
Calcite	CaCO ₃	22.1%	Ca, Mg, Sr
Dolomite	CaMg(CO ₃) ₂	—	Ca, Mg, Sr
Ankerite	CaMg _{0.27} Fe _{0.73} (CO ₃) ₂	—	Ca, Mg, Fe, Sr

^a 1. Abundance of Dolomite + Ankerite = 4.7%; 2. Quartz is stable during chemical weathering of acidic forest soils, and is expected to make insignificant contributions to the chemical evolution of the soil solution. Virtually all of the Si in solution is expected to arise from the weathering of aluminosilicates.; 3. Although Al generally behaves conservatively during weathering, all aluminosilicates are expected to provide small quantities of Al to solution.; 4. Most of the Ca, Mg, and Sr is due to carbonate weathering in the sediments.; 5. Clay fraction (<2 μm) of the sediments dominated by illite (56%), vermiculite (36%), and chlorite (8%); 6. Enrichment of As, Mo, and Te in the groundwaters, relative to snow, indicates that small amounts of metal sulfides are present in the glacial debris of the source area.; 7. Enrichment of U in the groundwaters, relative to snow, indicates that small amounts of apatite is present in the glacial debris of the source area.

in the samples collected previously and subsequently (unpublished data).

Groundwater metal concentrations in perspective

The trace element concentrations in the groundwaters described here are generally rather low, with many elements significantly below 10 ng/L, namely Cd, Co, Cr, Ga, Ge, Pb, Sb, and Sc (Table 1). For some elements, however, extremely low concentrations are found in the groundwaters, *e.g.* Ag, Be, Bi and Tl are each below 1 ng/L. An extensive list of trace elements was recently determined in 132 brands of bottled waters from 28 countries, using the same analytical methods and procedures;⁴³ compared to the median concentrations of trace metals in bottled waters collected worldwide and reported in that study, the groundwaters from Springwater and Tiny Townships contain significantly lower concentrations of Ag, Be, Cd, Co, Cu, Ge, Tl and V. The groundwaters analyzed here also contain far lower concentrations of Sb than bottled waters packaged in PET

plastic, because of leaching from the containers,^{28,29} and far lower concentrations of Pb than bottled waters in glass, again because of leaching.²⁷ The groundwaters of Springwater and Tiny Townships, therefore, provide a useful reference level against which other waters may be compared. The water samples from the Parnell flow in particular, adjacent to the planned landfill known as Site 41, should provide useful “baseline” values against which any data obtained in future may be compared.

Analytical implications for studies of trace elements in natural waters

The concentrations of many trace elements reported here for these groundwaters are comparable to the lowest concentrations found in ancient ice layers from the most remote regions of the arctic. Specifically, most of the elements reported in Table 1 have also been measured in an ice core collected on Devon Island in Nunavut, Canada. The average concentrations of many of the trace metals reported here for the groundwaters are comparable

to the concentrations found in the cleanest layers of ancient arctic ice. The median Pb concentrations in the groundwaters (Table 1), for example, are not significantly different from the Pb concentrations in arctic ice samples dating from the mid-Holocene, approximately 4000 to 8000 years ago, when rates of atmospheric metal deposition were at their lowest;¹⁰ the same is true of Co, Cr and V (unpublished data). Thus, the need for extreme analytical methods and precautions which are currently being employed to study trace metals in ice cores must also be employed in studying the same elements in groundwaters, to ensure the quality of the analytical data. Whether our interest concerns the predominant sources, transformations, and fate of trace metals, or to quantify exposure to humans or ecosystems, accurate data is required for trace metals in natural waters.

As we noted in a previous study, the Pb concentrations found in five samples of groundwater emanating from some of the artesian flows during 2004 and 2005 were <1 ng/L,²⁷ which are among the lowest values ever reported for Pb in water at the surface of the earth, and comparable to ancient ice from Antarctica.² The lowest Pb concentration found to date (700 pg/L) is approximately a factor of 50 lower than the average for deep groundwaters from Switzerland,¹⁸ a factor of 5 lower than the values reported for Pb in pristine groundwaters of the USA,¹⁹ and comparable to the lowest Pb concentrations ever measured in natural waters.⁴⁴ Trace metal concentrations in carbonate groundwaters have been likened to seawater⁴⁵ because the concentrations of elements such as Ag, Be, Bi, Cd and Pb are so low that even today they still present enormous analytical challenges.⁴⁶

Taken together these findings suggest that reliable measurements of Pb and other trace metals in uncontaminated groundwaters requires the comprehensive procedures, protocols and analytical methods developed for polar snow and ice. In particular the use of pre-cleaned sample bottles and vials, high-purity acid for cleaning and acidifying the water samples as well as systematic blank values and quality control measures have to be considered. In addition, the analytical protocols should provide detection limits well below the ng/L range to allow reliable quantification of trace elements in pristine groundwaters. 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.

To filter, or not to filter?

Although the common practice is to filter waters through a 0.45 µm membrane filter prior to measurement for trace metals,⁴⁷ the concentrations of Co, Cr, Ni and Pb in these groundwaters are so low that filtration represents a significant contamination risk. For example, the blank values for Pb leaching from most kinds of membrane filters, even when determined using high purity water in a Class 100 clean bench, are commonly one to two orders of magnitude greater than the average concentration of Pb in the groundwaters. Specifically, the filter blanks obtained using high purity deionized water, in a metal-free Class 100 clean air cabinet, employing three samples of each of four brands of 10 mm syringe filters, were 110 ± 10, 30 ± 30, 10 ± 10 and 4 ± 3 ng/L, respectively.⁴⁸ Even the filter which yielded the lowest blank values (4 ± 3 ng/L) is

unacceptable, given the extremely low concentrations of Pb found in these waters (Table 1). Thus, at this stage, a comparison of filtered and unfiltered groundwaters of this quality is not possible.

Natural purification of groundwater

Except for As, Mo, Te, and U which become enriched in the groundwater as a result of chemical weathering in the watershed, most trace metals, in particular Ag, Bi, Cd, Cr, Cu, Ni, Pb, Sb, Tl, V, and Zn, are strongly removed. The tritium concentrations in the groundwaters from the Parnell flow show that the waters are modern, ie certainly younger than 50 years, and probably younger than 30 years. Although the snow samples collected today are strongly contaminated with most of the potentially toxic trace elements (Ag, As, Bi, Cd, Cu, Mo, Ni, Pb, Sb, Te, Tl, V and Zn), in past decades the concentrations and extent of enrichments of these elements was even higher⁴⁹ Therefore, the waters emanating from the springs today probably started out with even greater element concentrations, and greater enrichments, than the snow samples suggest today. Given the young age of the water and the extent of trace element removal, the natural processes responsible for the purification, although poorly understood, are certainly efficient, and deserving of further study.

Acknowledgements

We are grateful to Stefan Rheinberger for expert technical support in the lab and to Tommy Nørenberg (Institute of Chemistry and Physics, Odense University, Denmark) for excellent support in the field. Discussions in Heidelberg with Andriy Cheburkin, Christian Scholz, and Margot Isenbeck-Schröter, and in Canada with Michael Powell, were helpful and sincerely appreciated.

References

- 1 M. Murozumi, T. J. Chow and C. C. Patterson, Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata, *Geochim. Cosmochim. Acta*, 1969, **33**, 1247–1294.
- 2 A. Ng and C. C. Patterson, Natural concentration of lead in ancient Arctic and Antarctic ice, *Geochim. Cosmochim. Acta*, 1981, **45**, 2109–2121.
- 3 C. F. Boutron, J.-P. Candelone and S. Hong, Past and recent changes in the large-scale tropospheric cycles of lead and other heavy metals as documented in Antarctic and Greenland snow and ice: a review, *Geochim. Cosmochim. Acta*, 1994, **58**, 3217–3225.
- 4 C. F. Boutron, J.-P. Candelone and S. Hong, Greenland snow and ice cores: unique archives of the large scale pollution of the troposphere of the Northern Hemisphere for lead and other heavy metals, *Sci. Total Environ.*, 1995, **160/161**, 233–241.
- 5 C. F. Boutron, J.-P. Candelone and U. Görlach, Ultra-trace analysis of heavy metals in ice and snow from the Antarctic and Greenland, *Analyst Mag.*, 1992, **20**, M24.
- 6 M. Krachler, J. Zheng, D. A. Fisher and W. Shotyk, Analytical procedures for improved trace element detection limits in polar ice from Arctic Canada using ICP-SMS, *Anal. Chim. Acta*, 2005, **530**, 291–298.
- 7 M. Krachler, J. Zheng, D. A. Fisher and W. Shotyk, Novel calibration procedure for improving trace element determinations in ice and water samples using ICP-SMS, *J. Anal. At. Spectrom.*, 2004, **19**, 1017–1019.
- 8 M. Krachler, J. Zheng, D. A. Fisher and W. Shotyk, Direct determination lead isotopes (²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb) in Arctic ice samples

- at pg/g levels using ICP-SMS coupled to a high efficiency sample introduction system, *Anal. Chem.*, 2004, **76**, 5510–5517.
- 9 W. Shotyk, J. Zheng, M. Krachler, C. Zdanowicz, R. Koerner and D. Fisher, Predominance of industrial Pb in recent snow from Devon Island, Arctic Canada, *Geophys. Res. Lett.*, 2005, **32**, L21814, DOI: 10.1029/2005GL023860.
 - 10 J. Zheng, W. Shotyk, M. Krachler and D. Fisher, 15,800 years of atmospheric lead deposition on Devon Ice Cap, Nunavut, Canada: Natural and anthropogenic enrichments, isotopic composition, and predominant sources, *Global Biogeochem. Cycles*, 2007, **21**, GB2027, DOI: 10.1029/2006GB002897, 2007.
 - 11 W. Shotyk and G. Le Roux. (2005) Biogeochemistry and Cycling of Lead. in “*Biogeochemical Cycles of the Elements*”, Vol. 43 of *Metal Ions in Biological Systems*, A. Sigel, H. Sigel, and R. K. O. Sigel, eds., M. Dekker, New York, pp. 240–275.
 - 12 J. O. Nriagu, Heavy metal pollution poisoning the biosphere?, *Environment*, 1990, **32**, 7–11, 28–33.
 - 13 H. Dörr and K. O. Münnich, Downward movement of soil organic matter and its influence on trace-element transport (^{210}Pb , ^{137}Cs) in the soil, *Radiocarbon*, 1989, **31**, 655–663.
 - 14 E. K. Miller and A. J. Friedland, Lead migration in forest soils: response to changing atmospheric inputs, *Environ. Sci. Technol.*, 1994, **28**, 662–669.
 - 15 E. X. Wang, F. H. Bormann and G. Benoit, Evidence of complete retention of atmospheric lead in the soils of northern hardwood forested ecosystems, *Environ. Sci. Technol.*, 1995, **29**, 735–739.
 - 16 S. I. Vinogradoff, M. C. Graham, G. J. P. Thornton, S. M. Dunn, J. R. Bacon and J. G. Farmer, Investigation of the concentration and isotopic composition of inputs and outputs of Pb in waters at an upland catchment in NE Scotland, *J. Environ. Monit.*, 2005, **7**, 431–444.
 - 17 M. C. Graham, S. I. Vinogradoff, A. J. Chipchase, S. M. Dunn, J. R. Bacon and J. G. Farmer, Using size fractionation and Pb isotopes to study Pb transport in the waters of an organic-rich upland catchment, *Environ. Sci. Technol.*, 2006, **40**, 1250–1256.
 - 18 B. Nowack, H. Xue and L. Sigg, Influence of natural and anthropogenic ligands on metal transport during infiltration of river water to groundwater, *Environ. Sci. Technol.*, 1997, **31**, 866–872.
 - 19 S. A. Sanudo-Wilhelmy, F. K. Rossi, H. Bokuniewicz and R. J. Paulsen, Trace metal levels in uncontaminated groundwater of a coastal watershed: importance of colloidal forms, *Environ. Sci. Technol.*, 2002, **36**, 1435–1441.
 - 20 R. M. Hirsch, P. A. Hamilton and T. L. Miller, U.S. Geological Survey perspective on water-quality monitoring and assessment, *J. Environ. Monit.*, 2006, **8**, 512–518.
 - 21 J. O. Nriagu, G. Lawson, H. K. T. Wong and J. M. Azcue, A protocol for minimizing contamination in the analysis of trace metals in Great Lake Waters, *J. Great Lakes Res.*, 1993, **19**, 175–182.
 - 22 G. Benoit, K. S. Hunter and T. F. Rozan, Sources of trace metal contamination artifacts during collection, handling, and analysis of freshwaters, *Anal. Chem.*, 1997, **69**, 1006–1011.
 - 23 Ontario Municipal Board (1989) *Reasons for Decision and Decision, Joint Board, Consolidated Hearings Act*, 1981. CH-87-03, 11. November, 1989. Ontario Municipal Board, Suite 1201, 2300 Yonge Street, Toronto, Ontario, Canada.
 - 24 M. Krachler, J. Zheng, C. Zdanowicz, R. Koerner, D. Fisher and W. Shotyk, Increasing enrichments of antimony in the Arctic atmosphere, *J. Environ. Monit.*, 2005, **7**, 1169–1176.
 - 25 M. Krachler, J. Zheng, D. Fisher and W. Shotyk, Natural background levels of atmospheric antimony, variation with climate change and modern enrichments revealed by age-dated snow and ice samples from Devon Island, Arctic, Canada, *Global Biogeochem. Cycles*, 2008, **22**, GB1015, DOI: 10.1029/2007GB002998.
 - 26 W. Shotyk, M. Krachler, B. Chen and J. Zheng, Natural abundance of Sb and Sc in pristine groundwater, Springwater Township, Ontario, Canada, and implications for tracing contamination from landfill leachates, *J. Environ. Monit.*, 2005, **7**, 1238–1244.
 - 27 W. Shotyk and M. Krachler, Lead in bottled waters: comparison with pristine groundwaters and contamination from glass, *Environ. Sci. Technol.*, 2007, **41**, 3508–3513.
 - 28 W. Shotyk, M. Krachler and B. Chen, Contamination of Canadian and European bottled waters with antimony leaching from PET containers, *J. Environ. Monit.*, 2006, **8**, 288–292.
 - 29 W. Shotyk and M. Krachler, Contamination of bottled waters with antimony leaching from PET increases with storage, *Environ. Sci. Technol.*, 2007, **41**, 1560–1563.
 - 30 R. J. W. Douglas. (1976). *Geology and Economic Minerals of Canada*. Department of Energy, Mines, and Resources, Ottawa.
 - 31 L. J. Chapman and D. F. Putnam. (1966). *The Physiography of Southern Ontario*. 2nd ed. University of Toronto Press, Toronto.
 - 32 County of Simcoe (2003) *Landfill Site 41, Jagger Hims Report, Supplemental Hydrogeological and Geotechnical Investigation*. County of Simcoe, Midhurst, Ontario, Canada.
 - 33 S. Hillier. (2002) *Spray drying for X-ray powder diffraction specimen preparation*. IUCR Commission on Powder Diffraction Newsletter No. 27. pp 7–9, June 2002.
 - 34 Oladipo Omotoso, Douglas K. McCarty, Stephen Hillier and Reinhard Kleeberg, Some successful approaches to quantitative mineral analysis as revealed by the 3rd Reynolds Cup contest, *Clays Clay Miner.*, 2006, **54**(6), 748.
 - 35 S. Hiller, Quantitative analysis of clay and other minerals in sandstones by X-ray powder diffraction (XRPD). International Association of Sedimentologists, *Spec Pub*, 2003, **34**, 213–251.
 - 36 W. Shotyk, D. Weiss, J. D. Kramers, R. Frei, A. K. Cheburkin, M. Gloor and S. Reese, Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace elements (Sc, Ti, Y, Zr, Hf and REE) since 12,370 ^{14}C yr BP, *Geochim. Cosmochim. Acta*, 2001, **65**(14), 2337–2360.
 - 37 W. Shotyk, M. Krachler, A. Martinez-Cortizas, A. K. Cheburkin and H. Emons, A peat bog record of natural, pre-anthropogenic enrichments of trace elements in atmospheric aerosols since 12,370 ^{14}C yr BP, and their variation with Holocene climate change, *Earth Planet. Sci. Lett.*, 2002, **199**, 21–37.
 - 38 M. Krachler, C. Mohl, H. Emons and W. Shotyk, Atmospheric deposition of V, Cr, and Ni since 12,370 ^{14}C yr BP recorded by a Swiss peat bog profile, *Environ. Sci. Technol.*, 2003, **37**, 2658–2667.
 - 39 W. Shotyk and M. Krachler, Atmospheric deposition of Ag and Tl since 12,370 ^{14}C yr BP recorded by a Swiss peat bog profile, and comparison with Pb and Cd, *J. Environ. Monit.*, 2004, **6**, 427–433.
 - 40 M. Krachler and W. Shotyk, Natural and anthropogenic enrichments of molybdenum, thorium, and uranium in a complete peat bog profile, Jura Mountains, Switzerland, *J. Environ. Monit.*, 2004, **6**, 418–426.
 - 41 M. Krachler, J. Zheng, D. Fisher and W. Shotyk, Atmospheric inputs of Ag and Tl to the Arctic: comparison of a high resolution record from a snow pit (AD 1994 to 2004) with firn (AD 1840 to AD 1996) and an ice core (previous 16,000 years), *Sci. Total Environ.*, 2008, **399**, 78–89.
 - 42 S. S. Goldich, A study in rock-weathering, *The Journal of Geology*, 1938, **46**, 17–58.
 - 43 M. Krachler and W. Shotyk, Trace and ultratrace metals in bottled waters: survey of sources worldwide and comparison with refillable metal bottles, *Science of the Total Environment*, 2008, **407**, 1089–1096.
 - 44 M. P. Field and R. M. Sherrell, Direct determination of ultra-trace levels of metals in fresh water using desolvating micronebulization and HR-ICP-MS: application to Lake Superior waters, *J. Anal. At. Spectrom.*, 2003, **18**, 254–259.
 - 45 V. E. Hodge, K. J. Stetzenbach and K. H. Johannesson, Similarities in the chemical composition of carbonate groundwaters and seawater, *Environ. Sci. Technol.*, 1998, **32**, 2481–2486.
 - 46 K. J. Stetzenbach, M. Amano, D. K. Kremer and V. E. Hodge, Testing the limits of ICP-MS: determination of trace elements in ground water at the part-per-trillion level, *Ground Water*, 1994, **32**, 976–985.
 - 47 A. J. Horowitz, K. R. Lum, J. R. Garbarino, G. E. M. Hall, C. Lemieux and C. R. Demas, Problems associated with using filtration to define dissolved trace element concentrations in natural water samples, *Environ. Sci. Technol.*, 1996, **30**, 954–963.
 - 48 N. Rausch, L. Ukonmaanaho, T. Nieminen, M. Krachler, G. Le Roux and W. Shotyk, Evaluation of samplers and filter materials for the establishment of trace metal concentration profiles in peat bog porewaters using inductively coupled plasma-mass spectrometry, *Anal. Chim. Acta*, 2006, **558**, 201–210.
 - 49 D. S. Jeffries and W. R. Snyder, Atmospheric deposition of heavy metals in Central Ontario, *Water, Air, Soil Pollut.*, 1981, **15**, 127–152.
 - 50 K. H. Wedepohl, The composition of the continental crust, *Geochim. Cosmochim. Acta*, 1995, **59**, 1217–1232.

Determination of trace element concentrations in natural freshwaters: How low is “low”, and how low do we need to go?

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Received 18th August 2009, Accepted 20th August 2009

First published as an Advance Article on the web 10th September 2009

DOI: 10.1039/b917090c

There is an on-going need for reliable concentration data for trace elements in natural freshwaters, including soil solutions and groundwaters, surface waters (wetlands, streams, rivers, and lakes), precipitation (fog, rain, and snow), and drinking water (including natural spring water as well as bottled water and tap water). Some of the trace elements of interest may be present in these waters at elevated concentrations due either to natural processes such as mineral weathering (*e.g.* As and U in groundwater), or because of human activities (*e.g.* atmospheric contamination of snow with Pb and Sb).

Introduction

Regardless of the cause of the enrichment of any given trace element in a natural water, it is sometimes desirable and often useful to be able to determine the “baseline” or “background” value for that parameter, for comparison, to be able to quantify and better understand any changes which may have taken place as the water evolves. In the case of many trace elements, this means being able to reliably undertake determinations at the part per trillion (ng/L) concentration level: accurate and precise measurements in this range requires limits of detection (LOD) at least a factor of ten lower. Because the concentrations of many trace metals in natural freshwaters are extremely low, both sensitive analytical methods combined with clean lab methods and procedures are of paramount importance.

A precedent was established for measuring Pb at extremely low concentrations in ancient layers of polar ice by Claire Patterson who documented in excruciating detail the extraordinary precautions that are needed to measure Pb reliably at the ng/L (part per trillion) concentration range.¹ Subsequently, laboratories dedicated to studies of metals in polar ice have incorporated many of these pioneering discoveries and developments.² Using metal-free “clean lab” methods combined with ICP-SMS allows the simultaneous determination of a broad range of trace elements, as well as Pb isotope ratios (²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb) to be measured reliably in ancient layers of polar ice.^{3–5}

The snow and ice which has accumulated since the Industrial Revolution, even in the most remote regions of the Arctic, is profoundly contaminated by such potentially toxic elements as Pb⁶ and Sb⁷ and therefore would provide a misleading starting point for any discussion of trace elements in “natural” freshwaters. In contrast, ancient layers of polar ice widely are considered to be the “cleanest water on earth”. To put trace element concentrations into perspective, it is helpful to use this material as a reference point, to provide a baseline against which other waters may be compared. In this commentary, we use ancient

layers (*ca.* 3.3 to 7.9 K years old) of ice from Devon Island, Nunavut, Canada, as a starting point for the discussion. A detailed description of the purpose built Ti corer, and mechanical decontamination of the outer layers of the ice core samples, is given elsewhere.⁸

1. Ancient arctic ice

In general, for most trace elements, the lowest concentrations found during the past 15 000 years are in the ice layers from the mid-Holocene.^{9–12} Here we present the average concentrations in six samples dating from 3278 to 7947 years BP *i.e.* Before Present (Table 1). For the present discussion, we ignore the fact that Ag (and Cd) are enriched during this period, compared to still older ice layers dating from the Late Glacial.¹⁰

First, notice that the average concentrations of trace elements during this time period may be very low *e.g.* Ag, Bi, Mo, Sb, Sc, Tl and U are all present at levels below 1 ng/L. Second, despite the obvious analytical challenge presented by these low concentrations, notice that the LODs obtained using appropriate clean lab methods and ICP sector-field mass spectrometry (ICP-SMS) are more than adequate; in all cases, the average concentration of any given trace element in the cleanest layers of ancient arctic ice is at least a factor of 10 greater than the LOD.

The average concentration of trace elements in ice layers from the mid-Holocene of the Arctic is the point of reference for the remainder of the discussion.

2. Groundwater

Also given in Table 1 is a summary of the average abundance of selected trace elements in groundwater from two artesian flows in Simcoe County, Ontario, Canada: the Johnson Farm in Springwater Township and the Parnell Farm in Tiny Township. Both of these artesian flows are described in more detail elsewhere.¹³ It is important to state clearly and to emphasize at the outset that none of the groundwater samples were filtered, and that waters were sampled only from flowing, artesian wells. The data for Al, Ba, Fe, Li, Mn, Sr, Ti and Zn are not presented here simply because they are present in the part per billion

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Table 1 Trace elements in groundwater, surface water, arctic ice, and contemporary snow (Southern Canada)^{a,c,e}

Element	Average ice, Devon Island, 3.3K to 7.9K BP (n = 6)		Average Groundwater, Johnson (n = 1)		Average Groundwater, Parnell (n = 12)		Surface Water, Kawagama Lake (n = 13) ^d		Snow (Johnson n = 6, Parnell n = 3)	
	Std. dev.	LOD	Std. dev.	Johnson (n = 1)	Std. dev.	Parnell (n = 12)	Std. dev.	Kawagama Lake (n = 13) ^d	Std. dev.	Snow (Johnson n = 6, Parnell n = 3)
Ag	0.67	0.02	0.19	0.95	0.47	0.08	n.d.	2.8	1.0	
As	3.0	0.3	73	1591	244	38	137	71	22	
Be	n.d.	0.03	0.06	0.55	0.56	0.11	6.4	1.4	0.5	
Bi	0.10	0.002	0.10	0.13	0.83	0.17	0.25	7.6	3.0	
Cd	2.3	0.01	0.9	4.9	2.3	0.5	8	35	27	
Co	2.5	0.01	0.9	8.6	17	3	12	18	9	
Cr	4.1	0.015	3.9	7.7	4.6	2.2	75	116	39	
Cu	19	0.1	77	64	17	9	470	852	584	
Ga	n.d.	0.5	0.06	8.0	4.2	0.8	n.d.	8.4	2.2	
Ge	n.d.	0.01	0.3	4.0	5.9	1.0	8.6	3.8	1.1	
Mo	0.82	0.01	108	673	453	122	8.1	75	26	
Ni	n.d.	1.0	12	48	26	5	289	336	261	
Pb	5.1	0.06	3.6	5.9	3.4	1.9	57	672	264	
Re ^b	n.d.	0.001	0.0	1.4	5.2	0.1	n.d.	n.d.	n.d.	
Sb	0.10	0.006	0.2	1.4	2.2	0.4	30	31	18	
Sc	0.65	0.006	0.5	1.3	0.75	0.13	6.5	2.3	0.9	
Te	n.d.	0.2	2	12	2.6	0.8	1.4	1.8	0.7	
Th	n.d.	0.01	0.9	2.0	0.07	0.02	3.9	1.8	0.7	
Ti	0.24	0.008	0.29	0.67	0.43	0.06	4.9	2.5	1.4	
U	0.50	0.002	28	843	1299	221	4.2	4.0	2.3	
V	4.9	0.007	3	25	9.1	1.7	62	172	105	
W ^b	n.d.	0.06	13	61	11	5	0.38	0.09	n.d.	

^a NOTES: Al, Ba, Fe, Li, Mn, Br, Ti and Zn not included because they are generally present in groundwaters in the part per billion concentration range and therefore less problematic. n.d. = not determined. ^b Re and W measured for the first time in these groundwaters in March of 2009 (Johnson, n = 3; Parnell, n = 6). ^c Detection limits for Ga, Mo, Ni and Th not yet determined. ^d Unfiltered Kawagama Lake surface water sampled in triplicate on 10.8.08. ^e All concentrations in ng/L (ppt).

concentration range and therefore are less problematic to be measured reliably than most of the elements listed in Table 1; these data, however, are presented elsewhere.¹⁴

Notice that the concentrations of Ag, Bi, Cd, Cr, Cu, Pb and Sc in groundwaters are effectively identical to those of ancient arctic ice (Table 1). Even Tl and V are within a factor of two of the values in ancient arctic ice. The point which we would like to stress here is that the extraordinary efforts which are needed to measure trace metals in ancient arctic ice,¹ and the extreme care needed to avoid contamination of the samples,² are also needed to reliably determine the abundance of many trace elements in natural groundwaters. Hodge *et al.*¹⁵ have compared the concentrations of trace elements in carbonate groundwaters to seawater, reminding us of the severity of analytical challenges facing chemical oceanographers.

As noted elsewhere,¹⁴ the differences between the groundwaters emanating from Parnell *versus* Johnson are reproducible and have been found consistently during the past five years of sampling and testing. Consider the case of Ag, for example: even though the average Ag concentrations are at or below 1 ng/L at both sites, frequent sampling and measurement has shown that the concentrations of Ag in the groundwaters from the Johnson flow are *ca.* twice those found at Parnell (Table 1); in other words, these are meaningful values which reflect real differences in the chemical composition of the waters; these can be clearly seen, even at extremely low concentrations, when great care is invested in sample collection, handling, preparation, and measurement.

The abundance of Re in these waters provides further illustration of the differences between these groundwaters. The concentrations of Re and U in replicate samples from these plus

a third artesian flow (Archer) are shown in Fig. 1. Notice how reproducible these values are; precise data can be obtained even at extremely low concentrations, provided that all of the necessary precautions and prerequisites are employed. The detection limit for Re is 1 pg/L (*i.e.* part per quadrillion) and notice again the significant difference between the Johnson and Parnell flows. In the groundwaters at the Archer flow, the abundance of Re is only 0.40 ± 0.01 ng/L ($n = 3$).

Comparison with other groundwater data

It would be desirable to obtain other data for groundwaters in the area, but there is very little data available for comparison. For example, the Groundwater Monitoring Program of the Ontario Ministry of the Environment (MOE) has no data whatsoever for most of the trace elements listed in Table 1. For some of the trace elements given in Table 1 such as Co, Cr, and Cu, there is MOE data available for groundwaters in this region of Simcoe County, but the concentrations reported by the MOE are far higher. For example, the Cr concentrations in the groundwaters from the Johnson and Parnell flows are below 10 ng/L (Table 1), but the MOE data (unpublished) shows concentrations in the range of 0.3–3 $\mu\text{g/L}$ ie values which are approximately 100 to 1000 times greater.¹⁶ A direct comparison of our data with that of the MOE is not possible because the samples are different, having been collected at different sites, and no consideration can be given to possible effects of the diverse Quaternary geological history of this region. Moreover, the MOE data is obtained from standing wells where the water has to be pumped and then filtered prior to testing. In contrast, our data is from flowing artesian wells, and represents unfiltered samples.

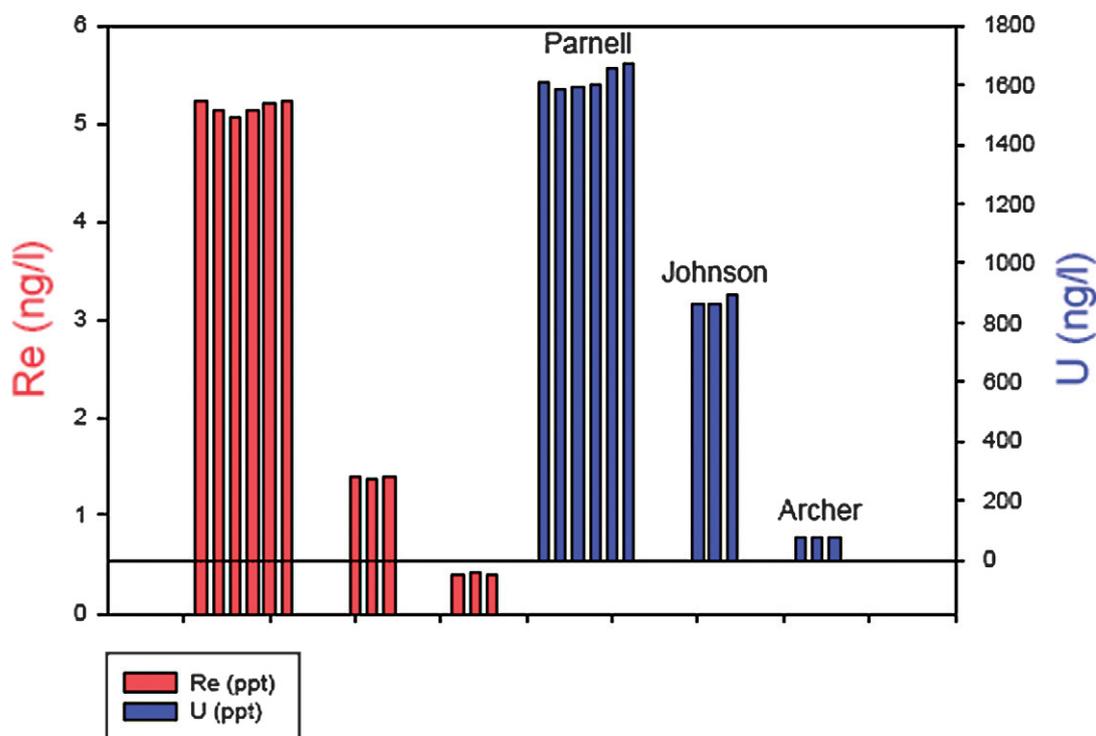


Fig. 1 Comparison of Re and U concentrations in groundwaters from three artesian flows (Parnell, Johnson, Archer). Six samples were collected at the Parnell flow, while the other two were sampled in triplicate.

Thus, we avoid altogether the temptation to compare the results, except to say that the concentrations are very different.

Given that the concentrations of trace metals found in unfiltered groundwaters from flowing, artesian wells in this area are so low (Table 1), and in fact comparable to the concentrations found in ancient Arctic ice, one has to ask what procedures need to be in place in order to be able to pump and filter groundwaters of this quality, without contaminating them.

Effects of colloids on trace metal concentrations

Site 41 is an engineered landfill being constructed in Tiny Township, in an area of groundwater discharge, adjacent to the Parnell farm. In April of 2006 we were given permission to collect groundwater samples from three flowing wells on the Site 41 property, namely 3A-1, 5A-1 and GL-1-B; the latter is a natural, artesian flow. The two constructed wells (3A-1 and 5A-1) were purged and water allowed to run for one hour before collection into either pre-cleaned bottles provided by a consulting engineering firm (3A-1, 5A-1 and GL-1-B) or directly into our own bottles (3A-1-ME, 5A-1-ME and GL-1-B-ME).

The results show that the two different bottles yield only small differences (Fig. 2). Of much greater importance is the fact that the water samples from the 3A well are distinctly different, yielding far greater concentrations of Al, Sc, Cr, V, Cu and Pb, as well as Cd and Tl (not shown). All of these waters originate in the same shallow aquifer, and we assume that the composition of the water underlying the landfill at Site 41 is fairly uniform; the similar Mg and Ca concentrations in the waters from all three wells supports this interpretation. The large differences in trace metal concentrations, therefore, appear to be entirely an artefact of the method of sample collection.

The groundwaters at Site 41, as well as those from the Johnson and Parnell artesian flows (Table 1) are in equilibrium with calcite and have a pH of 8. The expected concentration of Al at pH 8, assuming that the waters are in equilibrium with gibbsite, is approximately 10^{-7} M,¹⁷ or 3 µg/L. Groundwaters from the Johnson farm average 3.5 µg/L and from the Parnell flow 0.5 µg/L.¹⁴ Moreover, water samples collected from six additional artesian flows in the area (Belluz, Burgsma, Pigeon, Stone, Temolder, and Hwy 27) show similar Al values, and all yield Al concentrations below 3.5 µg/L (unpublished data). In contrast, the waters from the 5A and GL wells have significantly higher Al concentrations (ca. 10 to 20 µg/L). The 3A samples, in particular, containing up to 340 µg/L (ie 100 times more Al than the waters from any of the artesian flows), would be very difficult to explain based on either the geochemistry of the waters, or the geochemistry of Al. Instead, the elevated Al concentrations are an obvious indication of colloidal material having been introduced into the water, probably during purging of the wells. Notice that Sc, an element whose behaviour during hydrolysis is comparable to that of Al¹⁸ shows the same effect; at Johnson and Parnell, Sc concentrations are on the order of 1 ng/L (Table 1). In contrast, in the waters from the 3A well, the Sc concentrations exceed these values by 100× (Fig. 2). Again, we know of no logical explanation for such anomalous values based either on the geochemistry of the groundwaters or the geochemistry of Sc.

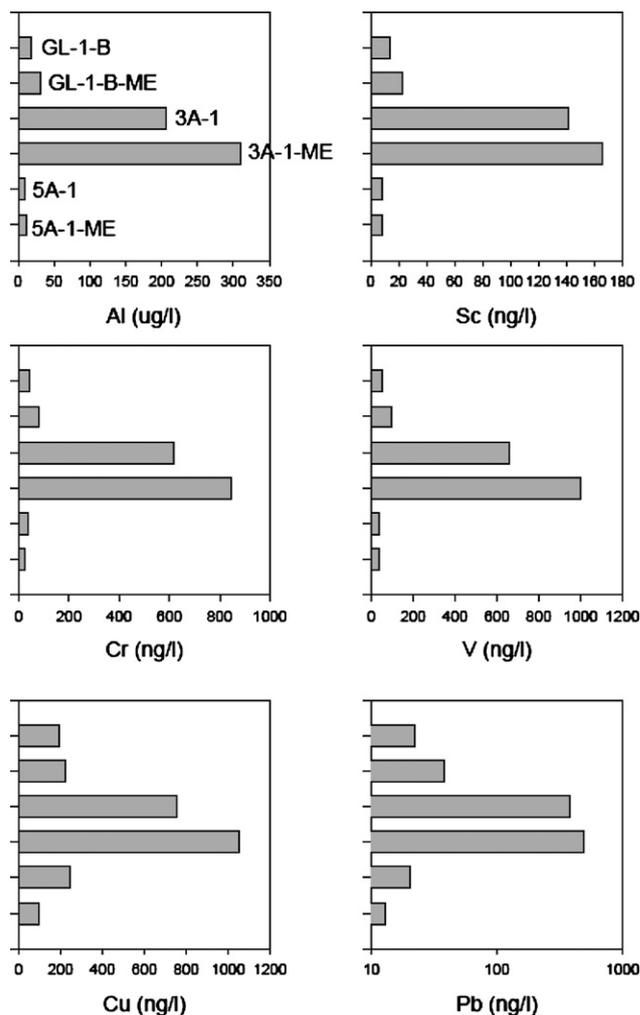


Fig. 2 Al, Sc, Cr, V, Cu, and Pb concentrations from three wells at Site 41, an engineered landfill now being constructed on the property. Aluminium concentrations given in µg/L, others in ng/L. Each bar represents the average of three samples.

The introduction of colloidal material during purging and its effect on *e.g.* Al and Sc, would explain the anomalous concentrations of Cr and V (Fig. 2) as well as Cu and Pb (Fig. 2). Cd and Tl are similarly affected, but not shown. The data shown in Fig. 2, therefore, shows that the method of sample collection can have a profound effect on the apparent abundance of trace metals in groundwaters, with the trace metal concentrations a sensitive reflection of the abundance of colloidal materials.¹⁹ The data from the 3A well most certainly do not reflect the chemical composition of the groundwater, but rather the concentration of colloids added to the water by purging the well.

While the introduction of colloids has a profound effect on trace metals associated with them (such as Pb), notice that the anionic trace elements (As, Mo, U) are much less affected (Fig. 3). The introduction of colloidal matter during sampling, therefore, is especially problematic, because not all of the trace elements will be affected to the same extent.

Regarding geochemical studies of the natural chemical composition of the groundwaters in the vicinity of Site 41, and the evolution of the fluids, we are confident that the data from the

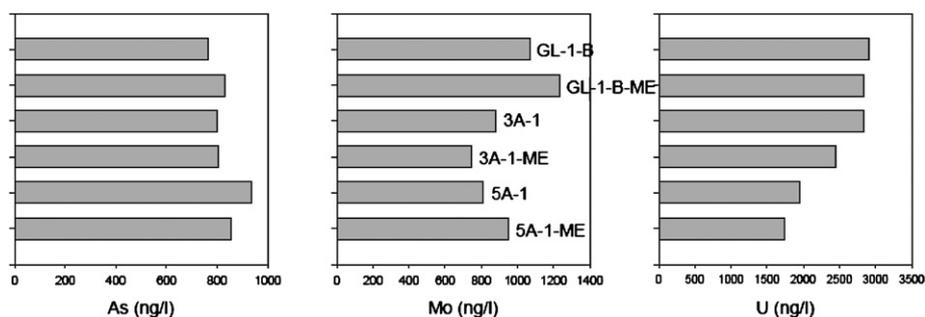


Fig. 3 As, Mo, and U (ng/L) at the same site. Again, each bar represents the average of three samples.

artesian flow on Parnell farm which is adjacent to Site 41, provides a reasonable indication of the quality of groundwater in this area today.

Effects of water sample filtration

The data in Table 1 shows that the natural abundance of many trace elements in several kinds of water samples (snow, surface water, groundwater) may be comparable to the cleanest layers of ancient arctic ice. While we certainly understand the importance of removing particulate material from water samples prior to testing, to allow the determination of “dissolved” concentrations of trace elements,²⁰ this raises two important issues: first, the problem of introducing colloidal materials capable of passing through 0.45 μm membrane filters. Second, the challenges faced when attempting to clean the filters prior to use,²¹ to be able to achieve the blank values necessary to measure trace elements reliably at these extremely low concentrations. Although commercially-available filters for online groundwater monitoring are certified to yield a maximum blank value for any given element, in many cases these values are several orders of magnitude beyond the concentrations of many of the elements shown in Table 1. Thus, although commercially available, pre-cleaned, on-line membrane filters may be adequate for the kinds of compliance testing noted above, blank values must be carefully evaluated on an element by element basis for any rigorous scientific studies.

Objectives of water sampling

In fairness to the MOE, it is their obligation to ensure that landfill sites are in compliance with water quality guidelines. The purpose of the monitoring wells, therefore, is simply to confirm that the water quality guidelines are being met, and the accuracy and precision of the chemical analyses must only be sufficient to complete such an assessment. Thus, from the perspective of a regulatory agency, it is not necessary to obtain the absolute value of any given parameter, but rather simply to ensure that the parameter has a concentration less than the guideline to complete the assessment.

At the same time, however, it is important to realise that any trace element concentration data obtained from these kinds of monitoring programs, may provide little, if any information about the true chemical composition of the waters, and cannot be used in geochemical studies of the origin and evolution of the fluids.

3. Surface water

As noted elsewhere,¹⁴ contemporary snow in southern Ontario contains elevated Pb concentrations and Pb/Sc ratios, with values up to 1000 \times greater than crustal values, due to atmospheric pollution. Many other chalcophile trace elements show comparable enrichments, relative to crustal values, due to industrial emissions. Measuring the concentrations of chalcophile trace elements in contemporary snow in southern Canada is much less of a challenge compared to ancient Arctic ice.

Despite the elevated atmospheric inputs, however, lake surface waters of southern Ontario today may exhibit Pb/Sc ratios approaching crustal values because of a variety of removal processes within the watershed. Taking the example of Kawagama Lake, the Pb concentrations in surface waters are sometimes as low as 10 ng/l, compared to 5 ng/l in ancient Arctic ice (Table 1). In massive water bodies such as the Great Lakes, such low Pb concentrations have been documented in the past,^{22–24} but these removal processes seem to also be operating effectively in much smaller watersheds.²⁵

Further, in surface waters the concentrations of trace elements may also be extremely variable, because of particle removal and scavenging processes. At Kawagama Lake, for example, Pb concentrations and Pb/Sc in the streams entering the lake may easily be 100 \times greater than the values found in the lake waters themselves, simply because of the physical removal of Pb-bearing particles, probably reflecting the change in water velocity from stream to lake. Thus, the analytical methods which are adequate for measuring Pb in stream waters^{26–28} may be entirely inadequate for studies of lake waters within the same watershed. Cobalt is an excellent example of extreme variations in concentrations: at Kawagama Lake, for example, the variations in concentration extend over nearly three orders of magnitude, with nearly 10 $\mu\text{g/L}$ (ppb) in seepage water and streams, and only a few ng/L (ppt) in the lake (Fig. 4). Geochemical studies of element flows in watersheds, therefore, also require the analytical sensitivity as well as the extreme care to avoid contamination as the great efforts which are needed to measure trace metals in ancient arctic ice.

Comparison of surface water and groundwater

As noted elsewhere,¹⁴ As, Mo, and U are enriched in groundwater, relative to snow, thus the determination of these elements in groundwater is rendered somewhat less difficult.

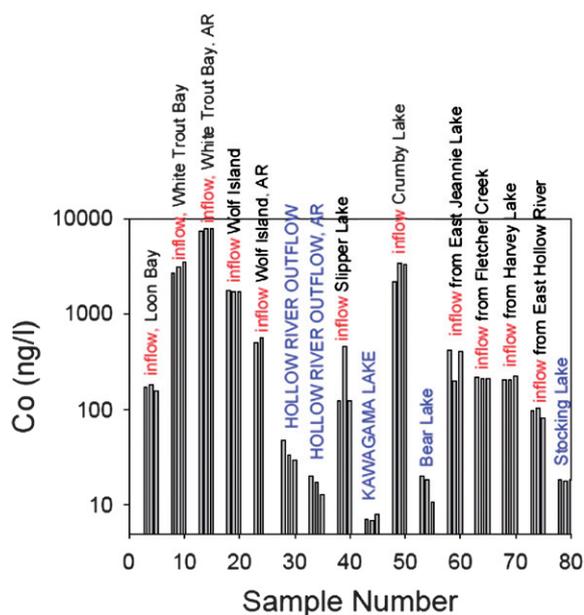


Fig. 4 Co concentrations (ng/L) in surface waters from the Kawagama Lake watershed. Each site was sampled in triplicate. Although source waters contain up to 10 $\mu\text{g/L}$, the samples from the middle of Kawagama Lake itself averaged 7.4 ± 0.6 ng/L: this is comparable to the groundwater samples (Table 1) and within a factor of 3 of the values found in ancient Arctic ice (Table 1). AR = sampled after rain event.

Recently we measured W in the groundwaters of Simcoe County for the first time, and the values (Table 1) are much greater than in snow from the area, suggesting that W, too, may be naturally enriched in the groundwaters. Despite this, W concentrations in the waters tested thus far are below 100 ng/L,

so under no circumstances are these measurements trivial. In contrast, in the surface waters of Kawagama Lake, W concentrations are approximately two orders of magnitude lower than in the groundwaters (Fig. 5), with the average concentration only 0.38 ± 0.09 ng/L. Thus, the methods suitable for measuring some trace elements in groundwaters (such as As, Mo, U and W which become enriched in the example given here) may be unsuitable or inadequate for testing surface waters for the same elements.

Bottled water

The concentrations of some trace elements in bottled waters (*e.g.* Ag, Te, Th) can be very low (a few ng/L or less), and many trace elements, in particular Li, Be, Ge and U, reveal very large variations in abundance.²⁹ Although some constituents in bottled waters may reflect their abundance in the groundwater prior to packaging (assuming that the waters have not been filtered or otherwise treated), others simply reflect contamination from the packaging: PET plastic releases Sb^{30,31} whereas glass may release Pb³² as well as Th and Zn.²⁹ The median concentration of Pb in bottled waters packaged in PET plastic, however, is only a few ng/L³² and probably reflects the natural abundance of this element in the waters prior to packaging. Thus, depending on the packaging and duration and storage, some elements in bottled waters may reflect their natural abundance in groundwaters; this means that the range in concentrations may be comparable to the values shown in Table 1. Once again, therefore, the reliable determination of many trace elements in bottled water requires the sensitivity as well as the extreme care to avoid contamination as the great efforts which are needed to measure trace metals in ancient arctic ice and uncontaminated groundwaters.

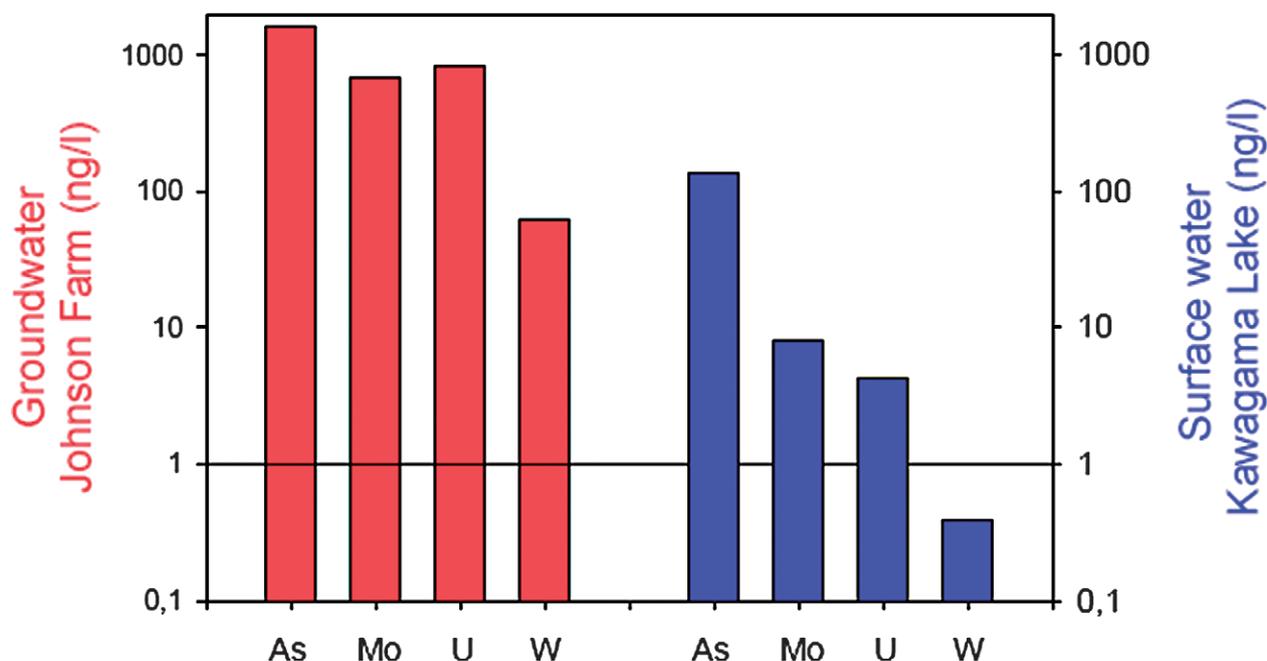


Fig. 5 As, Mo, U, W in groundwaters (artesian flow, Johnson farm) versus surface waters (Kawagama Lake). These two areas are far removed from one another and hydrologically independent, and are compared only to illustrate the different concentration ranges characteristic of the waters.

Conclusions

In natural waters, the concentrations of very many trace elements can be extremely low, in the range of a few ng/L or below. Although some chalcophile elements may be highly enriched in rain and snow because of atmospheric contamination, many of these may be efficiently removed by soils, leading to very low concentrations in groundwater (e.g. Ag, Bi, Cd, Cu, Pb, Sb, Tl). While some lithophile elements (Li, U) and chalcophile elements (As, Mo) can become naturally enriched in groundwaters due to chemical weathering, surface waters may exhibit very low concentrations of many trace elements because of the physical removal of metal-bearing particles within a watershed. Thus, a wide range of trace elements, including some commonly measured metals such as Cr, are present in many kinds of waters (surface waters and groundwaters) at concentrations comparable to those of ancient polar ice. The significance of this, of course, is that the extreme care required to measure trace elements in ancient arctic ice, is also needed for the reliable determination of trace elements in many other kinds of water samples.

Using the clean lab methods and ICP-SMS which has been successfully applied to polar ice, a broad range of trace elements can be measured simultaneously and reliably, in all other natural waters, including rain and snow, surface waters, and groundwaters. Although the lower limits of detection provided by the ICP-SMS are more than adequate for accurate and precise measurements of virtually all trace elements found in natural freshwaters, sensitivity alone does not ensure representative data. In fact, the risk of sample contamination will always represent a far greater challenge than adequate limits of detection. Moreover, the need to remove particulate matter without contaminating the water sample or introducing colloidal materials, remains a daunting task.

References

- 1 M. Murozumi, T. J. Chow and C. C. Patterson, *Geochim. Cosmochim. Acta*, 1969, **33**, 1247–1294.
- 2 C. F. Boutron, J.-P. Candelone and U. Görlach, *Analisis Mag.*, 1990, **20**, M24.
- 3 M. Krachler, J. Zheng, D. A. Fisher and W. Shotyk, *J. Anal. At. Spectrom.*, 2004, **19**, 1017–1019.
- 4 M. Krachler, J. Zheng, D. A. Fisher and W. Shotyk, *Anal. Chem.*, 2004, **76**, 5510–5517.
- 5 M. Krachler, J. Zheng, D. A. Fisher and W. Shotyk, *Anal. Chim. Acta*, 2005, **530**, 291–298.
- 6 W. Shotyk, J. Zheng, M. Krachler, C. Zdanowicz, R. Koerner and D. Fisher, *Geophys. Res. Lett.*, 2005, **32**, L21814, DOI: 10.1029/2005GL023860.
- 7 M. Krachler, J. Zheng, C. Zdanowicz, R. Koerner, D. Fisher and W. Shotyk, *J. Environ. Monit.*, 2005, **7**, 1169–1176.
- 8 J. Zheng, D. Fisher, E. Blake, G. Hall, J. Vaive, M. Krachler, C. Zdanowicz, J. Lam, G. Lawson and W. Shotyk, *J. Environ. Monit.*, 2006, **8**, 406–413.
- 9 J. Zheng, W. Shotyk, M. Krachler and D. Fisher, *Global Biogeochem. Cycles*, 2007, **21**, GB2027, DOI: 10.1029/2005GL023860.
- 10 M. Krachler, J. Zheng, D. Fisher and W. Shotyk, *Global Biogeochem. Cycles*, 2008, **22**, GB1015, DOI: 10.1029/2005GL023860.
- 11 M. Krachler, J. Zheng, D. Fisher and W. Shotyk, *Sci. Tot. Environ.*, 2008, **399**, 78–89.
- 12 M. Krachler, J. Zheng, D. Fisher and W. Shotyk, *Global Biogeochem. Cycles*, 2009, DOI: 10.1029/2009GB003471.
- 13 W. Shotyk, M. Krachler, B. Chen and J. Zheng, *J. Environ. Monit.*, 2005, **7**, 1238–1244.
- 14 W. Shotyk, M. Krachler, W. Aeschbach-Hertig, S. Hillier and J. Zheng, *J. Environ. Monit.*, 2009, DOI: 10.1039/b909723f.
- 15 V. E. Hodge, K. J. Stetzenbach and K. H. Johannesson, *Environ. Sci. Technol.*, 1998, **32**, 2481–2486.
- 16 Ontario Ministry of the Environment, *Provincial Groundwater Monitoring Program*, unpublished data.
- 17 G. Faure, *Principles and applications of inorganic geochemistry: a comprehensive textbook for geology students*. Upper Saddle River, N.J., London, Prentice Hall, 1998.
- 18 C. F. Baes, Jr. and R. E. Mesmer, *The Hydrolysis of Cations*. 512p., John Wiley and Sons, New York, 1976.
- 19 S. A. Sanudo-Wilhelmy, F. K. Rossi, H. Bokuniewicz and R. J. Paulsen, *Environ. Sci. Technol.*, 2002, **36**, 1435–1441.
- 20 A. J. Horowitz, K. R. Lum, J. R. Garbarino, G. E. M. Hall, C. Lemieux and C. R. Demas, *Environ. Sci. Technol.*, 1996, **30**, 954–963.
- 21 N. Rausch, L. Ukonmaanaho, T. Nieminen, M. Krachler, G. Le Roux and W. Shotyk, *Anal. Chim. Acta*, 2006, **558**, 201–210.
- 22 J. O. Nriagu, G. Lawson, H. K. T. Wong and J. M. Azcue, *J. Great Lakes Res.*, 1993, **19**, 175–182.
- 23 M. P. Field and R. M. Sherrell, *J. Anal. At. Spectrom.*, 2003, **18**, 254–259.
- 24 G. Benoit, K. S. Hunter and T. F. Rozan, *Anal. Chem.*, 1997, **69**, 1006–1011.
- 25 W. Shotyk and M. Krachler, *Geochim. Cosmochim. Acta*, 2009, submitted.
- 26 S. I. Vinogradoff, M. C. Graham, G. J. P. Thornton, S. M. Dunn, J. R. Bacon and J. G. Farmer, *J. Environ. Monit.*, 2005, **7**, 431–444.
- 27 J. Klaminder, R. Bindler, H. Laudon, K. Bishop, O. Emteryd and I. Renberg, *Environ. Sci. Technol.*, 2006, **40**, 4639–4645.
- 28 M. C. Graham, S. I. Vinogradoff, A. J. Chipchase, S. M. Dunn, J. R. Bacon and J. G. Farmer, *Environ. Sci. Technol.*, 2006, **40**, 1250–1256.
- 29 M. Krachler and W. Shotyk, *Sci. Tot. Environ.*, 2009, **407**, 1089–1096.
- 30 W. Shotyk, M. Krachler and B. Chen, *J. Environ. Monit.*, 2006, **8**, 288–292.
- 31 W. Shotyk and M. Krachler, *Environ. Sci. Technol.*, 2007, **41**, 1560–1563.
- 32 W. Shotyk and M. Krachler, *Environ. Sci. Technol.*, 2007, **41**, 3508–3513.