

Natural abundance of Sb and Sc in pristine groundwaters, Springwater Township, Ontario, Canada, and implications for tracing contamination from landfill leachates†

William Shotyk,* Michael Krachler, Bin Chen‡ and James Zheng§

Institute of Environmental Geochemistry, University of Heidelberg, INF 236, D-69120 Heidelberg, Germany. E-mail: shotyk@ugc.uni-heidelberg.de; Fax: +49 (6221) 54 5228; Tel: +49 (6221) 54 4803

Received 1st July 2005, Accepted 17th October 2005

First published as an Advance Article on the web 9th November 2005

Using ICP-SMS and the clean lab methods and procedures developed for determining trace element concentrations in polar snow and ice, a lower limit of detection (LOD) of 30 pg l^{-1} for Sb and 5 pg l^{-1} for Sc was achieved, allowing the natural abundances of Sb and Sc to be measured in pristine groundwaters. Water samples were collected from natural flows and wells between Elmvale and Wyevale in Springwater Township, Ontario, Canada. The water in this region is derived from chemical reactions between meteoric fluids and the Quaternary sediments which cover the bedrock (dolomitic limestone) to depths of more than 100 m. The chemical composition of these waters (pH 8) is primarily a reflection of reactions between the percolating fluids with calcite and dolomite. The maximum concentration of Sb was 5.0 ng l^{-1} , and the average of all samples collected was $2.2 \pm 1.2 \text{ ng l}^{-1}$ ($n = 34$). The average concentration of Sc was $8.6 \pm 4.7 \text{ ng l}^{-1}$ ($n = 28$). The paucity of published Sb concentration data available for comparison is probably because most of the analytical methods commonly used to date, including GFAAS, HG-AAS, HG-AFS, INAA, and ICP-QMS, have lower limits of detection which are inadequate for reliably determining the natural abundance of Sb in many uncontaminated groundwaters. Also, the measurement of extremely low concentrations of Sb requires extra care to avoid possible contamination. Given the extensive use of Sb in plastics, we show that some of the containers used to collect and store samples, and for handling and preparing samples for chemical analyses, may be important sources of contamination in the laboratory. The Sb and Sc concentrations reported here should serve as reference values for this region, against which contamination by various human impacts in future could be compared.

Introduction

One of the main goals of environmental geochemistry is to understand in a quantitative way the effects of human activities on the geochemical cycles of the elements. This objective cannot be met unless the natural geochemical cycle of the element under consideration is clearly understood. With respect to the environmental geochemistry of Sb, there have been remarkably few studies, compared to most other potentially toxic trace metals, and the contemporary significance of this element appears to have been underestimated by a considerable margin.¹ There are many gaps in our knowledge of the geochemical cycle of Sb,² one of them being the fate of Sb in the hydrocycle.

Antimony is one of the elements commonly enriched in leachates from landfills. This topic has been studied in some detail by Looser *et al.*³ who reported Sb concentrations in leachates from landfills in Switzerland. The maximum concentrations of Sb in the leachates were as follows: rural and urban landfills, *ca.* $1 \text{ } \mu\text{g l}^{-1}$; industrial landfills, *ca.* $300 \text{ } \mu\text{g l}^{-1}$; “co-disposal” landfills containing both urban and industrial wastes,

ca. $10 \text{ } \mu\text{g l}^{-1}$. The groundwaters which are impacted by these leachates contain several hundred ng l^{-1} of Sb.³ To put these values into perspective, however, the natural abundance of Sb in pristine waters is also needed, for comparison. Attempts to measure Sb in uncontaminated groundwaters failed;³ even though a double-focussing sector-field ICP MS was used, the



William Shotyk was born in the Village of Swansea, now part of the City of Toronto, in Ontario, Canada, in 1958. He received his BSc (Agr) in Soil Science and Chemistry from the University of Guelph in 1981, a PhD in Geology from the University of Western Ontario in 1987, and a Habilitation in Geochemistry from the University of Berne, Switzerland, in 1995. Since October of 2000 he has been Professor (C4) at the University of Heidelberg and Director of the Institute of Environmental Geochemistry. His research group is responsible for Inorganic and Radiogenic Isotope Geochemistry. His main research interests focus upon human impacts on the exogenic geochemical cycles of potentially toxic trace elements such as Pb, Sb, As, Cd and Hg.

† This work was presented at the First International Workshop on Antimony in the Environment, Heidelberg, Germany, 16th to 19th May 2005.

‡ Present address: Department of Environmental Health Sciences, School of Public Health, University of Michigan, 109 Observatory Street, Ann Arbor, MI 48109, USA.

§ Present address: GSC Northern Canada, Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada K1A 0E8.

limit of detection (LOD) for Sb was 100 ng l^{-1} which was too high for this purpose.

In the comprehensive compilation and review of the occurrence of Sb in natural waters,^{4,5} there are remarkably few data published for pristine groundwaters. The data available to date, derived mainly from early work using pre-concentration techniques and neutron activation analyses, range from tens to hundreds of ng l^{-1} , with the lowest reported value in groundwaters being 10 ng l^{-1} .⁴ More recently, Sb has been reported in a range of uncontaminated groundwaters.^{6,7} In a study of more than 1600 groundwater samples collected from areas of crystalline bedrock of Norway, Sb concentrations ranged from $<2 \text{ ng l}^{-1}$ up to a few $\mu\text{g l}^{-1}$.⁶ From Fig. 7 of that publication, the median concentration of Sb appears to be approximately 30 ng l^{-1} . The range in Sb concentrations reflects the geological, mineralogical, and hydrological diversity of the terrain which they investigated. In a more recent investigation of 138 samples of well water from Ethiopia,⁷ the median Sb concentration was 28 ng l^{-1} Sb, with a range of $<2 \text{ ng l}^{-1}$ to $1.28 \mu\text{g l}^{-1}$. In both of these studies, the LOD obtained using ICP-QMS was 2 ng l^{-1} , and this was found to be inadequate for many of the samples in both studies. Taken together, the results from these most recent studies show that quantitative determinations of Sb concentrations in pristine groundwaters require lower limits of detection which will allow Sb to be measured reliably at concentrations below 2 ng l^{-1} . At such extremely low concentrations, not only is analytical sensitivity a considerable challenge, but sample contamination is also a serious concern.

Compared to Sb, there is even less Sc data available for comparison. Scandium is one of the most sensitive elements which can be measured using neutron activation analysis,⁸ and 10 ng l^{-1} has been given as a typical concentration for freshwaters.⁹ Recent attempts to measure Sc concentrations in groundwaters using ICP-QMS have failed⁶ because of the number of molecular interferences in the mass spectrum. However, using high mass resolution provided by ICP-SMS, all of these molecular interferences can be overcome,¹⁰ and this should allow Sc to be measured quantitatively down to extremely low concentrations.

Recently, clean lab methods and procedures were developed to allow both Sb and Sc to be determined in polar snow and ice from the Canadian arctic.^{11,12} Using ICP-SMS with a high efficiency, desolvating sample introduction system (APEX Q), a LOD of 30 pg l^{-1} was achieved for Sb, and 5 pg l^{-1} for Sc.¹³ With the help of this instrumentation and clean lab protocols, we now report the natural abundance of Sb and Sc in some pristine groundwaters from Springwater Township, Ontario. The locations which were sampled include those which have been selected for the construction of a municipal waste disposal site (Site 41), in an area of groundwater discharge.¹⁴ The main objective of this study is to determine the natural abundances of Sb and Sc in the groundwaters of this region, in their pristine condition, to provide a reference level against which any changes in future can be compared. A second objective is to illustrate some of the risks of Sb contamination to water samples by plastic containers and handling equipment commonly available in most laboratories.

Materials and methods

The waters were collected from natural flows and wells between Elmvale ($44^{\circ}35'00'' \text{ N}$, $79^{\circ}51'57.0'' \text{ W}$) and Wyevale ($44^{\circ}39'13.8'' \text{ N}$, $79^{\circ}55'34.4'' \text{ W}$), in Springwater Township, Ontario, Canada (Fig. 1a). This area of Simcoe County, approximately 120 km north of Toronto, was occupied by the native Wendat (Huron) people until *ca.* 1650; by this time, they had been eliminated by disease introduced by the French arrival in 1603, and war with their rivals from the Five Nations.¹⁵ The area remained a wilderness until *ca.* 1850 when European settlers

arrived and began to clear the forests and cultivate the land for farming.¹⁶ The area has remained agricultural ever since, and there is effectively no industry. Agriculture and related occupations, retail and commercial services, and recreation and tourism are the dominant sectors of the local economy. This region contains an abundance of groundwater, giving rise to the appellation Springwater Township. These waters are the source of many of the streams and lakes in the area, and ultimately flow into Georgian Bay of Lake Huron, one of the Great Lakes.

Part of the St. Lawrence Platform, this region of southern Ontario is underlain by Ordovician limestones and dolostones.¹⁷ The dominant physiographic zones are the Simcoe Lowlands and the Simcoe Uplands.¹⁸ Once part of glacial Lake Algonquin, the surficial deposits of the Lowlands (2816 km^2) 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 feature of the lowlands.¹⁸ Here, where we collected our samples (Fig. 1b), many of these fine-textured soils are imperfectly drained and the water table is close to the soil surface. In the vicinity of Site 41, soils consisting of silty clays and clayey silts extend to depths of *ca.* 5 to 15 m, but are underlain by several metres of permeable sand which constitutes a confined aquifer; these materials, in turn, overlie *ca.* 80 or 90 m of glacial till.¹⁴ This is an area of groundwater discharge: the water in the sand aquifer below the clay soils are under pressure, giving rise to upward gradients and many natural flows and springs.

In contrast, the Uplands (1024 km^2) 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.¹⁸ The till in the uplands consists mainly of Precambrian bedrock derived from the Canadian Shield 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. With respect to the flows and wells which we have studied (Fig. 1b), the recharge area for the Wyevale samples, taken adjacent to Site 41, is believed to be in the uplands centred around Waverley ($44^{\circ}38'28.8'' \text{ N}$, $79^{\circ}49'21.8'' \text{ W}$).

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).

Water samples from the aquifer at Site 41 were collected between 1999 and 2002 from boreholes and yielded the following average values: pH 8.0, 182 mg l^{-1} carbonate alkalinity, major element cations and anions (mg l^{-1}) Ca 47.6, Mg 17.6, Sr 5.0, Na 6.4, K 3.6, SO_4^{2-} 17.9, Cl^{-} 1.2, DOC 1.1.¹⁹

Sample collection

The water samples collected for this study were collected from the stations listed in Table 1 during 2004 and 2005. The samples collected during 2004 were part of a preliminary study of the waters from this region, and employed a single sample from each site. The samples collected in 2005 at the Old Johnson Farm and the flow from the field at the Parnell farm are more representative of the waters in this area as they consist of a number of replicates (Table 1). Wearing 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,

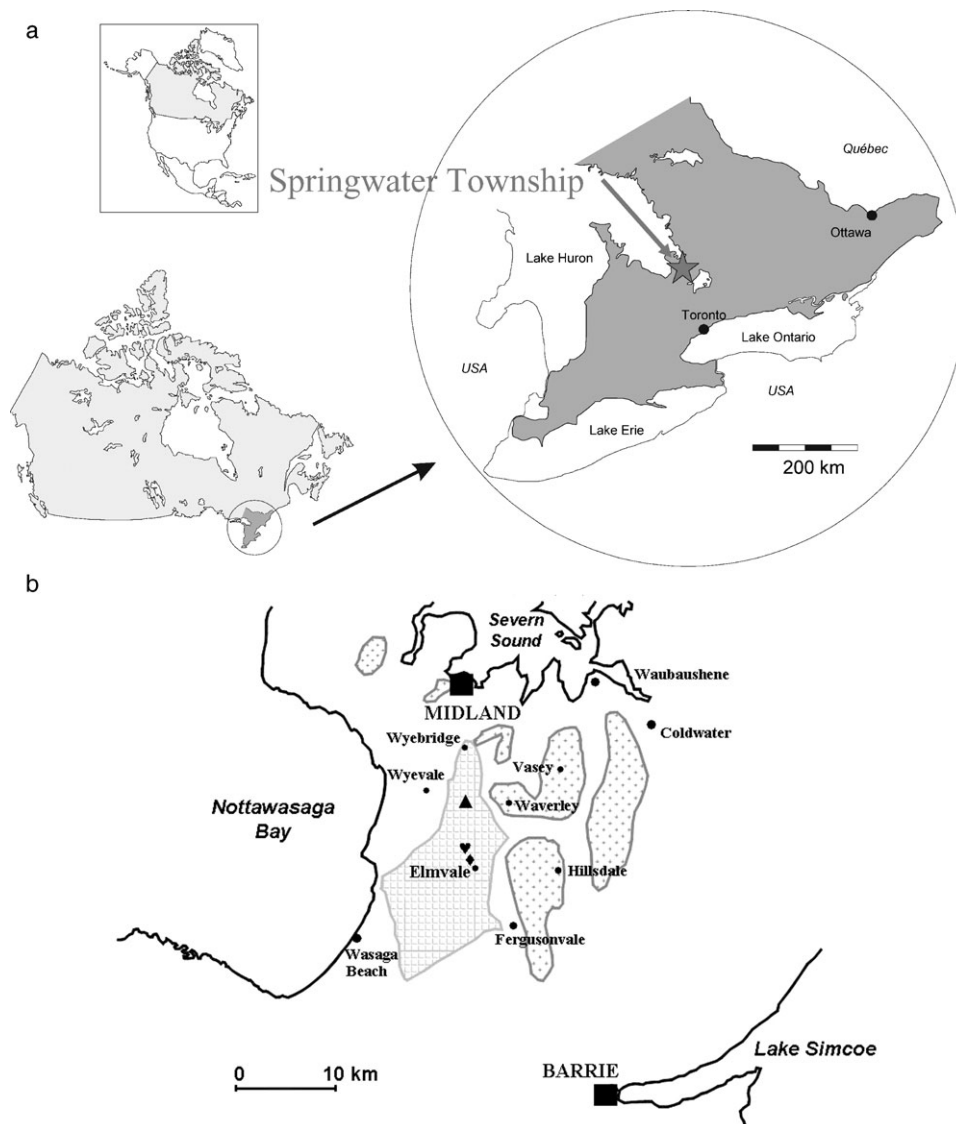


Fig. 1 (a) Location of Springwater Township, Ontario, Canada. (b) Location of sampling sites. The hatched area corresponds to the Elmvale Clay Plain (Chapman and Putnam, 1966) which is an area of groundwater discharge. The stippled areas are part of the Simcoe Uplands and represent an area of groundwater recharge. The solid diamond (◆) shows the location of the flow beside County Road 27, the heart (♥) the location of the Old Johnson Farm; these are the “Elmvale” samples. The solid triangle (▲) shows the approximate location of the “Wyevale” samples which were collected adjacent to Site 41.

and has an average Sb concentration of $<30 \text{ pg l}^{-1}$. Addition of $100 \mu\text{l}$ of this acid to 100 ml of water from the old Johnson Farm (Table 1) reduced the pH to 1.7 which is sufficient to stabilise the trace metals until the samples could be measured. To minimise the risks of contamination, none of the water samples were filtered.

The flow beside County Road 27 (Elmvale) and the flow in the Parnell field (Wyevale) run continuously. At these sites, therefore, there is no concern about leaching of Sb from the steel pipes used to channel the flow of groundwater to the surface; also, these water delivery systems do not employ any valves. The flow at the Old Johnson farm (Elmvale) also runs continuously, but was sampled from a brass faucet. Samples were collected from this source in July of 2005 after allowing the water to flow for 0, 5, 10, 15, 30, 60, and 120 min. The first sample taken (0 min) contained 16.3 ng l^{-1} Sb; all the other samples contained $\leq 2.0 \text{ ng l}^{-1}$ Sb. The first sample also contained elevated concentrations of Cu, Zn, and Pb, and it is assumed that the elevated Sb in this first sample reflects either the influence of the brass tap or the solder used to attach it to the pipe. Because all of the other water samples collected from this source were collected after the water was allowed to

run for at least 5 minutes, prior to sample collection, we have every confidence that the measured Sb concentrations reported for the 2005 samples reflect the original abundance of this element in the water. The water samples collected from the rural households in the Wyevale area were also allowed to run prior to sampling. Given that comparable Sb concentrations were found in samples from continuous flows and from the households sampled, it appears unlikely that solder which might have been used to connect the plumbing²⁰ has contributed significant Sb to the household samples.

Water samples were packed into two (2004) or three (2005) 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.

For comparison with the groundwaters, samples of surface water were also collected from the spring which feeds a small swamp ($44^{\circ}38'13.0'' \text{ N}$, $79^{\circ}52'15.2'' \text{ W}$), adjacent to Site 41, as well as Macdonald Creek which drains the swamp; this creek was sampled downstream from Baseline Road ($44^{\circ}39'02.8'' \text{ N}$, $79^{\circ}52'36.4'' \text{ W}$).

Table 1 Abundance of Sb and Sc in the pristine groundwaters from Springwater Township

Sample	Date of collection	Depth/m	Sb/ng l ^{-1a}	Sc/ng l ^{-1b}
Old Johnson farm (44°36'15" N, 79°52'57")	August, September, October 2004	Unknown	4.4 ± 1.4 (n = 3)	14.4 ± 2.1 (n = 3)
Old Johnson farm	1 April 2005	Unknown	1.4 ± 0.4 (n = 6)	9.0 ± 2.9 (n = 6)
Old Johnson farm	26 July 2005	Unknown	1.9 ± 0.1 (n = 6)	4.7 ± 0.6 (n = 6)
Old Johnson farm	7 September 2005	Unknown	2.1 ± 0.1 (n = 3)	4.5 ± 0.2 (n = 3)
Leonard household	24 September 2004	19	5.0	14.4
Greidanus household ^c	7 October 2004	80	3.4	17.2
Nahuis household	7 October 2004	25	1.4	19.5
Parnell farm (continuous flow, in field)	7 October 2004	Unknown	4.0	13.9
Parnell farm	1 April 2005	Unknown	1.9 ± 0.7 (n = 6)	6.2 ± 2.4 (n = 6)
Lot 5, Concession 9, County Rd. 27 (continuous flow, adjacent to highway)	1 January 2005	56 ^d	1.8 ± 1.1 (n = 6)	N/A
Swamp	7 October 2004	Surface	12.4	11.5
Macdonald Creek	7 October 2004	Surface	23.4	18.9

^a LOD = 30 pg l⁻¹. ^b LOD = 5 pg l⁻¹. ^c Chemical composition on 31.5.03 as follows: pH 8.05, 186 mg l⁻¹ alkalinity (as CaCO₃). Major elements (mg l⁻¹) 37.4 Ca, 18.8 Mg, 8.2 Na, 2 K, 11.6 SO₄²⁻, 0.6 DOC, <0.5 Cl⁻. N/A not available. ^d Described in the Water Well Record by the Ontario Ministry of Environment as follows: 0–1 m, top soil; 1–6.7 m, brown clay; 6.7–34.7 m, blue clay; 34.7–55.5 m, silty sand; 55.5–56.5 m, sand and gravel. Casing is 16 cm id and flow is ca. 1 l s⁻¹.

Determination of Sb in groundwaters using ICP-SMS

All cleaning procedures and sample manipulations were carried out in clean benches of US 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 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.

The average concentration of Sb in 15 independent blank solutions containing 0.5% HNO₃ was 43 ± 10 pg l⁻¹ and mainly reflects the contribution of Sb from the high purity water and not that of the acid. Analyses of different HNO₃ concentrations (0.5%, 1%, 2%, 5%, 10%) produced comparable signals, *i.e.* increasing acid concentrations had no detectable influence on the Sb signal intensity. Therefore, Sb contributions from HNO₃ are below the detection limit of 30 pg l⁻¹.

Antimony and Sc 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.¹³ 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. Details about instrument settings, acquisition and evaluation parameters are given elsewhere.¹³

For quality control purposes, SLRS-4, a certified, standard reference material (river water) was analyzed twice. The measured concentrations of Sb (245 ± 9 ng l⁻¹) and Sc (10.1 ± 0.6 ng l⁻¹) agree well with the certified (Sb: 230 ± 40 ng l⁻¹) and reference values (Sc: 11.3 ± 0.6 ng l⁻¹ according to ref. 12), respectively.

Determination of Sb in plastic using INAA

Selected specimens of plastic were measured for Sb concentrations using instrumental neutron activation analysis at ACTLABS, Ancaster, Ontario, Canada, prior to collection of the water samples.

Determination of Sb in HCl dispensed from a glass bottle using HG-AFS

The release of Sb from a plastic dispenser was evaluated using hydride generation-atomic fluorescence spectrometry (HG-AFS). For the determination of Sb by HG-AFS, an aliquot (30 ml) of the sample was transferred into a 50-ml PE volumetric flask. One ml of L-cysteine (50 g l⁻¹) solution was added before it was filled up to 50 ml with 10 mol l⁻¹ HCl. Stibine was generated in a continuous flow system using NaBH₄ (1.0%, m/v) solution (stabilized with 0.04% m/v NaOH) and 4 mol l⁻¹ HCl as carrier solution. The analyte solution (flow rate: 9 ml min⁻¹) and carrier solution (NaBH₄ flow rate: 4.5 ml min⁻¹ and HCl flow rate: 9 ml min⁻¹) were simultaneously pumped into the sample valve for mixing.²¹

Results and discussion

Abundance of Sb in pristine groundwaters from Springwater Township

The maximum concentration of Sb found was 5.0 ng l⁻¹ (Table 1), and the average of all samples collected was 2.2 ± 1.2 ng l⁻¹ (n = 34). The average concentration of Sb in these waters, however, is *ca.* two orders of magnitude greater than the LOD (0.03 ng l⁻¹). The methods and procedures employed here, therefore, are certainly capable of reliable measurements of Sb concentrations in pristine groundwaters. These Sb values provide a reference level for the waters of this area, against which any changes in future can be compared. With Sb concentrations in landfill leachates³ up to five orders of magnitude greater than the natural background abundance of Sb in the pristine groundwaters of Springwater Township (≤5 ng l⁻¹), Sb should provide a useful basis for monitoring any changes to the quality of these groundwaters in future.

A comparison of the abundance of Sb in these waters with the LODs which have been obtained using other analytical procedures indicates that previously published methods are not capable of directly measuring Sb reliably at these low concentrations (Table 2). Even using ICP-QMS, the lowest LODs reported to date (2 ng l⁻¹) are clearly inadequate, given that the

Table 2 Lower limits of detection for various analytical methods and procedures used to determine concentrations of Sb (ng l⁻¹) in waters

Analytical method	LOD, Sb/ng l ⁻¹	Reference
INAA after PbS precipitation	1000	Majola and Zikovsky ²²
ICP-QMS	1000	McCarty <i>et al.</i> ³⁵
GFAAS	300	Filho <i>et al.</i> ³⁶
ICP-QMS	120	Dabeka <i>et al.</i> ²³
HR-ICP-MS	100	Looser <i>et al.</i> ³
HR-ICP-MS	60	Cheng <i>et al.</i> ³⁷
ICP-QMS after pre-concentration	20	Lee <i>et al.</i> ³⁸
HG-AFS	20	Sun <i>et al.</i> ³⁹
ICP-QMS	10	Naohara ⁴⁰
HG-AFS	8	Chen <i>et al.</i> ²¹
ICP-QMS	2	Misund <i>et al.</i> ²⁴
ICP-QMS	2	Frengstad <i>et al.</i> ⁶
ICP-QMS	2	Reimann <i>et al.</i> ⁷
ICP-SMS	0.03	This study

average abundance of Sb in these waters is only 2.2 ± 1.2 ng l⁻¹ ($n = 34$). The minimum concentration of Sb found in the waters described here was 0.9 ng l⁻¹ (in a sample from the Old Johnson Farm), and reliable measurements of Sb require LODs which are at least a factor of ten lower than this. Any published values of Sb in uncontaminated natural waters at concentrations approaching the LOD, therefore, should be viewed with caution.

Risks of Sb contamination by plastics commonly used in the laboratory

All of the plastic bottles used in this study, as well as their lids, contain Sb in concentrations below the limit of detection of 0.1 µg g⁻¹ provided by INAA. However, the red lid from a plastic jar designed for urine samples was found to contain 106 µg g⁻¹ of Sb. The HCl used for HG-AFS analyses was found to contain approximately 21 ng l⁻¹ Sb when it was sampled directly from the glass bottle. However, the Sb concentrations obtained in HCl from the same bottle *via* the plastic dispenser were up to 3810 ng l⁻¹. These two simple examples illustrate the risks of sample contamination in measuring Sb concentrations at trace and ultratrace concentrations from the plastics commonly found in most laboratories. Given the extremely low concentrations of Sb in pristine groundwaters, such as those described here, there is a clear need for scrupulous contamination control, and blank values from plastics must duly be considered.

All of the water samples collected from the Old Johnson Farm in 2005 (April, July, and September) were kept refrigerated until they could be measured. All of the ICP-SMS determinations were performed during the week of October 10–14, 2005. The average concentrations of Sb in these samples (Table 1), however, does not reflect their time of storage (6, 3, and 1 month, respectively). Subsequent to sample collection, therefore, leaching of Sb from the acid-cleaned LDPE containers used in this study, was negligible.

Sb in bottled natural waters

For comparison with the data presented here, there has been a number of reports of Sb in bottled natural waters. In a study of trace element concentrations in bottled waters from Canada, the US, Europe, and Africa, a median Sb concentration of 2 µg l⁻¹ and a range of 1 to 50 µg l⁻¹ was reported.²² Some of these values exceed the Maximum Allowable Concentration (MAC) set by the World Health Organization (WHO) of 5 µg l⁻¹. However, the data are close to the limit of detection of the method which they employed (INAA after precipitation with

PbS) and are not considered further here. A more recent study of bottled waters sold in Canada²³ reported much lower values: 42 mineral waters averaged 0.32 µg l⁻¹, 102 springwaters averaged 0.30 µg l⁻¹, and 11 tap waters 0.17 µg l⁻¹; the limit of detection (ICP-QMS) was 0.12 µg l⁻¹. All of these values are high, relative to the average abundance of Sb in pristine groundwaters reported here (2.2 ± 1.2 ng l⁻¹). In a study of 56 bottled waters from Europe,²⁴ the median was 0.165 µg l⁻¹, compared with a median concentration of 0.028 µg l⁻¹ Sb in groundwaters from Norway. Comparison of the data presented here (≤ 5 ng l⁻¹) with published data from bottled waters leads us to ask whether the Sb concentrations reported for the bottled waters reflect the Sb concentrations originally present in the natural waters, or whether they possibly reflect an additional contribution from the containers in which many of the waters are sold. Given this uncertainty, it may well be that the concentrations of Sb in pristine natural waters are in general far lower than commonly believed.

Sb/Sc in the pristine groundwaters of Springwater Township

The Sb/Sc ratio (1 : 4) in the pristine waters exceeds the crustal ratio (1 : 45) by at least a factor of ten. In other words, using Sc as a lithogenic reference element, there is a natural enrichment of Sb in the waters, relative to its abundance in crustal rocks. The abundance of Ca, Mg, and bicarbonate in these waters, and the high pH (8) indicates that the chemical composition of the waters is dominated by reactions between the percolating fluids and carbonate minerals. The abundance of Sb in carbonate and silicate minerals is very similar,²⁵ and comparable to the crustal abundance (0.3 ppm) of this element.²⁶ However, it is the dissolution of the carbonate phases, and not the silicates, which dominates the weathering inputs to the waters. The dominant source of Sb to the waters, therefore, is most likely the carbonate mineral fraction.

Magnesium in the waters is derived primarily from the dissolution of dolomite [Ca, Mg(CO₃)₂]. Taking the Mg concentration in Table 1 as being representative of these waters generally, it is estimated that 0.10 mmole of dolomite has dissolved per litre of fluid. This would provide the waters not only with Mg (19 mg l⁻¹) but also Ca (4 mg l⁻¹). The remaining Ca (34 mg l⁻¹) must be derived from the dissolution of calcite [CaCO₃]. The amount of calcite dissolution is thereby estimated at 0.85 mmol l⁻¹. Assuming that all of the dissolved Sb is derived from the calcite, the calcite would only have to have an average Sb concentration of *ca.* 35 ng g⁻¹ to account for the abundance of Sb in these fluids. This value is at the lower end of the range presented for Sb in sedimentary rocks.²⁵ As a first approximation, therefore, the natural abundance of Sb in these waters can be explained simply by the dissolution of calcite. The dissolution of other soluble, sedimentary minerals such as dolomite and gypsum containing trace concentrations of Sb, could similarly be invoked to help account for the natural abundance of Sb in these waters.

Scandium is *ca.* ten times more abundant in silicate minerals, compared to carbonates,²⁵ with most primary, rock-forming silicate minerals containing Sc in concentrations comparable to its crustal abundance (15 ppm). However, using the arguments presented earlier for Sb, the average concentration of Sc in these waters could be explained by the dissolution of calcite containing *ca.* 100 ng g⁻¹ Sc. Taken together, the dissolution of calcite containing only 35 ng g⁻¹ Sb and 100 ng g⁻¹ Sc would be sufficient to account for the Sb and Sc concentrations of these waters. The solubility of Sc(OH)₃ is comparable to that of Al(OH)₃,^{25,27} yet the Al concentrations in these waters (average 150 µg l⁻¹) are four orders of magnitude greater than those of Sc. The Al concentrations in the waters reflect saturation with respect to amorphous Al hydroxide [Al(OH)₃] at pH 8.²⁸ With respect to Sc(OH)₃, the waters are apparently undersaturated by a factor of *ca.* 10³. The difference in the saturation states between

Al and Sc in these waters is consistent with the differences in their relative abundances in the sediments: the crustal abundance of Al is 8 weight percent *versus* 15 mg kg⁻¹ Sc.²⁶

Sb/Sc in groundwaters as a possible tracer of contamination from landfill leachates

Antimony is used in a broad range of industrial and commercial products and processes.^{29,30} For example, it is used in semiconductors, diodes and infrared detectors, and as an alloying ingredient to harden Pb and other metals. Alloys of Sb are used in the manufacture of batteries, cable sheathing, bearings, castings, sheets and pipes, plumbing solder and antifriction materials. Antimony trisulfide is used in the manufacture of safety matches. Automotive brake linings may contain several weight percent Sb which is added to improve their heat-resistance. Non-metallic Sb products include paint pigments, ceramic enamels, plastics, glass, pottery, ammunition primers and fireworks. Some Sb compounds are used in the vulcanising of rubber; other organic Sb compounds may be bactericides or fungicides. The single greatest use of Sb today (*ca.* two-thirds of total Sb production) is as a flame retardant: antimony trioxide (Sb₂O₃) is added to plastics such as polyvinyl chloride (PVC), especially in car components, televisions, electrical insulation, furnishing fabrics, and other synthetic fibres, and cot mattresses. Antimony trioxide is also the catalyst used to manufacture polyethylene terephthalate (PET); this material may contain a few hundred parts per million of Sb. Total global production of Sb is 140 000 tonnes per annum. Given the broad range of uses, Sb will be commonly found in many of the materials entering waste streams, including those at Site 41.

It is well known that both the trivalent and pentavalent oxides of Sb are rather soluble.³¹ According to Wedepohl,²⁵ the solubilities of Sb₂O₃ and Sb₂O₅ are 1.3 and 8.8 mg l⁻¹, respectively, at 35 °C. Except in anoxic environments, Sb(OH)₆⁻ will be the predominant species over the entire pH range which characterises natural waters.^{5,32} As a soluble anion, Sb should exhibit a considerable degree of mobility in soil-water systems. Sequential extraction of shooting range soils contaminated with Sb have recently confirmed that this element is comparatively mobile.³³ Although Ca antimonate Ca[Sb(OH)₆]₂ is a possible solubility control, at pH 8 this too, would permit mg l⁻¹ concentrations of dissolved Sb.³³ Taken together, an enrichment of Sb in leachates from landfills can be anticipated, relative to the composition of pristine waters, as has already been documented in Switzerland.³

In contrast to Sb, industrial uses of Sc are negligible, with total global Sc production amounting to only 45 kg per year.³⁰ In fact, there are effectively no commercial or industrial uses of this element. Scandium is a lithogenic trace element which behaves conservatively during the chemical weathering of crustal rocks.³⁴ Scandium has no preference for specific mineral phases (only seven Sc minerals are known, and they are all rare), but instead is widely distributed in all of the primary and secondary minerals at the surface of the Earth.

Given the abundance of Sb in waste materials and the solubility of its oxides, and the exclusive association between Sc and rock-forming minerals and the low solubility of its hydroxides, the ratio of Sb to Sc might be more useful index of contamination than the concentrations of Sb alone. In the pristine waters which are described here, the ratio of Sb to Sc is currently between 1 : 2 and 1 : 5. This ratio might prove to be a useful parameter in future, for monitoring impacts on groundwater quality by leachates from landfills and other sources of contamination.

Summary and conclusions

The natural abundance of Sb in the groundwaters of this region of Springwater Township is very low (≤ 5 ng l⁻¹).

Measuring Sb reliably at the low concentrations characteristic of pristine groundwaters presents two challenges: first, the obvious problem of being able to detect this element at such low concentrations. A less obvious challenge is that of contamination control, as many of the plastics found in laboratory use, in the form of sample containers as well as dispensers, contain Sb and pose a risk for quantitative determinations at such low concentrations. The procedures and methods developed in our lab for measuring Sb in polar snow and ice allow the abundance of Sb in pristine natural waters to be reliably determined. It is possible that some earlier reports have overestimated the natural abundance of Sb in similar natural waters, partly because of the poor precision of measurements near the lower limit of detection, but also because of contamination by Sb-containing plastics commonly found in labs.

The published reports of the abundance of Sb in leachates from landfills reveal concentrations of Sb which are up to five orders of magnitude greater than the natural values presented here, indicating that Sb should be a sensitive and possibly valuable tracer of any possible impacts on water quality in future. The average ratio of Sb to Sc is currently 1 to 4. Because of the low solubility of Sc, and because there are no industrial or commercial uses of this element, the ratio of Sb to Sc might be a useful parameter to detect impacts of the landfill leachates on these pristine groundwaters.

The concentrations of Sb reported in many determinations of Sb in bottled waters are much higher than those presented here. While these differences certainly may reflect geological, mineralogical, and hydrological variability, the possibility that these values are artefacts created by the contamination of these waters with Sb from the containers warrants investigation.

Acknowledgements

The support of the Alexander von Humboldt Foundation to B. C. is gratefully acknowledged. Thanks to Darrell Leonard for logistical support, and to families Leonard, Greidanus, Naihus, and Parnell for allowing their water sources to be sampled. The major element chemistry was provided by the County of Simcoe (special thanks to Mark Aitken and Robert McCullough). Thanks also to A. K. Cheburkin for helpful discussions regarding the geology of the area, M. Isenbeck-Schröter for critically reading an early version of the manuscript, Stefan Rheinberger for technical support in the lab, and Emma Shotyk for helping to collect the 2005 water samples. We are indebted to Dr Bernd Kober for designing and the University of Heidelberg for constructing a unique clean laboratory and providing related instrumentation which has made this work possible. W. S. wishes to dedicate this paper to his father, Michael, who has cared for the Johnson farm since he bought it in 1972, for a lifetime of unfailing support and encouragement and for instilling a love of nature.

References

- 1 W. Shotyk, M. Krachler, and B. Chen. Anthropogenic Impacts on the Biogeochemistry and Cycling of Antimony, in *Biogeochemistry, Availability, and Transport of Metals in the Environment*, ed. A. Sigel, H. Sigel, and R. K. O. Sigel, M. Dekker, Vol. 44 of *Metal Ions in Biological Systems*, New York, 2005, pp. 172–203.
- 2 R. W. Boyle and J. R. Jonasson, *J. Geochem. Explor.*, 1984, **20**, 223.
- 3 M. O. Looser, A. Parriaux and M. Bensimon, *Water Res.*, 1999, **33**, 3609.
- 4 M. Filella, N. Belzile and Y.-W. Chen, *Earth-Sci. Rev.*, 2002, **57**, 125.
- 5 M. Filella, N. Belzile and Y.-W. Chen, *Earth-Sci. Rev.*, 2002, **59**, 265.
- 6 B. Frengstad, D. Banks and U. Siewers, *Sci. Total Environ.*, 2001, **277**, 101.
- 7 C. Reimann, K. Bjorvatn, B. Frengstad, Z. Melaku, R. Tekle-Haimanot and U. Siewers, *Sci. Total Environ.*, 2003, **311**, 65.

- 8 H. J. M. Bowen and D. Gibbons, *Radioactivation Analysis*, Clarendon Press, Oxford, 1963.
- 9 H. J. M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, New York, 1979.
- 10 T. Prohaska, S. Hann, C. Latkoczy and G. Stingeder, *J. Anal. At. Spectrom.*, 1999, **14**, 1.
- 11 M. Krachler, J. Zheng, D. A. Fisher and W. Shotyk, *J. Anal. At. Spectrom.*, 2004, **19**, 1017.
- 12 M. Krachler, J. Zheng, D. A. Fisher and W. Shotyk, *Anal. Chim. Acta*, 2005, **530**, 291.
- 13 M. Krachler, J. Zheng, C. Zdanowicz, F. Koerner, D. Fisher and W. Shotyk, *J. Environ. Monit.*, 2005, **7**, DOI: 10.1039/b509373b.
- 14 Ontario Municipal Board, *Reasons for Decision and Decision*, Joint Board, *Consolidated Hearings Act*, 1981, CH-87-03, 11th November 1989, Ontario Municipal Board, Toronto, ON, Canada, 1989.
- 15 C. Heidenreich, *Huronian: A History and Geography of the Huron Indians 1600–1650*, McClelland and Stewart, Toronto, 1971.
- 16 A. F. Hunter, *A History of Simcoe County*, Historical Committee of Simcoe County, Barrie, 1948.
- 17 R. J. W. Douglas, *Geology and Economic Minerals of Canada*, Department of Energy, Mines, and Resources, Ottawa, 1976.
- 18 L. J. Chapman and D. F. Putnam, *The Physiography of Southern Ontario*, University of Toronto Press, Toronto, 2nd edn., 1966.
- 19 County of Simcoe, *Landfill Site 41, Jagger Hims Report, Supplemental Hydrogeological and Geotechnical Investigation*, County of Simcoe, Midhurst, ON, Canada, 2003.
- 20 C. E. Herrera, J. F. Ferguson and M. M. Benjamin, *J. Am. Water Works Assoc.*, 1982, **74**, 368.
- 21 B. Chen, M. Krachler and W. Shotyk, *J. Anal. At. Spectrom.*, 2003, **18**, 1256.
- 22 J. Majola and L. Zikovsky, *J. Radioanal. Nucl. Chem.*, 1997, **220**, 145.
- 23 R. W. Dabeka, H. B. S. Conacher, J. F. Lawrence, W. H. Newsome, A. McKenzie, H. P. Wagner, R. K. H. Chadha and K. Pepper, *Food Addit. Contam.*, 2002, **19**, 721.
- 24 A. Misund, B. Frengstad, U. Siewers and C. Reimann, *Sci. Total Environ.*, 1999, **244**, 21.
- 25 *Handbook of Geochemistry*, ed. K. H. Wedepohl, Springer, Heidelberg, 1969, 5 vol.
- 26 K. H. Wedepohl, *Geochim. Cosmochim. Acta*, 1995, **59**, 1217.
- 27 C. F. Baes, Jr and R. E. Mesmer, *The Hydrolysis of Cations*, John Wiley and Sons, New York, 1976.
- 28 W. L. Lindsay, *Chemical Equilibria in Soils*, John Wiley and Sons, New York, 1979.
- 29 A. Stwertka, *Guide to the Elements*, Oxford University Press Inc., New York, 1998.
- 30 J. Emsley, *Nature's Building Blocks: An A–Z Guide to the Elements*, Oxford University Press Inc., New York, 2001.
- 31 I. Bodek, W. I. Lyman, W. F. Reehl and D. H. Rosenblatt, *Environmental Inorganic Chemistry. Properties, Processes, and Estimation Methods*, Pergamon Press, New York and Oxford, 1988.
- 32 M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, New York, 1966.
- 33 A. Johnson, H. Moench, P. Wersin, P. Kugler and C. Wenger, *J. Environ. Qual.*, 2005, **34**, 248.
- 34 W. Shotyk, D. Weiss, J. D. Kramers, R. Frei, A. K. Cheburkin, M. Gloor and S. Reese, *Geochim. Cosmochim. Acta*, 2001, **65**, 2337.
- 35 K. M. McCarty, D. B. Senn, M. L. Kile, Q. Quamruzzaman, M. Rahman, G. Mahiuddin and D. C. Christian, *Environ. Health Perspect.*, 2004, **112**, 809.
- 36 V. R. A. Filho, M. de M. Fernandez and J. A. G. Neto, *Atom. Spectrosc.*, 2002, **23**, 7.
- 37 Z. Cheng, Y. Zheng, R. Motlock and A. van Geen, *Anal. Bioanal. Chem.*, 2004, **379**, 512.
- 38 K. H. Lee, M. Oshima and S. Motomizu, *Jpn. Soc. Anal. Chem.*, 2000, **49**, 529 (in Japanese).
- 39 H. W. Sun, J. Ha, J.-M. Sun, D.-Q. Zhang and L.-L. Yang, *Anal. Bioanal. Chem.*, 2002, **374**, 526.
- 40 J. Naohara, *Mizu Kankyo Gakkaishi*, 1998, **21**, 536 (in Japanese).