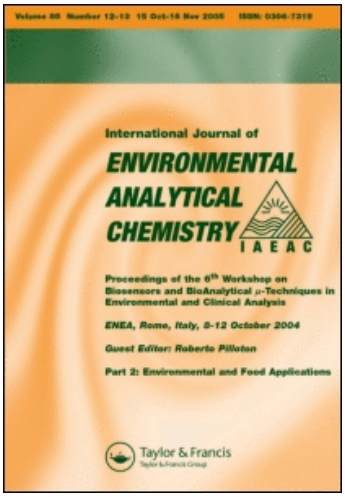

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ANTIMONY SPECIES IN ENVIRONMENTAL SAMPLES

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Antimony was extracted from environmental biota samples from Yellowknife, NWT and Meager Creek, BC, Canada. Extraction efficiencies ranged from 0.7 to 37% for all samples except for a cattail sample, from which 95% of antimony was extracted. Speciation analysis was carried out by using hydride generation-gas chromatography-atomic absorption spectrometry (HG-GC-AAS). The major antimony species in all samples, including biota extracts and water, was Sb (V). Sb (III) and methylated antimony species were detected in some samples as well. The presence of methylated antimony species in moss from Yellowknife and a water sample from Yellowknife was confirmed by using HG-GC-AAS at a second absorption wavelength, increasing the likelihood that the peaks obtained are due to the presence of antimony compounds. A headspace HG-GC-mass spectrometric (MS) method was developed for the speciation of antimony compounds and this was used to successfully confirm methylantimony species in the headspace following HG of extracts of moss and snail samples from Yellowknife.

Keywords: Antimony; speciation; plants; snails; mass spectrometry

INTRODUCTION

Antimony can enter the environment as a result of rock weathering, soil runoff and through effluents from mining and smelting. Its compounds are used as flame retardants in plastics and textiles, as additives in metal alloys, as doping agents in semiconductors, and as antiparasitic drugs[1]. Because of the toxicity of

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some of its compounds, antimony is listed by the United States Environmental Protection Agency (US-EPA) as a priority pollutant[2]. The determination of antimony species in the environment is necessary in order to assess the toxicity and mobility of antimony.

Usually concentrations of naturally occurring antimony are about 5–10% those of arsenic[3] and the two elements are often found together in mineral deposits[4]. Elevated levels of arsenic are found in the environment surrounding Meager Creek hot springs in British Columbia, Canada[5]. Another area, in Yellowknife, Northwest Territories, Canada, has been affected by gold mining activities and contains elevated levels of arsenic[6,7], as well as antimony in biota[8]. We were interested in analyzing samples from these two areas to glean more information about the behaviour of antimony in the environment. Although methods for antimony speciation by using HPLC with element specific detection have been developed[9,10,11], determination of methylantimony species other than Me_3SbCl_2 by using these methods have not been successful[12]. Therefore, we chose to use the method of hydride generation-gas chromatography (HG-GC) with atomic absorption spectrometric (AAS) and mass spectrometric (MS) detection for the analysis of antimony in environmental samples, in spite of the limitations and problems associated with this speciation method[8,13,14].

EXPERIMENTAL

Chemicals and reagents

Antimony (V) and (III) standards were obtained as potassium hexahydroxyantimonate, $KSb(OH)_6$(Aldrich), and potassium antimonyl tartrate, $K_2Sb_2(C_4O_6H_2)_2$ (Aldrich). Me_3SbCl_2 was synthesized as described elsewhere[15]. Stock solutions were made by dissolving these compounds in deionized water and diluting the resulting solutions to 1000 or 100 mg L^{-1} as Sb. Standard working solutions were made by diluting the stock solution with deionized water as necessary.

For hydride generation analysis, $NaBH_4$ (reagent grade, Aldrich) was dissolved in deionized water fresh daily to provide a concentration of 2% w/v. Ammonium citrate buffer at a concentration of 0.05 M and pH 6 (1 M ammonium hydroxide, MicroSelect, Fluka, and analytical reagent grade citric acid, BDH) and 1 M HCl (Environmental grade, Alfa Aesar) were used for pH adjustment during derivatization.

Sampling and sample preparation

Maps depicting sampling locations are shown in Figure 1. Sampling was carried out at Meager Creek (MC) for one day each time in September 1996, November 1996 and July 1997. Water was sampled from three hot spring sources, and from streams created by source runoff (see Figure 1a). A flowering plant, *Mimulus* sp. was picked from a location between streams, growing in soil that was made up of organic detritus and microbial mats that covered the streams.

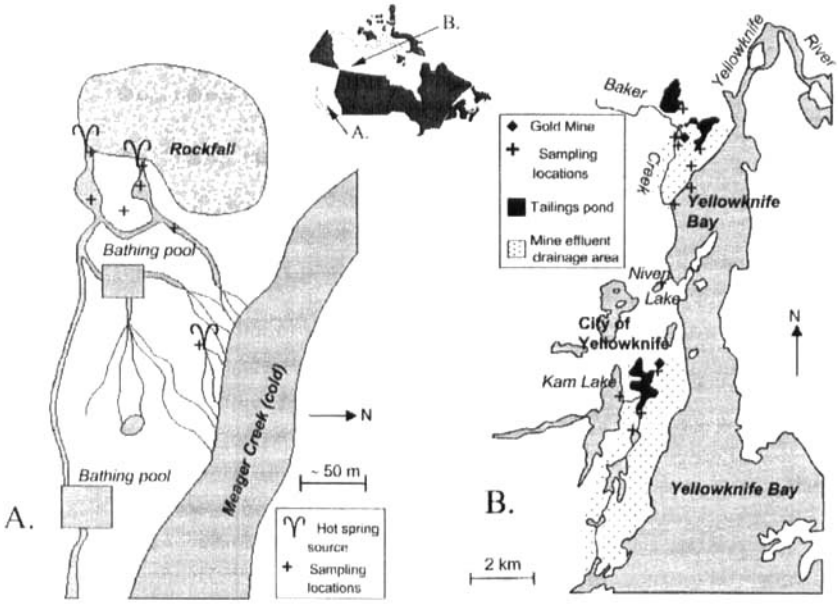

FIGURE 1 Map of Meager Creek (A) and Yellowknife (B)

Sampling was also carried out in Yellowknife (YK) for one week in June 1997 and August 1997. Water samples were collected from streams and puddles receiving mine effluent, and from a pond (Niven Lake) which was formerly a sewage pond and now supports prolific plant growth and wildlife, in the City of Yellowknife (Figure 1b). Biota were sampled from some of the same locations as the water samples, as well as from a lake adjacent to mine property and used by residents of the city (Kam Lake), from the body of water on which Yellowknife is situated (Yellowknife Bay), and from mine tailings (Figure 1b). The biota sampled from Yellowknife included moss (*Funaria hygrometrica* and *Drepanocladus* sp.), snails (*Stagnicola* sp.), emergent vascular plants (cattail *Typha*

latifolia and bur-marigold *Bidens cernua*), submergent vascular plants (duckweed *Lemna minor*, water milfoil *Myriophyllum* sp., Richardson's pondweed *Potomogetan richardsonii*, and bur-reed *Sparganium augustifolium*) and fungi (lichen, pixie cup lichen *Cladonia* sp., puffball mushroom *Lycoperdon* sp. and shaggy mane mushroom *Coprinus comatus*).

Water was sampled by hand into polypropylene bottles that had been acid washed previously. Biota were sampled by hand, stored in Ziploc® bags and kept cool until processing. They were washed thoroughly with tap water to remove soil and other particles, rinsed with deionized water, and frozen. The samples were freeze-dried and pulverized to a fine powder for analysis. Snails from Yellowknife were dissected to remove the soft tissue prior to freezing. Biota were identified by using field guide books[16–19], with assistance from experts for some samples.

Samples were digested with acid for the determination of total antimony content. The freeze-dried powders were accurately weighed (0.5 g ± 0.5 mg) into a 500 mL round bottomed flask (RBF). Concentrated nitric acid (3 mL, doubly distilled in quartz, Seastar, Sidney, BC) and hydrogen peroxide (3 mL, 30% in water, reagent grade, Fisher) were added to each sample. The samples in the RBFs were boiled for 3 hours by using a heating mantle and a reflux apparatus[20]. After all the samples had cooled, the clear solutions remaining were diluted to 25 mL with deionized water and stored at 4°C until analysis.

Extractions were carried out by weighing 0.5 g (± 0.5 mg) of the dried powders into 50 mL or 15 mL centrifuge tubes, adding 10–15 mL MeOH/water (1:1), sonicating for 20 minutes, centrifuging for 20 minutes, and decanting the liquid layer into a RBF. Each sample was sonicated and centrifuged a total of 5 times. The decanted extracts for each sample were pooled and rotovapped to near dryness (1–2 mL) and then diluted to 5 or 10 mL with deionized water. Moss (*Drepanocladus* sp.) and snails (*Stagnicola* sp.) from Yellowknife were extracted in a larger quantity to permit analysis by using HG-GC-AAS and HG-GC-MS. Masses of 1 or 2 g were weighed out and extracts were made up to a final volume of 20 mL or 40 mL, respectively.

Analysis of samples

Acid digested samples and water samples were analyzed by ICP-MS for total antimony content. A VG Plasmaquad PQ2 Turbo ICP-MS (VG Elemental) outfitted with a peristaltic pump and injection loop for flow injection introduction was used. Parameters for the ICP-MS are given in Table I. The m/z monitored were 121 (Sb) and 103 (Rh). Acid digested samples were diluted with 1% nitric acid (doubly distilled in quartz, Seastar) and Rh (10 ppb) was added as an inter-

nal standard to diluted samples and water samples. Quantification was carried out by using an external calibration curve derived from Sb standards made in 1% nitric acid and containing 10 ppb Rh.

TABLE I Operation parameters for ICP-MS

Feature	*Parameter*
Forward radio-frequency power	1350 W
Reflected power	<10 W
Cooling gas (Ar) flow rate	13.8 L/min
Intermediate (auxiliary) gas (Ar) flow rate	0.65 L/min
Nebulizer gas (Ar) flow rate	1.002 L/min
Nebulizer type	de Galan
Quadupole pressure	9×10^{-7} mbar
Expansion pressure	2.5 mbar

Hydride generation-gas chromatography-atomic absorption spectrometry (HG-GC-AAS) analysis was carried out for antimony speciation. The apparatus was composed of a semi-continuous flow, hydride generation system developed for arsenic analysis[21], coupled to an atomic absorption spectrometer (Varian AA1275) fitted with an Sb lamp (Varian), operating at a wavelength of 217.6 nm, or at 231.4 nm for a few samples. One modification was made to the basic apparatus in the form of using a gas-liquid separator[22] that resulted in less analyte carryover. The apparatus consisted of Tygon tubing for the peristaltic pump, and PTFE tubing (1/8″ OD) for the remainder. Data were collected from the AAS and processed directly by using an HP 3390A integrator, or were analyzed with the aid of Shimadzu EZChrom software run on a PC.

A peristaltic pump was used to deliver standard or sample solution (ranging from 5 μL to 200 μL for standards, and from 1 mL to 100 mL for samples) to mix with the acid or buffer and then to mix with a solution of $NaBH_4$ (2% w/v) in a reaction coil. The gases evolved were separated in the gas-liquid separator and then swept by a flow of helium into a PTFE U-tube, where they were trapped at −196°C. Continuous hydride generation and trapping were carried out for 3 minutes. The peristaltic pump was then stopped (making the system semi-continuous) and the U-tube was heated to 70°C, allowing the gases to be swept with He at a flow rate of 40 mL/min onto a Poropak PS column, which was then heated from 70°C to 150 °C at a rate of 30 °C/min, whereby the gases were separated. They were then detected by AAS. Semi-quantitative amounts were calculated by using external calibration curves.

HG-GC coupled to mass spectrometric (MS) analysis was used for confirmation of methylantimony species. Extracts of samples and standard solutions of Me_3SbCl_2 were reacted with $NaBH_4$ to form methylantimony hydrides. The reactions were performed in a 15 mL vial (sealed with a PTFE-faced silicone or neoprene septum, 16mm, Supelco) by using the appropriate volume of sample (5 mL for moss extracts and 10 mL for snail extract) or Me_3SbCl_2 standard solution, and 1 mL deionized water (for standards) and then injecting 0.5 mL of 6% $NaBH_4$ solution through the septum. All reactions were carried out without the addition of acid or buffer, with the exception of one reaction in which Me_3SbCl_2standard solution was first made acidic by adding an equal volume of 1 M HCl, in order to generate $MeSbH_2$ and Me_2SbH in addition to Me_3Sb. These methods were qualitative only.

For the analysis, a GC-MS system consisting of a Star 3400 Cx gas chromatograph (Varian), equipped with a 1078 temperature programmable injector (Varian) and interfaced to a Saturn 4D ion-trap mass spectrometer (Varian) was employed. A gas tight syringe (1.0 mL, Gastight #1001, Hamilton) was rinsed with 5 mL of lab air and was then used to inject 1 mL of headspace generated from the samples onto a capillary column (PTE™-5,30 m × 0.32 mm, 0.25 μm, Supelco 2–4143, poly (5% diphenyl / 95% dimethylsiloxane)). The injector was kept at 100 °C. The temperature program started at 40 °C, and stopped at 150 °C with a heating ramp of 15 °C/min. The parameters used are shown in Table II.

TABLE II GC-MS parameters

GC method	
Injector temperature	100 °C
Column temperature program	40 °C, 15 °C/min to 150 °C
Transfer line temperature	200 °C
Column	PTE™-5, 30 m × 0.32 mm, 0.25 μm, Supelco
MS method	
Mass range	115–180 m/z
Scan time	0.4 s
Segment length	4.5 min
Ion Mode	Electron Impact
Multiplier	2150 V
Target	15 400
Ionization current	20 μA
Manifold temperature	260 °C

RESULTS AND DISCUSSION

Antimony species and total antimony in environmental samples

The semi-quantitative amounts of antimony species in environmental samples detected by using the method of HG-GC-AAS, as well as total antimony, determined by using ICP-MS, are shown in Table III. The antimony contents in biota and water from Yellowknife and Meager Creek are summarized in Table IIIa (biota) and Table IIIb (water). Absolute detection limits of 1 ng for Sb (III) and methyl antimony species were estimated and relative standard deviations between replicate analyses can be estimated to be 20%.

In all biota sample extracts and water samples, inorganic Sb (V) is the major antimony species (Table IIIa and IIIb). Very few biota samples have been speciated for antimony previously[8,23], but other researchers have also shown that Sb (V) is the major antimony compound in water samples[3,11,24,25,26]. Thermodynamically, Sb (V) is predicted to be the most stable oxidation state under most environmental, oxygenated conditions (pH 5 to 8)[27] and therefore it is not surprising to find that Sb (V) is the most abundant extractable species of antimony in these samples.

Inorganic Sb (III) is present in *Drepanocladus* sp. (moss) samples from Yellowknife as shown in Table IIIa. Sb (III) is also present in all Meager Creek (MC) waters, as well as pond and effluent receiving waters from Yellowknife (Table IIIb). Other studies have shown that Sb (III) is produced in the photic zone of an estuarine inlet, which may indicate that biological activity is responsible for the presence of Sb (III)[28]. In the same study, reducing conditions, including the presence of H_2S, did not result in significant reduction of Sb (V) to Sb (III) in water, although the formation of Sb(III)-S compounds was postulated[28]. In the present study, water from Meager Creek was sampled from locations near microbial mats, which have been shown to exist under reducing conditions[5] and to produce Me_3Sb[29]. Reducing conditions and microbial metabolism may lead to the presence of Sb (III) in these waters.

Methylated antimony species were detected in a few samples by using HG-GC-AAS. Biota samples containing methylantimony species include moss and snails from YK locations (Table IIIa). The moss samples from Yellowknife that contain methylantimony compounds were all identified as the same species of *Drepanocladus* sp. The discovery of methylantimony compounds in snails (*Stagnicola* sp.) represents, to our knowledge, the first finding of methylated antimony in an animal.

TABLE IIIa Total antimony, extracted[a] antimony species, and percent Sb species extracted of total Sb, for environmental biota samples (ppm dry weight). YK = Yellowknife; MC = Meager Creek; na = not analyzed Percent Sb species of total represents the amount of antimony in extracts detectable by HG-GC-AAS, calculated by using (Sum of Sb species)/(Total Sb) × 100%

Sample	*Sb (V)*	*Sb (III)*	*Me_3Sb-*	*Me_5Sb-*	*Sum of Sb species*	*Total Sb (acid digested)*	*% Sb species of total*
YK-Mine Effluent Drainage Locations							
Funaria hygrometrica	1.4	<0.007	<0.007	<0.007	1.4	190	0.7
Drepanocladus sp., June	2.5 (0.6)[b]	0.009	0.046	<0.004	2.56	12	21
Drepanocladus sp., Aug	2.82 (0.05)[b]	0.011	0.044	<0.004	2.88	60	4.8
Drepanocladus sp., Aug (standing water location)	2.0	0.012	0.17 (0.01)[b]	<0.004	2.18	28	7.8
Stagnicola sp.	0.7	<0.002	0.005	0.024	0.73	6	12
YK-Kam Lake							
Typha latifolia sp.	0.19	<0.004	<0.004	<0.004	0.19	0.20	95
YK-Niven Lake							
Bidens cernua	0.031	<0.01	<0.01	<0.01	0.031	0.7	4.4
Lemna minor	0.05	<0.01	<0.01	<0.01	0.05	0.39	13
Myriophyllum sp.	0.032	<0.02	<0.02	<0.02	0.032	0.28	11
YK-Yellowknife Bay							
Potomogetan richardsonii	0.028	<0.01	<0.01	<0.01	0.028	0.8	3.5
Sparganium augustifolium	0.096	<0.01	<0.01	<0.01	0.096	0.26	37

Sample	*Sb (V)*	*Sb (III)*	*Me_3Sb-*	*Me_3Sb-*	*Sum of Sb species*	*Total Sb (acid digested)*	*% Sb species of total*
YK-mine tailings							
Lichen	5	<0.01	<0.01	<0.01	5	120	4.2
Cladonia sp.	0.046	<0.01	<0.01	<0.01	0.046	1.4	3.3
Lycoperdon sp.	0.46	<0.005	<0.005	<0.005	0.46	60	0.8
Coprinus comatus sp.	5	<0.005	<0.005	<0.005	5	34	15
MC Biota sample							
Mimulus sp.	0.07	<0.007	<0.007	<0.007	0.07	0.5	14

[a]Samples were extracted by using MeOH/water (1:1) and antimony species were detected by using HG-GC-AAS as described in as described in experimental section.
[b]Value in parentheses is standard deviation, calculated from duplicate analyses.

TABLE IIIb Total antimony, antimony species[a], and percent Sb species of total Sb, in environmental samples of water (ppb). See TABLE IIIa for abbreviations. Percent Sb species of total represents the amount of antimony detectable by HG-GC-AAS, calculated by using (Sum of Sb species)/(Total Sb)× 100%

Sample	*Sb (V)*	*Sb (III)*	*Me_2Sb-*	*Me_3Sb-*	*Sum of Sb species*	*Total Sb*	*% Sb species of total*
YK mine effluent runoff	240	<0.03	<0.03	<0.03	240	260	92
YK mine effluent runoff	220	<0.03	<0.03	<0.03	220	na	na
YK mine effluent runoff	300	<0.03	<0.03	<0.03	300	380 (50)[c]	79
YK mine effluent runoff (standing water)	30	0.10 (0.02)[b]	0.335 (0.007)[b]	0.13 (0.05)[b]	30.6	50	60
YK-Niven Lake	1.3	<0.03	<0.03	<0.03	1.3	3.7	35
YK-Niven Lake	0.38	0.08	<0.03	<0.03	0.46	1.8 (0.2)[c]	26
YK-mine effluent	18	<0.03	<0.03	<0.03	18	31	58
MC-stream, Sept. 1996	6 (4)[b]	0.08	<0.03	<0.03	6	na	na
MC-stream, Sept. 1996	8.2 (0.9)[b]	0.34	<0.03	<0.03	8.5	5	170
MC-source, Nov. 1996	2.4	0.06	<0.03	<0.03	2.5	5	50
MC-source, July 1997	6	0.09	<0.03	<0.03	6	na	na
MC-source, July 1997	4.3	0.05 (0.02)[b]	<0.03	0.04	4.4	na	na
MC-source, Sept. 1996	1.2	0.14	<0.03	<0.03	1.3	12	11
MC-stream, July 1997	3.0	0.07	<0.03	<0.03	3.1	na	na

[a]Antimony species detectable by using HG-GC-AAS analysis.
[b]Value in parantheses is standard deviation, calculated from duplicate analyses.
[c]Value in parantheses is standard deviation, calculated from analysis of duplicate samples.

Methylantimony compounds in biota have been observed rarely in past studies. One such finding was the postulated presence of a $Me_3Sb(V)$ species in a soil extract following high performance liquid chromatography (HPLC)-ICP-MS analysis[10]. Dodd *et al.* identified predominantly a trimethylantimony compound in one sample and a dimethylantimony compound in another sample of the same species of macrophyte from Yellowknife[8]. The results from the present study differ from that by Dodd *et al.*[8] because the methylated antimony is consistent for all three moss samples, namely, a dimethylantimony species.

Methylated antimony compounds were also found in two water samples (Table IIIb). The chromatogram in Figure 2 shows stibine, dimethylstibine and trimethylstibine that were hydride generated from a standing water sample (YK), then separated and detected by GC-AAS. A trimethylantimony compound is present in a water sample from a MC hot springs source (Table IIIb). Monomethylantimony and dimethylantimony compounds, assumed to be methylstibonic acid and dimethylstibinic acid, have been observed in river, estuary and sea water sampled by other researchers and their presence was attributed to biological activity[28,30].

The dimethylantimony compound present in the Yellowknife water sample may be similar to the dimethyl compound in the moss sampled from the same location, and its presence in both samples may indicate uptake and/or excretion. From these results it is impossible to differentiate between the possibility of the moss forming a dimethylantimony species as a metabolite and excreting it into the water, and the possibility of microorganisms in the water or sediment forming the compound and its being taken up by the moss. Both scenarios are possible.

The presence of trimethylantimony species in Meager Creek water may be a result of the production of Me_3Sb by the microbial mats nearby. Recent studies have indicated that Me_3Sb would be oxidized rapidly to Me_3SbO[31,32], but other studies suggest that if the Challenger mechanism is followed for the methylation of antimony the final reduction step to Me_3Sb takes place only to a very small extent[12]. Therefore the trimethylantimony compound in the Meager Creek water sample may be present as a result of oxidation following Me_3Sb production in the mats, or of biological antimony methylation only as far as Me_3SbO.

The percent antimony species of the total antimony in a sample was calculated and can be an approximation of extraction efficiency for biota samples. Using this calculation, extraction efficiencies for antimony from biota are estimated to range from 0.7 to 95%. For all biota samples except one, however, values are below 37% (Table IIIa), indicating that the extraction method using MeOH/water (1:1) might be inadequate to extract antimony from these samples. Antimony may be strongly bound to cellular components such as lipids, cellulose, lignin or

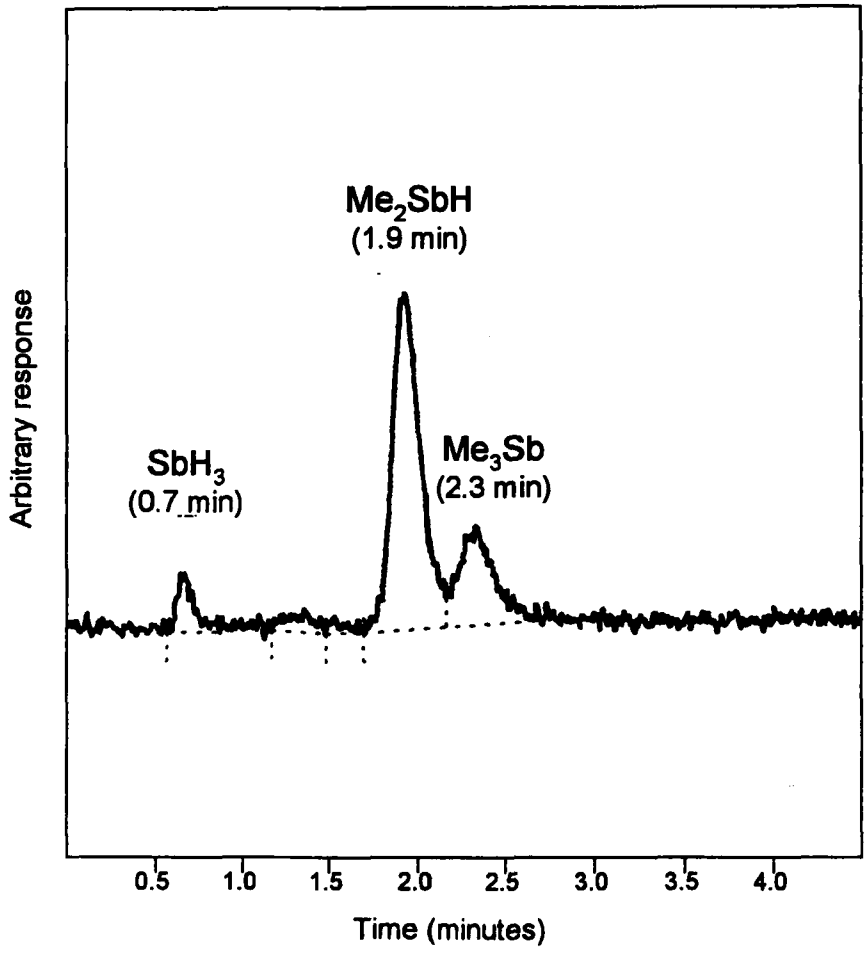

FIGURE 2 Chromatogram obtained by using HG-GC-AAS (217.6 nm) showing stibines generated at neutral pH from 100 mL of a sample of standing water from Yellowknife

carbohydrates. For example, metals are known to bind strongly to fungal cell walls[33], and antimony may thus be strongly bound to cellular components. Accordingly, extraction efficiencies from fungus samples (lichen and mushrooms) range from 0.8 to 15% (Table IIIa). *Typhus* sp. (cattail) from YK was extracted nearly quantitatively (Table IIIa).

Some of the antimony extracted from these samples may not have been detected by using HG-GC-AAS. The inability of HG-GC-AAS to detect all antimony may account for the differences in amounts detected in waters by using this method compared with the levels of total antimony in waters (Table IIIb, last

column). Arsenic species that are "hidden" to HG-GC-AAS detection, without strong digestion techniques (e.g., UV photolysis or microwave digestion), have been found in sediment pore water samples from Yellowknife[34]. This arsenic was suggested to be bound to colloidal organic matter, or in the form of organoarsenic compounds (such as arsenocholine or arsenosugars)[34]. In the same way, antimony that is complexed strongly to organic groups may not form hydrides under the conditions used, or Sb-S compounds may exist as well. Sb(III)-S compounds have been proposed to be present in estuarine and interstitial waters, detected by acidifying and degassing samples before HG-GC-AAS analysis at pH 6[28]. This method was not carried out in the present study and hence the possibility has not been ruled out that such compounds are present.

Confirmation of antimony in samples containing methylantimony compounds by using HG-GC-AAS and headspace HG-GC-MS

The presence of methylantimony species in samples was confirmed by two methods: (a) by using HG-GC-AAS at a different wavelength to corroborate that peaks are due to antimony compounds and not the result of spectral interferences, and (b) by using HG-GC-MS to confirm the structure and presence of hydrides derived from samples. Three moss samples and a water sample from Yellowknife were analyzed by using HG-GC-AAS with the AAS operating at a wavelength of 231.4 nm, which is a secondary absorption line specific to antimony. Peaks appeared at the same retention times as those found at a wavelength of 217.6 nm, and in similar abundances, as summarized in Table IV. The snail extract was not analyzed because of limited sample size.

To confirm the presence of methyl antimony compounds by using headspace-HG-GC-MS, Me_3Sb was generated in sealed vials from standard solutions of Me_3SbCl_2 by using hydride generation methodology. A sample of the headspace was then injected into the GC-MS for structural information. A detection limit of 0.08 ng Sb for Me_3Sb was obtained, corresponding to 1 ng Sb in solution before derivatization. However, the analysis of headspace following hydride generation suffers from imprecision, since RSD values no better than 20% were observed for 5 replicate analyses.

In Figure 3, a chromatogram and mass spectrum are shown, corresponding to standard trimethylstibine (30 ng Sb as Me_3Sb) generated by using 30 μL of 1000 ppb Me_3SbCl_2 solution with 1 mL of deionized water and 0.5 mL of 6% (w/v) $NaBH_4$ solution. The dominant characteristic of all mass spectra involving antimony compounds is the appearance of the isotopic pattern due to masses of 121 and 123 (naturally occurring at about 52:48) in all Sb-containing fragments. This isotopic pattern is observed in Figure 3at m/z 165/167, corresponding to

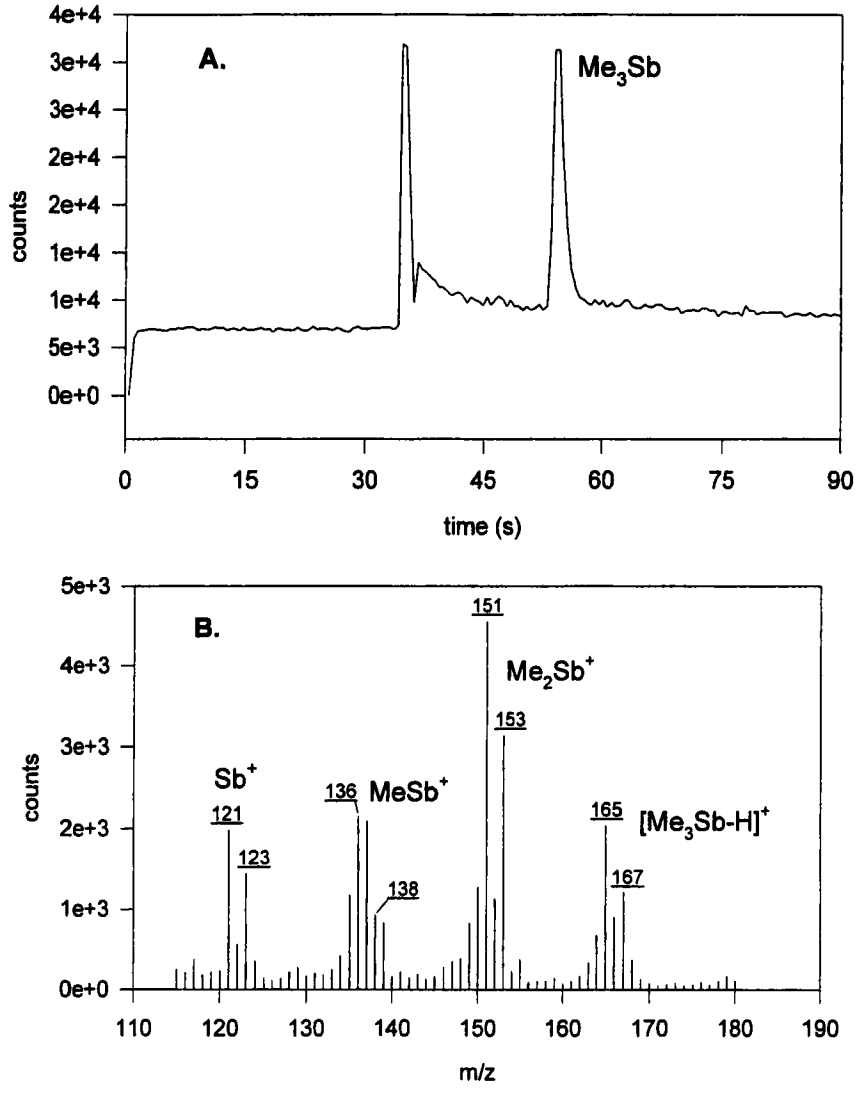

FIGURE 3 A. Total ion chromatogram resulting from headspace-HG-GC-MS analysis showing Me_3Sb generated from 30 ng Me_3SbCl_2 (neutral). B. Mass spectrum at 54.60 s corresponding to Me_3Sb

$[Me_3{}^{121}Sb\text{-}H]^+/[Me_3{}^{123}Sb\text{-}H]^+$; at m/z 151/153 corresponding to $Me_2{}^{121}Sb^+/Me_2{}^{123}Sb^+$; at m/z 136/138, corresponding to $Me^{121}Sb^+/Me^{123}Sb^+$; and at m/z 121/123 corresponding to $^{121}Sb^+/^{123}Sb^+$. This mass spectrum is simi-

lar to one obtained previously by using the same GC-MS[35] and also to spectra obtained by using a quadrupole mass spectrometer[8]. The loss of a methyl group from methylstibines is the prevalent fragmentation pattern and is considered to be typical for methylated organometallic compounds[36].

TABLE IV Relative amounts (% of sum of methyl species, estimated by normalizing area counts) for methyantimony peaks in moss and water samples. "nd" = not detected

Sample (YK location #)	*Sb (III) (RT=0.7)*	*Me_2Sb- (RT=1.9)*	*Me_3Sb- (RT=2.3)*
AAS at 231.4 nm			
Drepanocladus sp. June	12	88	nd
Drepanocladus sp., Aug.	10	90	nd
Drepanocladus sp., Aug. from standing water location	5	95	nd
Standing water, Aug.	17.5	59	23.5
AAS at 217.6 nm			
Drepanocladus sp., June	17	83	nd
Drepanocladus sp., Aug.	23	77	nd
Drepanocladus sp., Aug. from standing water location	6	94	nd
Standing water, Aug.	17.5	59	23.5

Enhanced demethylation of trimethylstibine is observed when the hydride generation reaction is performed at low pH[13]. Therefore, acidic HG conditions resulting in demethylation can be used to generate mass spectra for methylstibine and dimethylstibine. In Figure 4, the chromatogram obtained from hydride generation of Me_3SbCl_2 (100 ng Sb) at low pH (Figure 4a) and the mass spectra obtained for the peaks assumed to be methylstibine (Figure 4b) and dimethylstibine (Figure 4c) are shown. The fragmentation pattern for dimethylstibine is similar to that observed for trimethylstibine, because the most abundant m/z appears as a result of methyl loss ($MeSb^+$ from Me_2SbH). The mass spectrum for the peak at a retention time of 39.27s most likely corresponds to the one expected for $MeSbH_2$, even though the high background levels obscures a clear, characteristic fragmentation pattern. However, fragments at m/z 121/123 and 136/138 were observed, corresponding to Sb^+ and $MeSb^+$, respectively.

Past studies have included the use of HG-GC-MS for the identification and confirmation of methylated antimony species in plant samples from Yellowknife[8]. Another study involved the direct injection of fractions of gas samples

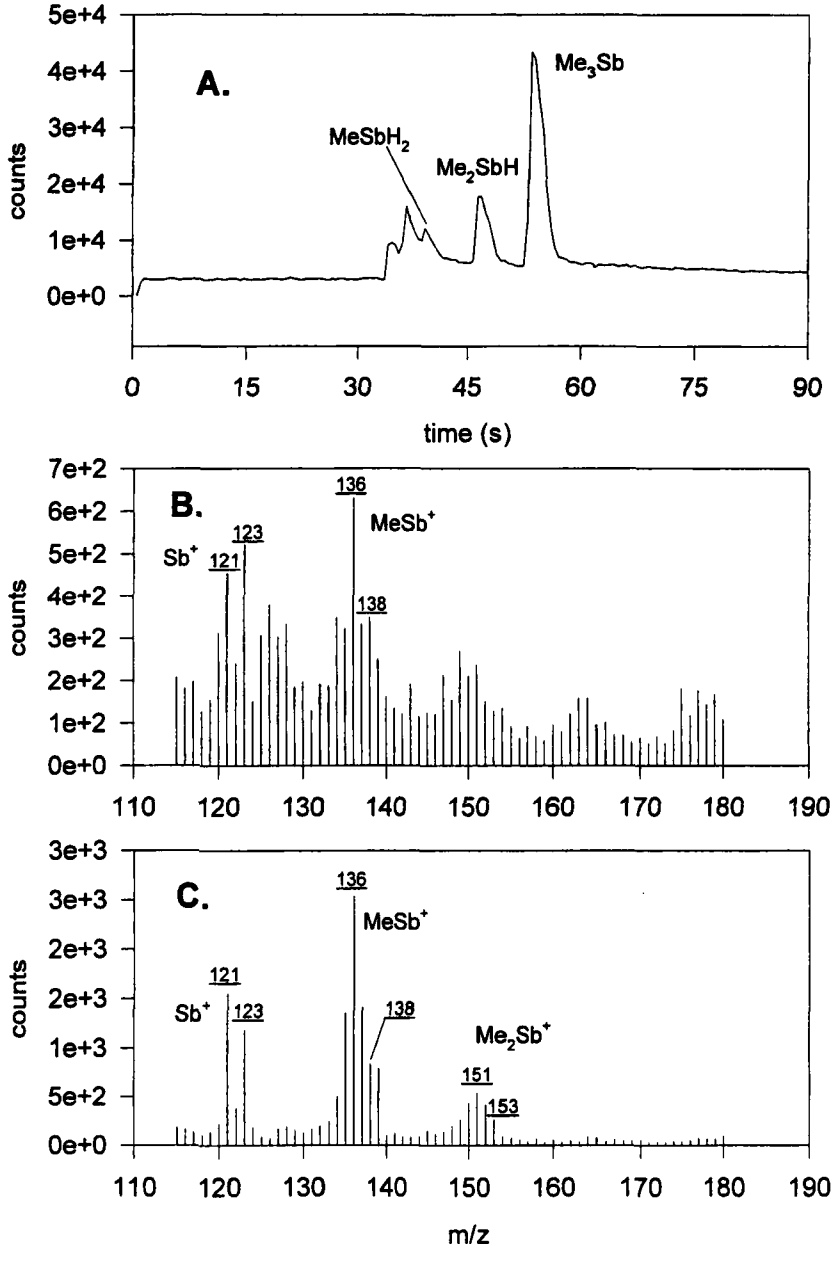

FIGURE 4 A. Total ion chromatogram resulting from headspace-HG-GC-MS analysis showing stibines generated from 100 ng Me_3SbCl_2 (1 M HCl). B. Mass spectrum at 39.27 s corresponding to $MeSbH_2$. C. Mass spectrum at 49.61 s corresponding to Me_2SbH

into an ion trap GC-MS, resulting in the conclusive identification of trimethylstibine, trimethylbismuthine and methyltin compounds in landfill and fermentation gases[35]. Hence, the headspace HG-GC-MS method developed in this work was anticipated to provide information about the presence of methylstibines following HG of Yellowknife samples.

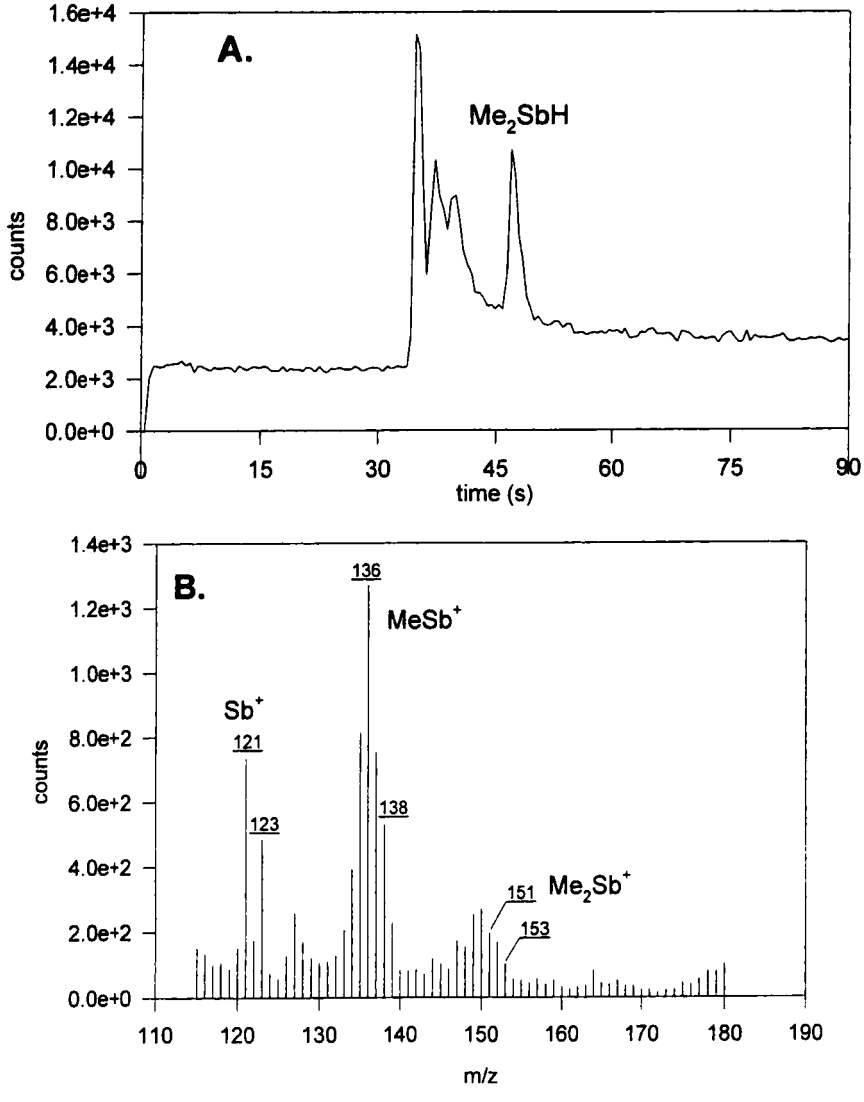

FIGURE 5 A. Total ion chromatogram resulting from headspace-HG-GC-MS analysis of 5 mL of a moss extract from Yellowknife showing Me_2SbH. B. Mass spectrum at 46.90 s corresponding to Me_2SbH

Chromatograms[37] and mass spectra for peaks corresponding in retention time to dimethylstibine for a moss sample from Yellowknife are shown in Figure 5. Similar chromatograms and mass spectra were obtained for the other moss samples that were suggested to contain methylantimony species. The mass spectra indicate that the compound found in the headspace following hydride generation of the sample extracts is indeed dimethylstibine, by comparison with the mass spectrum shown in Figure 4c.

The chromatogram and mass spectra for the peaks corresponding in retention time to dimethylstibine and trimethylstibine for the snail extract are shown in Figure 6. Again, comparison of the mass spectra with those for standards (Figures 3b and 4c) indicates the presence of dimethyl- and trimethylstibine following HG of the extract. Differences in m/z abundances are probably due to interfering ions causing slightly different fragmentation patterns. For example, in Figure 6c (the mass spectrum for the peak corresponding to trimethylstibine) m/z 166 and 168 are observed (corresponding to Me_3Sb^+) rather than 165 and 167 (corresponding to $[Me_3Sb\text{-}H]^+$), which were the m/z observed for the standard compound (Figure 3b). For this sample, background subtraction was necessary to isolate the major m/z of interest, because of low levels of antimony in the extract and large amounts of other matrix components. Therefore HG-(headspace)-GC-MS was successful in confirming the presence of methyl antimony species in environmental samples.

Because of the abundance of *Drepanocladus* sp. at the location from which it was sampled, and the seasonal consistency in its methylantimony content, this species of moss can be used as a laboratory standard for dimethylantimony. Future work is planned involving the use of moss extracts to study HPLC behaviour of the dimethylantimony compound present in the moss by using ICP-MS detection or MS detection for structural information.

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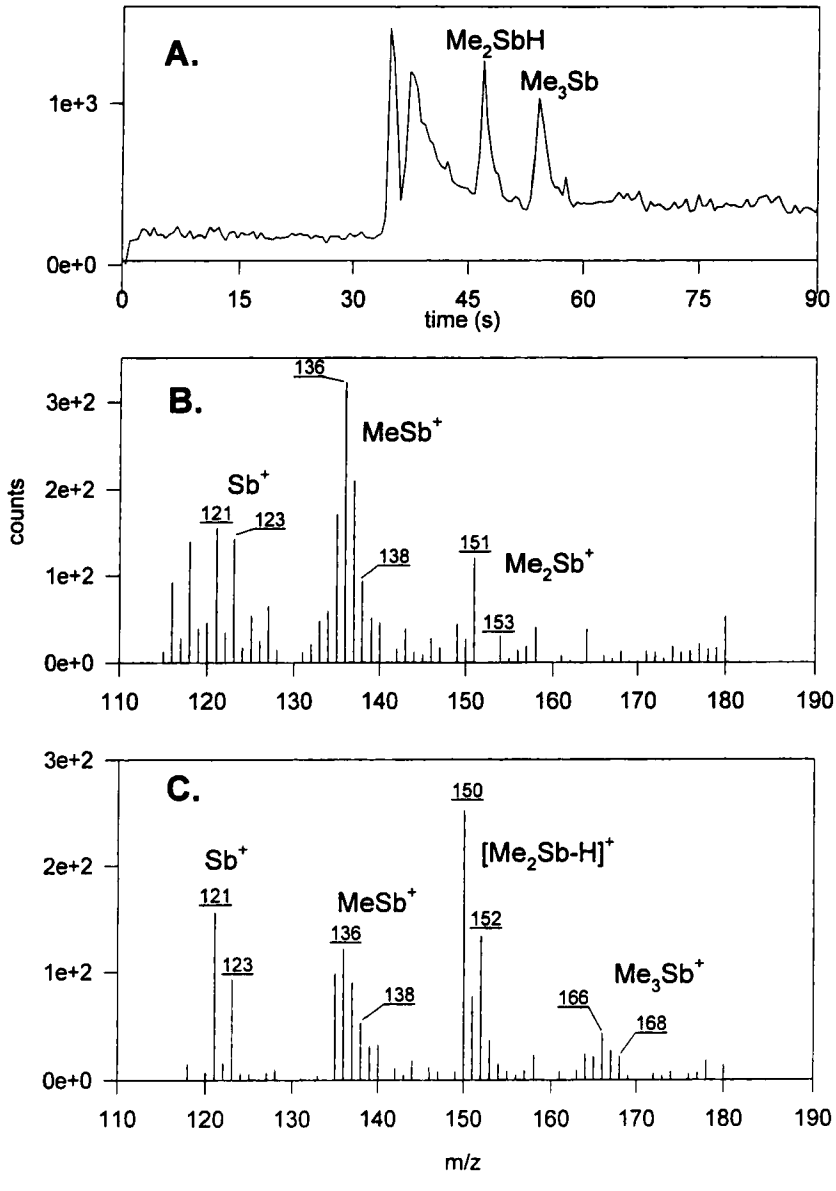

FIGURE 6 A. Chromatogram (sum of Sb containing ions) resulting from headspace-HG-GC-MS analysis of 10 mL of snail extract (YK Location 1+3) showing Me_2SbH and Me_3Sb. B. Background corrected mass spectrum at 46.96 s corresponding to Me_2SbH. C. Background corrected mass spectrum at 54.05 s corresponding to Me_3Sb

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