DETERMINATION OF MERCURY CONTENT IN A SHALLOW FIRN CORE FROM GREENLAND BY ISOTOPE DILUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Abstract. The total mercury content was determined in 6 cm sections of a shallow 7 m firn core and in surrounding surface snow from Summit, Greenland (elevation: 3238 m, 72.58°N, 38.53°W) collected in May 2001 by isotope dilution cold-vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS). The focus of this research was to evaluate the capability of the ID-CV-ICP-MS technique for measuring trace levels of Hg typical of polar snow and firn. Highly enriched ^{201}Hg isotopic spike is added to approximately 10 mL melted core and thoroughly mixed. The Hg^{2+} in the sample is reduced on line with tin(II) chloride ($SnCl_2$) and the elemental Hg ($Hg°$) vapor pre-concentrated onto gold gauze using a commercial amalgam system. The Hg is then thermally desorbed and introduced into a quadrupole ICP-MS. The blank-corrected Hg concentrations determined for all samples ranged from 0.25 to 1.74 ng/L (ppt) (average 0.59 ± 0.28 ng/L (1σ)) and fall within the range of those previously determined by Boutron *et al.* [Geophys. Res. Lett. 25, 1998, 3315–3318] ($\leq$0.05–2.0 ng/L) for the Summit site. The average blank value was 0.19 ± 0.045 ng/L ($n = 6$, 1σ) and the method detection limit was 0.14 ng/L. The Hg values specifically for the firn core range from 0.25 to 0.87 ng/L (average 0.51 ± 0.13 ng/L (1σ)) and show both values declining with time and larger variability in concentration in the top 1.8 m.

Keywords: firn core, Greenland, isotope dilution, mercury, trace

1. Introduction

The trace metal mercury is a pollutant of global concern because of its relatively long atmospheric residence time (approximately 1 year) and its potential to form highly toxic methylmercury which bioaccumulates in the aquatic food chain. Hg in the environment is derived from both natural and anthropogenic sources with natural sources contributing an estimated 9 Mmol per year (e.g. land surface (soil degassing) and oceanic evasion) and anthropogenic contributing roughly 13 Mmol/year (combustion sources (fossil fuels, medical waste incineration)) (Lamborg *et al.*, 2002, p. 1116). The dominant species of Hg in the atmosphere is elemental mercury ($Hg°$) (at a concentration of 1.6 ng/m^3) (Lindqvist, 1991; Schroeder *et al.*, 1998) and this relatively inert $Hg°$ can be transported long distances prior to chemical

transformation and consequently has global environmental influence. Once the mercury is chemically or photochemically oxidized to reactive gaseous mercury (RGM) and/or particle-associated mercury (PM) (Lindberg *et al.*, 2001) it is highly water soluble resulting in enhanced deposition via wet and dry processes. In the Arctic, oxidized mercury accumulates in the snowpack to be later released via snowmelt in the summer season where it can be transformed to methylmercury and becomes available to the terrestrial ecosystem. The principal route of human exposure to methylmercury compounds is via fish and shellfish consumption (EPA, 1997). Ingestion of methylmercury by humans can cause central nervous system damage and endocrine system disruption (NRC, 2000). High levels of Hg have been found in Arctic food supplies and elevated levels have been observed in the native people (approximately 80% of the Greenland population has levels in blood that exceed 50 μg/L) of the circumpolar countries including Greenland whose populations consume large amounts of fish and piscivorous species (AMAP, 1998; UNEP, 2002, p. 62).

Low concentrations of oxidized mercury play an important role in the biogeochemical cycling of this metal because of the increased solubility and enhanced deposition to the environment. The mercury concentrations in certain regions of the Arctic (e.g. elevated sites in Greenland) are low and require measurement techniques capable of high precision and accuracy for understanding mercury cycling within these environments. Typical concentrations in natural waters (rainfall, snow, and ice) are non-detectable to 0.5 μg/L range, which presents a challenge to many of the analytical techniques available for Hg determination (ATSDR, 1999; Mann *et al.*, 2003). Cold-vapor atomic absorption spectrometry (CVAAS) and cold-vapor atomic fluorescence spectrometry (CVAFS) have very low limits of detection (sub-ng/L range) and have been used successfully in the measurement of Hg in snow and ice, where concentrations can be in the ng/L (ppt) range (Boutron *et al.*, 1998; Ferrari *et al.*, 2000; Schuster *et al.*, 2002; Shanley *et al.*, 2002). Recently, inductively coupled plasma mass spectrometry (ICP-MS) has been used for the determination of Hg in various matrices such as bovine blood, fish tissue, coal and other fossil fuels, and bottled water (Christopher *et al.*, 2001; Long and Kelly, 2002; Kelly *et al.*, 2003; Mann *et al.*, 2003). The very high sensitivity (instrument detection limit <0.1 ng/L, 3σ) of this method combined with the inherently accurate isotope dilution method allowed for the ultra trace (parts per trillion, ppt) levels of Hg encountered in bottled waters to be determined with relatively high accuracy and precision (Mann *et al.*, 2003). Using isotope dilution obviates the need to perform yield studies since 100% yields are unnecessary for accurate quantification. In the present work, the method has been employed for the determination of trace levels of Hg in a shallow firn core and surface snow samples obtained from Summit, Greenland to evaluate the capability of the isotope dilution cold-vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) technique for measuring the trace levels of Hg of polar snow and firn. The Summit site was chosen because of the documented low Hg levels ($\leq$0.05–2.0 ng/L) previously measured by CVAFS (Boutron *et al.*, 1998, p. 3315).

2. Experimental

2.1. SAMPLE COLLECTION

In the course of a broader study of accumulation at this location, samples were taken from a 7 m firn core recovered from Summit, Greenland (elevation: 3238 m, 72.58°N, 38.53°W) by Mann and Shuman using a fiberglass hand auger in May 2001 (Figure 1). The core was cut in the field into 3 cm sections and two sections were taken for Hg analysis every 15 cm. The sections were transferred to pre-cleaned low density polyethylene (LDPE) bottles and transported frozen to the NIST laboratory where the samples remained frozen until analysis. The bottles were washed in a sequence of rinsing and soaking three times with Milli-Q 18 mΩ water. The Hg content was determined in 8 surface snow samples and 34 firn core samples. The samples were dated using the method described by Shuman et $al.$ (1995, 1998), which pairs variations in oxygen (δ^{18}O) and hydrogen isotope (δD) record of the core with automatic weather station (AWS) temperature records.
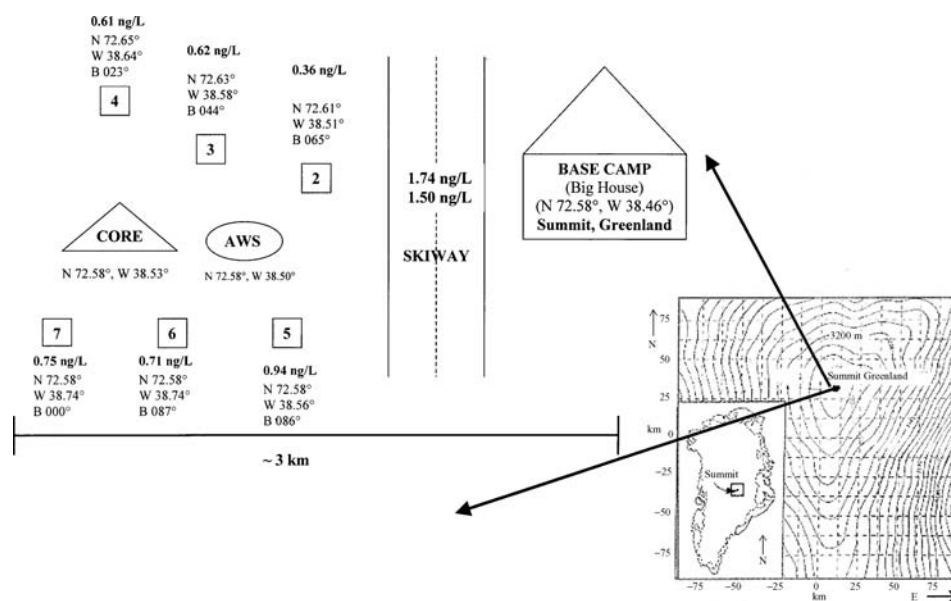
Figure 1. Map showing latitude and longitude for the eight surface samples collected. The highest Hg concentrations were in the samples collected from the skiway. In general, the Hg concentrations begin to decline with distance from the skiway. All sample sites were approximately 1 km from each other and the latitude, longitude and bearing are listed for each surface sample collected. Automated Weather Station (AWS). Contour interval = 10 m.

2.2. SAMPLE AND BLANK PROCESSING

Approximately 10 g of thawed sample was weighed into a 50 mL polypropylene centrifuge tube. All samples were thawed in the dark. The sample was then spiked with a weighed aliquot (approximately 0.35 g) of ^{201}Hg-enriched stock solution (50 pg/g) using a plastic syringe. All measurements were completed within few hours of preparation to reduce the risk of Hg loss. Blank contribution was assessed by adding 10 g of Milli-Q 18 mΩ water that was taken into the field and approximately 0.35 g of the ^{201}Hg spike to a polypropylene centrifuge tube and processing through the analytical procedure. All processing was performed in a Class 10 laboratory. Loss of Hg to the wall of the plastic centrifuge tube during a time period of a week was found to be negligible based on ion intensities compared to pure solutions. These same type containers have been used for Hg in our laboratory for three years for all previously published work.

2.3. ISOTOPIC SPIKE AND CALIBRATION MATERIALS

The ^{201}Hg enriched spike (95.5% atom fraction ^{201}Hg, 2.8% atom fraction ^{202}Hg – atomic weight 200.982) is a solid mercuric oxide purchased from Oak Ridge National Laboratory, Oak Ridge, TN. A stock solution (50 pg/g) was prepared from the spike by dissolution in high-purity nitric acid and serial dilution with a preservative solution containing 0.05% (w/v) potassium dichromate ($K_2Cr_2O_7$) in 3% (v/v) nitric acid. The spike was calibrated by reverse isotope dilution using serially diluted SRM 3133, Mercury Standard Solution (Standard Reference Materials, NIST, Gaithersburg, MD).

2.4. INSTRUMENTATION AND ISOTOPE RATIO MEASUREMENTS

The details of the ID-CV-ICP-MS technique have been described previously by Christopher *et al*. (2001) and Long and Kelly (2002) and specifically for bottled drinking water by Mann *et al*. (2003). Mercury vapor ("cold" vapor) was generated using tin(II) chloride reductant (10% w/v in 7% v/v HCl) and separated from the liquid phase using a commercial CETAC (Omaha, NE) glass reaction/separator cell. Approximately 10 g of sample was consumed for analysis. The Hg vapor was preconcentrated on gold gauze using a commercial amalgam system (Bodenseewerk Perkin-Elmer GmBH) and transferred directly to a VG PQ2 (VG Elemental, Winsford, Cheshire, UK) ICP-MS system with 1/16″ id Viton tubing, using an argon carrier gas flow rate of approximately 100 mL/min. The system was rinsed for approximately 2 min and baked out for approximately 30 s between each sample. The argon carrier gas was passed through a tube containing gold-coated sand to remove Hg contamination. The gold trap was periodically heated to purge trapped Hg. The combination of high-efficiency transfer of Hg from the sample to the plasma source, increased ionization under dry plasma conditions, and decreased memory between

samples improved the sensitivity. The ^{201}Hg and ^{202}Hg isotopes were monitored in a pulse counting Time-Resolved-Analysis mode (TRA) to recover the individual ion count rates. Typical net intensities were 3000 counts for the unspiked isotope (^{202}Hg) per pg/mL (600,000 ions/(s pmol mL)). Instrument mass discrimination was measured by generation of Hg vapor from an isotopic calibration standard.

3. Results

The measurement results for the 34 firn core samples are shown as a function of depth in Table I and Figure 2 and results for the 8 surface snow samples are shown in Figure 1. The total blank-corrected Hg concentration, including the firn and surface samples, ranged from 0.25–1.74 ng/L (*average* $= 0.59 \pm 0.28$ ng/L (1σ)), with Hg concentrations ranging from 0.25–0.87 ng/L (*average* $= 0.51 \pm 0.13$ ng/L (1σ)) in the firn core and 0.36 to 1.74 ng/L (*average* $= 0.90 \pm 0.48$ ng/L (1σ)) in the surface snow samples. The highest Hg concentrations observed were in surface snow samples collected along the airplane skiway located adjacent to Summit base camp. These samples were chosen deliberately to check for contamination from the LC-130 and other aircraft engines. The remaining surface samples were collected to evaluate the change in Hg concentration from base camp to the core collection site. In general the Hg concentrations decrease with distance from base camp and the skiway. The expanded uncertainties ranged from 0.05 to 0.18 ng/L (approximately 20% relative) for the firn core samples (Table I; Column 3) and 0.08 to 0.35 ng/L (approximately 20% relative) for the surface samples (Figure 1) (ISO GUM, 1995). The expanded uncertainties are expressed as 95% confidence intervals. The values fall within the range of those previously reported for the same region ($\leq$0.05–2.0 ng/L) (Boutron *et al.*, 1998). Six total blanks were run concurrently with the samples. The blanks ranged from 0.11 to 0.24 ng/L with an average of 0.19 ± 0.045 ng/L (1σ). All blanks are based on 10 mL aliquots. The method detection limit was 0.14 ng/L (based on three times the standard deviation of the blanks). The detection limit of the instrument was approximately 0.04 ng/L (this can vary by a factor of 2 or 3 from day to day). The reproducibility of the technique is 0.13 ng/L based on measurements of bottled water of similar concentration levels (Mann *et al.*, 2003).

The Hg data are shown in Figure 3a with the composite δD and the automatic weather station temperature (Figure 3b) records that are used to correlate the depth profile to time. The dating method in this study relies on the relationship of the stable isotope depth series to surface temperature at a site. This record is a proxy for the surface temperature record assuming accumulation occurs throughout the year, which is the case at Summit. Comparison is made between the proxy temperature δD record and the actual surface temperature record obtained from the nearby automated weather station (AWS) (located approximately 1 km from the field site) record using a qualitative point-pairing technique that is directed by the maxima, minima,

TABLE I

Mercury concentrations of firn core

Depth (m)	Hg (ng/L)	[a]Expanded uncertainty (ng/L)
Firn core		
0.18	0.68	0.14
0.39	0.26	0.06
0.60	0.37	0.08
0.81	0.59	0.12
1.02	0.38	0.08
1.23	0.33	0.07
1.44	0.25	0.05
1.65	0.47	0.10
1.86	0.59	0.12
2.07	0.34	0.07
1.98	0.46	0.10
2.19	0.34	0.07
2.40	0.51	0.11
2.61	0.46	0.10
2.82	0.45	0.09
3.03	0.51	0.11
3.24	0.48	0.10
3.45	0.56	0.12
3.66	0.51	0.11
3.87	0.47	0.10
4.08	0.67	0.14
4.29	0.55	0.11
4.50	0.50	0.10
4.71	0.63	0.13
4.92	0.56	0.12
5.13	0.56	0.12
5.34	0.51	0.11
5.55	0.57	0.12
5.76	0.56	0.12
5.97	0.60	0.12
6.18	0.87	0.18
6.39	0.55	0.11
6.60	0.66	0.14
6.81	0.63	0.13

[a]The uncertainties expressed in the table are expanded uncertainties at 95% confidence level (k). Uncertainties include Types A and B. Type A components of uncertainty (ISO GUM, 1995) include the measurement precision, the calibration of the spike solution, and correction for the blank contribution. Type B components include the purity of the primary calibrant, instrument mass discrimination, correction for dead time effects, weighing measurements and correction for instrument background. The largest source of the uncertainty was from the blank contribution and the instrument background correction. The average relative uncertainty was approximately 25%.
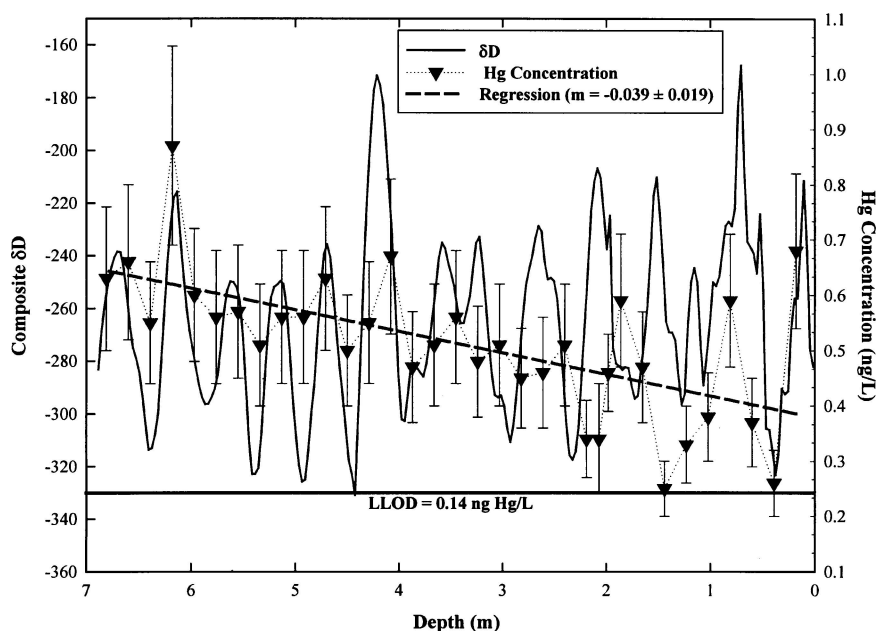
Figure 2. A decreasing trend in Hg concentration with decreasing depth (depth as proxy for time); deeper: older. The error bars are the expanded uncertainties at 95% confidence level. The reproducibility of the method based on measurements of Hg in bottled waters of the same concentration level is 0.13 ng/L. The regression uncertainty is a 95% confidence interval.

and inflections in the shape of the profiles. The tie lines between the two records have been omitted from Figure 3 and replaced with vertical solid black lines highlighting time in Figure 3a. The core extends back approximately 11 years to 1989. The uncertainty in the dates is approximately ± 2 weeks for the top portion of the core and ± 1 month for the bottom portion of the core (Shuman *et al.*, 1995, 1998).

4. Discussion

The data appear to show (1) a decreasing trend in the Hg concentration through the recent past (*slope* $= -0.039 \pm 0.019$) (Figure 2) and (2) greater variability in concentration in the top 1.8 m of the core (Figure 4). The declining trend observed could be explained by both chemical and physical mechanisms as well as by a reduction in source contribution. The chemical and physical mechanisms include: (1) oxidation of Hg° contained in the interstitial air of the snowpack causing an increase in the Hg (II) (RGM or PM) concentration with depth (age of snow), (2) movement or settling of Hg/aerosols within the snowpack, and (3) inadequate sampling resolution. An additional explanation is declining anthropogenic Hg emissions to the atmosphere over recent time. The variability observed in the top portion of the
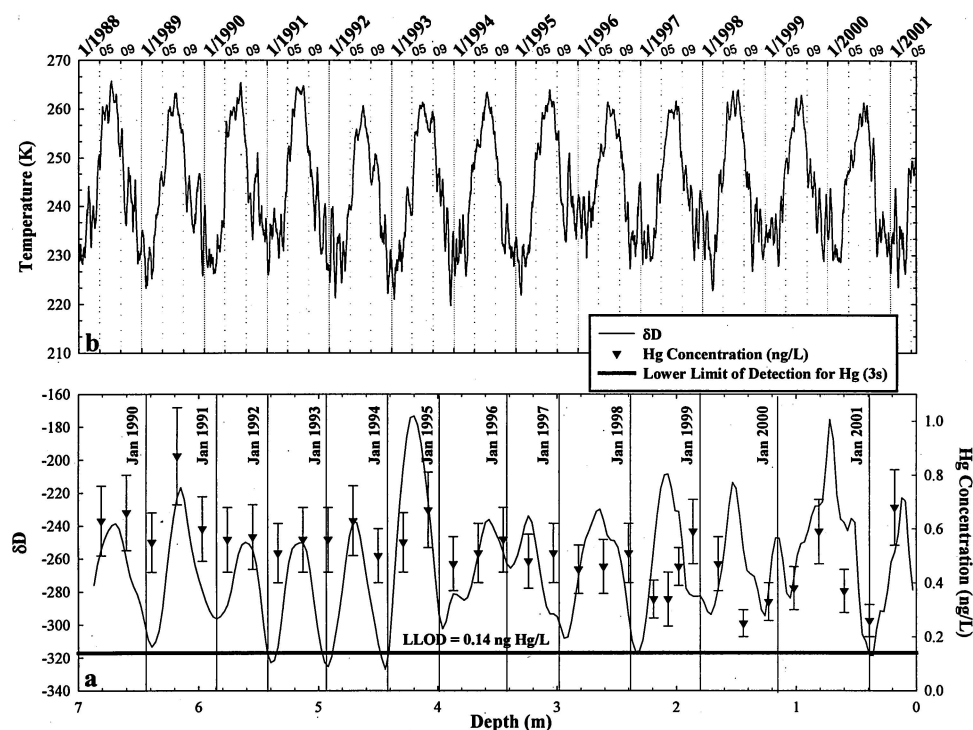
Figure 3. Hg data are shown in (a) with the composite δD record used to link the depth profile to time. The vertical solid black lines highlight time, (b) shows the composite temperature record (14-day average) from the automated weather station located approximately 1 km from the firn core collection site (72.58°N, 38.50°W).

core may reflect the seasonal variations of Hg° in the atmosphere. This signature may be related to Arctic polar Mercury Depletion Events (MDEs) where during polar sunrise Hg° is oxidized to reactive Hg(II) in the atmosphere that can then be deposited to the snow surface causing spring/summertime peaks in the mercury content within the snowpack.

4.1. Causes of Hg loss or gain

4.1.1. *Mercury Oxidation*
The oxidation of Hg° contained in interstitial air of the snowpack could cause an increase in Hg(II) concentration with depth (age of snow) resulting in the declining Hg trend observed. As a part of the ALERT 2000 study Kemp *et al.* (2000) measured the depth profiles of gaseous elemental mercury (GEM) in the interstitial air of the snowpack. They found that GEM decreased with increasing depth (age of snow). Lindberg *et al.* (2002), Ferrari *et al.* (2002) and Dommergue *et al.* (2003) have observed similar trends in the depth profiles of GEM in other regions including
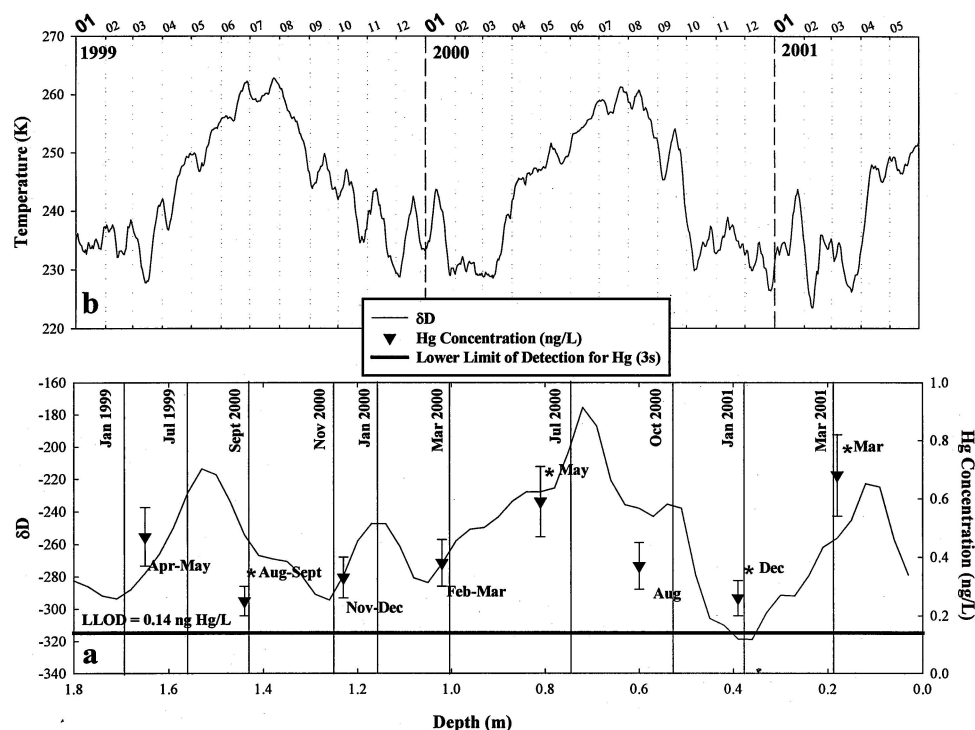
Figure 4. Hg data are shown in (a) with the composite δD record used to link the depth profile to time. The vertical solid black lines highlight time, (b) shows the composite temperature record (14-day average) from the automatic weather station located approximately 1 km from the firn core collection site for the time frame represented in the top 1.8 m of the firn core (<3 years).

Barrow, Station Nord, Greenland, and Kuujjuarapik, Quebec. This GEM has the potential to be rapidly oxidized by halogen compounds within the snowpack. In this case elemental Hg oxidation during diffusion produces a reactive divalent species that can be rapidly deposited to the snowpack. The concentration of halogen atoms and/or highly reactive halogen oxides (BrO and ClO) that participate in photochemical oxidation of Hg° to Hg(II) are expected to be relatively small at Summit due to distance and elevation from the marine source providing these catalysts. Douglas and Sturm (2004) recently noted that wind direction and storm tracks govern the availability of ocean-derived halogens and their participation in Hg oxidation and deposition. Sea-salt contributions to Summit have typically been <10% during industrial times (Patris *et al.*, 2002, p. ACH 6–5) based on sulfur isotopic studies. In addition, the concentration of these compounds with depth in the snowpack is expected to decrease with reduced permeability and interstitial pore space, particularly below approximately 3 m at Summit (Albert and Shultz, 2002). Consequently, the reduced availability of these compounds both from the source and with depth reduces the chance for these photochemically driven oxidation reactions

to occur. If Hg° oxidation were to occur, the Hg(II) increase is likely to be small to negligible with depth (below 2 to 3 m) at this location.

4.1.2. *Movement/Settling of Hg*

Loss of Hg from near-surface snow via percolation of meltwater or settling of aerosols to deeper layers are other potential mechanisms that could explain the trend observed. Percolation of meltwater is an unlikely mechanism for this region because air and snow temperatures very rarely exceed 0 °C at Summit (Alley and Anandarkrishnan, 1995). In addition, major element concentrations do not exhibit any systematic decrease with depth contrary to the Hg record; thus, settling of aerosols cannot account for the Hg trend.

4.1.3. *Inadequate Sampling Resolution*

Another possible physical mechanism responsible for the trend observed is the limited sampling resolution. Samples obtained from the firn core for Hg analysis were taken in 15 cm intervals. For the top portion of the core that has better age constraints (± 2 weeks), the interval of snow accumulation is likely to be the same. With depth and increased age uncertainty (± 1 month) the interval of snow accumulation for each sample may not correspond to exactly the same time interval. As a result the variability in the Hg concentrations is probably associated with seasonal changes. Furthermore, due to the relatively low-resolution at which the samples were taken, fine-scale changes in the Hg concentration with depth may not have been captured. As a consequence, the observed declining trend may in fact be due to inadequate sampling resolution but statistical tests suggest the declining trend to be significant at the 95% confidence level ($P = 0.00017$).

4.1.4. *Anthropogenic Mercury*

Declining anthropogenic Hg emissions to the atmosphere may also cause the observed decrease in total Hg concentration. Boutron *et al*. (1998, p. 3317) found that Hg concentrations in snow from the 1980s at Summit to be lower in Hg (factor of 1.7 lower) than snow dated from the late 1940s to the mid 1960s. They attribute this decrease, based on a similar decline recorded in lake sediments and peat bogs from the United States (Engstrom and Swain, 1997), to a decline in emissions due to a shift in coal combustion to electric utilities and the reduction in industrial use of Hg. Our data appear to show a similar decline, about a factor of 1.5 decrease (Figure 2), in the Hg concentration over about a decade period 1989–2001. The main sources of anthropogenic Hg to the Arctic are from Eurasia and North America, with Eurasian emissions governing the levels of anthropogenic contribution since the 1950s (Fischer *et al*., 1998b). Coal is the largest contributor of Hg to the atmosphere followed by industrial processes (e.g. chloro-alkali plants). Since 1992 coal consumption in Eurasia has declined by almost 27% from 689 (1992) to 506 (2002) million tonnes oil equivalent (BP, 2003, p. 33). In the early 1990s a drastic reduction occurred in the industrial emissions from Eastern Europe and the former Soviet Union due to social and economic upheaval (Pirrone *et al*., 1996,

p. 2984). Due to the residence time of Hg° in the atmosphere and the resulting long-range transport the decline in the emissions of anthropogenically-derived Hg from the Eurasian region, would likely manifest in reduced Hg levels in ice cores of Greenland. The decline of global oil and gas supplies, coupled with increasing demand for energy, will almost certainly result in a corresponding increase in coal consumption. This will likely result in increased anthropogenic Hg contribution to the global atmosphere with a concomitant increase in ice cores.

4.2. MERCURY VARIABILITY IN THE TOP 1.8 m

In addition to the decline in Hg concentrations, the top 1.8 m of the core appear to show larger variability as demonstrated by the extremes in Hg concentration from low (approximately 0.30 ng/L) to high (0.60 ng/L), than the lower portion of the core. This variability may result from seasonal effects such as those responsible for Arctic Mercury Depletion Events (AMDEs). During polar sunrise Hg° is oxidized to reactive Hg(II) in the atmosphere resulting in depletion of gaseous Hg (Hg°) (Schroeder *et al.*, 1998; Lu *et al.*, 2001; Lindberg *et al.*, 2002; Steffen *et al.*, 2002). The reactive Hg(II) can be rapidly deposited to the snow surface either as RGM or PM causing peaks in the mercury content within the snowpack (Lindberg *et al.*, 2001) as observed in Figure 3. In addition, photochemical production of trace gases such as alkenes, halocarbons, and alkyl nitrates change the oxidative capacity to a highly reactive oxidizing environment within the snowpack itself during polar sunrise. This can potentially oxidize near surface Hg° within the snowpack to Hg(II) for deposition to the snow; thus, resulting in increased Hg(II) concentrations during the spring months. This seasonal trend is likely not observed with depth due to compaction of the firn and to lower sampling resolution both of which cause the interval of snow accumulation for each sample to be variable and thus not correspond to exactly the same time interval.

5. Summary and Conclusions

The primary focus of this research was to test the capability of the ID-CV-ICP-MS technique for measuring ultra-trace levels of Hg typical of polar snow and firn. Cold-vapor generation coupled with the inherently accurate and precise isotope dilution method of analysis provides the sensitivity and reliability required for trace-level Hg quantitation. The low detection limit (0.14 ng/L) and small blank values (average: 0.19 ± 0.045 ng/L (1σ)) make this technique competitive with CVAAS and CVAFS with the added advantage of intrinsic accuracy of isotope dilution and is much improved over other methods for Hg analysis in waters (Al-Saleh *et al.*, 1998; Manzoori *et al.*, 1998; Allibone *et al.*, 1999; Misund *et al.*, 1999; De la Riva *et al.*, 2002; De Wuilloud *et al.*, 2002; Manganiello *et al.*, 2002). The data suggest: (1) Hg content has decreased during the past 11 years and (2) Hg exhibits a seasonal

signal near the surface (top 1.8 m) of the core. The decreasing trend observed is likely caused by the combination of decreased anthropogenic Hg emission and inadequate sampling resolution. Based on the dates of the core, the variability observed in the top 1.8 m may correspond with seasonal polar sunrise chemistry; however, higher sampling resolution is needed to determine this relationship. The demonstrated capability of this technique to measure low-level (ng/L) quantities of Hg in snow and firn strongly suggests the technique would be useful for this and other applications requiring high sensitivity such as urban atmospheric pollution. In addition newer generations of ICP-MS instruments are a factor of 5–10 more sensitive which may allow the determination of lower concentrations if blanks are sufficiently reduced. For example, from Figures 2 and 4, a factor of 2 reduction in error bars and higher resolution sampling would allow the Hg trends observed to be better constrained.

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Disclaimer

Certain commercial equipment, instruments or materials are identified in this work to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for this purpose.

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