Pre-industrial and recent (1970–2010) atmospheric deposition of sulfate and mercury in snow on southern Baffin Island, Arctic Canada

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ABSTRACT

Sulfate (SO_4^{2-}) and mercury (Hg) are airborne pollutants transported to the Arctic where they can affect properties of the atmosphere and the health of marine or terrestrial ecosystems. Detecting trends in Arctic Hg pollution is challenging because of the short period of direct observations, particularly of actual deposition. Here, we present an updated proxy record of atmospheric SO_4^{2-} and a new 40-year record of total Hg (THg) and monomethyl Hg (MeHg) deposition developed from a firn core (P2010) drilled from Penny Ice Cap, Baffin Island, Canada. The updated P2010 record shows stable mean SO_4^{2-} levels over the past 40 years, which is inconsistent with observations of declining atmospheric SO_4^{2-} or snow acidity in the Arctic during the same period. A sharp THg enhancement in the P2010 core ca 1991 is tentatively attributed to the fallout from the eruption of the Icelandic volcano Hekla. Although MeHg accumulation on Penny Ice Cap had remained constant since 1970, THg accumulation increased after the 1980s. This increase is not easily explained by changes in snow accumulation, marine aerosol inputs or air mass trajectories; however, a causal link may exist with the declining sea-ice cover conditions in the Baffin Bay sector. The ratio of THg accumulation between pre-industrial times (reconstructed from archived ice cores) and the modern industrial era is estimated at between 4- and 16-fold, which is consistent with estimates from Arctic lake sediment cores. The new P2010 THg record is the first of its kind developed from the Baffin Island region of the eastern Canadian Arctic and one of very few such records presently available in the Arctic. As such, it may help to bridge the knowledge gap linking direct observation of gaseous Hg in the Arctic atmosphere and actual net deposition and accumulation in various terrestrial media.

1. Introduction

The Arctic is subject to long-range atmospheric contamination by air pollutants from lower-latitude anthropogenic sources (Law and Stohl, 2007). Pollutants such as sulfate aerosols (SO_4^{2-}) impact the radiative balance and water content of the Arctic atmosphere (Quinn et al., 2008), whereas others such as mercury (Hg) can biomagnify and bioaccumulate in marine or terrestrial ecosystems, which increases the risks of toxic exposure in northern populations (Douglas et al., 2012). Although atmospheric SO_4^{2-} and Hg share some common sources (e.g., coal combustion), their emission histories have followed different paths over the last century and reflect an evolving technological and economic context (Hirdman et al., 2010; Smith et al., 2011; Streets et al., 2011). The monitoring of SO_4^{2-} aerosols and gaseous elemental Hg (GEM or Hg^0) in the Arctic atmosphere is presently limited to a few stations, and the longest continuous time series of observations only extends to the early 1980s for SO_4^{2-} (Quinn et al., 2009) and to the mid-1990s for Hg^0 (Cole et al., 2013). This limitation makes identification of long-term trends challenging. Furthermore, changing levels of Hg^0 do not necessarily translate to changing net Hg deposition rates in environmental media because of the high reactivity and volatility of Hg species. However, proxy records of airborne pollution developed from archives such as polar firn and ice cores can serve as useful surrogates for direct measurements of historical Arctic air pollution (e.g., Goto-Azuma and Koerner, 2001) and can determine the atmospheric response to pollution control measures, such as the detection of atmospheric lead (Boutron et al., 1995). Furthermore, net accumulation rates of Hg in the vast glaciated terrestrial areas of the Arctic (~20% of land cover) are presently poorly known. With the

recent adoption of the international Minamata Convention on Mercury (UNEP, 2013), reliable baseline estimates of Hg levels and accumulation rates in various media in the Arctic environment must be established so that the possible impact of future constraining measures on Hg releases may be evaluated.

SO_4^{2-} aerosols have a relatively short atmospheric lifetime of a few weeks (Quinn et al., 2008) and are irreversibly deposited in polar snow by both wet and dry processes (except when snow scouring by wind occurs); however, atmospheric Hg can exist as Hg^0 as well as in its divalent (Hg^{2+}) gas or particulate (Hg_p) phases, and these forms have vastly different atmospheric lifetimes of a few days (Hg^{2+} and Hg_p) to over a year (Hg^0). Furthermore, a large fraction (possibly > 80%) of the Hg deposited in snow may be rapidly re-emitted to the atmosphere because of photochemically-driven changes in the Hg oxidation state (Steffen et al., 2008). The SO_4^{2-} and Hg that accumulate in polar firn, therefore, represent a time-varying fraction of the atmospheric burden of these contaminants. Factors controlling the accumulated SO_4^{2-} fraction in firn include the dry/wet deposition ratio, surface wind strength and snow accumulation rate (e.g., Fischer et al., 1998; Harder et al., 2000). The situation for Hg is more complex because its net deposition rates are linked to ozone and halogen photochemistry in the atmospheric boundary layer (Brooks et al., 2011; Durnford et al., 2012; Toyota et al., 2013).

At present, most historical reconstructions of Hg accumulation in Arctic environments are based on lake sediments or ombotrophic peat, and these archives have their merits and shortcomings (reviewed by Goodsite et al., 2013). Comparatively few archives of Hg accumulation in polar firn and ice exist; however, discontinuous measurements of THg in firn have been reported from central Greenland (e.g., Boutron et al., 1998; Brooks et al., 2011) and a 66-year record of Hg^0 in interstitial firn air was recently developed from the same region (Faïn et al., 2008). Although the latter documents the changing Hg^0 levels in the Arctic air, it does not provide any information on the changing rates of Hg accumulation in the polar firn. Hence, current knowledge of Hg accumulation trends in the vast glaciated regions of the Arctic remains extremely poor.

To address this knowledge gap, a project was initiated as part of the 2007–08 International Polar Year initiative to recover glacial firn and ice cores from multiple sites across the Canadian Arctic Archipelago (CAA) and Greenland, extend earlier glacial records of climatic variables and atmospheric pollution to the present day and define the spatial and recent temporal variability in previously-undocumented trace elements, Hg in particular. One of the sites studied was Penny Ice Cap (~66° N, 6410 km^2), which is the southernmost large ice cap in the CAA and the only one on Baffin Island with an accumulation zone from which ice-core records have been obtained. This region of the CAA is experiencing rapid changes in sea-ice cover (Kinnard et al., 2006; Tivy et al., 2011), which could have an impact on SO_4^{2-} and Hg accumulation in the polar firn.

In previous studies, a Holocene record of atmospheric SO_4^{2-} and nitrate (NO_3^-) deposition on Penny Ice Cap was developed, which extended into the early 1990s (Goto-Azuma and Koerner, 2001; Goto-Azuma et al., 2002). In this article we present an update of the SO_4^{2-} record from Penny Ice Cap, and a new ~40-year record (1970–2010) of total Hg (THg) and monomethyl mercury (MeHg) accumulation from the same site. The study presented here builds on results from an earlier pilot investigation of Hg deposition and release on Penny Ice Cap (Zdanowicz et al., 2013). Findings from the new P2010 core are compared with earlier published results for SO_4^{2-} and THg data measured in earlier historical and pre-historical archived core samples from this site.

2. Materials and methods

2.1. Study site

Penny Ice Cap is located on Cumberland Peninsula (Fig. 1), a mountainous region with deeply incised fjords and glacial valleys. The ice cap
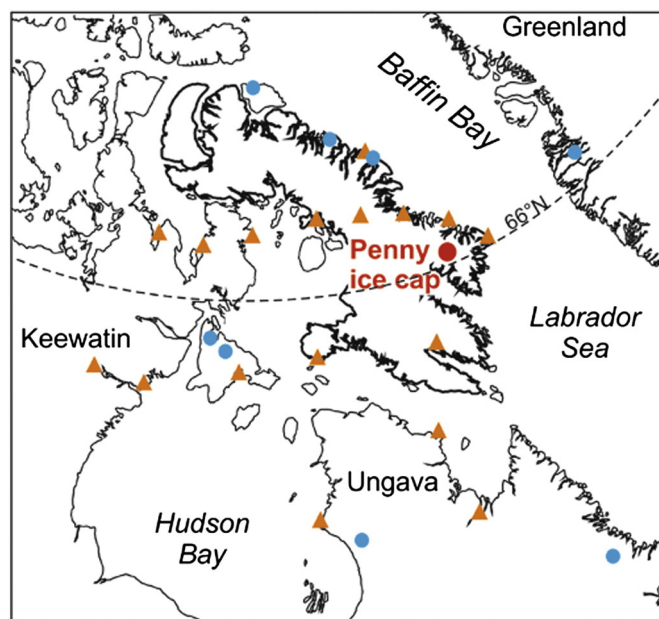

Fig. 1. Location map of the Baffin Island region showing the position of Penny Ice Cap on Cumberland Peninsula. Blue dots indicate sites from which the archives of lake sediment Hg accumulation were developed (Bindler et al., 2001; Cooke et al., 2012; Muir et al., 2009), and orange triangles denote weather stations from which data were obtained for the present study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

summit (~1825 m asl) experiences a mean annual air temperature of −16 °C and accumulation rate of ~0.40 m H_2O a^{-1} (see Section 2.3). Presently, a large part of the winter accumulation at the summit melts in summer and the meltwater percolates into the firn to refreeze as infiltration ice. This process leads to an unquantified vertical redistribution of water-soluble impurities and imposes limits on the temporal resolution of firn and ice core records (Zdanowicz et al., 2012, 2013).

2.2. Firn coring and sampling

A 22.7-m firn core (P2010) was recovered in April 2010 from the summit of Penny Ice Cap using a fiberglass corer (Kovacs Instruments, Lebanon, NH). The coring site was the same site (within GPS error) from which deeper cores were obtained in 1995 (cores P95 and P96: Fisher et al., 1998; Goto-Azuma et al., 2002). Prior to sampling, the corer was cleaned repeatedly in untouched snow and firn. The core was recovered in 0.85-m segments (average) that were measured, weighted, bagged in polyethylene, placed inside opaque coolers and returned frozen to the Geological Survey of Canada (GSC) laboratories in Ottawa where they remained stored in a −25 °C freezer until they were processed. First, the structure, density and electrical conductivity of the core segments were measured (Zdanowicz et al., 2012). The core segments were then sampled inside a metal-free clean cold room at −10 °C by operators wearing non-particulating suits and disposable powder-free gloves. To remove possible external contamination on the core, the following protocol was adapted from previous experiments (Zheng et al., 2006): the outer 2- to 3-mm of each core segment was removed with a stainless steel scalpel, and the shavings from selected cores were collected in sealable, Hg-free Teflon bags (Welch Fluorocarbon, Dover, NH, USA) for analysis. Next, a second 2- to 3-mm thick layer was removed in the same manner, and the shavings were saved in Whirl-Pack bags to be used for major anion (Cl^- and SO_4^{2-}) analyses. These bags have been used and tested routinely for many years and proven to be contamination-free for the determination of major ions at low (ppb) levels. The remaining scraped inner core segments were cut into 10-cm samples (average) with a clean stainless steel saw, placed into Teflon bags and returned to the cold dark storage until