

Polar firn air reveals large-scale impact of anthropogenic mercury emissions during the 1970s

Xavier Faïn^{a,1}, Christophe P. Ferrari^{a,b}, Aurélien Dommergue^{a,b}, Mary R. Albert^c, Mark Battle^d, Jeff Severinghaus^e, Laurent Arnaud^a, Jean-Marc Barnola^a, Warren Cairns^f, Carlo Barbante^{f,g}, and Claude Boutron^{a,h}

^aLaboratoire de Glaciologie et Géophysique de l'Environnement (Unité Mixte de Recherche 5183 Centre National de la Recherche Scientifique/Université Joseph Fourier), 54 Rue Molière, B.P. 96, 38402 St. Martin d'Hères Cedex, France; ^bPolytech' Grenoble, Université Joseph Fourier, 28 Avenue Benoît Frachon, B.P. 53, 38041 Grenoble Cedex, France; ^cGeophysical Sciences Division, Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, 72 Lyme Road, Hanover, NH 03755; ^dDepartment of Physics and Astronomy, Bowdoin College, 8800 College Station, Brunswick, ME 04011-8488; ^eThe Scripps Institution of Oceanography, University of California at San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0244; ^fInstitute for the Dynamics of Environmental Processes CNR, Calle Larga Santa Marta 2137, I-30123 Venice, Italy; ^gEnvironmental Sciences Department, University of Venice, Calle Larga Santa Marta, 2137, I-30123 Venice, Italy; and ^hUnité de Formation et de Recherche de Physique, Université Joseph Fourier, B.P. 53, 38041 Grenoble Cedex, France

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Mercury (Hg) is an extremely toxic pollutant, and its biogeochemical cycle has been perturbed by anthropogenic emissions during recent centuries. In the atmosphere, gaseous elemental mercury (GEM; Hg⁰) is the predominant form of mercury (up to 95%). Here we report the evolution of atmospheric levels of GEM in mid- to high-northern latitudes inferred from the interstitial air of firn (perennial snowpack) at Summit, Greenland. GEM concentrations increased rapidly after World War II from $\approx 1.5 \text{ ng m}^{-3}$ reaching a maximum of $\approx 3 \text{ ng m}^{-3}$ around 1970 and decreased until stabilizing at $\approx 1.7 \text{ ng m}^{-3}$ around 1995. This reconstruction reproduces real-time measurements available from the Arctic since 1995 and exhibits the same general trend observed in Europe since 1990. Anthropogenic emissions caused a two-fold rise in boreal atmospheric GEM concentrations before the 1970s, which likely contributed to higher deposition of mercury in both industrialized and remotes areas. Once deposited, this toxin becomes available for methylation and, subsequently, the contamination of ecosystems. Implementation of air pollution regulations, however, enabled a large-scale decline in atmospheric mercury levels during the 1980s. The results shown here suggest that potential increases in emissions in the coming decades could have a similar large-scale impact on atmospheric Hg levels.

atmosphere | Greenland | past century | pollution

Mercury (Hg) is a worldwide pollutant globally dispersed in the environment. Lake and ocean sediment profiles, peat bogs, and ice—in both remote and industrialized regions—suggest that natural background levels of mercury have increased during the past 150 years (1). Based on these observations, global-scale Hg cycling models show that anthropogenic emissions have substantially perturbed the global biogeochemical mercury cycle since preindustrial times (2). Recently, efforts have been made to reduce Hg emissions from industry and power plants in both North America and Europe. Direct anthropogenic sources such as coal combustion, however, still release large amounts of inorganic mercury into the atmosphere, either as gaseous elemental mercury (GEM; Hg⁰) or as divalent gaseous mercury species (Hg²⁺) (3).

GEM, with an atmospheric lifetime in the range of 5–24 months, can be transported across long distances to remote locations before conversion to divalent Hg species by atmospheric oxidation processes (4). Divalent Hg species are subject to rapid wet and dry deposition in terrestrial ecosystems. Some of the Hg²⁺ deposited in aquatic systems and sediments is transformed into organic methylmercury (5). Although inorganic Hg species have severe health effects on humans, methylmercury is thought to be the highly toxic species involved in bioaccumulation in aquatic food chains. In thousands of lakes in North America, Europe, and Asia, methylmercury contamination of fish negatively impacts the health of humans and wildlife,

particularly affecting populations whose traditional diet is based on seafood (e.g., in the Arctic) (5).

Many factors affect fish mercury levels (5), and the response of fish methylmercury concentrations to changes in mercury deposition has been difficult to establish. Harris et al. (6) recently reported, however, a whole ecosystem study demonstrating a rapid and direct change in mercury levels in fish resulting from a change in atmospheric mercury. Thus, recent evolution of the atmospheric mercury burden, strongly influenced by anthropogenic emissions, could have played a key role in contamination of many ecosystems. This linkage is of prime importance because many organizations (e.g., United Nations Environmental Program) and nations (e.g., the United States, Europe, and Canada) are presently debating the implementation and extension of mercury emission regulations and implementation of a global network to monitor mercury pollution.

To better assess the global influence of anthropogenic mercury emissions, new methodological approaches are needed. In particular, historical evolution of atmospheric GEM concentrations during the last few decades remains poorly characterized, even though GEM represents as much as 95% of the atmospheric mercury burden (4). The first direct measurements of total gaseous mercury (TGM, including GEM and divalent gaseous mercury species) were reported in the late 1970s during ship cruises across the Atlantic Ocean (7), but real-time atmospheric continuous monitoring at various European and Arctic locations was only initiated in the early 1990s (8). Lake sediment (9, 10), peat bog (11, 12), and ice and snow (13, 14) records have been powerful tools to reconstruct past evolution of atmospheric deposition of Hg²⁺ species at specific locations, although their interpretation is still debated (15, 16). These archives, however, do not inform directly about GEM, the major atmospheric Hg species. In this paper, we present results from a natural archive that provides a unique history of gaseous elemental mercury concentrations at middle and high northern latitudes. Specifically, we examined polar firn air as an archive for investigating the impact of anthropogenic emissions on the mercury cycle.

Results and Discussion

The potential of polar ice sheets to serve as an archive for reconstruction of past atmospheric compositions has been well

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¹To whom correspondence should be sent at the present address: Division of Atmospheric Sciences, Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512. E-mail: xavier.fain@dri.edu.

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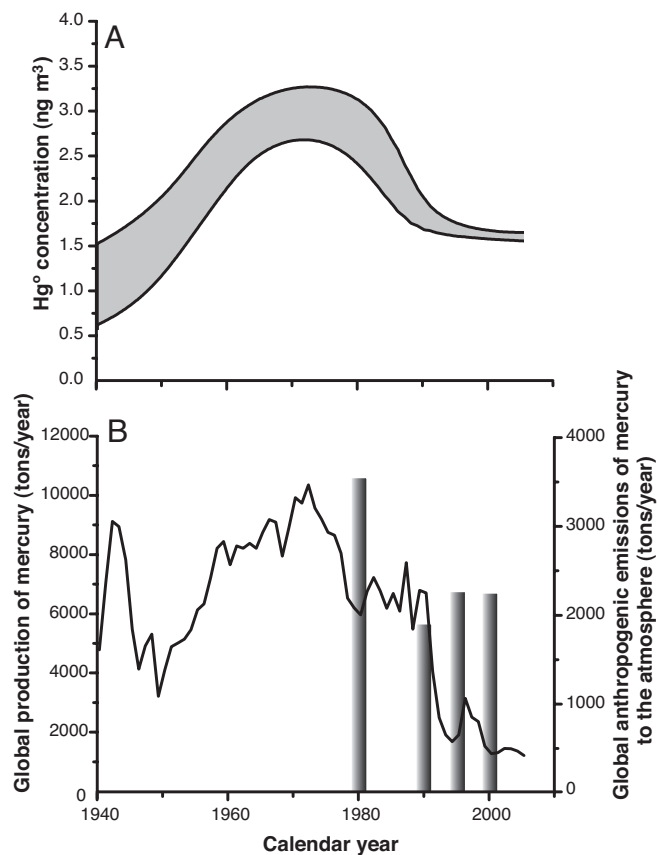


Fig. 2. Impact of human emissions on the atmospheric mercury reservoir during recent decades. (A) Envelope of modeled concentrations for atmospheric GEM inferred from Summit firn air, central Greenland, during the last 66 years (gray area). (B) Global anthropogenic emissions of mercury to the atmosphere in 1980, 1990, 1995, and 2000 (ref. 3 and references therein) (gray bars) and worldwide production of mercury (black line) (49). Global anthropogenic emissions of mercury presented here are based on emission inventories and include industrial emissions as well as coal combustion. Worldwide production refers to the mercury extracted from geological reservoirs for industrial uses (including mining). Only a fraction of the mercury produced is transferred to the atmosphere by industrial processes.

a negligible effect on GEM production in the interstitial air of alpine snow (31). How snow composition impacts mercury chemistry is still under challenge (32). Higher levels of sea salts favor reduction processes and thus GEM destruction in the snow interstitial air (30), but no long-term trends have been reported for sea salt impurities deposited on the Greenland ice sheet during the last century (33). Recent evolution of surface snow composition at Summit has been dominated by human-driven pollutants, but Hg²⁺ concentrations measured in a firn core dated from 1949 to 1989 exhibited low values and limited variation (range: 0.05–2.0 pg g⁻¹; mean: 0.43 pg g⁻¹) (13).

GEM does not adsorb on ice surfaces, as demonstrated by both field and laboratory measurements (34, 35), and we showed that present chemical processes in the shallow firn do not perturb the long-term record of past atmospheric GEM (21). We cannot eliminate the possibility that slow evolution of environmental conditions (e.g., surface temperature and irradiation) and snow composition (e.g., sea salts levels) induced slight evolution in chemical processes involving GEM in the shallow firn during recent decades. However, such processes are unlikely during winter and occur during a limited period of the year (typically from late spring to early fall, 21), and we argue that their past

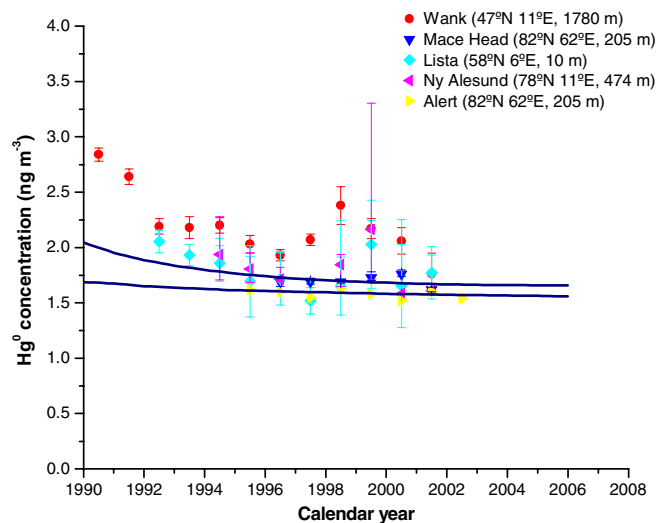


Fig. 3. Envelope of GEM atmospheric concentrations inferred from Summit firn air (blue curves), and atmospheric monitoring of GEM available for the Northern Hemisphere and Arctic sites since 1990. Dots and error bars represent the median and 95% confidence intervals. Data are reproduced from Slemr et al. (8) and Steffen et al. (38).

evolution will have a negligible impact on the deep firn atmospheric record. Thus, we conclude the firn air is a reliable archive to investigate historical changes of GEM atmospheric concentrations during the last ≈ 70 years.

Atmospheric trends inferred from polar archives inform about boundary layer levels, and the lack of information about free tropospheric background could be a concern for many gaseous species. Conversely, specific oxidation processes can lead to depletion of GEM in the upper troposphere and lower stratosphere (36), and GEM concentrations in the boundary layer could be relevant information when measured far from large pollution sources (e.g., at Summit). Active atmospheric chemistry has been reported for polar coastal areas: the so-called Atmospheric Mercury Depletion Events (AMDEs), occurring simultaneously with the postsolar sunrise destruction of ozone, can lead to complete depletions of atmospheric GEM during springtime (32). No atmospheric ozone depletion events were observed at Summit (37); and, consequently, AMDEs are unlikely to occur in central Greenland. No strong variations in atmospheric GEM concentrations are thus expected throughout the year at Summit. Furthermore, firn air in the lock-in zone has the useful property that it averages surface gas concentrations for a decade or so, due to diffusion in the firn.

GEM atmospheric monitoring available from the Arctic at Alert (82°N, 62°E, 205 m, Canada) (38) and Ny-Ålesund (78°N, 11°E, 474 m, Spitzbergen) (8) as well as the GEM history reconstructed from the firn air at Summit exhibit stable GEM concentrations of about 1.7 ng m⁻³ during the last 10 years (Fig. 3). In Europe, atmospheric GEM monitoring started at the summit of the Wank mountain (47°N, 11°E, 1780 m, Germany), at Lista (58°N, 6°E, 10 m, Norway), and at Mace Head (53°N, 9°W, 10 m, Ireland) in 1990 (39), 1993 (40), and 1996 (41), respectively. The Wank station is located in a central and continental area and is more strongly influenced by regional sources than the Lista and Mace Head stations. From 1990 to 1996, a decrease in atmospheric GEM concentrations was observed at both the Wank and Lista stations, with higher levels at Wank (Fig. 3). This trend has been related to the 45% decrease in European anthropogenic emissions reported between 1990 and 1995 (42). Atmospheric GEM history reconstructed from

containing devices may considerably escalate Hg emissions in Asia. As was observed during the 1970s, we expect an increase in GEM concentrations at mid-northern latitudes as a result. This trend is likely to increase in the future, impacting high-northern latitude areas. Long-range transportation of mercury from Asia is already reported in the United States (55). Recently, more than 140 nations decided to begin negotiations for a mercury-limiting treaty in the framework of the United Nations Environment Program (UNEP). Implementation of such global regulations may be an effective strategy to avoid contamination of populated and remote areas up to the Arctic in the future.

Materials and Methods

Firn Air Sampling. From May 25 to May 31, 2006, we investigated GEM in the firn air at a remote location 10 km away from Summit Station, central Greenland (72.6°N, 38.5°W, 3200 m elevation). We sampled firn air using established methods (18, 19, 56) from one borehole at depths of 15, 25, 30, 40, 50, 58, 63, 66, 70, 72, 74, 76, 78, and 79.5 m. A 4-m long bladder was lowered into the borehole after drilling to the sampling depth and pressurized with air from the bottom of the hole, effectively sealing the hole. Two Dekabon (polyethylene/aluminum composite) lines were used to pump firn air from a space left immediately below the bladder. These lines drew air from two separate openings above and below a horizontal stainless steel baffle that was nearly as wide as the borehole. Air was pumped from the upper opening at 20 L min⁻¹ and directed to waste after measuring CO₂ concentration (in situ measurements using an NDIR analyzer). When CO₂ levels stabilized, indicating effective removal of contamination by younger and/or ambient air, sampling from the lower opening was initiated. Firn air was first collected in flasks for additional measurements (e.g., CH₄ and CFCs) before GEM sampling actually started. Pumping from the upper opening continued during sampling (at 20 L min⁻¹) to remove any air leaking from within or around the bladder. This technique also served to keep sampled air out of contact with the bladder itself.

GEM Analysis. A gas phase mercury analyzer 2537A (Tekran Inc.) was used for determination of GEM concentrations in firn air. The prefiltered air stream (0.2- μ m Teflon particle filter) was collected on two gold cartridges. GEM was thermally desorbed and detected by cold vapor atomic fluorescence spectrometry at 253.7 nm. Use of dual gold cartridges allowed alternate sampling and desorption, resulting in continuous measurement of GEM on a predefined time base. Set-up, accuracy, and precision of this instrument have been evaluated previously during field comparisons at an urban/industrial site (57) and a remote marine background location (58). The Tekran analyzer was operated with a five-minute sampling frequency, and the air was sampled at a flow rate of 1 L min⁻¹. The analyzer was calibrated every 25 h with an internal automatic permeation source. The detection limit for GEM in this operation mode is about 0.15 ng m⁻³. Since the internal pump of the 2537A Tekran analyzer was not strong enough to pump firn air, particularly from deeper layers, a PTFE pump (MZ-2C; Vacuubrand, Inc.) was connected to the firn sampling line, upstream to the Tekran analyzer. This pump delivered firn air to the inlet of the 2537A at the desired flow rate of 1 L min⁻¹. We measured blanks of the PTFE pump before and after sampling at all depths to quantify any contamination introduced by this additional pump.

At each depth, we sampled firn air for 40 min, resulting in approximately eight GEM measurements. We checked blanks of the Dekabon sampling line both at the beginning and end of the fieldwork; they were 0.08 \pm 0.13 ng m⁻³ (n = 8, before sampling, on May 25, 2006) and 0.01 \pm 0.06 ng m⁻³ (n = 18, after sampling, on June 1, 2006).

Diffusion Modeling. We used a one-dimension gas diffusion model in Eulerian coordinates developed by Rommelaere et al. (24) to infer the atmospheric record of GEM from firn air concentrations (Fig. 1). Processes taken into account

included (i) air mixing by pressure and temperature gradients down to a few meters below the surface (i.e., the so-called convection zone); (ii) molecular diffusion in the open pore space and gravitational fractionation (entrainment toward the deeper firn depends on concentration gradients, diffusivities, and molar mass); and (iii) a downward air flux in the open porosity zone due to bubble closure removing air from the open pores. Note that this removed air has to be replaced by air coming from the upper parts of the firn, thus creating a downward flux. We set temperature and accumulation rate to their present-day values [respectively, 241°K (20) and 224 kg m⁻² year⁻¹ (22)] and assumed these rates were constant throughout the model run. We used firn structure parameters (density and closed porosity) from the EUROCORE drilling (20) (see Fig. S2).

GEM diffusivity in firn air depends on both GEM diffusivity in air and firn tortuosity. Tortuosity of a porous medium represents the complexity of the pathway and is commonly calculated as the ratio of the mean path length to the minimum possible (straight line) path length. We used an inverse method (24, 59) to compute tortuosity at all depths in the firn from the CO₂ atmospheric trend and from CO₂ concentrations measured in the firn at Summit. In other words, we obtained a site specific, tortuosity-depth relationship by adjusting diffusivity until the model reproduced the observed CO₂ firn-air profile when driven by the independently derived atmospheric CO₂ history (see Fig. S3). We sampled air for CO₂ analysis at the same depths as GEM.

We validated parameterization of the model diffusivity using CH₄ and three halocarbon species (CFC11, CFC113, and CCl₄) for which atmospheric histories have been estimated from emission scenarios and real-time measurements (60–62). Concentration-depth profiles were determined for these four species using the adjusted diffusivity-depth profile in the diffusion model, and good agreement with concentrations-depth profiles actually measured in the Summit firn was obtained (see Figs. S4 and S5).

Monte Carlo Modeling. Little information is available about past atmospheric levels of GEM, but real-time measurements reported since 1977 (8) and industrial production figures (49) suggest that GEM concentrations could have peaked within the last 50 years. Thus, we chose a mathematical parameterization of atmospheric GEM history from 1940 to 2006 (firn air model input)—which allowed for the possibility of a constant level, monotonic increase or decrease, or peak concentration of GEM concentration during this timeframe, depending on the choice of parameter values. We tested a wide range of parameter values with the forward firn air model previously described (Monte Carlo approach), representing widely varying scenarios for atmospheric evolution of GEM concentrations. We then modeled a profile of GEM concentrations in the firn from each atmospheric history tested. Agreement between a modeled firn profile and the experimental firn profile (Fig. 1) was estimated using the χ^2 parameter (see *SI Text*). According to Tarantola theory (63), we were able to associate a probability density with each atmospheric scenario tested. We finally assessed probability distributions for GEM concentrations with a 1-year time resolution, and we calculated means and standard deviations from all distributions (i.e., every year from 1940 to 2006) (see *SI Text*). The envelope of atmospheric GEM concentrations presented in this study corresponds to the mean concentrations plus or minus one standard deviation.

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