Atmospheric Mercury Deposition during the Last 270 Years: A Glacial Ice Core Record of Natural and Anthropogenic Sources

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Mercury (Hg) contamination of aquatic ecosystems and subsequent methylmercury bioaccumulation are significant environmental problems of global extent. At regional to global scales, the primary mechanism of Hg contamination is atmospheric Hg transport. Thus, a better understanding of the long-term history of atmospheric Hg cycling and quantification of the sources is critical for assessing the regional and global impact of anthropogenic Hg emissions. Ice cores collected from the Upper Fremont Glacier (UFG), Wyoming, contain a high-resolution record of total atmospheric Hg deposition (ca. 1720−1993). Total Hg in 97 ice-core samples was determined with trace-metal clean handling methods and low-level analytical procedures to reconstruct the first and most comprehensive atmospheric Hg deposition record of its kind yet available from North America. The record indicates major atmospheric releases of both natural and anthropogenic Hg from regional and global sources. Integrated over the past 270-year ice-core history, anthropogenic inputs contributed 52%, volcanic events 6%, and background sources 42%. More significantly, during the last 100 years, anthropogenic sources contributed 70% of the total Hg input. Unlike the 2−7-fold increase observed from preindustrial times (before 1840) to the mid-1980s in sediment-core records, the UFG record indicates a 20-fold increase for the same period. The sediment-core records, however, are in agreement with the last 10 years of this ice-core record, indicating declines in atmospheric Hg deposition.

Introduction

Atmospheric transport and fate of mercury (Hg) and subsequent methylmercury bioaccumulation in the environment are critical contamination issues (*1*). Of continuing debate is whether atmospheric Hg deposition is due to local, regional,

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or global sources (*2*, *3*). Recent estimates indicate that anthropogenic emissions of Hg have exceeded natural inputs since the onset of the industrial period (*4*). The potential effectiveness of proposed Hg emission reductions hinges on an accurate estimate of the function of current atmospheric deposition from "manageable" sources. A significant question facing scientists and environmental agencies is the relative contribution of natural and anthropogenic sources to atmospheric Hg. Mercury concentrations in glacial ice provide a direct measurement and historic record of atmospheric Hg deposition (*5–7*). Research on total Hg in glacial ice, especially in the midlatitudes, is scarce. Although some polar ice cores have provided a limited record of past Hg deposition, polar ice cores are, at best, proxy indicators of historic Hg deposition in the midlatitudes.

Increasingly, ice cores from low- and midlatitudes are becoming recognized as valuable tools for reconstructing paleoclimatic and paleoenvironmental records (*8–15*). These records, however, are uncommon; the Hg record presented here is the first and most comprehensive of its kind yet to be available in North America. To underscore the importance and uniqueness of these records, increasing global temperatures are threatening the existence and integrity of low- and midlatitude glaciers, which are receding rapidly. If recession continues at these rates, the Dinwoody Glacier, about 3 km north of the Upper Fremont Glacier (UFG), will be gone in about 20 years (*16*). Other estimates show that the remaining glaciers in Glacier National Park, Montana, will no longer exist in 50−70 years (*17*) and that high alpine glaciers in the Andes of South America (i.e., Quelccaya) will be severely compromised by meltwater processes (*13*). This irreplaceable paleoenvironmental resource may literally melt away in the near future, releasing an additional and potentially large reservoir of Hg trapped in snow and ice to the environment.

The dynamics of Hg in glacial ice are not well-known. Although Hg deposition to polar cores has been investigated (*5–7*), it is recognized that, unlike polar ice cores, meltwater processes can influence the chemical stratigraphy of alpine glaciers. This process is described in terms of an elution sequence (*18*) and may "dampen" or complicate the environmental signal by mobilizing or removing solutes. A complete removal of chemical signal from the ice by meltwater processes limits paleoenvironmental interpretation in that it is impossible to know if an environmental signal initially existed. Therefore, any chemical signal preserved in the ice, albeit possibly stratigraphically shifted, may have potentially been much larger during deposition. To date, there has been no work to place metals such as Hg in the elution sequence. Thus, the mobility of Hg in temperate ice, in relation to other ions, is largely unknown. Despite these potential problems, previous studies (*8–11*, *19*) indicate that the UFG preserves chemical stratigraphy with sufficient resolution to support the interpretation of valuable paleoenvironmental records. Moreover, Hg concentrations in ice cores are not subject to controversial diagenetic processes that may affect Hg concentrations in sediment cores, peat bogs, and soils (*20–21*). Hg(0) is sparingly soluble (equilibrium concentrations with typical air concentrations are about 2−6 pg/L) and, with respect to other solutes, the solubility of Hg(II) and HgO is low, suggesting that movement in glacial ice due to meltwater is minimal.

Experimental Section

Continuous ice cores were collected from UFG in the Wind River Range, Wyoming (Figure 1), in 1991 and again in 1998.
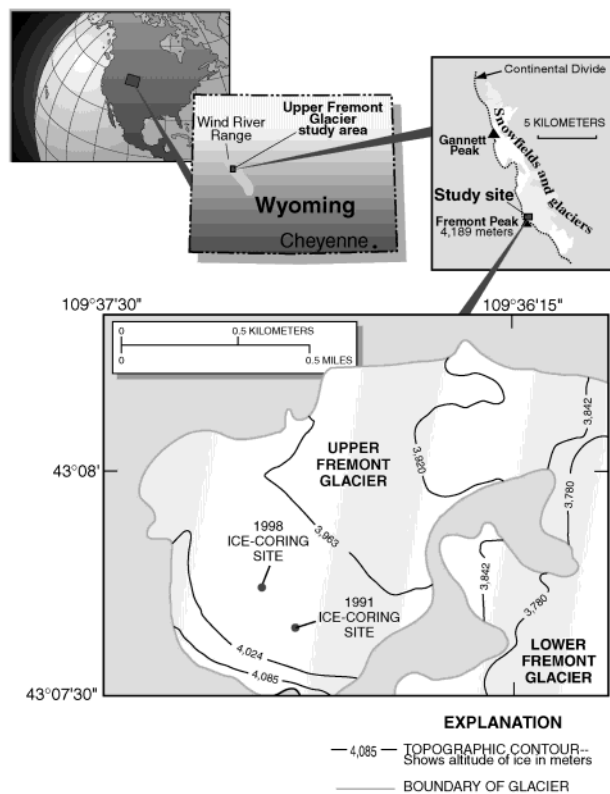
FIGURE 1. Map showing the location of the 1991 and 1998 ice-core drilling sites. Each site was located at about the same altitude separated by about 220 m.

FIGURE 2. Location of the Upper Fremont Glacier showing very little impact from upwind local sources of atmospheric Hg.

For a temperate glacier, the UFG has some unique qualifications conducive to preserving paleoenvironmental signal. The drill site elevation is 4100 m. Minimum, maximum, and average annual air temperatures during 5 years of record were −36, 13, and −7 °C, respectively. Temperature profiles from snow pits, conducted on an intermittent basis, on the UFG indicated that the snowpack was typically isothermal at 0 °C during the summer months. During the winter months, the snowpack was below 0 °C, ranging from −7 to −2 °C. The net accumulation rate is 96 cm ice equivalent/year, based on the 29-m depth of ice (the 1963 tritium peak) divided by time. The glacial surface gradient is near level, reducing crevassing and fracturing of the ice strata (9). These characteristics reduce the potential for meltwater to alter any paleoenvironmental signal. Because the remoteness of the site limits the influence of local sources of atmospheric Hg deposition to the UFG, the location is favorable for measuring historical regional and global deposition of total Hg from the atmosphere (Figure 2) (22).

Typically, ice cores are recovered with electromechanical drills, and deep polar cores require the use of liquid lubricants such as fuel oil or antifreeze to keep the drill hole open. The UFG cores, located about 220 m apart roughly along the same contour elevation, were recovered with a 7.6-cm diameter thermally heated aluminum coring device (9). The thermal drilling process excludes the use of lubricants, reducing the potential for Hg contamination. The drill winch cable was a Kevlar braid protected by an outer Nylon braid. All bolts on the core barrel were stainless steel, and silver was a major component of the thermal blade. The metals exposed to the ice-core surface during recovery and processing were composed of aluminum and stainless steel. To assess possible Hg contamination from these metals, "veneer experiments" similar to those reported for polar ice (23) were performed on a 20-cm piece of archived UFG ice (ca. 1855) from a depth of 103 m. Four successive ∼1 cm layers (i.e.,
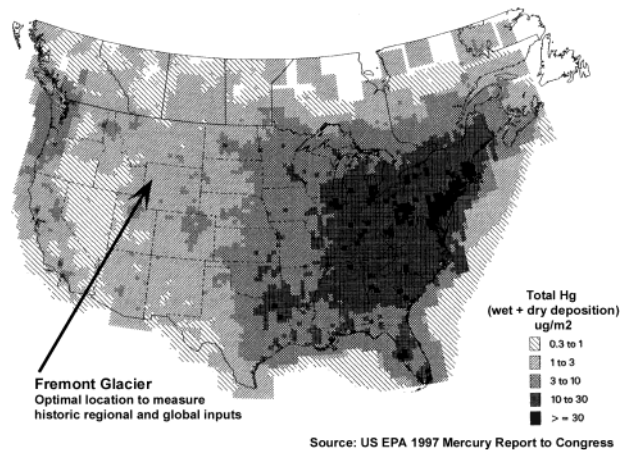
concentrai rings) were scraped from the sample using a titanium blade onto a Teflon working platform inside a laminar-flow hood. Powder-free Latex gloves were worn throughout the procedure (24). The scrapings were collected into acid-boiled 250-mL Teflon bottles and allowed to melt at room temperature. The melted samples, ranging in volume from 51 to 71 mL, were analyzed for Hg using internationally adopted and proven analytical methods (25). Rinse water from the titanium blade was measured at 0.35 ng/L. Selected metal concentrations (including rare earths) were measured by ICP-MS. Mercury concentrations from the veneer experiment ranged from 9.3 to 11.2 ng/L with no obvious trend in those data, and the average concentration was within 6% of the composite sample taken from the same horizon for the development of the Hg profile. The uniform concentrations through the thickness of this ice-core sample suggest two possibilities: (1) the source of Hg is from atmospheric deposition and represents an uncontaminated signal, or (2) an Hg source from the core barrel has penetrated the entire thickness of the core. The latter is unlikely for three reasons: (1) Hg(0) is sparingly soluble and, with respect to other solutes, the solubility of Hg(II) and HgO is low, and reducing movement in ice, a solid-phase exchange process would be required; (2) the significant variations in Hg concentrations observed throughout the length of the core would be masked or dampened by a constant source of contamination; and most significantly, (3) if a contamination source existed, concentrations of these constituents would decrease from outer to inner core (23); this trend was not observed in the UFG ice core. Aluminum and zinc, two major components of the core barrel and saw blade, also showed no decreasing trends from the outer layers to the ice-core center. Moreover, silver, a major component of the thermal blade, and chromium, a component in stainless steel, were not detected. Aluminum did not correlate with the rare earth elements La, Ce, and Nd in the outermost layer as a function of radius from the center, suggesting that a fraction of this aluminum is from the core barrel. The next five layers to the center of the core, however, show that aluminum is correlated to these rare earth elements, indicating that the source is natural or crustal earth. Although the potential for Hg contamination exists, based on these results, removal of the outer layer of the ice-core samples (discussed next) greatly reduces the potential for Hg contamination from recovery and processing techniques used for the UGF ice cores.

After the ice core was removed from the aluminum core barrel, 1-m sections were quickly sealed in polyethylene bags and placed in core tubes by personnel wearing Tyvek suits and powder-free Latex gloves. During the entire process, "clean hands" protocol was used (24). To prevent melting,

the core tubes were stored at 0 °C in snow vaults on the glacier. Immediately after drilling was complete, the cores were transported to a freezer truck via a 10-min helicopter flight to storage in the National Ice Core Lab (NICL) storage room (−36 °C) in Denver, CO, until processing and analysis.

All processing took place in the clean −24 °C environment of NICL. The cores, totaling 160 m in length, were cut into 7-cm sections with a stainless steel band saw cleaned with methanol. A total of 57 samples and 40 samples were removed from the 1991 and 1998 cores, respectively. The sections were placed in Hg-free clean polyethylene bags and shipped frozen on dry ice overnight to the U.S. Geological Survey's Wisconsin District Mercury Research Lab (WDMRL) in Middleton, WI. Temperature recorders were placed in the shipping containers, and the temperature inside the containers during shipment did not exceed 0 °C.

At the WDMRL, ice samples were removed from the bags with gloved hands and rinsed with about 50 mL of WDML deionized water (total Hg ≤0.1 ng/L) to remove any potential contamination from field procedures. After rinsing, the samples were placed in Hg-clean (25) Teflon jars. Four milliliters of bromine monochloride (BrCl) was added to oxidize all species of Hg to Hg(II), the jars were capped, and the samples were allowed to thaw at room temperature. Samples ranged in volume from 25 to 75 mL. Although there are small variations in ice density, this is not the main reason for sample-volume variation. In some sections of the ice core, demands for ice to address other research interests (i.e., chlorine-36 studies and paleoclimate and paleoenvironmental studies) limited the volume of ice available for Hg research. Because all samples were run in duplicate for Hg analysis and the likely possibility Hg concentrations would be relatively low in many preindustrial samples (<1 μg/L), creating further demand for a maximum volume needed for accurate Hg analysis, 50 mL of rinse water was used to remove the potentially contaminated outer core layer. Once thawed, the liquid was transferred to Hg-clean Teflon bottles that were placed in an oven at 50 °C overnight to ensure complete oxidation of all mercury species. Analysis for total Hg was performed with dual amalgamation cold vapor atomic fluorescence spectrometry (25) with a method detection limit (MDL) of 0.04 ng/L (26).

Quality control (QC) check samples were analyzed at the beginning of the run, at least every 10th sample, and at the end of the run to establish daily statistical control. QC checks were prepared with WDMRL deionized water and a known amount of Hg standard from a source other than that used for standardization. The QC standards measure any possible instrument drift and provide an external check on the accuracy of the calibration standards. Four jar blanks (process blanks) were run during the period of analysis. A jar blank consisted of brominated deionized water that was allowed to sit in a clean jar for the time it took for the ice to melt and then was transferred into a Teflon bottle and treated like a sample. Results from the jar blanks were used to determine the contribution of Hg from the oxidant BrCl and any Hg sources from the jars. The blanks ranged in concentration from 0.30 to 0.86 ng/L (mean = 0.66, std dev = 0.25, n = 4). After blank subtraction of the mean blank value, the lowest total Hg concentration from 97 samples was 1.21 ng/L, which is still significantly above the highest blank value. All samples were analyzed in duplicate. If the percent difference between the two duplicates was greater than 10%, the sample was analyzed a third time. In all cases, the relative standard deviation between the three replicates was less than 10%. On each work day, at least one sample was spiked and the percent recoveries ranged from 90 to 111 (mean = 99, std dev = 6, n = 15).

Results and Discussion

Ice Core Chronology. Accurate ice-core chronology is essential to paleoenvironmental interpretation. Unlike polar ice cores from Greenland and Antarctica, which are more likely to preserve visual stratigraphy in the form of annual summer dust layers (27, 28), annual dust layers in the UFG were not always visible, thereby making visual age-dating methods unreliable. Although long-term trends in the water isotopes appear to be preserved, there is no evidence that seasonal isotopic signatures have been preserved in the UFG ice (8, 9). Instead, the chronology of the UFG was determined using other isotopic and chemical age-dating techniques. The 1963 tritium (8) and 1958 chlorine-36 (10) peaks were found at depths of 28 and 32 m respectively. A carbon-14 value from a grasshopper leg found at 152 m yielded a most probable age of 221 ± 95 years (8). These dates, in combination with estimated snow accumulation and ablation measurements (9), established a low-resolution chronology for the UFG cores. Additional time markers of volcanic origin at 88 and 123 m were identified through electrical conductivity measurements (ECM), establishing a confident age−depth relationship and refining the ice-core chronology to prediction limits of ±10 years (90% confidence level) and confidence limits of 2−3 years (11). Although the resolution of the UFG ice cores is considered low by polar ice-core research standards, it provides a chronology of sufficient resolution over its 270-year record to support the conclusions made about historical changes in Hg deposition. Development of the UFG ice-core chronology is described in detail in other work (8, 9, 11, 29).

Hg Concentrations in the UFG. The remote location and high elevation of the UFG (Figure 1) most likely reduce the contributions from local anthropogenic influences of atmospheric Hg (Figure 2) (22). As such, Hg concentrations in ice cores from the UFG reflect regional and global atmospheric inputs. Although the range of Hg concentrations found in the UGF ice cores (Figure 3) were much greater than those found in Antarctic and Greenland ice, preindustrial or background concentrations not influenced by volcanic activity, however, were similar to those found in Antarctic ice and Greenland ice (5, 6), indicating that the large ranges of Hg concentrations found in the UFG are not an artifact of contamination but rather reflect natural and anthropogenic deposition of atmospheric Hg at this latitude. Total Hg measured in 97 ice-core samples spanning 160 m provided an average Hg profile resolution of 3 years. The detailed chronology of the UFG cores, coupled with analytical advances in measuring trace levels of Hg, together with a 3-year profile resolution, provide a clear and direct measure of historical natural and anthropogenic contributions to atmospheric Hg deposition. Furthermore, the continuity of the Hg profile from the 1991 core to the 1998 core indicates that Hg is preserved in the ice (Figure 3).

By integrating the peak areas identified as separate atmospheric sources of Hg, the relative contributions of these sources were quantified. Eighteen preindustrial (before 1840) measurements of Hg were used to extrapolate a background value (3 ng/L) through the ice-core record. Background concentrations contributed 42% of the total Hg in the ice core during its 270-year record.

Volcanic Sources of Hg. Volcanic eruptions are a known atmospheric Hg source (30, 31); however, their importance on a global scale has remained unresolved. Three distinct peaks in the ice-core Hg profile are coincident (within the chronology prediction limits of ±10 years) with increased chloride and sulfate concentrations and ECM (Figure 4) (11). ECM is a direct measurement of the acidity of the ice (32). Volcanic eruptions increase the acidity of precipitation, resulting in increased ECM of the ice. Strong ECM signals,
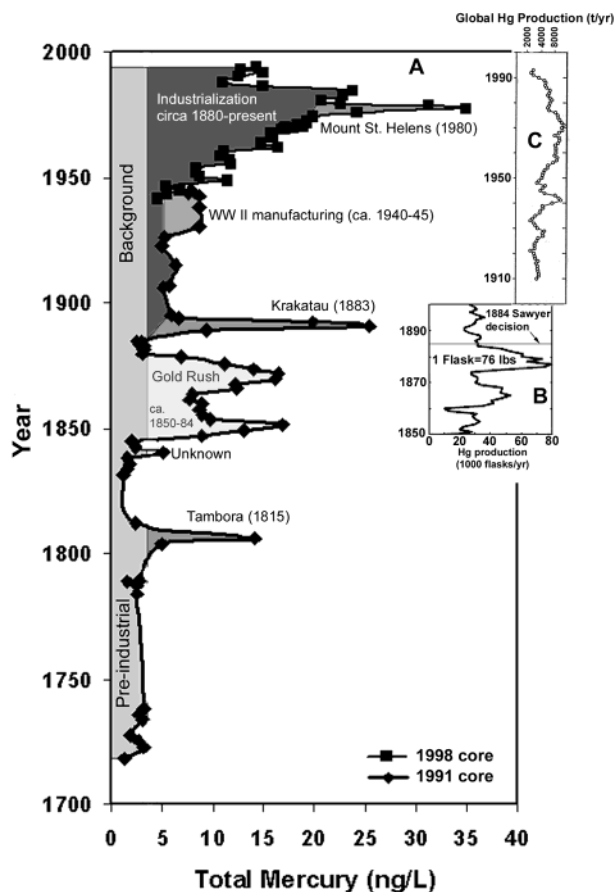
FIGURE 3. (A) Profile of historic concentrations of Hg in the Upper Fremont Glacier. A conservative concentration of 4 ng/L was estimated as preindustrial inputs and extrapolated to 1993 as a background concentration. Age−depth prediction limits are ±10 years (90% confidence level); confidence limits are 2−3 years (*11*). (Inset B) Hg production during the California Gold Rush (adapted from Figure 5 in ref *39*). (Inset C) World production of Hg in tons per year during the last century (adapted from Figure 4B in ref *43*).

along with increased chloride and sulfate concentrations in the ice-core profile suggest that the snow falling on the glacier surface at that time contained volcanic fallout.

The two largest eruptions in recorded history, Krakatau (1883 AD) and Tambora (1815 AD), albeit in the southern hemisphere 20 000 km from the UFG, reached well into the stratosphere with global effects. The ship, Medea, measured the Krakatau eruption column height to be up to 26 km (*33*). The Tambora event, perhaps the largest eruption in the last 10 000 years, injected volcanic material to a height estimated to be as high as 44 km into the stratosphere (*34*). Historical observations of remarkable sunsets in Europe, North America, and Hawaii and optical effects for up to 2 years after each eruption were another indication that the dust columns reached the stratosphere (*35*). Fallout from the Tambora and Krakatau events has been identified in Antarctic and Greenland ice cores (*36*, *37*). These natural geologic events were point sources in terms of Hg origin but were followed by global scale deposition. The Mount St. Helens eruption (1980), although orders of magnitude smaller in scale, was only 600-km distant and directly upwind of the UFG, blanketing the region with volcanic ash (*9*). The proximity of Mount St. Helens to the UFG qualifies the corresponding Hg peak as a regional Hg source. The peak's superposition on elevated concentrations due to near-peak anthropogenic Hg emissions resulted in the profile's highest measured Hg concentrations (Figure 3). Differences in Hg loads among the three volcanic peaks may have been due to differences in volcanic dust

compositions as indicated by differences in chloride, sulfate, and ECM peaks. Whether the volcanic source of Hg was regional, global, or altered by postdepositional processes, it is clear that these globally impacting natural events have "punctuated" the historical Hg record in the UFG and likely elsewhere.

Integrating the peak areas attributed to volcanic activity with global impact (Figure 3), these natural atmospheric Hg sources were quantified. During the past 270 years, three major volcanic events (Tambora, Krakatau, and Mount St. Helens) contributed 6% of the total Hg measured in the ice cores. It is likely, however, that 6% is an underestimate. There are three main possibilities for this underestimate. (1) There have been numerous smaller volcanic events (*38*) during the past 270 years. Some of these events undoubtedly had some global impact, but the volcanic signal was likely masked by the background or anthropogenic signal. (2) Only 6.7 m of a total length of 160 m of ice was sampled for Hg throughout the length of the core. The Hg signal from a volcanic source is of short duration (1−2 years). Thus, it is likely that some volcanic events were not sampled. (3) It is also possible that elution processes (described earlier) dampened the volcanic Hg signal of the three major volcanic eruptions identified in the UFG ice core.

Anthropogenic Sources of Hg. Mercury was used on a large scale to recover gold from mining operations throughout the western United States beginning around 1850. These activities peaked around 1860 and then again around 1877 (Figure 3, inset B) (*39*). The bimodal nature of these activities was reflected in the ice-core Hg profile, showing significant increases coincident with peak Hg production in California during this period. The age−depth prediction limit for the UFG ice cores is ±10 years, thus accounting for the slight offsets among Figure 3A and insets B and C. Mercury production decreased significantly in 1884 with the introduction of legislation (The Sawyer Decision) (*39*) that greatly reduced the use of Hg for gold extraction in California. A precipitous drop in UFG ice-core Hg concentrations coincided with this period.

Most sediment-core studies do not indicate an increase in Hg concentrations coincident with the start of the California Gold Rush. There are some studies, however, that do record a "jump" in the sediment Hg profile ca. 1850 (*40*, *41*). Nriagu (*42*) explains that most of the Hg would have blown west, describing this transport as a "grasshopper-like dispersal pattern". The mercury−gold amalgamation practices during the California gold rush during the mid-to-late 1800's were unregulated and unrivaled by any other mining activity up to that time (*39*). During this time, unknown amounts of Hg were volatilized to the atmosphere. The depositional pattern of atmospheric Hg from this source would be, in a large part, dependent on storm trajectories and jet stream patterns for which there is obviously no data for that period. On the basis of (1) today's general knowledge that it is not uncommon for storm trajectories and the jet stream to migrate north and south, (2) the UFG's proximity to the California mining belts, and (3) the magnitude of the estimates of Hg volatilized into the atmosphere for 30 years (ca. 1849−1884), it is suggested that the source of elevated Hg concentrations measured in the UFG ice core coincident with the same time period is Hg from California mining activities (Figure 3). If the source of these elevated Hg concentrations is from California gold-mining activities, as suggested by Figure 3, then the integration of the profile indicates that the mercury−gold amalgamation activities during the California Gold Rush contributed 13% of the total Hg in the 270-year ice-core record. These data suggest that
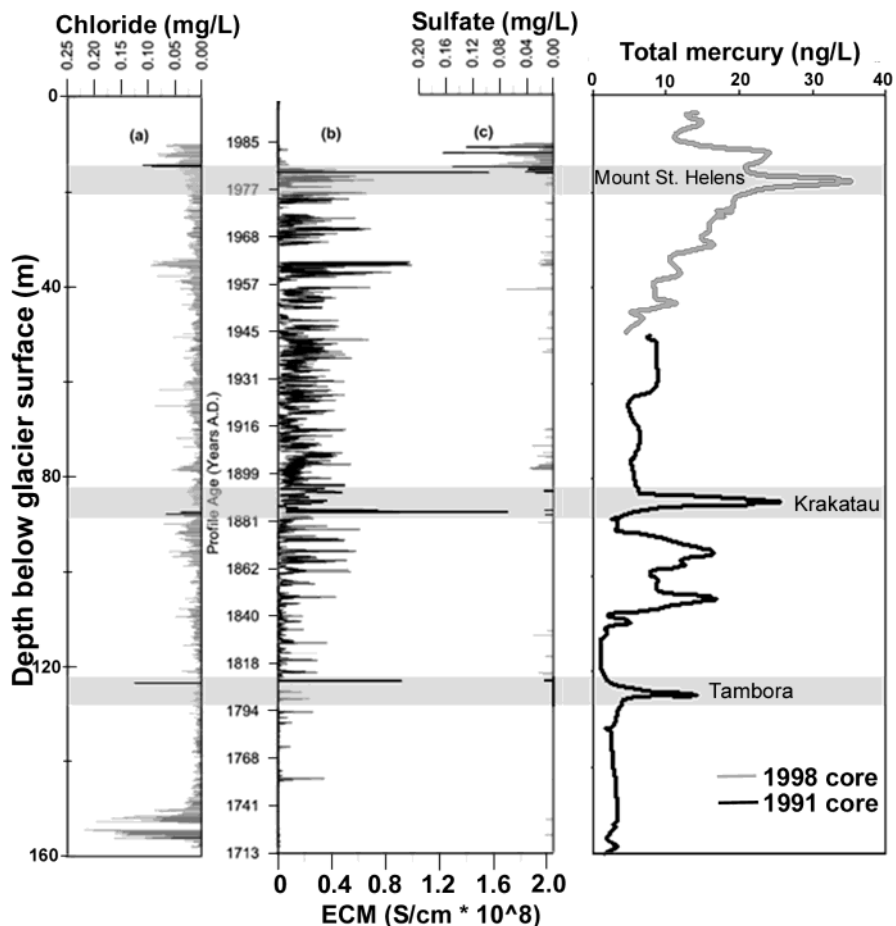
FIGURE 4. Profiles for Hg compared to chloride, sulfate, and electrical conductivity measurements (ECM). The *y* axis is scaled with the age–depth relation ship, thus giving the Hg profile a slightly different appearance from Figure 3. ECM is a measure of the acidity of the ice. A correlation among chloride, sulfate ECM, and Hg is a strong indication of a volcanic source. Age–depth prediction limits are ±10 years (90% confidence level); confidence limits are 2–3 years (*10*) (adapted from Figure 3 in ref *11*).

the California Gold Rush had a significant regional impact in terms of atmospheric Hg deposition in the western United States.

At the turn of the 20th century, atmospheric Hg levels remained elevated as compared to preindustrial (before ca. 1840 AD) or background values. Increases in anthropogenic Hg emissions during the past century have been attributed mainly to coal-burning power plants, waste incineration, and chlor-alkali plants (*3, 43, 44*). The next significant increase in ice-core Hg concentrations coincided (within the ±10 year prediction limits) with increased global Hg production (Figure 3, inset C), most likely in response to industrial mobilization for World War II. There was a post-WWII decline in global Hg production, once again coincident with decreases in ice-core Hg concentrations. The last half of the 20th century up until 1990 shows a consistent increase in both global Hg production and Hg concentrations in the UFG ice cores.

Volcanic eruptions contributed to the global Hg pool for brief periods (<2 years) and, thus, cannot account for the substantial increase in ice-core Hg concentrations during the last century. The volcanic inputs, albeit competitive with industrial inputs, were short in comparison to the chronic levels of elevated Hg concentrations during the last 100 years, indicating that anthropogenic inputs have had the greatest influence on the atmospheric Hg deposition record in the UFG. During the past 270 years, anthropogenic inputs contributed 52% of the Hg accumulation in the core. More significantly, during the last 100 years, anthropogenic sources contributed 70% of the total Hg input. A post-1990 decline in the ice-core Hg concentrations is discussed next.

Hg Deposition Rates to the UFG. Historical Hg deposition rates were calculated from Hg concentrations measured in the ice cores (Table 1). The calculated rates of deposition assume an average accumulation rate of 1 m of ice equivalent to the UFG per year. Obviously, this rate varies from year to year. However, on the basis of average measurements of accumulation and ablation rates (*8, 9*) this estimate is not unreasonable. Moreover, up to 50% of seasonal snowfall accumulation is lost through ablation (*9*). This process, although difficult to quantify, would, most likely, lead to an underestimate of Hg deposition calculated from concentrations in the ice core.

There is a down-core change in the age–depth relationship due mostly to glacial flow processes leading to layer thinning with depth. Basically, the same 7-cm section of ice-core sample represents more time with depth. Considering the calculation of Hg deposition rates and utilizing the age–depth relationship (*11*), a ratio (change in age/change in depth) was calculated and applied to Hg deposition results to develop corrected Hg deposition rates using eq 1

$$(A_i - A_{i-1})/(D_i - D_{i-1}) \qquad (1)$$

where A is the calculated age (years) (*10*), D is the ice-core depth (meters), and i denotes the sequential Hg sample (1–97). At the base of the core (the 97th Hg sample), the ratio is 2.88. Thus, at this depth, 1 m of ice represents approximately 2.88 years. Equation 1 was applied to Hg deposition rates as a correction factor to compensate for down-core changes of

TABLE 1. Mercury (Hg) Deposition Measured among Three Sample Media

site	sample media	episode (reference)	year(s) (AD)	average [Hg] (ng/L)	deposition[a] (μg/m^2/year)	change from preindustrial (fold)
UFG	ice	Clean Air Act	1986–1993	9	11.4	11
UFG	ice	industrial max	1984	20	20.3	20
UFG	ice	Mt. St. Helens	1980	11[b]	12.7§	12
UFG	ice	industrial	1900–1993	10	11.0	11
UFG	ice	WWII	1938–1946	7	4.73	5
UFG	ice	Krakatau	1883	21[c]	18.2§	18
UFG	ice	Gold Rush	1850–1878	8	4.84	5
UFG	ice	Tambora	1815	10[c]	8.60§	8
UFG	ice	preindustrial	1719–1847	3	0.78	na[d]
Minnesota	wet ppt[e]	(49)	1997–1999	14	6.99	7
Colorado	wet ppt	(49)	1999	10	9.20	9
			<1880	na	80.0	na
Minnesota	lake sed**	(48)	>1880	na	170	2[#]
			<1850	na	3.70	na
Minnesota	lake sed	(45)	modern	na	12.5	3
			<1750	na	2.00	na
Arctic	lake sed	(47)	1980	na	12.5	6
			<1850	na	5.00	na
New York	lake sed	(46)	modern	na	8.90	2
			<1850	na	7.60	na
California	lake sed	(40)	>1980	na	38.0	5

[a] Deposition calculated using age–depth correction factor. [b] Preindustrial and industrial inputs subtracted to isolate volcanic signal; maximum input reported. [c] Preindustrial input subtracted to isolate volcanic signal; maximum input reported. [d] Not applicable or not available. [e] Wet precipitation. § Age–depth correction factor not used to calculate deposition rate. ** Sediment. [#] Change measured from "preindustrial" dated cores from cited study.

the age–depth relationship (due to thinning) on each 7-cm sample.

The ratio attained one at about 35 m. It is assumed there is no change in the age–depth relationship (due to thinning) from 35 m to the top of the core (1 m of ice ∼ 1 year). The residence time of Hg(0) in the atmosphere is on the order of a year (1). Thus, deposition from volcanic sources represents, at most, a 1-year period. Therefore, volcanic deposition values were calculated and reported without age–depth correction factors. Also, preindustrial (background) and industrial inputs were subtracted from the calculated volcanic deposition to isolate the volcanic signal. Using maximum input from each volcanic event and the conditions described previously, deposition rates from the volcanic events identified here indicate an 8–18-fold increase in Hg deposition over background due to globally impacting volcanic activity.

Again, assuming an accumulation rate of 1 m of ice/year (9) at the top of the ice core and accounting for changes in the age–depth relation down-core (11), there was a 20-fold increase from preindustrial times to an "industrial maximum" ca. 1984. During the last century, the average increase due to industrialization was 11-fold. Analysis of sediment cores from lakes (40, 45–48) and precipitation (49) also indicate increases in atmospheric Hg deposition (2–9-fold) since the 1700s. The increase in Hg deposition rates from preindustrial times to the mid-1980s, as indicated by the ice cores, are up to 10 times higher than increases determined from sediment cores and precipitation. Recent work indicates that ice-core response to changes in global atmospheric cycling masses and deposition may be amplified for snow (50). Although the mechanisms are unclear, the work concluded there is a positive relationship of altitude to Hg loading in snow. A more recent study, however, indicates that Hg in snow packs is susceptible to reemission due to photochemical redox reactions, resulting in reductions of Hg levels by 54% within 24 h after deposition (51). If this process does occur at the UFG, the estimated Hg deposition rates calculated from the UGF ice cores could be underestimated by as much as one-half. On the other hand, recent work has also shown that mercury deposition may be affected by altitude, resulting in

increases in atmospheric Hg deposition. Work in the Wasatch and Teton ranges near the UFG indicate that annual Hg accumulation rates increase from 100% to 175%, with an elevation gain of 1000 m (50). In addition, recent work on Denali (Mt. McKinley) in Alaska (Krabbenhoft, to be submitted for publication) showed a 30–75-fold increase in Hg concentrations in the surface snow with an elevation gain of about 5500 m; the ice-core site on the UFG is at an elevation of 4100 m (Figure 1). It appears that the altitude effect is much larger than the reemission processes indicated by LaLonde (51). This may by why there are measurable and distinct volcanic and anthropogenic Hg signals in the UFG ice cores and why this profile differs greatly from those found in sediment cores. The nearly 50% decline in mercury accumulation at the top of the ice core compares very favorably in magnitude with independent estimates of recent global declines of mercury production and use (43, 52). Lake sediments, on the other hand, retain only a small fraction of the total Hg deposition, and the remainder is generally recycled back to the lake (53). Moreover, uncertainties such as sediment focusing associated with using sediment cores to estimate accumulation rates prevent simple comparisons of the two methods.

Estimation of "Global Impact" Volcanic Hg Deposition. An estimated 21 km^3 of volcanic material was ejected during the 1883 Krakatau eruption (54). The 1815 Tambora event produced a bulk volume of approximately 150 km^3 of pumice and ash (55). Assuming that the ejecta and gases reached the stratosphere and were distributed evenly over the earth's hemisphere (56), an estimation of the atmospheric deposition attributed to these globally impacting volcanic events was calculated by eq 2

$$Hg_{vol}(\mu g/m^2) = [V_{eje}(cm^3)\rho_{plu}(g/cm^3)1/\rho_{str}(g/m^3)Hg_{plu}(\mu g/m^3)]/A_{hem}(m^2) \quad (2)$$

where Hg_{vol} is the atmospheric deposition from a globally impacting volcanic eruption, V_{eje} is the volume of volcanic ejecta, ρ_{plu} is the density of the volcanic plume, ρ_{str} is the

density of air at 5000-m elevation (pressure ~ 0.4 atm, and average air temperature in the volcanic plume is $\sim -20\ ^\circ$C (57)), Hg_{plu} is the concentration of Hg in the plume, and A_{hem} is the area of the earth's hemisphere.

On the basis of previous work (58−62), the concentration of Hg in an atmospheric volcanic plume or volcanic fumarolic gases can range from 1 to >7000 $\mu g/m^3$. For the sake of argument, a conservative value of 48 $\mu g/m^3$ (61) and a fine ash density of 1 g/cm^3 (56) were used in eq 2. Assuming conditions at 5000-m elevation (the approximate lower limit of the stratosphere), the estimated Hg deposition for the Tambora eruption is 25.6 $\mu g/m^2$; approximately 3 times the estimated Hg deposition calculated from Hg concentrations in the ice core (8.6 $\mu g/m^2$). In eq 2, if the atmospheric deposition (Hg_{vol}) is set equal to the estimated value from the ice core and the equation solved for the concentration of Hg in the volcanic plume (Hg_{plu}), a value of 16 $\mu g/m^3$ is calculated. When the same assumptions are applied to the Krakatau eruption, atmospheric Hg deposition is estimated to be 3.6 $\mu g/m^2$, almost 5 times less than the deposition calculated from ice-core Hg concentrations (18.2 $\mu g/m^2$). Again, setting atmospheric deposition equal to the Hg deposition estimated from the ice core in the equation and solving for the concentration of Hg in the volcanic plume (Hg_{plu}), a value of 244 $\mu g/m^3$ is calculated. On the basis of a limited number of studies measuring Hg concentrations in volcanic plumes, the volcanic plume estimate for the Krakatau eruption is comparatively high. The measurements made in previous studies (58−62), however, suggest that large ranges of Hg concentrations in volcanic ash plumes are possible. This estimation, although basic and oversimplified, demonstrates that the Hg deposition calculated from concentrations in the ice core attributed to the globally impacting volcanic eruptions of Tambora and Krakatau are not unreasonable. While individual volcanic events lead to short-term deposition rates similar to the industrial maximum (Table 1), the brief duration of the events limits their importance in overall deposition.

Recent Declines in Atmospheric Hg Deposition. Since the industrial maximum (ca. 1984), Hg concentrations in the UFG ice core have declined from the 20-fold increase since preindustrial times to an 11-fold increase during the 1990s. This decline is corroborated by recent declining trends observed in dated sediment cores (41, 43, 63) and precipitation (50). The declining trends recorded during the last 10 years are consistent with the last 7 years of precipitation data (22). The top 10 m of the ice core have a calculated average deposition rate of about 1 $\mu g/m^2$. Figure 2 shows the UGF region receiving 1−3 $\mu g/m^2$. The recent declines may be in response to emission controls implemented through the United States Clean Air Act of 1970 and the Clean Air Amendment of 1990 requiring pollutant scrubbers that also likely remove a fraction of the Hg in flue gases. If so, the results presented here suggest that further reductions are achievable.

Acknowledgments

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