Article

An ice core perspective on mercury pollution during the past 600 years

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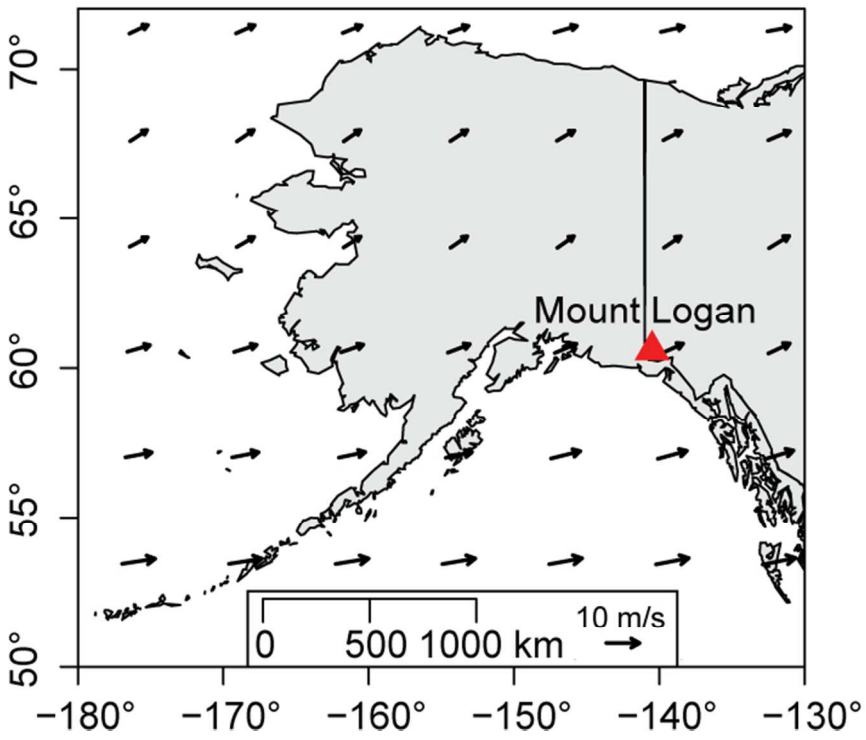

Location of Mount Logan (red triangle) in the St. Elias Mountains on the border of Alaska and Yukon, Canada. Arrows represent annual average vector wind at 500 mb from AD 1948–1998.[42]
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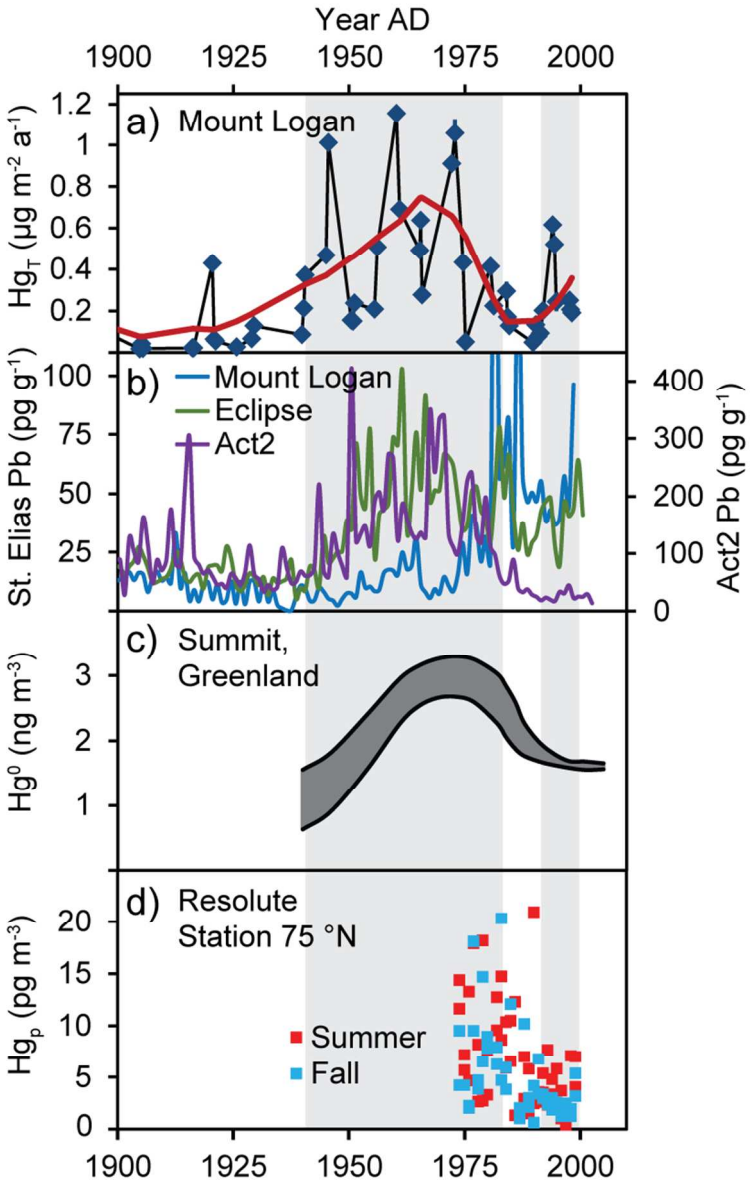

20th Century trends in atmospheric Hg deposition at Mount Logan compared with ice core records of Pb pollution and the longest available measurements of remote atmospheric Hg concentrations. a) Mount Logan HgT fluxes (blue points) with 1σ error bars and LOESS smoother (red line). Grey shading denotes two periods of elevated HgT fluxes. b) Annually averaged Pb concentrations in the Mount Logan ice core[18] and the Eclipse Icefield ice core[28], both in the St. Elias Mountains, and in the Act2 ice core in southern Greenland[29]. c) Modeled firn-air Hg0 concentrations in a core from Summit in central Greenland modified from Faïn et al.[30] d) Total filterable (particulate) Hg concentrations in air samples from Resolute in Arctic Canada modified from Li et al.[31]
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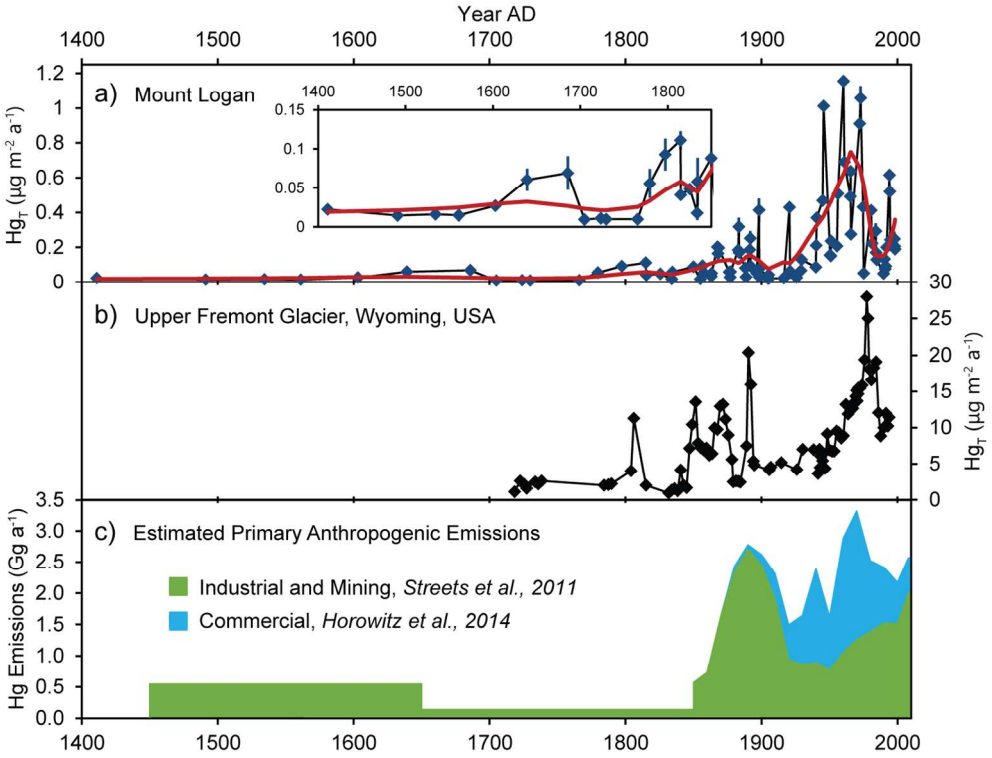

Multi-century HgT records from ice cores compared with estimates of primary anthropogenic emissions used in recent global Hg models. a) Mount Logan HgT fluxes (blue points) with 1σ error bars, LOESS smoother (red line), and inset with adjusted y-axis for the Preindustrial Period. b) HgT fluxes in the Upper Fremont Glacier ice core calculated using an assumed constant accumulation rate of 800 kg m-2 a-1 modified from Schuster et al.[14] c) Estimated primary anthropogenic Hg emissions from industrial and mining sources modified from Streets et al.,[7] and additional emissions from commercial Hg use modified from Horowitz et al.[8]

136x103mm (300 x 300 DPI)

An ice core perspective on mercury pollution during the past 600 years

Environmental Science and Technology

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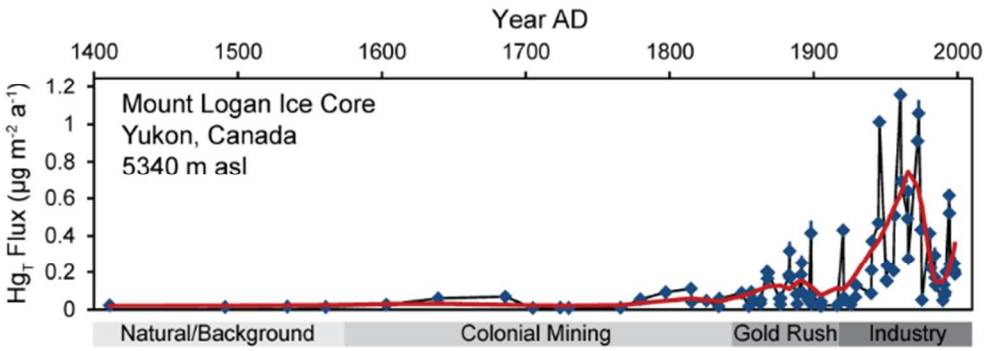

Abstract (150-200 words)

Past emissions of the toxic metal mercury (Hg) persist in the global environment, yet these emissions remain poorly constrained by existing data. Ice cores are high-resolution archives of atmospheric deposition that may provide crucial insight into past atmospheric Hg levels during recent and historical time. Here we present a record of total Hg (Hg_T) in an ice core from the pristine summit plateau (5340 m asl) of Mount Logan, Yukon, Canada, representing atmospheric deposition from AD 1410 to 1998. The Colonial Period (~1603–1850) and North American "Gold Rush" (1850–1900) represent minor fractions (8% and 14%, respectively) of total anthropogenic Hg deposition in the record, with the majority (78%) occurring during the 20th Century. A period of maximum Hg_T fluxes from 1940 to 1975 coincides with estimates of enhanced anthropogenic Hg emissions from commercial sources, as well as with industrial emissions of other toxic metals. Rapid declines in Hg_T fluxes following peaks during the "Gold Rush" and the mid-20th Century indicate that atmospheric Hg deposition responds quickly to reductions in emissions. Increasing Hg_T fluxes from 1993 until the youngest samples in 1998 may reflect the resurgence of Hg emissions from unregulated coal burning and small-scale gold mining.

1. Introduction

Atmospheric deposition of the globally distributed and toxic metal mercury (Hg) contaminates ecosystems throughout the world.[1] Hg is introduced to the environment by *primary* emissions from anthropogenic sources (e.g., coal burning, Hg mining, and silver and gold mining) and natural sources (e.g., volcanism and weathering). Primary emissions occur predominantly as gaseous Hg^0, with lesser quantities of reactive Hg^{2+} species that are either

gaseous or bound to particulates (Hg_p).[2] With a residence time in the atmosphere of ~1 year, Hg^0 can be transported globally before oxidation to Hg^{2+} causes deposition to the land/ocean surface in precipitation (wet deposition) or by particle settling (dry deposition).[3] Deposited Hg can be reemitted to the atmosphere through *secondary* emissions (e.g., ocean-air exchange and biomass burning), which actively cycles Hg between the ocean, land, and atmosphere.[4,5]

Recent works provide disparate accounts of past primary anthropogenic Hg emissions, which are thought to have occurred since at least AD 1570.[6] Framing this disparity are emissions estimates, based on historical records of metal production and industrial/commercial activity, and sediment records from remote lakes with small undisturbed watersheds. Emissions estimates indicate that mining during the Preindustrial Period (pre-AD 1850) and the North American "Gold Rush" (AD 1850–1920) represent ~30% and ~27%, respectively, of total primary anthropogenic Hg emissions, and that emission rates peaked in the 1970s.[7,8] Conversely, sediment records from remote lakes generally support background rates of atmospheric Hg deposition (~1 $\mu g\ m^{-2}\ a^{-1}$) until ~AD 1850 and a subsequent continuous increase to the present-day.[9] Uncertainties in past emissions propagate to global model determinations of anthropogenic Hg in the modern environment and predictions of the environmental response to future emissions scenarios.

Ice cores are archives of atmospheric Hg deposition over seasonal to millennial timescales, preserving a purely atmospheric signal with high temporal resolution and excellent chronological control through annual layer counting and distinct event stratigraphy. Although an unknown fraction of deposited Hg is reemitted to the atmosphere by photoreduction within the upper 3 to 60 cm of snowpack,[10] the remaining Hg that is preserved in glacial ice may reveal important information on past changes in atmospheric Hg deposition. Records of total Hg (Hg_T)

46 from ice cores have been developed since the 1970s, but work in the 1990s by Boutron et al.
47 using clean methods for sample handling in the field and laboratory demonstrated that many of
48 these earlier records were contaminated by orders of magnitude.[11] Clean sampling of remote
49 glacial snow and ice typically reveals Hg_T concentrations from <0.02 to ~4 pg g^{-1}.[11–13] To date,
50 the only published ice core Hg_T record covering the entire industrial period is from Upper
51 Fremont Glacier in Wyoming, United States.[14] This record has been used extensively in literature
52 on the global Hg cycle,[15] and it contains several unique characteristics including a prominent
53 "Gold Rush" peak, short-lived (2 to 3-year) peaks associated with explosive volcanic events in
54 both the Northern and Southern Hemisphere, and an abrupt decline in Hg_T concentrations in the
55 1980s.[14] However, the unique characteristics of the record, relatively high Hg_T concentrations
56 (1.2–35 pg g^{-1}), and the glacier's proximity to upwind historical mining and industrial Hg
57 sources have led to uncertainty about the record's representativeness of global trends in
58 atmospheric Hg.[9,15] New ice core Hg_T records from remote glaciers could provide useful
59 additional constraints on past global Hg emissions.
60 Here we present a record of Hg_T from AD 1410 to 1998 in an ice core from Mount
61 Logan, Yukon, Canada. The Mount Logan ice core, collected from the mountain's summit
62 plateau (5340 m asl), preserves deposition from the free troposphere sourced by winds traversing
63 the North Pacific Ocean (Figure 1).[16,17] The core's location, tightly constrained chronology, and
64 high-resolution co-registered geochemistry[18] allow us to interpret the Mount Logan Hg_T record
65 and assess its relevance to past global Hg emissions.

2. Materials and Methods

2.1. Core Collection

The Mount Logan ice core was collected from Prospector-Russell Col on the summit plateau (5340 m asl) of Mount Logan in the summers of 2001 and 2002 by the Geological Survey of Canada. The coring site is near the center of dividing glacier flow with low ice velocities (<0.2 m a^{-1}), and the site has persistent below-freezing temperatures based on automatic weather station data (mean annual: -29°C) and the lack of refrozen surface melt layers in the core.[19,20] The core was collected from a dry borehole using an electromechanical drill from 2 m depth until bedrock at 186 m depth. We focus on the depth range of 3 to 128 m that represents net snow accumulation between AD 1410 and 1998. Previous work established the depth-age model for this ice core based on annual layer counting of seasonal oscillations in $\delta^{18}O$ and Na and U concentrations between 1700 and 1998 (3–109 m depth) and an ice flow model constrained by well-dated volcanic signals between 1410 and 1700 (109–128 m depth).[18,21,22]

2.2. Core Decontamination

We sampled discrete sections of the ice core, with each section comprising at least one complete year of accumulation. Within the upper 100 m of the ice core, which included firn (3–45 m depth) and ice (45–100 m depth), the volume of material for each section required division into multiple samples that we plot individually. We melted firn and ice samples in 500-ml glass jars with PTFE septa and polypropylene caps which we pre-cleaned following Method B in Hammerschmidt et al.[23] Briefly, this cleaning method involved successive storage in a Citranox and >18.2 MΩ deionized (DI) water solution for 6 days, in 10% Trace-Metal Grade HCl for 6 days, and in 1% BrCl (made from reagent grade KBr, $KBrO_3$, and Optima HCl) for 1 day. All sample work was conducted in a HEPA-filtered laminar flow bench with a double layer of

activated carbon cloth covering the filter air intake. We cut firn and ice pieces that were longer than 10 cm with a stainless steel saw to accommodate the height of the glass jars. For firn samples (3–45 m), we manually removed the outer surfaces of each sample using ZrO ceramic knives (pre-cleaned with 10% HCl) in a -10 °C freezer before transferring the decontaminated firn to the pre-cleaned glass jars. For ice samples (45–128 m), we removed potentially contaminated outer ice surfaces by partially melting each sample for 1.5 hours at room temperature in Whirlpak bags before rinsing with DI water and transferring to the pre-cleaned glass jars. We tested contamination of outer ice core surfaces by partially melting selected ice samples in pre-cleaned glass jars instead of Whirlpak bags, and then treating the cleanly collected meltwater from the outer core surfaces as samples. We made procedural blanks by freezing low-Hg (<0.02 pg g^{-1}) DI water in pre-cleaned glass jars and processed them following the decontamination methods for either firn or ice. Before melting, we added concentrated BrCl to each sample or procedural blank to a final concentration of 0.1% BrCl.[24]

2.3. Hg_T Analysis

Within 72 hours of melting, we measured Hg_T in ~24 ml sample aliquots using Purge and Trap with Cold Vapor Atomic Fluorescence Spectrometry (Brooks Rand Automated Total Mercury Analyzer) following EPA Method 1631E. Hg_T refers to all BrCl-oxidizable forms of Hg present, including Hg^{2+}, Hg^0, organic Hg, and Hg adsorbed to particulates.[24] The instrumental detection limit was 0.02 pg g^{-1}, but the method detection limit (MDL; determined here as 3σ of the procedural blanks) ranged from 0.01 to 0.24 pg g^{-1} (median 0.06) depending on the method and day of sampling. Sample concentrations were considered detectable if their procedural blank subtracted concentrations exceeded the MDL.

2.4. Flux Calculations

We determine Hg_T fluxes as the product of measured Hg_T concentrations and water equivalent accumulation rates (ARs). In the Mount Logan ice core, ARs are calculated within the sub-annually resolved portion of the core (1700–1998) from measurements of density (kg m^{-3}) and annual layer thickness (m a^{-1}), and ARs are estimated within the annually resolved portion of the core (1410–1700) as the average of measured ARs from the sub-annually resolved portion (420 ± 90 kg m^{-2} a^{-1}) because annual layer thickness is not accurately determined at these depths.[18]

3. Results and Discussion

Of the 130 samples that we melted, 88 samples had detectable Hg_T concentrations (Table 1 and Figure S1). Table 1 shows the occasionally high and variable procedural blank values that limited detection of Hg_T in the remaining samples. We suspect that day-to-day changes in air quality within the HEPA-filtered laminar flow benches are responsible for this variability, highlighting the need for the many procedural blanks used in this study. Among the samples with detectable Hg_T concentrations, preservation of a signal from atmospheric Hg deposition is supported by similar Hg_T concentrations found in snow/ice from other remote glaciers[11–13] and by the order of magnitude concentration difference between the samples and the core exterior removed during decontamination (Table 1).

In the most recent samples from 1994 to 1998, Hg_T fluxes (0.19–0.52 μg m^{-2} a^{-1}) are an order of magnitude lower than recent measurements of wet deposition across the western United States (~1–9 μg m^{-2} a^{-1}) and in sub-Arctic Alaska and Canada (~1–5 μg m^{-2} a^{-1}).[25,26] This difference could be attributed to the relative inefficiency of gaseous Hg^{2+} scavenging by snow,[27] which is the only phase of precipitation at Mount Logan, and to the reemission of a fraction of

134 deposited Hg from the snowpack. Repeated sampling of surface snows generally indicate that
135 >50% of Hg is reemitted within 24 hours, although there is great variability both within
136 individual study sites and between geographic areas.[10] Nevertheless, we propose that multi-
137 annual variations in the Mount Logan Hg_T flux record reflect past changes in mid-tropospheric
138 atmospheric Hg^{2+} deposition based on several lines of evidence. First, the estimated Hg^0 content
139 in firn/ice air can account for only 0.2 to 7% of the measured Hg_T concentrations (see Supporting
140 Information). Hg_T concentrations are only weakly correlated with co-registered lithogenic
141 element and Pb concentrations ($r = 0.23–0.35$, $p < 0.05$), which are proxies for Hg_p from crustal
142 and industrial sources, respectively (Table S1). Hg_T concentrations are neither correlated with
143 co-registered chloride concentrations, nor with ARs (Table S1), both of which are thought to
144 affect Hg reemission from the snowpack.[10,28] Finally, the Mount Logan Hg_T flux record shows
145 striking similarities with two of the longest published records of remote atmospheric Hg levels
146 (Figure 2) and with historical changes in Hg use, which we discuss below. On shorter (sub-
147 annual to annual) timescales, the relatively high variability, or spikiness, of the Mount Logan
148 Hg_T flux record is likely the result of factors influencing Hg reemission from the snowpack.
149 Accordingly, we use a LOESS smoothed line to filter out this short-term variability and highlight
150 longer-term variations in the Mount Logan Hg_T flux record.

151 **3.1. The 20th Century**

152 Figure 2 shows the Mount Logan Hg_T record during the 20th Century, revealing near-
153 background Hg_T fluxes (0.02–0.06 μg m^{-2} a^{-1}) from 1900 to 1940, a broad peak between ~1940
154 and 1975 (maximum of 1.2 μg m^{-2} a^{-1} in 1960), decreasing fluxes during the 1980s, and a final
155 rise through the 1990s. Comparison with high resolution Pb records from the Mount Logan ice
156 core and other high northern latitude glaciers provide information on both the source and

speciation of Hg_T in the Mount Logan ice core. The mid-century peak in Mount Logan Hg_T fluxes is coincident with a period of maximum Pb deposition registered in ice cores from Greenland and from Eclipse Icefield (located ~50 km northwest of Mount Logan at 3017 m asl), attributed to industrial (e.g., coal burning) aerosol emissions from North America and Europe that increased from World War II until the enactment of environmental regulations in the 1970s (Figure 2b).[29,30] However, North American and European Pb aerosols did not reach the Mount Logan summit plateau during this time (Figure 2b) because of the relatively short (7-10 days) atmospheric residence time of Pb,[31] and the persistent air mass source from the west (North Pacific and Asia) due to the site's elevation in the free troposphere.[18] Different emissions sources for 20th Century Pb and Hg deposited on Mount Logan is also supported by the lack of correlation between the two co-registered records (Table S1). Rather, the mid-century peak in Mount Logan Hg_T fluxes mirrors a record of atmospheric Hg^0 concentrations from firn-air at Summit Greenland (Figure 2c). Altogether, these comparisons suggest a coherent change in high northern latitude atmospheric Hg levels during the 20th Century associated with industrial emissions from North America and Europe.

Subsequent to the mid-century peak, Hg_T fluxes decline during the 1980s and approach near-background fluxes (0.05–0.13 $\mu g\ m^{-2}\ a^{-1}$) between 1989 and 1991. Decreases during this time are similarly observed in the firn-air Hg^0 record from Summit Greenland[32] and in air measurements of Hg_p at Resolute Bay in the Canadian High Arctic (Figure 2d).[33] A record-maximum peak in Mount Logan Pb concentrations between 1980 and 1989, likely resulting from the transport and deposition of industrial aerosols from Asia,[18] is coincident with this period of depressed Mount Logan Hg_T fluxes and therefore indicative of negligible Hg_p contributions from Asia during this time. We sampled the Mount Logan ice core at continuous 0.5-year resolution

between late 1989 and late 1991 to examine a possible Hg_T pulse from the April 2, 1991 eruption of Mount Pinatubo that sent volcanic ash and sulfur-containing aerosols into the stratosphere.[34] Such a pulse is not evident in either the Mount Logan or the Upper Fremont Glacier records during the timing of this eruption.[14] A number of other major volcanic eruptions, including ones in the Southern Hemisphere, are identified as significant Hg_T spikes, in the Upper Fremont Glacier record,[14] but material from the Mount Logan ice core covering these events has been entirely consumed for other studies.

Increasing Mount Logan Hg_T fluxes from 1993 until 1998 (the age of the youngest samples) coincide with estimated increasing emissions of Hg^0, Hg_p, and Pb from coal combustion in Asia.[7,35] The trans-Pacific transport and deposition of industrial aerosols from Asia are thought to be responsible for increasing Pb concentrations in the Mount Logan ice core during the 1990s (Figure 2b).[18] We therefore infer that the increase in Hg_T fluxes between 1993 and 1998 is due, at least in part, to deposition of Hg_p associated with Asian industrial emissions.

3.2. The "Gold Rush" (AD 1850–1900)

Figure 3 displays the entire 600-year Mount Logan record, which shows, in addition to the mid-20th Century peak, a smaller irregular peak in Hg_T fluxes that begins in the 1860s, reaches a maximum of 0.32 μg m^{-2} a^{-1} in ~1883, and remains elevated until a return to background at the turn of the century. This 19th Century peak is largely synchronous with an estimated peak in primary Hg emissions from silver and gold mining in North America, and associated Hg production (mainly in Spain, Slovenia, and Italy), during the "Gold Rush" between 1860 and 1920 (Figure 3c).[7] The Upper Fremont Glacier Hg_T record (Figure 3b) also shows a "Gold Rush" peak, which the authors suggest is caused by the regional transport and deposition of Hg from gold mining in upwind California.[14] The synchronous response of the

Mount Logan Hg_T flux record to estimated global Hg emissions during the "Gold Rush", and the lack of major upwind Hg point sources during the time, support a distinct anthropogenic change in high northern latitude Hg levels caused by the "Gold Rush". However, the Mount Logan and Upper Fremont Glacier "Gold Rush" Hg_T peaks are both substantially smaller than their respective 20th Century peaks, whereas emissions estimates indicate that the "Gold Rush" included an extended period of some of the highest primary anthropogenic Hg emissions of the past 400 years (Figure 3).[7,8] Lower-than-estimated anthropogenic Hg emissions during the "Gold Rush" may explain the lack of such a signal in many lake sediment records.[9]

3.3. The Preindustrial Period (AD 1410–1850)

The inset of Figure 3a shows stable background Mount Logan Hg_T fluxes (0.015–0.023 $\mu g\ m^{-2}\ a^{-1}$) from ~1410 to ~1561, followed by a period of increased low-level variability in Hg_T fluxes lasting until ~1850, when the impact of industrial emissions becomes clearly apparent. The introduction in 1570 of liquid Hg^0 for silver mining in Colonial Spanish South America likely marked the first global distribution of anthropogenic Hg,[6,36,37] so we interpret the Mount Logan Hg_T fluxes prior to 1570 as representative of natural deposition and subsequent variations from this background as due to anthropogenic Hg emissions. The background pre-Colonial Hg_T fluxes are in good agreement with a few measurements of Hg_T (0.009 $\mu g\ m^{-2}\ a^{-1}$) during the early and middle Holocene in an ice core from Dome C, Antarctica.[38] The low-level increases in Mount Logan Hg_T fluxes between ~1600 and 1850 suggest that Hg emissions from Colonial silver mining were globally transported, however Hg_T fluxes during this time are at least an order of magnitude lower than Hg_T fluxes during both the "Gold Rush" and the late 20th Century.

3.4. Potential Global Hg Cycle Implications

Integrating the smoothed Mount Logan Hg_T flux record (Figure 3a) after subtracting average background (1410–1561) fluxes yields ~78% of anthropogenic Hg deposition registered by the ice core occurring during the 20th Century, ~14% during the "Gold Rush" (1850–1900), and ~8% during the Colonial Period (~1603–1850). This 20th Century dominance in the Mount Logan record differs significantly from estimates of primary anthropogenic Hg emissions from industrial, mining, and commercial sources, which combined show that the "Gold Rush" and Preindustrial Period contributed ~27% and ~30% of total anthropogenic emissions, respectively.[7,8] Hg releases to water and soil may emit additional anthropogenic Hg to the atmosphere, but estimates of these releases generally scale with total (commercial, industrial, and mining) primary emissions since 1850.[8] The potential for secondary emissions from the oceans and land to influence deposition across the time periods discussed here make this a first-order comparison. However, the relatively small anthropogenic Hg deposition registered by the Mount Logan ice core before 1900 suggests that current estimates of Hg emissions from Colonial and "Gold Rush" mining are erroneously high. In turn, global Hg models forced with these high emissions likely overestimate the influence of early mining on anthropogenic Hg in the modern global environment.

Rapid declines in the Hg_T flux records from both Mount Logan and Upper Fremont Glacier coincide with estimated decreases in primary anthropogenic emissions from mining following the "Gold Rush"[7] and from commercial sources in the 1970s[8] (Figure 3). However, global Hg models forced with these emissions estimates show relatively minor decreases in atmospheric Hg following the "Gold Rush" and the 1970s, which are the result of high emission forcings from early mining and secondary emissions that are estimated as approximately

247 equivalent to primary emissions during the present-day.[4,5,8,39] Similar to the ice core Hg_T records,
248 the Summit Greenland firn-air Hg^0 record (Figure 2c) exhibits a rapid decrease following the
249 1970s, but the extent of its recovery is difficult to assess because of the record's brevity and the
250 potential for smoothing by diffusion of gaseous Hg^0.[32] The rapid decreases in atmospheric Hg
251 deposition implied by the Mount Logan and Upper Fremont Glacier records may not be easily
252 detectable in lake sediment records due to lagged declines in watershed inputs.[40] However,
253 decreases following both the "Gold Rush" and the 1970s are apparent in Hg flux records from
254 two remote lakes with exceptional characteristics: the crater lake Challa in eastern equatorial
255 Africa (900 m asl) that has almost no surficial watershed,[9] and the tarn Yanacocha in southern
256 Peru (4900 m asl) that has a small, poorly vegetated watershed composed predominantly of
257 exposed bedrock.[41] Further research is needed to constrain net exchanges between the land,
258 oceans, and atmosphere that cause anthropogenic Hg to persist in the environment.

259 Rising Hg_T fluxes during the most recent part of the Mount Logan record, from 1993 to
260 1998, may reflect a new period of increasing primary Hg emissions, driven by coal burning in
261 Asia and small-scale gold mining in developing countries around the world, that is estimated to
262 have continued at least through 2008.[2,7] Remarkably, however, the majority of atmospheric
263 measurements, primarily from the Atlantic near sea level, reveal declining Hg^0 concentrations
264 from ~2000 to 2009.[42,43] New high-resolution records of atmospheric Hg deposition, in addition
265 to air measurements, are needed to document trends in global atmospheric Hg pollution and to
266 address fundamental deficiencies in our current understanding of the global Hg cycle. The
267 collection of new ice cores for this work demands urgency as glaciers around the world are
268 currently experiencing accelerated mass losses, and many may soon vanish.[44,45]

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Supporting Information Available

The primary data for this paper can be accessed in the Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org.

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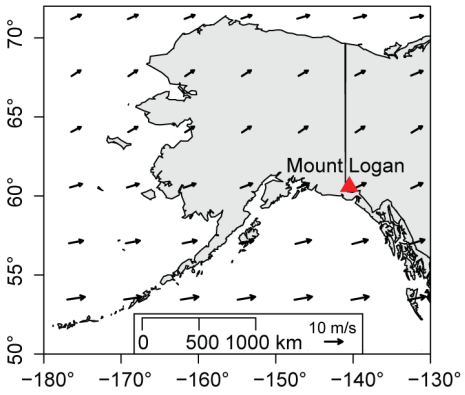
Tables

Table 1. Descriptive statistics for detectable Hg_T concentrations in samples, procedural blanks, and outer core material removed during decontamination of Mount Logan firn and ice. Concentrations for samples and the outer core are procedural blank corrected, whereas procedural blank concentrations are instrumental blank (0.02 pg g^{-1}) corrected.

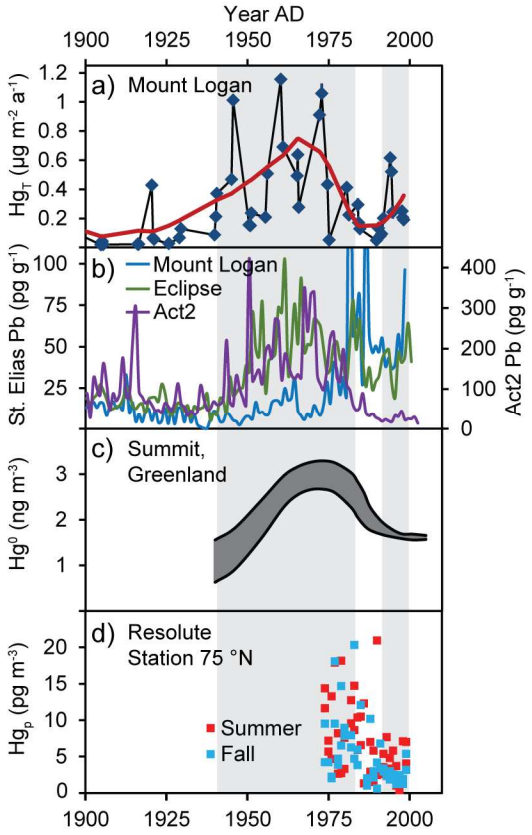
	Hg_T (pg g^{-1})				
	Firn		Ice		
	Samples	Proc. Blank	Samples	Proc. Blank	Outer Core
Max	3.52	0.33	1.06	0.34	9.41
Min	0.13	0.16	0.02	0.01	0.35
Mean	0.91	0.24	0.21	0.09	5.63
Median	0.66	0.23	0.14	0.04	5.41
Std. dev	0.82	0.06	0.23	0.10	2.29
n	37	12	51	43	13

422 # Figures



423

424 **Figure 1**. Location of Mount Logan (red triangle) in the St. Elias Mountains on the border of Alaska and
425 Yukon, Canada. Arrows represent annual average vector wind at 500 mb from AD 1948–1998.[46]



426

427 **Figure 2.** 20th Century trends in atmospheric Hg deposition at Mount Logan compared with ice core
428 records of Pb pollution and the longest available measurements of remote atmospheric Hg concentrations.
429 a) Mount Logan Hg_T fluxes (blue points) with 1σ error bars and LOESS smoother (red line). Grey
430 shading denotes two periods of elevated Hg_T fluxes. b) Annually averaged Pb concentrations in the Mount
431 Logan ice core[18] and the Eclipse Icefield ice core,[29] both in the St. Elias Mountains, and in the Act2 ice
432 core in southern Greenland.[30] c) Modeled firn-air Hg^0 concentrations in a core from Summit in central

Greenland modified from Faïn et al.[32] d) Total filterable (particulate) Hg concentrations in air samples from Resolute in Arctic Canada modified from Li et al.[33]

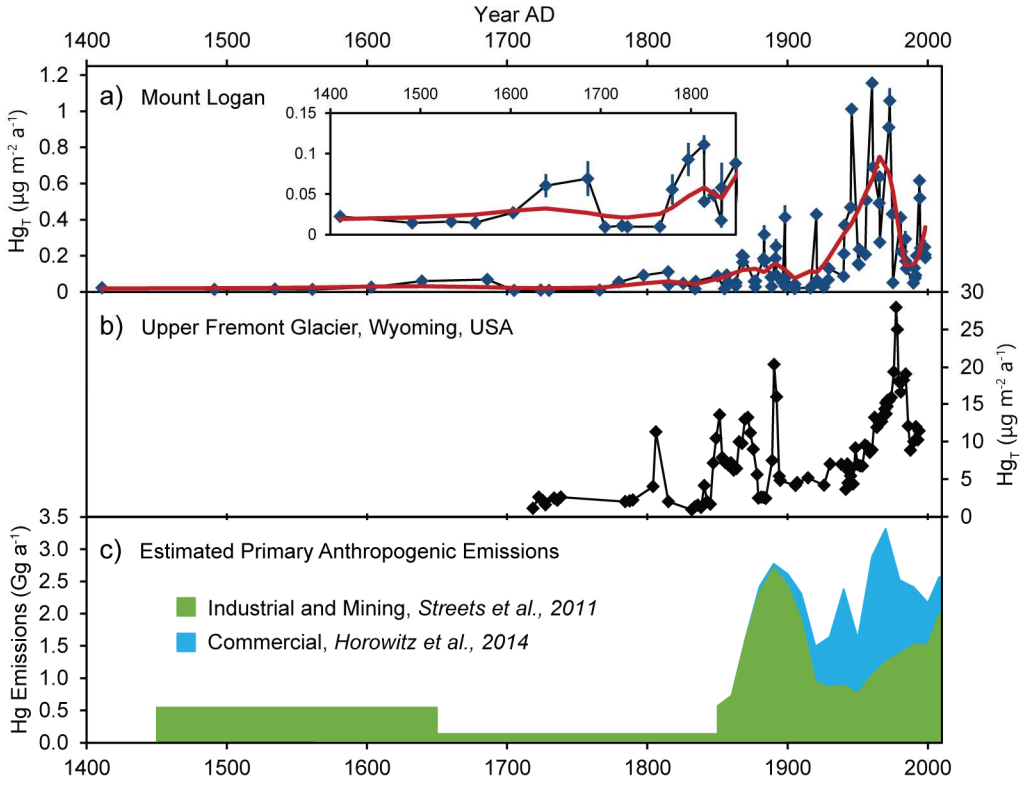
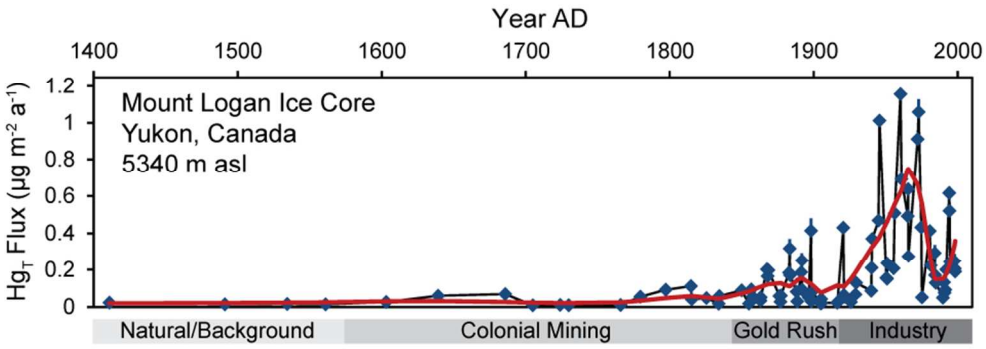


Figure 3. Multi-century Hg_T records from ice cores compared with estimates of primary anthropogenic emissions used in recent global Hg models. a) Mount Logan Hg_T fluxes (blue points) with 1σ error bars, LOESS smoother (red line), and inset with adjusted y-axis for the Preindustrial Period. b) Hg_T fluxes in the Upper Fremont Glacier ice core calculated using an assumed constant accumulation rate of 800 kg m^{-2} a^{-1} modified from Schuster et al.[14] c) Estimated primary anthropogenic Hg emissions from industrial and mining sources modified from Streets et al.,[7] and additional emissions from commercial Hg use modified from Horowitz et al.[8]



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