A 250-year high-resolution record of Pb flux and crustal enrichment in central Greenland

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[1] Records of contaminant deposition from ice cores document the impact of changing emissions on remote regions. While variations in Greenland ice core Pb concentrations before and after 1970 have been attributed primarily to leaded gasoline emissions, discontinuous coarse sampling in these studies provided limited temporal resolution. Using a continuous, high-resolution record of Pb and other trace element concentrations from 1750 to 1998, we show that large, sustained increases in Pb deposition in Greenland occurred >50 years before the introduction of leaded gasoline and that non-gasoline lead contamination likely accounted for >50% of the cumulative increase in lead deposition and crustal enrichment since industrialization. After 1970, mandated emission reductions led to a >75% decline in annual lead flux, with most of the decline occurring from 1970 to 1985. Additional elemental and isotopic tracers will be needed to provide Pb provenance.


1. Introduction

[2] Exposure to lead (Pb) is a significant health risk. Recent international efforts have resulted in large reductions in Pb emissions, primarily from the phase out of leaded gasoline. Because long-range transport results in widespread contamination, with Pb from lower latitude emissions extending into the Arctic [Barrie et al., 1992], records from polar firn and ice cores have been used to document the impact of changing emissions and recent observed changes in ice core Pb concentrations have been attributed primarily to leaded gasoline emissions [Wolff and Peel, 1988; Boutron et al., 1991; Rosman et al., 1994; Candelone et al., 1995]. Previous trace metal measurements in polar snow and ice, however, were based on discrete sampling methods. Because of the extensive decontamination procedures needed to prepare discrete samples and the large sample volumes required, these studies were limited both in depth resolution and the range of depths sampled (often spanning only a few years to decades). In the most exhaustive Pb studies, temporal resolution was generally no more than two samples yr−1 [Rosman et al., 1994; Lobinski et al., 1994]. Using a new method for making continuous measurements of trace element concentrations in ice cores [McConnell et al., 2002], we have developed a continuous record of Pb and other trace element concentrations in a central Greenland ice core extending from 1750 to 1998 with temporal resolution of ~25 samples yr−1.

2. Methods

[3] A 137-m ice core was collected in 1999 near Summit, Greenland (72.55°N, 38.31°W). The core was analyzed using a new method called Continuous Flow Analysis with Trace Elements (CFA-TE) [McConnell et al., 2002] that links a continuous ice core melter directly with a continuous flow analysis system (CFA) [Röthlisberger et al., 2000] and an inductively coupled plasma mass spectrometer (ICP-MS). Longitudinal samples of ice core (~3 by ~3 cm cross section) were melted in sequence, with the meltwater fed to the analytical instruments in real time. To minimize contamination from the outer core, the meltwater was split into three samples based on concentric regions. Melt from the innermost region was pumped to the ICP-MS for trace element analyses; melt from the middle region was sent to the CFA system; and melt from the potentially contaminated outermost region was discarded. Flow rates for each region were designed so that lateral flow across the melter head was strongly outward. Annual layer counting using winter Na maxima and H2O2 minima, verified with known volcanic events, was used to convert the glaciochemical record from depth to time.

[4] Contamination control during sample handling and analysis is critical for trace element measurements in snow and ice. While previous studies using discrete sample methods have included measurements of consecutive radial samples to monitor contamination [Boutron et al., 1991], this is not possible with real-time continuous measurements. Continuous Pb measurements are highly repeatable for analyses of adjacent parallel samples and no correlation between core breaks and concentration was found [McConnell et al., 2002], however, suggesting that contamination of the inner core was minimal. With our current analytical procedures and equipment, the absolute detection limit for Pb is ~5 ppt.

3. Results

[5] The 250-yr, continuous record of Pb concentrations provides unprecedented temporal detail and demonstrates that intra- and inter-annual variability in Pb deposition was high both before and after widespread industrialization
began in the mid-1800s (Figure 1). Increases in Pb deposition lasting from a few months to a few years resulted from fallout from explosive volcanism such as the well-documented 1783 Laki (Iceland) [Hong et al., 1996], 1844 Hekla (Iceland), and 1912 Katmai (Alaska) eruptions with no corresponding change in aluminium (Al) deposition (Figure 1C). Spring increases in continental dust transport to central Greenland [Davidson et al., 1993] and the corresponding sharp rise in Al deposition (Figure 1C), demonstrated a marked seasonal cycle in Pb deposition (Figure 1B). The Pb seasonal cycle was far more pronounced after industrialization than before, rising from ~10 ppt before 1850 to ~60 ppt from 1900 to 1970 and dropping to ~30 by 1990. In addition, summer minima increased more relative to pre-1870 levels than spring maxima during the past 150 years. Annual cycles in Al concentration showed no corresponding change. Our high-resolution measurements show that Pb deposition in Greenland responds very quickly to emission changes. During the period from 1930 to 1935, for example, both spring and summer concentrations of Pb dropped almost to pre-1870 levels (Figure 1B) because of the economic downturn of the Great Depression.

We used annual water accumulation rates and exactly coregistered elemental measurements of Al to compute both the annual average flux of Pb and crustal enrichment from the continuous, high-resolution record for central Greenland (Figure 2). Here, crustal enrichment is defined as the ratio of the Pb and Al concentrations, divided by the bulk Pb to Al ratio for crustal rocks [Taylor and McClenan, 1985]. Other than occasional increases associated with volcanic events, annual Pb flux was relatively low at 28 ng m$^{-2}$ yr$^{-1}$ prior to 1870 but was gradually rising. Beginning in 1870, Pb flux increased dramatically and reached ~112 ng m$^{-2}$ yr$^{-1}$ by 1890, a 300% increase from pre-1870 levels. Following the sharp, well-defined drop during the Great Depression (described above), Pb flux increased rapidly from 1940 to 1960 reaching a peak of >225 ng m$^{-2}$ yr$^{-1}$ in ~1970, a 700% increase from pre-1870 levels. By 1985, Pb deposition had declined to ~55 ng m$^{-2}$ yr$^{-1}$, undoubtedly in response to government-mandated emission reductions. Mean annual flux from 1985 to the late 1990s, however, was still ~200% of that observed prior to 1870. Hong et al. [1994] reported crustal enrichment of Pb of ~1 in central Greenland ice older than 3000 years, rising to ~5 in ice deposited in the late 15th century. Crustal enrichment in our high resolution record was ~30 prior to 1870, increasing to ~180 by 1890 and then to >500 by 1970, before dropping to ~100 by 1985 and remaining approximately constant through 1998. While Pb to Al ratios varying significantly in crustal material, these results suggest that ~4% of Pb in central Greenland before 1870 and ~0.2% in 1970 was of crustal origin, with current enrichment ~300% of that prior to 1870.

4. Discussion

[7] Validation of the contamination control and calibration procedures used in the new continuous method comes from comparison with previously reported discrete measurements from the Summit, Greenland area, although spatial variations in snow accumulation result in differences in glaciochemical records from site to site. The mean of the 26 ice core Pb measurements spanning the time period 1773 to 1974 reported by Candelone et al. [1995] was 58.2 ppt, compared with a mean of 59.6 ppt for our corresponding continuous measurements. Our continuous concentration measurements were somewhat lower than the 39 discrete measurements spanning 1960 to 1989 reported by Rosman et al. [1994], although differences in dating the discrete samples may account for some of the discrepancy. Assuming that the previously reported discrete measurements were 10 cm in length and dated to an accuracy of ±0.5 yrs [Lobinski et al., 1994], we computed an uncertainty...
between the continuous and discrete measurements based on intra-annual variability in the smoothed (10 cm boxcar filter) high-resolution data for ±0.5 yrs around each sample date. Chi-squared analyses of the resulting time series using these estimated concentration uncertainties showed highly significant temporal correlations (Q ~ 0.1) between the continuous measurements and the previously reported discrete measurements [Candelone et al., 1995; Rosman et al., 1994]. Validation of the more recent part of the continuous record comes from comparison with snow pit measurements corresponding to the period from summer 1989 to summer 1990 reported by Savarino et al. [1994]. The mean concentration for the 19 discrete pit samples was 21.6 ppt compared with 22.9 ppt for our continuous measurements during the same period. In addition, the annual concentration cycle in the pit samples closely matched the annual cycle in the continuous measurements with 1990 spring maxima of ~51 and ~47 ppt and 1989 and 1990 autumn minima of ~10 and ~11 ppt for the discrete pit and continuous ice core measurements, respectively.

A climatology of air-mass back trajectories indicates that the northern part of North America and the North Pacific are the primary source regions for aerosols reaching Summit [Kahl et al., 1997]. There is substantial seasonal variability, however, with the shortest ten-day trajectories during summer (originating over North America) and the longest during winter (originating over both North America and East Asia). Previous studies of Pb deposition during recent decades have assumed that leaded gasoline emissions were the dominant source of Pb in central Greenland [Boutron et al., 1991; Rosman et al., 1994]. As a result, U.S. and Canadian/European Pb isotopic signatures of leaded gasoline and limited available aerosol measurements were used to determine source regions [Rosman et al., 1994]. While there is no doubt that some of the Pb deposited in Greenland comes from leaded gasoline [Lobinski et al., 1994], our continuous measurements (Figures 1, 2) clearly demonstrate that ~50% of the increases in Pb flux and crustal enrichment from preindustrial levels to the 1970 maximum occurred from 1870 to 1890, more than 50 years before the introduction of leaded gasoline. Although continental-scale emissions are dominated by leaded gasoline combustion, our results suggest that Pb flux in central Greenland is determined more by regional emissions strongly influenced by smelter and other industrial processes.

In addition to leaded gasoline, possible sources of Pb emissions include non-ferrous metal processing and coal combustion, both of which began to grow rapidly in the U.S. and Canada in the 1860s and 1870s and continued at approximately the same levels until 1970 [Kelly et al., 2001; Milici, 1997]. Lead isotope ratios in emissions from coal combustion and smelter activities are highly variable from region to region and even smelter to smelter. Chow and Earl [1972] reported Pb 206/207 ratios in North American coals ranging from 1.18 to 1.25. Sturges and Barrie [1989] found that emissions from the Noranda copper smelter complex in northern Quebec (the largest single emitter of industrial Pb in Canada in the 1970s and 1980s) and the nearby Sudbury smelter complex were characterized by Pb 206/207 ratios of ~1.10 and 1.16, respectively. Both the Noranda and Sudbury complexes are well within the possible source areas for aerosols arriving at Summit [Kahl et al., 1997]. As suggested by the differences between the record of Pb flux in Greenland and the history of U.S. leaded gasoline emissions, a significant proportion of Pb deposited in central Greenland must have originated from smelter operations, coal combustion, and other industrial processes. Thus, a mixing model to characterize Pb deposition in central Greenland must include isotopic and elemental signatures for emissions from industrial processes in addition to leaded gasoline combustion.

Lead flux and crustal enrichment in central Greenland since 1970 closely match reductions in total U.S. Pb emissions, with mean annual flux declining more than 75% from 1970 to 1985 and then stabilizing from 1985 to 1998 (Figure 3). After peaking in 1972, total U.S. atmospheric Pb emissions declined by more than 98% from 1972 to 1998 [EPA, 2000]. Most of the decline in emissions came from the mandated phase-out of leaded gasoline, which dropped on-road vehicle emissions more than 99% from 156,003 metric tons in 1970 to 17 metric tons in 1998 [EPA, 2000]. Emissions from metal processing, the second largest source of U.S. emissions in 1970, dropped 91% from 21,976 to 1,903 metric tons during the same period. In both cases, ~90% of the declines occurred from 1970 to 1985. By 1987, gasoline accounted for less than 50% of U.S. lead emissions. Records of Canadian and Eurasian Pb emissions during the same period are not as comprehensive, although total Canadian Pb emissions in 1978 were only 13% of U.S. emissions and the proportion coming from leaded gasoline emissions was 63% [Jan and Sheffield, 1983] compared to 84% for the U.S. [EPA, 2000].

5. Conclusions

The close correspondence since 1970 between reductions in total U.S. Pb emissions and flux to the Greenland ice sheet is consistent with North America as the primary source of Pb in central Greenland. Since our continuous ice core analysis suggest that ~50% of the Pb flux in Greenland at the 1970 maximum did not come from leaded gasoline emissions, Pb isotopic ratios alone are not likely to provide details of sources and source regions. Rather, additional elemental and isotopic tracers (e.g., As, Sb, Se, V, Zn, Mn, ...
and In) measured continuously and at high resolution will be needed [Sturges and Barrie, 1989; Rahn and Lowenthal, 1985]. Such tracers have been used successfully in modern atmospheric studies to determine pollution aerosol sources and must be used in concert with stable Pb isotope ratios [Sturges and Barrie, 1989; Veron and Church, 1997] to establish sources and possible source areas for pollution recorded in ice cores. The development of new methods for making exactly coregistered, continuous elemental and isotopic measurements in ice cores is an important step in combining modern studies of atmospheric emissions and transport with long-term ice core proxies.

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References


