

8-134

Environment Canada

Water Science and Technology Directorate

Direction générale des sciences
et de la technologie, eau

Environnement Canada

Recent Metal Pollution in Agassiz Ice Cap

By:

V. Cheam, G. Lawson, J. Lechner, R. Desrosiers

NWRI Contribution # 98-134

TD
226
N87
No. 98-
134

98-134

MANAGEMENT PERSPECTIVE

- Title:** Recent metal pollution in Agassiz Ice Cap
- Authors:** Cheam, V., G. Lawson, Lechner, J., and Desrosiers, R.
- NWRI Publication #:** 98 - 134
- Citation:**
- EC Priority/Issue:** This work was done as part of the Green Plan Initiative for Preserving the Integrity of the Canadian Arctic and as part of Northern Ecosystems under the Science in Support of Large Ecosystem Initiatives. Have long-range transported pollutants of foreign origin such as metals affected the Arctic particularly since the industrial revolution ?
- Current Status:** The Canadian Arctic is far from being pristine. In spite of the implementation of unleaded gasoline since early 70s, the Agassiz Ice Cap still received a significant amount of lead in late 80s and early 90s relative to Antarctica and Central Greenland. Metal data for Pb, Zn, Al, Cd and Tl show seasonal variations of high levels in winter-early spring period and low levels in summer-fall period. Lead concentration follows the order Agassiz > Central Greenland > Antarctica.
- Next Steps:** Since the conclusions were based on our data covering a short time span coupled with other published data from nearby regions, it is recommended that a deep core of snow/ice covering the last 100 years be obtained from the Canadian Arctic, and Pb concentrations as well as its isotopic and organometallic characteristics be determined along with other toxic metals including Hg and Cd in order to generate an integrated historical record of metals pollution in this important Canadian ecosystem.

Recent Metal Pollution in Agassiz Ice Cap

V. CHEAM,*† G. LAWSON,†
J. LECHNER,† AND R. DESROSIERS‡

National Water Research Institute, Aquatic Ecosystem
Restoration Branch and Research Support Branch, Box 5050,
Burlington, Ontario, Canada L7R 4A6

Metal data for Pb, Zn, Al, Cd, and Tl show seasonal variations of high levels during the winter-early spring period and low levels during the summer-fall period. In terms of Pb magnitudes and seasonal variations, our data of the late 1980s and early 1990s (unleaded gasoline era) appear compatible with those of Murozumi et al. (Murozumi, M.; Chow, T. J.; Patterson, C. C. *Geochim. Cosmochim. Acta* 1969, 33, 1247-1294.) of the 1950s and 1965 (leaded gasoline era). This is probably due to the close proximity and similar elevation of the two areas (Agassiz Ice Cap, Canadian Arctic and Camp Century, northwest Greenland), which are likely subjected to the same polluted air masses. Despite the implementation of unleaded gasoline since the early 1970s, our data show that the Agassiz Ice Cap still received a significant amount of lead during the late 1980s and early 1990s; this is in contrast to Summit, Greenland, which saw a very drastic decrease of the element during similar periods. This is because of the different locations and altitudes, as well as different sources, mainly Eurasian for Agassiz versus mainly U.S. for Summit. Lead was determined by laser-induced fluorescence spectrometry via the direct injection of microliter sample sizes. Its fallout flux was estimated to be $1.2 \text{ ng cm}^{-2} \text{ year}^{-1}$. The lead concentration in the surface snow appears to follow the order of Agassiz and northwest Greenland > central Greenland > Antarctica.

Introduction

Historical changes in the aerosol composition above polar systems have been preserved in polar ice caps for several hundred thousand years. Past pollution above the caps can be reconstructed by investigating deep ice cores where seasonal stratification changes are minimal. In fact, there have been numerous heavy metal studies on deep cores as well as blocks and pits of polar ice/snow from Greenland (1-11) and Antarctica (1, 12-19). Some of these studies resulted in landmark discoveries, one example of which is the pioneering work by Murozumi et al. who produced the first reliable trace metal data that have stood the test of time (1). They studied massive snow blocks collected from northwest Greenland and showed that Pb pollution increased between the years 1753 and 1965 with the sharpest increase from about 1950 to 1965. This sharp increase reached Pb levels ~200 times that found in ancient ice that was 2800 years old. Their conclusion was that more than 99% of the

increase was directly caused by human activities, the principal culprit being leaded gasoline. This finding, at least partly, led to the implementation of unleaded gasoline in the early 1970s in the United States, Canada, and some other countries such as Japan and Brazil. The implementation subsequently has resulted in a significant decline in Pb levels in the atmosphere (4, 8).

Another example concerns the sources of metals polluting the polar regions. For Antarctica, lead pollution is linked to Brazil and Australia (19). For the Arctic, Boutron, Rosman, and co-workers (4, 9, 10) have demonstrated that a principal source of lead pollution over Summit, Greenland, during the early 1960s to mid 1980s is the United States. For the Canadian high Arctic, on the other hand, Barrie (20) and Barrie et al. (21) pointed to Eurasian sources for various pollutants particularly during the late winter-early spring period. As the Canadian Arctic receives different air masses than Greenland, particularly central Greenland, and since it has seen extremely few metal profiles investigated, it is important to carry out metal studies on snow and firn samples in the region; our data will shed some new light on the Arctic pollution and complement other published data especially those generated for Greenland.

This paper discusses metal pollution in recent snow and firn layers in the Agassiz Ice Cap, Northwest Territories, Canada. The chosen sampling location has been shown to possess the required conditions to ensure the minimum seasonal redistribution of pollutants and the reliable recording of entrapped aerosols (22-24). These conditions include, for example, minimum summer melt and maximum, but least disturbed, snow accumulation. Lead, as determined by laser-excited atomic fluorescence spectrometry, is discussed in detail and in relation to other findings from different ecosystems, and is tied in with other metals namely, Cd, Tl, Zn, and Al.

Experimental Section

Clean Room, Chemicals, and Sample Collection. The development of a class 100 clean room has been described in detail elsewhere, and clean room practices were followed (25). All bottles and relevant laboratory equipment were rigorously cleaned using such cleaning agents as soap, HCl, HNO₃, and ultrapure water; the procedure lasted over one week. The ultrapure Milli-Q water was produced using a 3-stage demineralization process: reverse osmosis (RO) distillation, redistillation of the RO water using quartz still, and final purification via the Milli-Q system. Very high-purity chemicals including doubly distilled nitric and hydrochloric acids (Seastar, Victoria, British Columbia) were used throughout. More details can be found elsewhere (26).

The collection of samples was done in March 1993 at the Canadian Arctic's Agassiz Ice Cap which is situated above the 80° N latitude and close to northwest Greenland. During all the sample collections, full clean garments (Saranex jumpsuit, polyethylene (PE) booties and gloves) were worn over cold weather clothing; all sampling sites were approached on foot from the downwind side; and any removed snow was discarded downwind. A systematic sampling of surface and subsurface snow samples was made at 1-km intervals east and west of the base camp (80° 40' N, 73° 30' W, 1.8 km above sea level). The camp had been in operation during springtime for 10 years. The wind direction is predominantly from the north-northwest (27, 28). A clean Teflon corer (10-cm diameter by 17-cm length) was used to scoop the immediate surface snow to a depth of about 5 cm, and to scoop subsurface snow to about 15 cm deep after 5 cm of snow was

* Corresponding author phone: (905)336-4755; fax: (905)336-6430; e-mail: ven.cheam@cciw.ca.

† Aquatic Ecosystem Restoration Branch.

‡ Research Support Branch.

scraped away with a clean scraper. Surface and subsurface samples were transferred into 1 L low-density polyethylene (LDPE) bottles.

A pit of ~1 m² area and 2.3 m deep was dug approximately 2 km upwind of the base camp. The pit was dug in stages of 75 cm using a stainless steel shovel with a plastic coated handle that had been previously rinsed with weak acid (<1%) and ultrapure water. To avoid cross-contamination between samples, the upwind face of the pit was sampled as follows. A pair of clean PE gloves and a clean Teflon scraper from the clean storage bag were used to scrape clean the snow face to be sampled. Clean snow faces were exposed only just before each sample depth was to be cored. The snow was sampled by pushing a clean corer into the side of the snow face. For trace metals, samples were taken from the top to the bottom of the pit about every 25 cm with no prior knowledge of the conductivity profile, which was obtained after all of the metal samples were taken. The snow was loosely broken up by squeezing the sides of the corer, and the sample was poured into a 1 L LDPE bottle. When full, it was tightly capped and placed into a PE sleeve and then back into its plastic storage box. Triplicate samples were obtained at 20-, 100-, and 225-cm depths; a single sample was taken at 195-cm depth, and duplicate samples were taken at all other depths. Water blanks were obtained in triplicate for the LDPE bottles.

All sample bottles were transported frozen to the class 100 clean laboratory, thawed, and acidified to pH 1.6 (0.2% HNO₃) using Seastar HNO₃. The stability of the samples and reference standards (including NIST SRM 1643c) was checked from time to time, and no change in concentrations was found over a period of more than one year. More details have been discussed earlier (27, 29).

Laser-Excited Atomic Fluorescence Spectrometer (LEAFS). A copper vapor laser-based LEAFS was described earlier (30, 31) and was used for the direct determination of Pb and Tl. A 6-kHz repetition rate was used. Normal operating power outputs of the lasers are 5–6 W for the CVL and 0.3–0.5 W for the dye laser. The approximate bandwidth of the laser is 3 pm. In the furnace, the approximate area of the laser beam is 2.1 mm², the pulse duration about 7 ns, and the peak irradiance about 23 kW/cm². The 511 nm line was used to optically pump a Rhodamine 6G dye laser for Pb and a Rhodamine 575 dye laser for Tl. The dye laser output (566 nm for Pb, 554 nm for Tl) was then frequency-doubled by a second harmonic generator to give the 283 nm light for Pb and the 277 nm light for Tl. The fluorescence light (406 nm for Pb and 353 nm for Tl) emitted by the excited atoms was collected, amplified, and interpreted.

LEAFS and AAS Analytical Methods. LEAFS methods were developed for the direct determination of Pb and Tl using only microliters of samples. The accuracy and precision of the methods have been reported using certified reference materials and spike recoveries. Detection limits of 0.03 pg/g for Tl (0.6 fg) and better than 0.4 pg/g for Pb (10 fg) were achieved (30, 31). Duplicate analyses were carried out for every sample. Lead results were generated using the Standard Calibration technique developed for lake waters (30). The results were also verified by the use of the known addition technique (32). Thallium results were generated using an in situ known addition technique (31). Cd, Zn, and Al were directly determined using a Graphite Furnace atomic absorption spectrometer. Multiple injections of 30 μL were made into the furnace (2, 33). The detection limits are 0.3 pg/g for Cd (10 multiple injections), 1.5 pg/g for Zn (single injection), and 0.07 ng/g for Al (single injection). The analysis of two certified reference materials, NIST 1643c and SLRS-2, produced excellent recoveries versus certified values: 125.3 ± 10.8 vs 129 ± 11 pg/mL for Pb; 7.8 ± 0.5 vs 7.9 ng/mL for

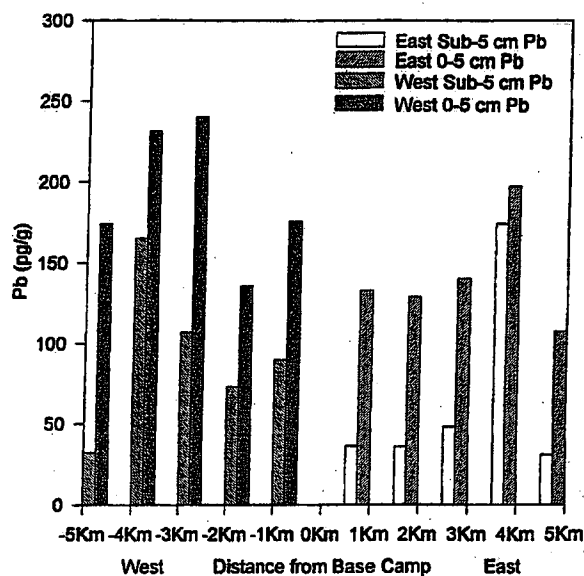


FIGURE 1. Lead in surface (0–5 cm) and subsurface (sub-5 cm) depth relative to the base camp.

Tl; 40.0 ± 2.5 vs 37.0 ± 0.5 pg/mL for Zn; 6.2 ± 0.7 vs 6.1 ± 0.5 pg/mL for Cd; and 4.5 ± 0.1 vs 4.2 ± 0.2 ng/mL for Al.

Blanks. Actual field blanks, representing the actual background contamination due to sampling, could not be obtained since it would involve the use of artificial snow samples with known metal concentrations which we do not have. We are not aware of any standard procedure to obtain such blanks for pit sampling. The field blanks were approximated as follows: during actual sampling, three clean empty bottles were exposed to air, capped after sample collection, later filled with water in the clean laboratory, and acidified as actual snow samples. These blanks were analyzed as samples and were found to contain 0.9 pg/g of Pb, 0.05 pg/g of Tl, <0.3 pg/g of Cd (10 multiple injections), 26 pg/g of Zn, and 0.14 ng/g of Al.

Results and Discussion

Lead and Other Metals in Surface and Subsurface Samples. Figure 1 shows Pb concentrations at various distances from the base camp for both surface and subsurface samples. The concentrations on the east side are fairly constant throughout for both surface and subsurface samples, except the 4-km samples, which show higher results for all five elements, Pb, Tl, Cd, Zn, and Al (Figure 1, Table 1). We have no explanation for this, though these high results do not seem to be representative of the east side samples. The west side concentrations (Figure 1, Table 1) are, in general, higher than the east side for all elements. This might have been caused by the plane which transported the research team and which landed southwest of the camp but closer to the west side sampling sites.

The concentration range for the east side surface snow is 105–205 pg/g of Pb and is somewhat smaller than 241–365 pg/g, the range reported by Sturgeon et al. (34) for their surface snow samples; these were collected in April 1992 from isolated pits dug on an ice floe north of Ellesmere Island. Our Pb results are also smaller than those reported by Murozumi et al. (150–420 pg/g) for the northwest Greenland snow samples collected during the summer, spring, and winter of 1965. These three sets of data are, however, about the same order of magnitude when compared to Antarctic snow concentrations which are <21 pg/g (Table 2). The three Arctic areas are close to each other and are likely under similar polluted air masses, which may explain the similar magnitude

TABLE 1. Concentrations of Metals in Surface and Subsurface Snow at Agassiz Ice Cap (March 1993)^a

Distance from base camp (km)	Surface Samples									
	Pb (pg/g)		Tl (pg/g)		Cd (pg/g)		Zn (pg/g)		Al (ng/g)	
	west	east	west	east	west	east	west	east	west	east
1	199.0	117.6	0.74	0.50	5.4	4.2	214	170	17.0	14.0
2	149.5	118.5	0.46	0.31	3.1	4.7	176	290	26.6	24.9
3	294.8	155.5	1.13	0.30	9.2	3.3	389	155	27.9	24.6
4	295.9	205.0	1.01	0.85	9.7	5.0	320	250	21.5	30.6
5	199.4	105.5	0.45	0.46	4.5	2.6	202	133	26.1	7.2
	Subsurface Samples									
1	90.5	42.3	0.20	0.24	4.6	1.5	124	59	6.8	2.6
2	88.9	39.8	0.38	0.10	2.4	1.9	107	62	5.7	2.3
3	117.2	53.0	0.48	0.16	3.2	1.8	140	56	17.8	1.9
4	221.9	204.6	0.85	0.91	5.3	8.9	203	307	19.5	33.9
5	28.8	36.9	0.02	0.08	1.9	1.9	50	77	5.4	2.1

^a The average of the % RSD's for these results are the following: 6% ± 4% for Pb; 8% ± 4% for Tl; 2% ± 2% for Zn; 8% ± 6% for Cd; and 4% ± 4% for Al.

TABLE 2. Metal Concentration Ranges (pg/g) for Fresh, Surface, or Recent Snow in Various Locations

sampling region	collection time	Pb	Cd	Tl	Zn	Al (ng/g)	reference
Agassiz Ice Cap, Canadian Arctic ice floe north of Ellesmere Island	1993 March, fresh snow	105-205	0.37-8.88	0.3-0.9	56.2-300.5	0.96-17.66	this work
	1992 April	241-365	7-18	1.3-2.2			34
Northwest Greenland	1965 summer, spring, and winter	150-420					1
Antarctic	1980 present day snow	2.6-9.8	0.12-2.3		1.0-7.4		2, 37
Antarctic (various sites)	1983 and 1984 January, surface snow	2.3-7.4				1.2-2.0	38
Antarctic, height >700 m (Terra Nova)	1988/89, 1989/1990, 1990/91 fresh snow			0.18-0.45			39
Antarctic (various sites)	1993/1994	7-21	3-4				18
Greenland-Spitsbergen area	1980 late summer, fresh snow	8-20	0.2-0.6				40
Greenland-Spitsbergen area	1979 old, accumulated snow	173-226	2.6-6				40
Dye 3, south-central Greenland	1978, 1979 summer	42-150	7.8-17		140-280		41
Dye 3, south-central Greenland	1982 June, fresh snow	160 ± 34	24 ± 12			2.80 ± 0.13	42
Greenland, near Dye 3	1983-1984 present day surface snow	5-86	0.2-1.3		7-47		2, 37
central Greenland	1990 spring-992 summer	0.6-44	0.08-2.5		9-194	<1-26	11

of results despite the large difference in sampling periods (1965 and early 1990s). Nineteen sixty-five was a year when the use of leaded gasoline was still on the rise. More on this topic will be discussed below.

Table 2 also lists Pb results from other areas of Greenland, keeping in mind the statement by Wolff and Peel (35) that much of the reported trace metals data up to the mid 1980s are questionable, with the possible exceptions of those by Patterson et al. (1, 36). Mart (40) reported a range of 8-20 pg/g for fresh snow collected during late summer of 1980 and a range of 173-226 pg/g for old snow accumulated in 1979 at the Greenland-Spitsbergen area. This indicates that the concentration in summer is low and smaller than that in other seasons, presumably in winter and spring. In contrast, at Dye 3, south-central Greenland, the concentrations during the summers are high (42-160 pg/g) as reported by Davidson et al. (41, 42); these results are also shown in Table 2. Wolff and Peel (2) also reported data for Dye 3 with a mean Pb value of 28 pg/g for one year of accumulation (1983-1984). In general, though, Pb concentrations at Dye 3 or central Greenland are less than 100 pg/g (Table 2, refs 2, 11, 34) and are below those observed in northwest Greenland and Ellesmere Island as discussed above. Thus, it appears that the Pb deposited on the three regions follows the order of the Canadian Arctic and northwest Greenland > central Greenland > Antarctica. Table 2 also compares the results for Cd, Tl, Zn, and Al for all these regions.

Seasonal Variations. The dating of snow samples was made according to the conductivity profile and the mor-

phology of the snow pit. Snow samples were obtained using PE vials pushed horizontally into the side of the snow pit at approximately 2-cm intervals, and the conductivity was measured at 0 °C. Summer ice layers were carefully noted and used as reference points. Figure 2 plots the conductivity readings (open circles) and the summer ice layers (solid diamonds) with respect to depth. It clearly shows the maximum readings corresponding to the winter-early spring periods and the minima to the summer-fall periods. Also, the figure shows Pb results (solid circles) at various depths, with the horizontal bars representing two standard deviations of the results obtained from the different replicate samples of each depth, and with the vertical bars representing the width of the snow sampled by the corer. As can be clearly seen, Pb values also peak out in the winter-early spring periods for the years 1993, 1992, 1990, and 1988.

These concentration peaks correspond to the Arctic haze episodes when the air is loaded with high levels of foreign pollutants and suspended particulates which often reduce visibility (43). The haze event is known to occur annually from about December to April, when the strong Siberian anticyclone drives the pollutant-containing air masses from Eurasia through the Arctic, where a fraction of pollutants is extracted by snowfalls and archived (20, 21). Atmospheric trace metals and major ions also have been shown (22) to peak during the Arctic haze period. Furthermore, Barrie et al. (23) showed that the historical conductivity and acidity values in ice cores from the Agassiz Ice Cap peaked, as does the Arctic air pollution, in the December-April periods.

TABLE 3. Results of Metals Found at Agassiz Ice Cap within the Approximate Periods of December–April and May–November^a

metal	period	1993	1992	1991	1990	1989	1988	1986
Pb	Dec–April	127.2	212.4		159.5		201.2	
	May–Nov		37.6, 19.2	29.3	73.1 ^b	48.7	13.2	37.8
Tl	Dec–April	0.34	0.77		0.54		0.84	
	May–Nov		0.15, 0.06	0.17	0.18 ^b	0.12	0.13	0.14
Cd	Dec–April	3.7	7.4		5.6		5.2	
	May–Nov		1.8, 1.5	1.8	2.8 ^b	1.3	0.4	1.1
Zn	Dec–April	153	301		243		273	
	May–Nov		63, 105	96	178 ^b	102	62	88
Al	Dec–April	17.7	12.2		9.0		7.2	
	May–Nov		2.2, 1.5	1.0	6.3 ^b	1.7	1.3	2.0

^a The within-sample % RSD's are <12% for all metals, except Cd with <25%. ^b These values are all higher than other years. It is probably because they are close to the winter values. The results are between-samples averages. The ranges of the between-samples % RSD's are the following: 8%–27% for Pb; 8%–41% for Tl; 1%–27% for Zn; 1%–51% for Cd; and 6%–39% for Al.

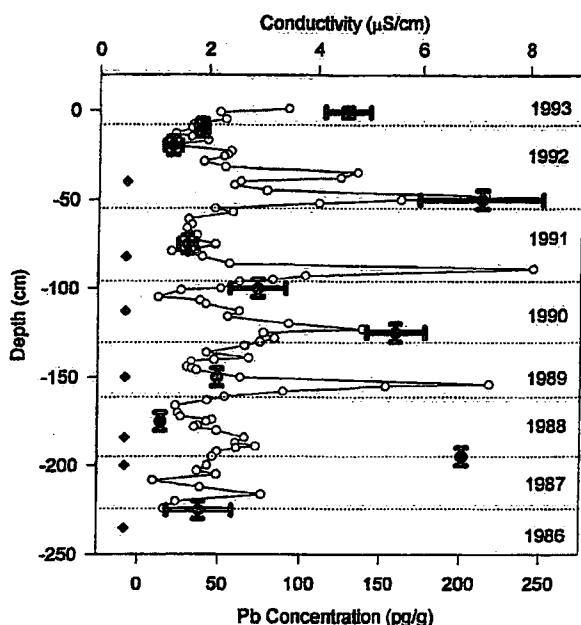


FIGURE 2. Lead concentration profile along with conductivity profile and summer ice layers: (●, lead; ○, conductivity; ◆, ice layers).

Therefore our Pb results from accumulated snow and firn layers mirror the historical air pollution and snow chemistry of the region. In fact all of the metal data (Pb, Zn, Al, Tl and Cd) presented in Table 3 show for all practical purposes the same seasonal pattern.

Compatibility of Pb Data and a Suggested Pollution Pattern. Since the main concern was on the seasonal variations, the annual snow accumulations were not collected. However, we had for the years 1988, 1990, and 1992 at least two values for each year; basically one value for winter and one or two for summer–fall (Figure 2). As a crude approximation, annual deposits were calculated, by averaging those values, and were found to be 107 pg/g, 116 pg/g, and 90 pg/g, respectively, for the years 1988, 1990, and 1992. The three values further average to 104 pg/g, which is almost an order of magnitude higher than the average of 15 pg/g for Summit, central Greenland, for the years 1990, 1991, and 1992 (11), or 18 pg/g for central Greenland for the years 1989–1990 (44). This difference seems high but may be real given the following facts: Agassiz is significantly lower than Summit, 1.8 vs 3.2 km above sea level; the Agassiz glacier is weathered with the Arctic haze and with polluted lower tropospheric air masses; and Summit, on the other hand, receives relatively unpolluted snow from the middle and upper troposphere (20, 23, 45, 46). Furthermore, Sturgeon

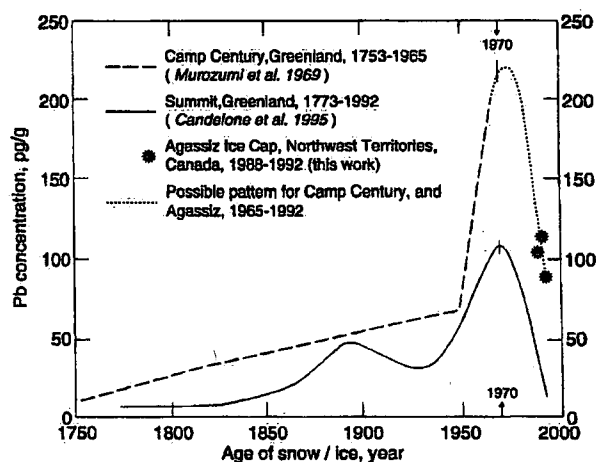


FIGURE 3. Time dependence of Pb concentrations in snow/ice at three different locations in the Arctic.

et al. (34) reported Pb values which are closer to ours for snow samples from an ice floe north of Ellesmere Island (83° 94' N, 61° 10' W). Their samples were collected in April 1992 from two different isolated pits of 30 cm deep, and their Pb results were 241/29 and 365/49 pg/g for top/bottom layers of the two pits.

Figure 3 shows Pb concentrations covering the past 250 years for three different Arctic areas: Camp Century, northwest Greenland (dashed line, ref 1); Summit, central Greenland (solid line, ref 8); and Agassiz Ice Cap (star symbols, this work). The dashed line was originally drawn by Murozumi et al. (1) for the period 1753–1965, where the data have been shown to be reliable over the years (8, 35, 47). The solid line is the original spline-smoothed curve representing the data by Candelone et al. (8) for the period 1773–1992. Since Camp Century is lower than Summit (1866 vs 3228 m above sea level) and is expected to receive more pollution, the relative position of the two lines is reasonable, the dashed line being higher than the solid one.

Since Camp Century and Agassiz have about the same altitude (1866 vs 1830 m) and are relatively close to each other, both locations are probably under the influence of the same polluted air masses. Then, our data should closely fit the pattern of Pb pollution reported by Murozumi et al. (Figure 3) and should correspond to a declining trend which had passed by a certain maximum concentration. Since our results for the 1990s approximate those of Murozumi et al. for 1950, the pattern of the dashed curve and that of the solid curve between these years (Figure 3) together suggest that this maximum occurred around 1970–1975 with an annual concentration near 225 pg/g. Accordingly, a possible Pb pollution pattern for Agassiz and Camp Century would follow

the dotted curve as shown in the figure from 1965 to the 1990s.

Lead Sources and Recommended Follow-Up. If Pb concentrations at Agassiz and Camp Century did peak in the early 1970s, the descent in Pb concentration would have occurred about mid 1970 (Figure 3) when the phase-in of unleaded gasoline was implemented in North America (48). Thus a link to the North American gasoline consumption seems obvious, especially when Boutron and co-workers (4, 9, 10) showed that the rise and fall of Pb concentration at Summit was directly associated with the use and discontinuance of leaded fuel in the United States. However, since Asia and Europe still used mostly leaded gasoline in the 1970s, and since the source of pollution in the Canadian Arctic is believed to originate in Eurasia (20, 21, 49), the hinted link to the U.S. source is seriously challenged or even ruled out by virtue of the isotopic evidences shown by Sturges and Barrie (50).

A possible scenario is that the rapid increase in Pb concentration from 1950, observed by Murozumi et al. (1), was a combination of sources from Eurasia and, to a lesser extent, eastern Canada and northeastern U.S. (43, 50) since the consumption of leaded gasoline increased rapidly in these sources. Also, nongasoline sources, such as emissions from metal productions, smelters, coal combustion, refineries, etc., still increased significantly in Eurasia. This scenario would explain the increased difference between the dashed curve (eastern Canadian, northeastern U.S., and Eurasian source mainly) and the splined curve (U.S. source mainly) from 1950 to 1965 as seen in Figure 3. This also supports the fact that our Pb values are higher than those of Candelone et al. (11) since the Eurasian source still contains Pb from the consumption of leaded petrol. But the descent of the dotted curve from 1975 to early 1990s seems too steep, which does not corroborate with the late (1987–1989) phase-in of the unleaded fuel in Eurasia (48). It could be that the data of Murozumi et al. of 200 pg/g (top of dashed line) might be too high, making the extrapolated peak of 225 pg/g too high also, thus the steep descent. A lower top of the dashed line would make the descent less steep, even less steep than the slope of the solid line from 1970 to early 1990s. This would verify the diminished U.S. source compared to the still very strong Eurasian source during this time span.

Obviously, additional reliable data are needed to elucidate this "nearly solved" question of Pb quantity and sources in this region. It seems therefore highly desirable that a deep core of snow/ice covering the last 100 years be obtained from the Canadian Arctic, and the concentrations of Pb as well as its isotopic and organometallic characteristics be determined along with other toxic metals including Hg and Cd.

Estimation of Metal Fallout Fluxes. Because the amount of annual snowfall differs from year to year, and because the concentration depends on the amount of snowfall, metal concentration alone could be a "weak" quantity to be used when comparing quantities from different times or different regions. Metal fallout flux, which is based on both the concentration and the amount of snowfall, would be a complementary quantity to be used for comparison purposes; it is defined as the product of annual metal concentration (pg/g) and annual snow accumulation ($\text{g cm}^{-2} \text{ year}^{-1}$). The annual snow accumulations were estimated from the fluxes and annual PAHs concentrations reported in 1995 by Peters et al. (28) for the Agassiz Ice Cap. For the top seven years (1993–1987), the annual snow accumulations were calculated yielding an average of $11.5 \text{ g cm}^{-2} \text{ year}^{-1}$. This accumulation, coupled with the Pb concentrations for the years 1988, 1990, and 1992, results in calculated Pb fluxes of 1.23, 1.33, and 1.04, averaging to $1.2 \text{ ng cm}^{-2} \text{ year}^{-1}$.

TABLE 4. Comparison of Metal Fluxes (Calculated Average \pm Standard Deviation), $\text{ng cm}^{-2} \text{ year}^{-1}$

metal	Agassiz ^a	Greenland ^b	Greenland ^c	antarctic ^d
Pb	1.2 \pm 0.2	0.39	0.85 \pm 0.10	0.07 \pm 0.03
Tl	0.005 \pm 0.001			
Cd	0.04 \pm 0.01	0.02		
Zn	2.0 \pm 0.3	1.2		
Al	70 \pm 20			

^a This work for the years 1988–1992. ^b Candelone et al. (8), central Greenland for year 1992. ^c Boyle et al. (57), central Greenland for the years 1988–1990. ^d Scarponi et al. (19), at Hercules Neve, east Antarctica for the years 1988–1991.

The flux of $1.2 \text{ ng cm}^{-2} \text{ year}^{-1}$ is reasonable when compared to the average flux of $0.85 \text{ ng cm}^{-2} \text{ year}^{-1}$ for central Greenland in the years 1988–1990 (57), and to $0.39 \text{ ng cm}^{-2} \text{ year}^{-1}$ for Summit in year 1992 (8). Also, it is approximately 18 times the average flux of $0.068 \text{ ng cm}^{-2} \text{ year}^{-1}$ for Hercules Névé, Antarctica, in the years 1988–1991 (19); this is reasonable given the fact that the Arctic is known to be significantly more polluted than the Antarctic. Table 4 compares the fluxes of Pb and other metals, and shows that our results are higher than those for central Greenland and Antarctica, which supports the fact that the Agassiz Ice Cap has received more polluted air masses as discussed above.

Acknowledgments

We thank the Geological Survey of Canada for the use of the base camp and Dr. D. J. Gregor for leading the expedition.

Literature Cited

- Murozumi, M.; Chow, T. J.; Patterson, C. C. *Geochim. Cosmochim. Acta* 1969, 33, 1247–1294.
- Wolff, E. W.; Peel, D. A. *Ann. Glaciol.* 1988, 10, 193–197.
- Hong, S.; Candelone, J. P.; Patterson, C. C.; Boutron, C. F. *Science* 1990, 265, 1841–1843.
- Boutron, C. F.; Gorlach, U.; Candelone, J. P.; Bolshov, M. A.; Delmas, R. J. *Nature* 1991, 353, 153–156.
- Heidam, N. Z.; Wahlin, P.; Kemp, K. *Atmos. Environ.* 1993, 27A, 3029–3036.
- Hong, S.; Candelone, J. P.; Patterson, C. C.; Boutron, C. F. *Science* 1994, 265, 1841–1843.
- Lobinski, R.; Boutron, C. F.; Candelone, J. P.; Hong, S.; Szpunar-Lobinski, J.; Adams, A. *Environ. Sci. Technol.* 1994, 28, 1467–1471.
- Candelone, J. P.; Hong, S.; Pellone, C.; Boutron, C. F. *J. Geophys. Res.* 1995, 100 (D8), 16605–16616.
- Rosman, K. J. R.; Chisholm, W.; Boutron, C. F.; Candelone, J. P.; Gorlach, U. *Nature* 1993, 362, 333–335.
- Rosman, K. J. R.; Chisholm, W.; Boutron, C. F.; Candelone, J. P.; Hong, S. *Geochim. Cosmochim. Acta* 1994, 58, 3265–3269.
- Candelone, J. P.; Jaffrezo, J.-L.; Hong, S.; Davidson, C. I.; Boutron, C. F. *Sci. Total Environ.* 1996, 163, 101–110.
- Boutron, C. F.; Patterson, C. C. *Geochim. Cosmochim. Acta* 1983, 47, 1355–1368.
- Boutron, C. F.; Patterson, C. C. *Nature* 1986, 323, 222–225.
- Gorlach, U.; Boutron, C. F. *J. Atmos. Chem.* 1992, 14, 205–222.
- Wolf, E. W.; Sutie, E. D. *Geophys. Res. Lett.* 1994, 21, 781–784.
- Scarponi, G.; Barbante, C.; Cescon, P. *Analysis* 1994, 22(7), M47–M50.
- Rosman, K. J. R.; Chisholm, W.; Boutron, C. F.; Candelone, J. P.; Patterson, C. C. *Geophys. Res. Lett.* 1994, 21, 2669–2672.
- Lanza, F.; Bocci, F.; Papoff, P. *Microchem. J.* 1996, 54, 429–443.
- Scarponi, G.; Barbante, C.; Turetta, A.; Gambaro, A.; Cescon, P. *Microchem. J.* 1997, 55, 24–32.
- Barrie, L. A. *Atmos. Environ.* 1986, 20, 643–663.
- Barrie, L. A.; Gregor, D.; Hargrave, B.; Lake, R.; Muir, D.; Shearer, R.; Tracey, B.; Bidleman, T. *Sci. Total Environ.* 1992, 122, 1–74.
- Barrie, L. A.; Hoff, R. M. *Atmos. Environ.* 1985, 19, 1995–2010.

- (23) Barrie, L. A.; Fisher, D.; Koerner, R. M. *Atmos. Environ.* 1985, 19, 2055-2063.
- (24) Woo, M.-k.; Heron, R.; Marsh, P.; Steer, P. *Atmos.-Ocean* 1983, 21, 312-325.
- (25) Nriagu, J. O.; Lawson, G.; Wong, H. K. T.; Azcue, J. M. *J. Great Lakes Res.* 1993, 19, 175-182.
- (26) Cheam, V.; Lechner, J.; Desrosiers, R.; Sekerka, I.; Nriagu, J.; Lawson, G. *Int. J. Environ. Anal. Chem.* 1993, 53, 13-27.
- (27) Nriagu, J.; Lawson, G.; Gregor, D. *Bull. Environ. Contam. Toxicol.* 1994, 52, 756-759.
- (28) Peters, A. J.; Gregor, D. J.; Teixeira, C. F.; Jones, N. P.; Spencer, C. *Sci. Total Environ.* 1995, 160/161, 167-179.
- (29) Cheam, V.; Lawson, G.; Lechner, J.; Desrosiers, R.; Nriagu, J. *Fresenius' J. Anal. Chem.* 1996, 355, 332-335.
- (30) Cheam, V.; Lechner, J.; Sekerka, I.; Desrosiers, R.; Nriagu, J.; Lawson, G. *Anal. Chim. Acta* 1992, 269, 129-136.
- (31) Cheam, V.; Lechner, J.; Desrosiers, R.; Sekerka, I. *Int. J. Environ. Anal. Chem.* 1996, 63, 153-165.
- (32) Cheam, V.; Lechner, J.; Sekerka, I.; Desrosiers, R. *J. Anal. At. Spectrom.* 1994, 9, 315-320.
- (33) Gorlach, U.; Boutron, C. F. In *Proceedings of the 7th International Conference on Heavy Metals in the Environment*; Vernet, J. P., Ed.; CEP Consultants Limited: Edinburgh, United Kingdom, 1989; pp 24-27.
- (34) Sturgeon, R. E.; Willie, S. N.; Zheng, J.; Kudo, A.; Gregoire, D. *C. J. Anal. At. Spectrom.* 1993, 8, 1053-1058.
- (35) Wolff, E. W.; Peel, D. A. *Analyst* 1994, 22, M41-M43.
- (36) Ng, A.; Patterson, C. C. *Geochim. Cosmochim. Acta* 1981, 45, 2109-2121.
- (37) Boutron, C. F. *Fresenius' J. Anal. Chem.* 1990, 337, 482-491.
- (38) Boutron, C. F.; Patterson, C. C. *J. Geophys. Res.* 1987, 92(D7), 8454-8464.
- (39) Baiocchi, C.; Giacosa, D.; Saini, G.; Cavalli, P.; Omenetto, N.; Passarella, R.; Poletti, A.; Trincerini, P. R. *Int. J. Environ. Anal. Chem.* 1994, 55, 211-218.
- (40) Mart, L. *Tellus* 1983, 35B, 131-141.
- (41) Davidson, C.; Chu, L.; Grimm, T.; Nasta, M.; Qamoos, M. *Atmos. Environ.* 1981, 15, 1429-1437.
- (42) Davidson, C.; Santhanam, S.; Fortmann, R.; Olson, M. *Atmos. Environ.* 1985, 19, 2065-2081.
- (43) Lockhart, W. L.; Wagemann, R.; Tracey, B.; Sutherland, D.; Thomas, D. J. *T. Sci. Total Environ.* 1992, 122, 165-243.
- (44) Savarino, J.; Boutron, C. F.; Jaffrezo, J.-P. *Atmos. Environ.* 1994, 28A, 1731-1737.
- (45) Davidson, C. I.; Schnell, R. C. *Atmos. Environ.* 1993, 27A, 2695-2699.
- (46) Barrie, L. A. In *Chemical Exchange Between the Atmosphere and Polar Snow*; Wolf, E. W., Bates, R. C., Eds.; NATO ASI Series; Springer-Verlag: Berlin Heidelberg, 1996; Vol I 43, pp 93-130.
- (47) Wolff, E. W. *Antarctic Sci.* 1990, 2, 189-205.
- (48) Nriagu, J. O. *Sci. Total Environ.* 1990, 92, 13-28.
- (49) Landsberger, S.; Vermette, V. G.; Stuenkel, D.; Hopke, P. K.; Cheng, M. D.; Barrie, L. A. *Environ. Pollut.* 1992, 75, 181-187.
- (50) Sturges, W. T.; Barrie, L. A. *Atmos. Environ.* 1989, 23, 2513-2519.
- (51) Boyle, E. A.; Sherrell, R. M.; Bacon, M. P. *Geochim. Cosmochim. Acta* 1994, 58, 3227-3238.

Received for review November 19, 1997. Revised manuscript received August 3, 1998. Accepted August 5, 1998.

ES971012W

Environment Canada Library, Burlington



3 9055 1018 1696 4



Environment
Canada

Environnement
Canada

Canada

Canada Centre for Inland Waters

P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada

National Hydrology Research Centre

11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

St. Lawrence Centre

105 McGill Street
Montreal, Quebec
H2Y 2E7 Canada

Place Vincent Massey

351 St. Joseph Boulevard
Gatineau, Quebec
K1A 0H3 Canada

Centre canadien des eaux intérieures

Case postale 5050
867, chemin Lakeshore
Burlington (Ontario)
L7R 4A6 Canada

Centre national de recherche en hydrologie

11, boul. Innovation
Saskatoon (Saskatchewan)
S7N 3H5 Canada

Centre Saint-Laurent

105, rue McGill
Montréal (Québec)
H2Y 2E7 Canada

Place Vincent-Massey

351, boul. St-Joseph
Gatineau (Québec)
K1A 0H3 Canada