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V. Cheam · G. Lawson · J. Lechner · R. Desrosiers
J. Nriagu

Thallium and cadmium in recent snow and firn layers in the Canadian Arctic by atomic fluorescence and absorption spectrometries

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Abstract Compared to the Antarctic and Greenland, the Canadian Arctic has seen extremely few trace metal studies on snow and ice. Surface, subsurface and depth samples of snow and firns were collected from the Agassiz Ice Cap, Ellesmere Island, Canada using clean room practices. Results for Tl (directly determined by LEAFS) and Cd (determined by GFAAS) are reported. To our knowledge, the thallium depth profile presented here is the first one so far reported for both polar systems, Greenland or other places. Tl concentrations peak in the winter-spring periods, when the Arctic atmosphere is loaded with foreign pollutants and suspended particulates which sometime severely reduce the visibility, creating a phenomenon commonly known as the Arctic haze. These results are in general accordance with the historical Arctic air pollution and acidity/conductivity data on ice cores. Surface concentrations of Tl range from 0.3 to 0.9 pg/g, which is a few times higher than those found in Antarctica. Cadmium shows seasonal characteristics similar to Tl although there is not a definite correlation between the two. However, there could be two predominant origins of metals which were deposited in the snow: Eurasian origin in January–April corresponding to high level metals (main deposition), and a less definite origin in May–December corresponding to low level metals.

1 Introduction

Numerous trace metal studies have been carried out for Antarctic and Greenland ice cores stimulated by the

pioneering work of Murozumi et al. in 1969 [1]. However, much of the trace metals data reported up to the mid-1980's are questionable, apparently because of analytical and contamination problems [2, 3]. Some possible exceptions to this are the works by Patterson et al. [1, 4]. Nevertheless, a wealth of informative, useful records have been unearthed [2, 5, 6].

Compared to Antarctica and Greenland, trace metal works on Canadian Arctic snow and ice are very rare even though it has been known for sometime that the Canadian Arctic is a transient “dumping ground” for the long-range transported atmospheric pollutants of outside origins [7–10]. Sturgeon et al. [11] evaluated electrothermal vaporization ICPMS techniques by analyzing some surface and subsurface snow samples from North of Ellesmere Island. Recently some Cd data were reported for snow and firn from the Agassiz Ice Cap, Canada [12].

This paper reports results for thallium directly determined by Laser-Excited Atomic Fluorescence Spectrometry (LEAFS) and additional data on cadmium (by GFAAS) for snow and firn samples taken from the same location reported earlier [12] as well as for several samples collected upwind and downwind with respect to this location. The samples include surface, subsurface and depth samples down to 2.3 m, which corresponds to a historical record of the past seven years. By following ultraclean laboratory and field practices, ultratrace levels of Tl were observed, whose depth profile is believed to be the first one reported for both polar systems or other regions.

2 Experimental

2.1 Laser-excited atomic fluorescence spectrometer. The details of the copper vapor laser-based spectrometer have been described elsewhere [13, 14]. The 511 nm line was used to optically pump a Rhodamine 575 dye laser. The dye laser output (553.58 nm) was then frequency-doubled by a second harmonic generator to give the 276.79 nm UV light. The fluorescence light (352.94 nm) was collected

V. Cheam (✉) · G. Lawson · J. Lechner · R. Desrosiers
National Water Research Institute (CCIW), Box 5050, Burlington,
Ontario, Canada L7R 4A6

J. Nriagu
University of Michigan, School of Public Health,
Department of Environmental and Industrial Health,
Ann Arbor, MI 48109-2029, USA

and measured via a narrow bandpass filter (1 nm)-monochromator-photomultiplier-boxcar system.

2.2 Analytical methods. A LEAFS method utilizes an in situ known addition technique, in which 5 μl of snowmelt sample is used to directly determine Tl [15]. Duplicate analysis was carried out for every sample. The method accuracy was demonstrated by successfully recovering more than 50 spikes made on six different water samples. Also a Reference Material (NIST 1643c) was analyzed undiluted and 2000-times diluted and was found to contain $7.8 \pm 0.5 \mu\text{g/l}$ and $4.18 \pm 0.36 \text{ ng/l}$ of Tl, which agree with the recommended values of $7.9 \mu\text{g/l}$ and 3.95 ng/l , respectively. The precision of 19 groups of replicate analyses gives a median relative standard deviation of 4.7%. A detection limit of 0.03 ng/l (0.6 fg) was achieved [15]. Cadmium was directly determined using a Graphite Furnace Atomic Absorption Spectrometer. Multiple injections of 30 μl were made into the furnace [16, 17]. The detection limit for 10 multiple injections is 0.3 pg/g . The method was successfully used earlier [12].

2.3 Sample collection. By using our expertise in clean room practices some representative samples from the Agassiz Ice Cap (Northwest Territories, Canada) were collected. All equipment and sample bottles were cleaned according to a decontamination procedure described earlier [18]. Full clean garments were worn over cold weather clothing. The sampling site was about 2 km upwind from our base camp ($80^{\circ}40'N$ $73^{\circ}30'W$) and about 1800 m above sea level. The site was chosen because the seasonal stratification is known to be minimally affected by snow drift and snow melt [19, 20], making the spatial study of metal accumulation meaningful.

A pit of $\sim 1 \text{ m}^2$ area and 2.3 m deep was dug in March 1993. For trace metals, sampling depths were about every 25 cm. The samples were collected with no prior knowledge of the conductivity profiles, which were obtained after all the metal samples were taken. The samples were obtained with a Teflon corer (10 cm diameter by 17 cm length) pushed horizontally into the side of the pit wall at specified depths and transferred into 1L low-density polyethylene (LDPE) bottles. The sample bottle was then placed back into its PE storage sleeve and placed into a PE box for transport. Water blanks were obtained in triplicate for LDPE bottles.

All samples were transported frozen to our class 100 clean lab, thawed and acidified to pH 1.6 (0.2% HNO_3) using double sub-boiled distilled HNO_3 (Seastar). The stability of the samples and standards (including the 2000-times diluted NIST SRM 1643c) was checked from time to time and no change in concentrations was found over a period of more than one year.

3 Results and discussion

3.1 Tl and Cd in surface and subsurface samples

Surface snow samples were obtained every km up to 5 km upwind and downwind with respect to the base camp. The corer was used to scoop the immediate surface snow to a depth of about 5 cm, and to scoop subsurface snow to about 15 cm depth after 5 cm of snow was scraped away. Upwind Tl concentrations are overall lower than those downwind of the base camp, which indicates contamination from the camp. This is true for both surface and subsurface samples. Also the surface concentrations are higher than those of the subsurface. The upwind surface concentration of Tl ranges from 0.3 to 0.9 pg/g . These results are higher than those ($0.18\text{--}0.45 \text{ pg/g}$ of Tl) reported by Baiocchi

et al. [21] for snow samples taken from several locations in Antarctica with height $\geq 700 \text{ m}$ above sea level. These authors believe that their results are higher than the “true” content of the snow and attributed the excess to the possible sampling contamination, contribution from marine spray and aerosol, leaching from particulate matter, as well as crustal contribution, but not to the long-term storage. This renders our results (Arctic) a few times higher than theirs (Antarctic), which seems reasonable as the Arctic is known to be more polluted than the Antarctic [3].

The average Cd values for upwind surface samples is 3.7 pg/g whereas that of subsurface samples is 1.8 pg/g . These values are somewhat lower than those ($2.6\text{--}6 \text{ pg/g}$) reported by Mart [22] for accumulated snow in the area of Greenland-Spitsbergen. The reason could be that their sampling sites are closer to the Eurasian sources (see below) and are at sea level.

3.2 Conductivity and dating of firn layers

The snow samples were dated according to the conductivity profiles and the morphology of the snow pit. Samples were obtained using PE vials pushed horizontally into the side of the snow pit at approximately 2 cm intervals. Conductivity measurements were made on the melted samples at 0°C using a portable conductivity meter (Metrohm-Herisau E587). Obvious morphological details, in particular summer ice layers were recorded and used as reference points. Figure 1 shows the conductivity profile and the summer ice layers. As can be seen the maxima correspond to the late winter-early spring period and the minima to the summer-fall period.

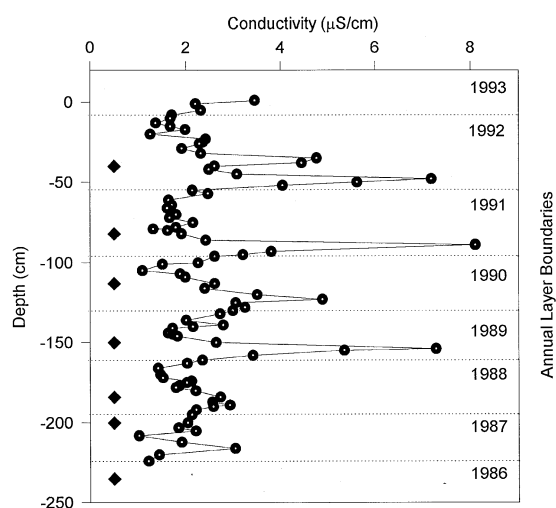


Fig. 1 Conductivity profile and identification of annual snow and firn layers; ● conductivity, ◆ summer ice layer, annual boundary

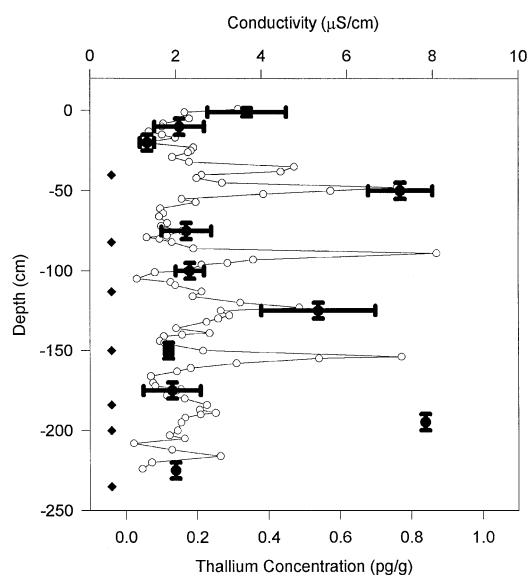


Fig. 2 Thallium profile with respect to conductivity and summer ice layers. ● thallium, ◆ summer ice layer, ○ conductivity

3.3 Thallium and cadmium profiles

Figure 2 shows Tl results (solid circles) at various depths along with the conductivity values (open circles). 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. We took replicate samples to give a measure of the sampling blank. A horizontal bar represents 2 standard deviations of the results obtained from the replicate samples of each depth, whereas a vertical bar represents the width of the snow sampled by the corer. As the standard deviation is generally small, it is reasonable to assume that the sampling blank is also small. Furthermore the analysis of the triplicate water blanks gave a very small value of 0.03 ng/l of Tl.

It is obvious from Fig. 2 that for the samples corresponding to the late winter-early spring period, the Tl values peak out the same way as the conductivity. Four such peaks are evident and coincide with the years 1993, 1992, 1990, and 1988 (Fig. 1). These points correspond to occasions when Arctic air is loaded with high levels of foreign pollutants and suspended particulates which often reduce visibility [23]. This phenomenon is known as the Arctic haze, which recurs 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 deposited [7, 24]. Earlier observations [19] showed that atmospheric trace metals and major ions in the Canadian Arctic also peak during the Arctic haze period. Also, the historical conductivity and acidity values in ice cores from the Agassiz ice cap peak as the Arctic air pollution does in December–April period [20]. Thus Tl results in accumulated snow layers are in

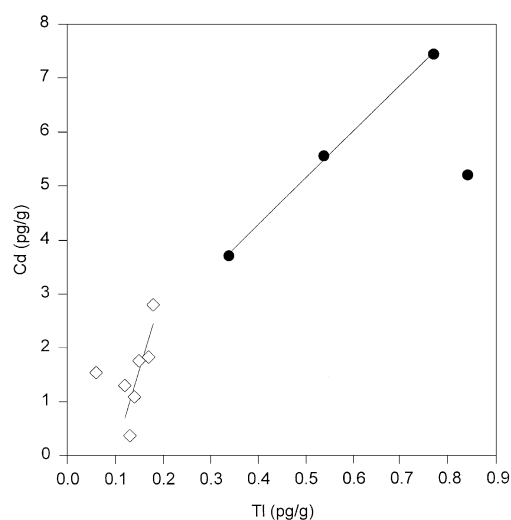


Fig. 3 A correlation plot between Cd and Tl, ◇ May to December, ● January to April

general accordance with the historical air pollution and snow chemistry. However, we are unaware of any other Tl profile reported for snow and ice in polar systems, Greenland or other ecosystems.

The cadmium profile also shows the same seasonal variations as the thallium profile which is evident in a plot of the concentration of Cd vs. Tl (Fig. 3). Although there is not a clear correlation between Tl and Cd, it does appear that two distinct lines may be drawn which could represent two predominant origins of metals, each origin being common to both metals. One line is for the points corresponding to the four thallium peaks discussed above (solid circles, January–April, Eurasian origin, main deposition), and one corresponding to low level Tl (open squares, May–December, uncertain origin, minor deposition).

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