Earth Sciences Scholarship

Earth Sciences

12-2001

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Recommended Citation

K. Yalcin and C. P. Wake, "Anthropogenic signals recorded in an ice core from eclipse Icefield, Yukon territory, Canada," Geophysical Research Letters, vol. 28, no. 23, pp. 4487–4490, Dec. 2001.

Anthropogenic signals recorded in an ice core from Eclipse Icefield, Yukon Territory, Canada

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Abstract. Trends in the annual flux of sulfate and nitrate in a new ice core collected at an elevation of 3017 m on Eclipse Icefield, 45 km northeast of Mt. Logan were examined to determine the effect of anthropogenic activity on precipitation chemistry in the remote northwest North America mid-troposphere. The annual flux of both sulfate and nitrate at Eclipse began increasing in the 1940s, demonstrating, for the first time, the anthropogenic sulfate and nitrate pollution of the northwest North American Arctic in an ice core from this region. Comparison of the Eclipse record with regional emission estimates for total sulfur and nitrogen oxides suggests that Eurasia is the dominant source of pollutants reaching Eclipse. The available data does not permit a confident assessment of the relative importance of European versus Soviet emissions in producing the observed trends in sulfate and nitrate at Eclipse.

1. Introduction

Ice core studies of sulfate and nitrate have revealed twentieth century increases in these species at nearly all northern hemisphere sites, reflecting the influence of fossil fuel combustion on precipitation chemistry in the remote troposphere. These sites include south Greenland [*Neftel et al.*, 1985; *Finkel et al.*, 1986; *Mayewski et al.*, 1986; *Mayewski et al.*, 1990; *Mayewski et al.*, 1993], central and north Greenland [*Mayewski et al.*, 1993; *Legrand and Mayewski*, 1997; *Fischer et al.*, 1998], Baffin Island [*Goto-Azuma and Koerner*, 2001], Ellesmere Island [*Barrie et al.*, 1985; *Koerner et al.*, 1999], and Spitsbergen [*Goto-Azuma et al.*, 1995]. The timing of these increases varies from site to site, allowing source regions to be identified by comparison with regionalized emissions data [*Goto- Azuma and Koerner*, 2001]. North America has been identified as the principal source region for south Greenland and Baffin Island [*Finkel et al.*, 1986; *Mayewski et al.*, 1986; *Mayewski et al.*, 1990; *Goto-Azuma and Koerner*, 2001], Eurasia for Ellesmere Island and Svalbard [*Barrie et al.*, 1985; *Koerner et al.*, 1999]; and both North America and Eurasia for central and north Greenland [*Legrand and Mayewski*, 1997; *Goto- Azuma and Koerner*, 2001]. Meanwhile, an ice core collected at an elevation of 5340 m on Mt. Logan in northwest North America showed no discernable increase in either species, suggesting the upper troposphere in this region remains unaffected by anthropogenic sulfate or nitrate [*Holdsworth and Peake*, 1985; *Mayewski et al.*, 1993].

The seasonal buildup of Arctic haze has been intensively studied since the 1970s throughout the Arctic [*Raatz and Shaw*, 1984; *Barrie*, 1986; *Lowenthal and Rahn*, 1985; *Shaw*, 1995], including sites in northwest North America. Arctic haze consists of anthropogenic sulfur, nitrogen, heavy metals, and organic compounds derived mostly from Eurasian sources, with concentrations highest during winter. Since Arctic haze is mostly confined to the lower 5 km of the troposphere, it is not surprising that an increasing trend in sulfate and nitrate associated with pollution of the Arctic air mass is not recorded on the summit of Mt. Logan as it lies above the influence of most continental aerosols [*Holdsworth and Peake*, 1985].

In this paper we use a new ice core from the Yukon Territory to evaluate the anthropogenic effect on precipitation chemistry in the remote northwest North America mid-troposphere.

2. Methods

A 160 m firn and ice core was recovered from Eclipse Icefield (60.51° N, 139.47° W, 3017 m elevation) in the summer of 1996 (Figure 1). Visible stratigraphy (location and thickness of ice layers) and density measurements were made in the field, and then the core was shipped frozen to the University of New Hampshire. The core was continuously sampled in 10 cm segments using stringent core processing techniques [*Mayewski at al.*, 1993] to ensure that samples were contamination free at the ng g^{-1} level. Blanks prepared on a frequent basis showed no contamination of samples during processing of the core. Samples were analyzed for
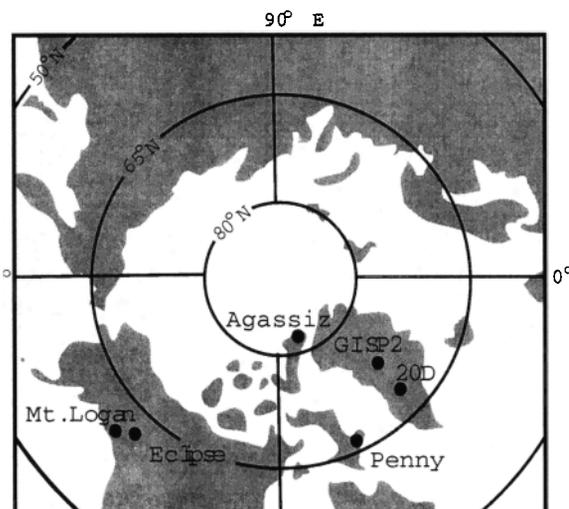

Figure 1. Location of circum- Arctic ice core records discussed in this paper.
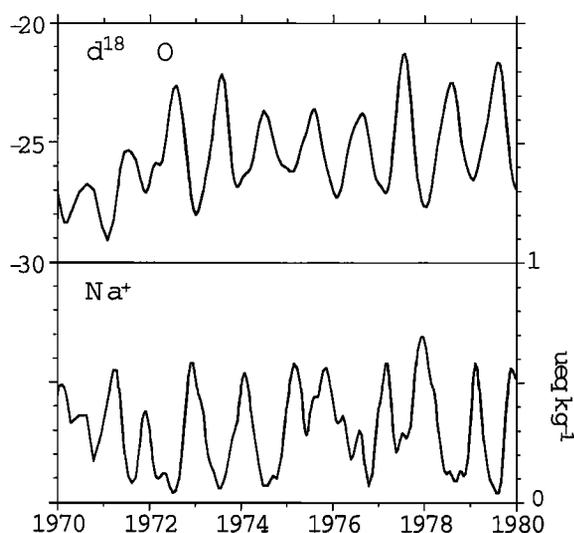
Figure 2. Seasonal signals in the smoothed oxygen isotope and sodium records from the Eclipse ice core used to date the core via annual layer counting.

major ions (Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$, SO$_4^{2-}$) using an ion chromatograph at the University of New Hampshire and for oxygen isotopes at the Department of Geophysics, University of Copenhagen, Denmark. A section of the core from 50 m to 76 m depth was analyzed for beta activity.

Analysis of the beta activity profile and comparison with real-time precipitation measurements from Whitehorse, YT [*Holdsworth et al.*, 1984] shows clear identification of the 1961 and 1963 beta activity peaks from atmospheric thermonuclear weapons testing. Average annual accumulation from 1963 to 1996 was 1.38 m water equivalent. The presence of discrete ice layers in the Eclipse ice core accounting for 5% of the net accumulation by weight suggests that a limited amount of surface melting occurs at the Eclipse site during summer. Meltwater percolation does not significantly alter the major ion records as evidenced by the preservation of clear seasonal signals in the major ion and oxygen isotope records, allowing dating of the core via annual layer counting (Figure 2). Several volcanic horizons are evident in the major ion record, including Redoubt, Alaska, 1989; Hekla, Iceland, 1947; and Katmai, Alaska, 1912; and have been identified by the major oxide composition of associated tephra [*Yalcin*, 2001]. Chronology of the Eclipse ice core is based on annual layer counting, the 1963 and 1961 beta activity reference horizons, and SO$_4^{2-}$ reference horizons provided by volcanic eruptions. Dating error in the core is estimated to be no more than +/- one year.

Trends in the annual flux of sulfate and nitrate at Eclipse were examined to determine the effect of fossil fuel burning on the glaciochemistry at Eclipse. Major ions were partitioned into sea- salt and non- sea- salt (nss) fractions using the ratios in bulk seawater [*Keene et al.*, 1986]. Sodium was the limiting species in 92% of the samples, with eight percent of the sulfate in the Eclipse ice core from sea salt. Samples with nss sulfate greater than one standard deviation above the mean were attributed to the effects of volcanic eruptions and removed. Annual mean concentrations of both nitrate and sulfate were then calculated and converted to fluxes, using the accumulation rate of the same year. We present fluxes rather than concentrations to facilitate comparison of our record to other ice core records with substantially different accumulation rates.

3. Results and Discussion

From the turn of the century through 1940, no overall trend is observed in either the sulfate or nitrate flux at Eclipse (Figure 3). The average annual flux during this period is 50 kg km^{-2} yr^{-1} of sulfate and 30 kg km^{-2} yr^{-1} of nitrate. Annual fluxes of both sulfate and nitrate began to increase in the 1940s and exhibit greater interannual variability. Annual sulfate fluxes reach a maximum around 80 kg km^{-2} yr^{-1} in the late 1960s and early 1970s, representing an increase of 30 kg km^{-2} yr^{-1} above earlier levels. Since that time, a decreasing trend in sulfate is suggested, with the exception of a high sulfate flux in 1995. Meanwhile, the annual nitrate flux has risen to near 70 kg km^{-2} yr^{-1}, more than a doubling of early twentieth century values. Nitrate fluxes peak in the mid 1970s, and have remained high through the mid 1990s.

To determine the seasonal timing of these increases, we calculated seasonal fluxes of both species for each year of our record. This was done by calculating an average winter and summer concentration for each year and multiplying by the accumulation for that season. Seasons were defined using the seasonal oscillations of the oxygen isotope record. These calculations reveal that the bulk of the increase in both species has taken place during the winter half of the year. Conversely, there is no clear trend in either species during the summer half of the record. These observations are consistent with
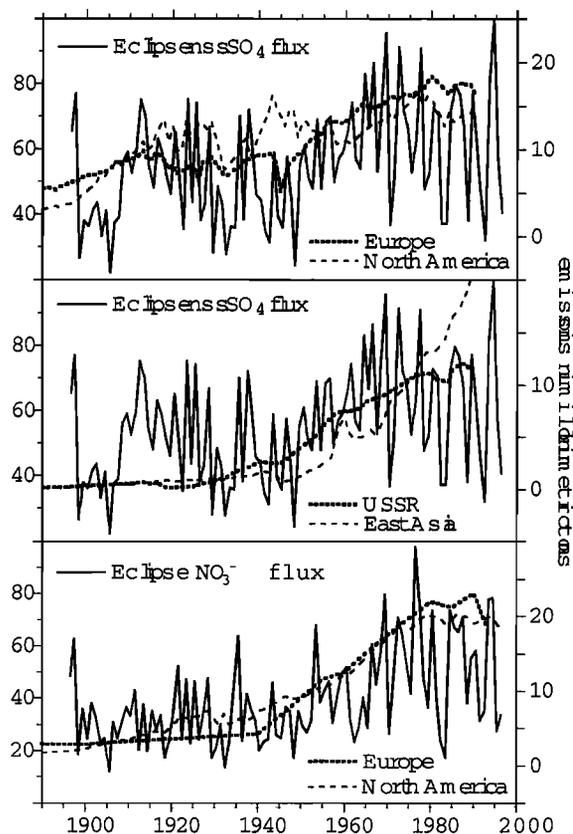

Figure 3. Annual fluxes of sulfate (top and middle) and nitrate (bottom) at Eclipse compared to anthropogenic emissions of sulfur [*Lefohn et al.*; 1999] and nitrogen oxides [*Erisman and Draaijers*; 1995; *U.S. EPA*; 1997] from potential source regions.

Table 1. Correlation Coefficients Between
Eclipse Sulfate Flux and Regional Emissions.

	Europe	USSR	North America	East Asia
before 1940	0.32	0.01	0.26	0.01
after 1940	0.44	0.45	0.03	0.29
overall	0.46	0.43	0.31	0.35

published reports on the seasonality of secular increases in sulfate and nitrate in circum- Arctic ice cores [*Koerner et al.*, 1999] and the occurrence of pollution aerosols in the high northern latitudes [*Barrie*, 1986].

We compared our ice core sulfate and nitrate records to regional emission estimates to determine if the increases in the ice core records are consistent with an anthropogenic source and to identify the dominant source region. Estimates of annual total sulfur emissions are available by country for the period 1850 –1990 [*Lefohn et al.*, 1999]; from this database we constructed regional emission estimates by year for four potential source regions: North America, Europe, the former Soviet Union, and East Asia. A regression analysis (Table 1) was used to help identify the principal source region(s) for anthropogenic sulfate deposition at Eclipse. During the period of consistently higher sulfate fluxes after 1940, the Eclipse sulfate flux correlates best with European and Soviet sulfur emissions, suggesting these regions are the most important anthropogenic sulfate sources at Eclipse. Meanwhile, the correlation is lower for East Asia and nearly zero for North America, suggesting these regions are less important sulfur contributors. Prior to 1940, the correlation is best with European emission trends, suggesting Europe is the most important anthropogenic sulfur source to Eclipse during this period. Our findings are consistent with previous studies on the origin of Arctic haze showing that Eurasia and in particular the former Soviet Union is the principal source of anthropogenic emissions responsible for Arctic haze [*Barrie*, 1986; *Raatz and Shaw*, 1984; *Lowenthal and Rahn*, 1985; *Shaw*, 1995].

There is a scarcity of long- term estimates of nitrogen oxide emissions; to our knowledge such estimates exist only for the United States [*U.S. EPA*, 1997] and Eurasia [*Erisman and Draaijers*, 1995]. Trends in nitrogen oxide emissions from both Eurasia (Europe and the former Soviet Union) and the United States closely resemble the pattern of nitrate increase at Eclipse. The similarity of Eurasian and U.S. nitrogen oxide emission trends makes it difficult to identify the predominant source region. Since Eurasia is clearly the major source region for anthropogenic sulfate reaching Eclipse, it is logical to assume that Eurasia is also the principal source region for anthropogenic nitrate. However, this cannot be conclusively demonstrated with the data available at present.

Comparison of our results with other circum- Arctic ice cores (Figure 4) demonstrates that Eclipse has seen increases in both sulfate and nitrate comparable to twentieth century increases observed in ice cores from Greenland [*Mayewski et al.*, 1990; *Mayewski et al.*, 1993] and the eastern Canadian Arctic [*Koerner et al.* 1999; *Goto- Azuma and Koerner*, 2001]. In calculating the annual fluxes shown in Figure 4 we did not estimate a non- sea- salt fraction or remove samples containing volcanic SO_4^{2-} as data from other ice cores was

only available to us at low resolution and/or only for anions. We stress that the sulfate fluxes in Figure 4 include a small sea- salt contribution and in years with major eruptions (i.e. Tambora 1815, Katmai 1912) are dominated by volcanic SO_4^{2-}. For consistency and to facilitate comparisons between sites, the Eclipse sulfate record presented in Figure 4 also represents the total sulfate flux without estimation of a non-sea- salt fraction or removal of volcanic SO_4^{2-}.

Fluxes of total sulfate and nitrate are higher at Eclipse than at other Arctic ice coring sites due to higher accumulation rates, more efficient rain- out, and closer proximity to ice-free areas. However, the 30 kg km^{-2} yr^{-1} increase in sulfate flux at Eclipse attributable to anthropogenic emissions is of the same magnitude as increases seen at other circum- Arctic sites. The Eclipse sulfate record is most similar to the sulfate record from Agassiz Ice Cap, Ellesmere Island. Both records show no definitive increasing trend in sulfate flux until the middle part of the twentieth century. Likewise, a decreasing trend in sulfate between 1910 and 1935 is seen at both Eclipse and Agassiz. Conversely, earlier increases in sulfate flux are seen at Penny Ice Cap as well as the 20D and GISP2 sites in Greenland. Although the magnitude of increase is similar between Eclipse and other Arctic ice coring sites, the records themselves are not, suggesting a unique source region(s) for anthropogenic sulfate at Eclipse. The nitrate increase at Eclipse is also comparable in both timing and magnitude to the increases seen in the 20D, GISP2, and Agassiz Ice Cap cores. Curiously, only a slight increase in nitrate flux is seen in the Penny Ice Cap core, for which no explanation is available at present [*Goto- Azuma and Koerner*, 2001].

Despite the proximity of Eclipse to Mt. Logan, it is not surprising that anthropogenic signals are recorded only at
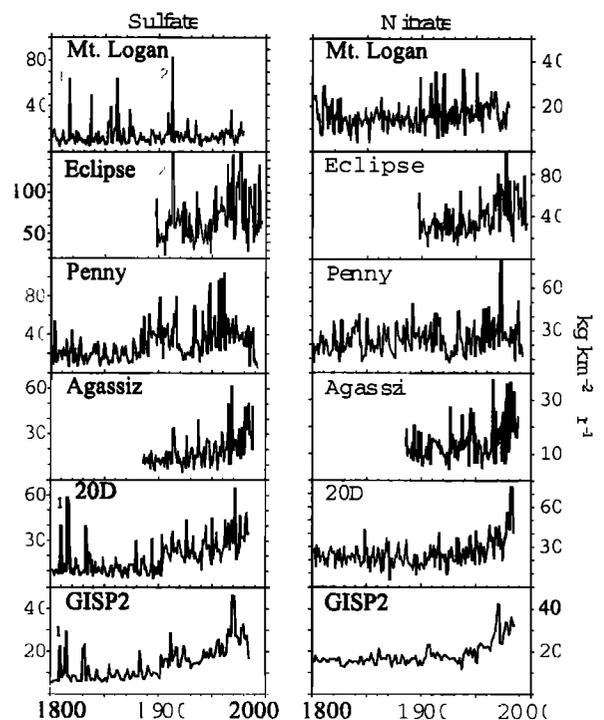

Figure 4. Circum- Arctic ice core records of sulfate (left) and nitrate (right) presented as annual flux in kg km^{-2} yr^{-1}. High sulfate fluxes prior to the onset of anthropogenic deposition are associated with major volcanic eruptions, notably 1. Tambora (1815) and 2. Katmai (1912) [*Simkin and Seibert*, 1994].

Eclipse. At an elevation of 3017 m, Eclipse is more than two kilometers below the ice core site at 5340 m on Mt. Logan. Aerosol concentrations, including the pollutants associated with Arctic haze, are known to decrease exponentially with height, to less than 30% of the near surface value above 5000 m [*Holdsworth et al.*, 1984]. Therefore, little in the way of anthropogenic sulfate and nitrate emissions reaches the summit plateau of Mt. Logan. Less snowfall and more windscour at the Mt. Logan site suggests that less anthropogenic sulfate and nitrate will be preserved as glaciochemical signals. Further evidence that Eclipse and Mt. Logan are sampling distinct types of air masses comes from earlier snowpit studies showing that Chernobyl nuclear fallout, the 1986 eruption of St. Augustine, and biomass burning plumes were recorded in snow at Eclipse but not at Mt. Logan [*Holdsworth et al.*, 1985]. Likewise, a comparison of the volcanic signals recorded in the Eclipse and Mt. Logan ice cores over their eighty year period of overlap reveals a detectable glaciochemical signal from at least thirty- two different eruptions at Eclipse but only eight at Mt. Logan [*Yalcin*, 2001]. These studies suggest that Eclipse provides a more detailed record of continental emissions than Mt. Logan due to its lower elevation, higher accumulation, and limited windscour. However, the Mt. Logan site provides a good record of distant aerosols since it samples the free troposphere, and is uniquely situated near the 500 millibar level for teleconnection studies [*Moore et al.*, 2001].

4. Conclusions

The Eclipse ice core provides, for the first time, a glaciochemical record of the anthropogenic sulfate and nitrate pollution of the northwest North American Arctic, giving a historical perspective to direct measurements of Arctic haze at Barrow and elsewhere. The principal source region of pollution aerosols reaching Eclipse appears to be Eurasia, consistent with previous work on the origin of Arctic haze. Future deep drilling efforts at a range of elevations in the St. Elias region of the southwest Yukon Territory will provide the longer glaciochemical records needed to place our record from Eclipse in the context of Holocene changes in precipitation chemistry in northwest North America.

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