

# The Arctic Atmosphere : Sulphur and Trace Metals

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## Article abstract

The atmosphere is the principal transport path to the Arctic of sulphur, toxic heavy metals and chlorinated organic compounds. One of the consequences of these pollutants is the winter phenomenon of arctic haze. Once a pollutant is emitted into the atmosphere, its transport to the Arctic is determined by the position of the polar front. In winter, the front expands to occupy a large fraction of the North American and Asian continents. Anthropogenic sulphur and metal input to the Arctic peaks in the winter half of the year and aerosol studies point to Eurasia as the major source region. By adding to these data, trace metal and other isotopic information indicative of particular sources (e.g., V, Pb,Zn), apportionment may become possible. Precipitation and lichen monitoring activities could provide useful additional information for characterizing change in the Arctic atmosphere.



## The Arctic Atmosphere: Sulphur and Trace Metals

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### SUMMARY

The atmosphere is the principal transport path to the Arctic of sulphur, toxic heavy metals and chlorinated organic compounds. One of the consequences of these pollutants is the winter phenomenon of arctic haze. Once a pollutant is emitted into the atmosphere, its transport to the Arctic is determined by the position of the polar front. In winter, the front expands to occupy a large fraction of the North American and Asian continents. Anthropogenic sulphur and metal input to the Arctic peaks in the winter half of the year and aerosol studies point to Eurasia as the major source region. By adding to these data, trace metal and other isotopic information indicative of particular sources (*e.g.*, V, Pb, Zn), apportionment may become possible. Precipitation and lichen monitoring activities could provide useful additional information for characterizing change in the Arctic atmosphere.

### RÉSUMÉ

L'atmosphère est la principale voie d'accès à l'Arctique des sulfures, des métaux lourds toxiques et des composés organochlorés. La brume arctique en hiver est l'une des conséquences de la présence de ces polluants atmosphériques. Une fois dans l'atmosphère, le transport du polluant jusque dans l'Arctique dépend de la position du front arctique. En hiver, le front s'étend et occupe une grande portion de l'Amérique du Nord et de l'Asie. L'apport maximal des sulfures anthropogéniques et des métaux en Arctique se situe dans la moitié hivernale

de l'année, et les études sur les aérosols indiquent que l'Eurasie en serait la source principale. En ajoutant à ces données celles sur les métaux traces et sur les profils isotopiques des particules, il est possible d'établir la répartition des points d'origine des particules (par ex. V, Pb et Zn). L'étude des précipitations et des lichens peut également fournir des informations additionnelles utiles permettant de caractériser les changements atmosphériques dans l'Arctique.

### INTRODUCTION

The arctic environment is extremely sensitive to perturbations from outside; signatures of climate change are expected to occur there first (Arctic Interactions, 1988). Its physical, ecological and chemical components are in delicate balance, governed by slow rates of biogenesis and chemical turnover. Arctic air pollution, commonly observed as arctic haze, is a well-documented phenomenon first observed 40 years ago. It is widespread and covers large parts of the northern hemisphere in the cold half of the year, peaking in the period from January to April (Barrie, 1986). While the absolute concentrations of pollutants are comparatively small and may not pose an immediate health threat to arctic residents, their effects on the radiation balance and chemistry of the atmosphere, as well as the potential for biomagnification, make them of concern.

The first symposium on arctic air pollution was held in Norway in 1977. This initiated the establishment of an international arctic aerosol sampling network. Since that time, several circumpolar, multidisciplinary studies have responded to this interest in arctic atmospheric chemistry. The ground-level monitoring network in North America had been collecting and archiving aerosol measurements at Point Barrow, Alaska since 1976 but additional stations were established in Alert, Mould Bay and Igloolik in Canada in 1980. Since 1981, four arctic air chemistry specialty symposia have been held in the United States, Canada, Norway and Denmark. The Arctic Gas and Aerosol Sampling Program (AGASP) operated during 1983. In 1988 the National Aeronautics and Space Administration-sponsored Global Tropospheric Experiment-Arctic Boundary Layer Expedition (GTE-ABLE 3A) extended the ground-level measurements to an altitude of 6 km over Alaska. In 1990, ABLE 3B was performed over the mid continental and

eastern regions of Canada and, in recognition of the fact that arctic atmospheric chemical reactions change quite drastically between winter and summer, the Polar Sunrise Experiment was initiated in 1992. Its primary objective was to investigate lower tropospheric ozone depletion at Alert around polar sunrise, but was also concerned with characterization of long-range transport of air pollutants to the high Arctic (Barrie *et al.*, 1994). The Northern Contaminants program of the Canadian Arctic Environmental Strategy is in the last year of 6 years. Measurements of numerous organochlorines (*e.g.*, PCBs, pesticides and herbicides) have been taken at Alert, NWT, Tagish, Yukon (near Whitehorse), and Cape Dorset, NWT. In addition, measurements of metals and organochlorines were made for 2 years in eastern Russia at Dunai Island.

The purpose of this paper is to summarize the state of knowledge with respect to the Canadian arctic atmosphere in general, and its pollution in particular. It will focus on two types of atmospheric contaminants: sulphur and trace metals. Organic compounds including PCBs and PAHs, as well as UVB penetration, will be dealt with in future in separate contributions. This review will begin with a characterization of arctic haze including its composition and spatial and temporal variability. Meteorological factors affecting transport to the Arctic will then be addressed with probable source regions identified. This will be followed by a treatment of source identification and apportionment techniques including the stable isotopes of sulphur and lead, multivariate statistics, and chemical enrichment factors. Finally, suggestions for future work will be proposed.

### ARCTIC HAZE

Anthropogenic pollution that reaches the Arctic through the atmosphere and causes a reduction in visibility has been labeled "arctic haze." When the air is clear, one can theoretically see 200-300 km through the atmosphere. Haze can decrease this distance to less than 50 km. Preliminary investigations into the source of arctic haze were based on its chemical composition. Rahn *et al.* (1977) determined that while the particulate matter in air between distinct haze layers was of anthropogenic origin, the haze layers themselves were of crustal composition, likely originating from Asian deserts. These results were thought to mean

that the haze was primarily of natural origin. However, during the winter of 1976-1977 Rahn and McCaffrey (1979, 1980) noticed a strong seasonal variation in the haze particles. They were 20-40 times more abundant in winter than summer, and a marked enrichment in combustion-derived vanadium indicated that they were almost exclusively of anthropogenic origin. Only in summer were particles dominated by the natural sources of sea salt and crustal dust.

The major component of arctic particulate matter is sulphate. The density of particles <1mm equivalent scattering diameter (ESD) is consistent with a composition of sulphuric acid or ammonium bisulphate. These fine particles also contain black carbon, lead and many other anthropogenic metals (Barrie, 1996). In the polluted winter, black carbon comprises between 2.8% and 11% of the total aerosol mass. Larger particles are a mixture of wind-blown dust and sea salt particles. Typical concentration profiles for three stations in the Canadian Arctic are presented in Table 1. Sulphate is usually associated with acid deposition and based on a few precipitation measurements taken during the summer and fall; it is considered to be the dominant source of acidity in the Arctic (Galloway *et al.*, 1982; Dayan *et al.*, 1985). The acidity of snow has also been measured on the Agassiz glacier on northern Ellesmere Island. It is well correlated with depth of measurement and shows a strong seasonal variation paralleling that of arctic air pollution. Maximum ice core acidity has been compared with sulphur dioxide emissions in Europe and Asia, suggesting the origin of the correlation (Barrie *et al.*, 1985). However, this is not the primary reason for concern over atmospheric sulphur compounds in the arctic atmosphere. Sulphate particulate matter scatters solar radiation, thus reducing visibility, and soot particles both trap solar radiation in the atmosphere and increase the blackness of the snowpack (Clarke and Noone, 1985). Both of these features make arctic sulphur of more concern to the issue of global warming than acidification. Furthermore, sulphates may affect the hydrological cycle by altering the size distribution and hence, fallout rate, of diamond dust snow crystals (Blanchet and Girard, 1995).

Atmospheric sulphur at any site potentially combines natural and anthropogenic components, and can exist as solid or liquid particulate matter or as a gas.

Natural sources of emissions to the atmosphere include sea spray ( $\text{SO}_4^{2-}$ ), biological sources [dimethyl sulphide (DMS), carbonyl sulphide (COS), hydrogen sulphide ( $\text{H}_2\text{S}$ )], and volcanoes [sulphur dioxide ( $\text{SO}_2$ )]. Anthropogenic emissions to the atmosphere are mainly released as  $\text{SO}_2$  (a small fraction is released in the form of particulate sulphate) and are generated by industrial processing of native sulphur, sulphide ores, coal and petroleum.  $\text{SO}_2$  is irreversibly oxidized to  $\text{SO}_4^{2-}$  either in the gas phase by OH radicals or in the aqueous phase by  $\text{H}_2\text{O}_2$  or  $\text{O}_3$  in cloud and rain droplets. This process is much slower in the winter in the absence of sunlight, so the abundance of  $\text{SO}_4^{2-}$  relative to  $\text{SO}_2$  is expected to be greater in the sunlit half of the year than in the remaining dark half.

Sulphur transport to the Arctic was modelled by Barrie *et al.* (1989) as a function of month, longitude and altitude. A primary objective was to determine the frac-

tion of anthropogenic sulphur emissions released from mid-latitudes that enters the Arctic. The results are given in Table 2 and confirm the qualitative evidence pointing to Eurasia as the main source of sulphur entering the Arctic. On an annual basis, 4.8% of the anthropogenic emissions of North America and Eurasia enter the Arctic, contributing 6% and 94%, respectively.

The size distribution of the haze offers some insight into processes governing its formation and removal. The most abundant particles are in the range of 0.005-0.2 mm in diameter (Barrie and Bottenheim, 1991). This overlaps two size ranges in the distribution of aerosol mass. Particles from 0.005-0.05 mm are in the "nucleation mode." The rest of the haze particles belong to the lower size range of what is known as the "accumulation mode" (0.05-1 mm). Accumulation mode particles scatter solar radiation more efficiently, and have the longest

**Table 1** Mean annual concentrations ( $\text{ng}/\text{m}^3$ ) of Canadian Arctic aerosol constituents.

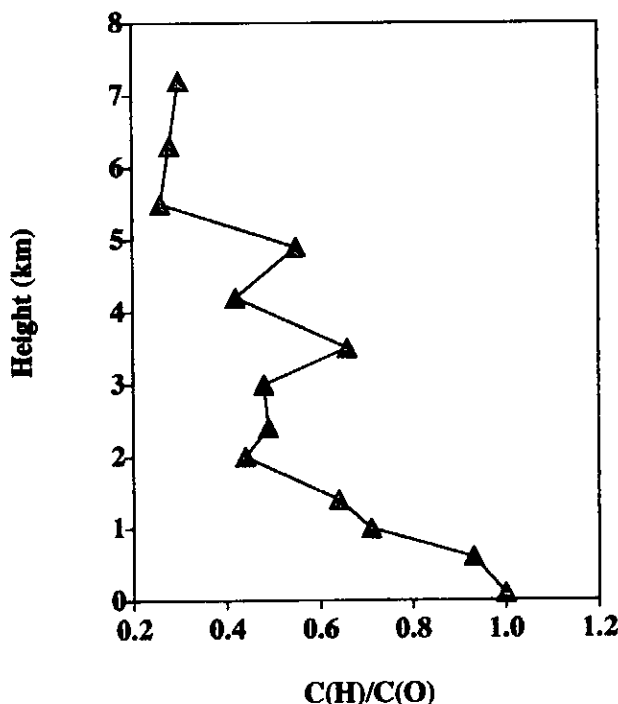
Substance	Alert	Igloolik	Mould Bay
<b>ANTHROPOGENIC</b>			
Cr	0.30	0.15	0.32
Cu	1.33	1.13	1.02
Mn	1.49	0.71	0.87
Ni	0.38	0.27	0.45
Pb	1.70	3.84	3.22
Sr	0.57	0.67	0.41
V	0.62	0.47	0.56
Zn	3.48	3.45	3.79
H <sup>+</sup>	7.4	5.9	9.2
$\text{NH}_4^+$	102	95	125
$\text{SO}_4^{2-}$	1052	966	1036
$\text{NO}_3^-$	74	71	67
<b>HALOGENS</b>			
Br	8.9	14	16
I	0.49	1.03	0.46
F	7.0	5.8	6.7
<b>SEA SALT</b>			
Na	158	313	243
Cl	182	505	354
K	16	31	11
Mg	84	129	63
<b>SOIL</b>			
Al	146	—	—
Ba	0.37	0.21	0.47
Ca	139	94	29
Fe	86	21	29
Ti	1.31	—	0.24
P	1.67	0.93	1.12

Adapted from Barrie and Hoff (1985)

**Table 2** Sulphur emissions and flux to the Arctic from the Northern Hemisphere.

Source Region	SO <sub>2</sub> Emissions (Mt a <sup>-1</sup> )		Flux to Arctic (Mt a <sup>-1</sup> )		% Emissions Entering Arctic
		%		%	
Western Europe	10	21	0.56	25	5.5
Eastern Europe	11	23	0.63	27	5.9
Former Soviet Union	11	24	0.96	42	8.5
North America	15	32	0.12	06	0.8

Adapted from Barrie (1988)



**Figure 1** Mean vertical profile of anthropogenic aerosol concentration based on aircraft measurements of particulate carbon (C) during March and April, 1984. The concentration of carbon at height H or C(H) is normalized to the concentration at the surface or C(O) (from Barrie, 1986).

residence time of any particle size in the atmosphere (Ibrahim *et al.*, 1983). Most of the total mass of particulate NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, V, Ni, Cr, Pb, Cu, Br and I is in the accumulation mode. Na<sup>+</sup>, Mg<sub>2</sub><sup>+</sup> and sea salt Cl<sup>-</sup> dominate the super micrometre particles. Barrie (1986) published data on the average vertical distribution of suspended particulate matter in the arctic atmosphere based on aircraft observations of light scattering. Most of the pollution is concentrated in the troposphere below 5 km, with the highest concentrations in the lowest 2 km (Fig. 1). Spatially, there is a minimum in sulphate concentration located in the Greenland and eastern Canadian Arctic, between the influence of Eurasian and eastern North American sources. On average, sulphate concentrations measured in the winter haze are a factor of 2-3 lower than those measured in rural areas of eastern Canada and the United States.

While sulphate is the most abundant constituent, trace metals are also an important component of arctic particulate pollution. Metals accumulate in the environment, altering the conditions under which plants and wildlife grow. Six important metals of primarily anthropogenic origin are zinc (Zn), vanadium (V), mercury (Hg), cadmium (Cd), lead (Pb) and arsenic (As) (Table 3). They are all of concern because of their potential for immediate or long-term toxicity to humans and animals. Metals are also important as tracers of long-range transport of pollution to the Arctic (see below). Hg exists in the atmosphere primarily in the gas phase. Anthropogenic sources include Zn, Cu and Pb smelting; burning of fossil fuels; chlorine production in chlor-alkali plants; production and use of agricultural pesticides; and waste incineration (Lindqvist and Rodhe, 1985). Hg also enters the air through natural degassing processes in aquatic and marine environments. Annual emissions of natural and anthropogenic Hg to the at-

**Table 3** Primary sources of elements typically measured in arctic aerosols.

Element	Primary Sources	Interference Factor*
Aluminum	crustal	
Antimony	combustion	
Arsenic	volcanic, anthropogenic	300
Barium	crustal, diesel fuel	
Bromine	sea salt, car exhaust	
Cadmium	mixed anthropogenic	760
Lead	smelters, (gasoline)	2,400
Manganese	crustal, (gasoline)	52
Mercury	smelting, combustion	100-200
Nickel	crustal, oil combustion	180
Sodium	sea salt	
Vanadium	crustal, oil combustion	320
Zinc	combustion, smelting	78,500

\* Interference Factor =  $\frac{\text{Anthropogenic sources}}{\text{Natural sources}}$

mosphere are estimated to be 3600 tonnes and 2600 tonnes, respectively (Nriagu and Pacyna, 1988). Most anthropogenic Cd comes from coal and oil combustion, Cu-Ni-Zn production, waste incineration, and cement manufacture. Anthropogenic and natural emissions are estimated to be 7600 tonnes per year and 1200 tonnes per year, respectively (Nriagu and Pacyna, 1988). Anthropogenic emissions of Pb greatly exceed natural emissions to the atmosphere (332,000 tonnes per year *versus* 18,000 tonnes per year). Major anthropogenic sources are automobile exhaust, non-ferrous metal production and fossil fuel combustion. Since the 1970s auto exhaust Pb emissions have been essentially eliminated in North America and reduced by 30% to 50% in Europe. Arsenic exists in the atmosphere mostly as particulate matter (Sweet and Gatz, 1987) although its exact chemical form is poorly known. It has both natural and anthropogenic sources with annual emissions estimated at 6.4 tonnes and 19 tonnes, respectively. These include coal combustion, Cu-Ni smelting and agricultural pesticides. Vanadium and zinc are associated with oil combustion; wood burning and incineration are also important for zinc.

Most concentration and deposition information on these metals has been gathered from aerosol work done in Canada (Barrie and Hoff, 1985; Barrie and Barrie, 1990), Greenland (Heidam, 1984), Barrow, Alaska (Bodhaine, 1986), Sweden (Heintzenberg *et al.*, 1986) and Norway (Ottar and Pacyna, 1986; Maenhaut *et al.*, 1989) and from measurements made on arctic snowfall (Mart, 1983). Pb has been extensively measured (Sturges and Barrie, 1989). Aerosol measurements have been made in the Canadian Arctic since 1980. Excess sulphate and non-crustal vanadium concentrations vary seasonally as do other anthropogenic constituents (Cr, Cu, Mn, Ni, Pb, Zn). Concentrations peak in late January-February. Halogen concentrations (Br, I, F) peak later in the spring (March-April) while sea salt constituents (Na, Cl, Mg, K) peak between September and January. These variations are similar to and in phase with observations made in Alaska and the Norwegian Arctic, although concentrations in Canada are 15 - 25% lower. Soil constituents (Al, Ba, Ca, Fe, Ti) do not display regular seasonal variation.

The fluxes of three anthropogenic

trace metals (Cd, Pb and V) to the Arctic were modelled by Akeredolu *et al.* (1994) based on emission fields for Eurasian sources and air mass back trajectories. The results are displayed in Table 4. Fluxes were highest in the lower troposphere, below 1 km. Between 11% and 22% of the trace metals entering the Arctic are estimated to be deposited there.

#### METEOROLOGY OF ARCTIC AIR POLLUTION

Once a pollutant is emitted into the atmosphere, meteorological conditions determine its mixing and transport. Atmospheric circulation controls the movement of substances into, through and out of the arctic ecosystem. The Arctic can be defined (for pollution purposes) in terms of its meteorological boundary termed the polar front. The arctic air mass is characterized by: 1) sub-zero temperatures during much of the year; 2) little precipitation; 3) stable stratification preventing strong vertical mixing; and 4) low levels of solar radiation, especially during the winter. Strong thermal inversions are a common occurrence in the Arctic and sub-Arctic. These inversions act as barriers to mixing and dilution of atmospheric pollutants which can lead to elevated, and at times hazardous, concentrations. The main type of inversion is caused by radiative cooling of the Earth's surface. If this heat loss is not compensated for by solar insolation (*i.e.*, at night or during the winter), substantial cooling of the surface occurs and an inversion develops (Jaffe, 1991). Boundary layer inversions also occur in the Arctic, mainly in the summer, due to warm maritime air overriding cooler continental air. The polar front separates the tropical and Arctic air masses. In winter it lies between 40°N and 50°N while in summer it shifts to between 60°N and 70°N (Fig. 2). Winter flow patterns are driven by the strong Siberian anticyclone favoring movement from the Eurasian continent into the Arctic and then out over the North

American continent, or into major cyclonic regions in the Aleutians and southern Greenland (Barrie *et al.*, 1992). In summer, strong south-to-north transport is replaced by weaker flow in the opposite direction as the Siberian high dissipates. During this season, movement into the Arctic from the North Pacific and North Atlantic is more frequent.

The characteristics of the arctic air mass in summer and winter make the problems of the Arctic unique. Seasonal variation in position of the polar front results in a weak connection of the Arctic to source regions located to the south of the front in the summer, whereas in the winter the same source regions are located north of the front. Eurasian sources that are available to the Arctic in winter are more than double those in North America. In winter, when the Arctic is most polluted, the predominant pathway of windborne pollution from the high emission areas of eastern North America to the pole is east over the Atlantic, whereas Eurasian pollution travels north-east over snow-covered land-ice areas. The former path is exposed to more precipitation or aerosol removal opportunities resulting in a smaller chance of the aerosol reaching the Arctic.

#### MEASURING DEPOSITION

Pollutants are deposited to the arctic ecosystem through precipitation scavenging from the air and dry deposition to the surface. Information on deposition amounts can be obtained directly through analysis of precipitation and snowpack samples, or indirectly by measuring concentrations in air and estimating deposition using various parameterization schemes which describe the deposition process. Data have been successfully obtained from air, snowpack and glacial ice sampling but there is a distinct lack of routine precipitation chemistry measurements (Barrie, 1986). There are two reasons for this: one is that very little precipitation falls during the winter (typically

**Table 4** A comparison of arctic flux of trace elements with their estimated deposition.

Element	Arctic Flux (t a <sup>-1</sup> )	European Emissions (t a <sup>-1</sup> )	Estimated Deposition (t a <sup>-1</sup> )	%
Cd	47	1140	7	14
Pb	2400	80,839	258	11
V	474	27,374	102	22

Adapted from Akeredolu *et al.* (1994)

<5 mm liquid water equivalent per month); the second is that quality control is very difficult owing to practical problems such as blowing snow and low pollutant concentrations.

Since direct sampling of the arctic atmosphere through aerosols or precipitation may not always be possible or convenient, other kinds of sample types may be employed. Among the most promising of these is lichen. Lichens afford an opportunity for sampling on a time scale possibly long enough to effectively monitor changes in atmospheric composition over tens to hundreds of years, depending on the species. Lichens are slow growing and extremely effective in absorbing soluble and insoluble mineral nutrients from ambient air and precipitation with little subsequent loss (Easton, 1994). In fact, some genera have annual branching patterns.

It is usually assumed that the origin of

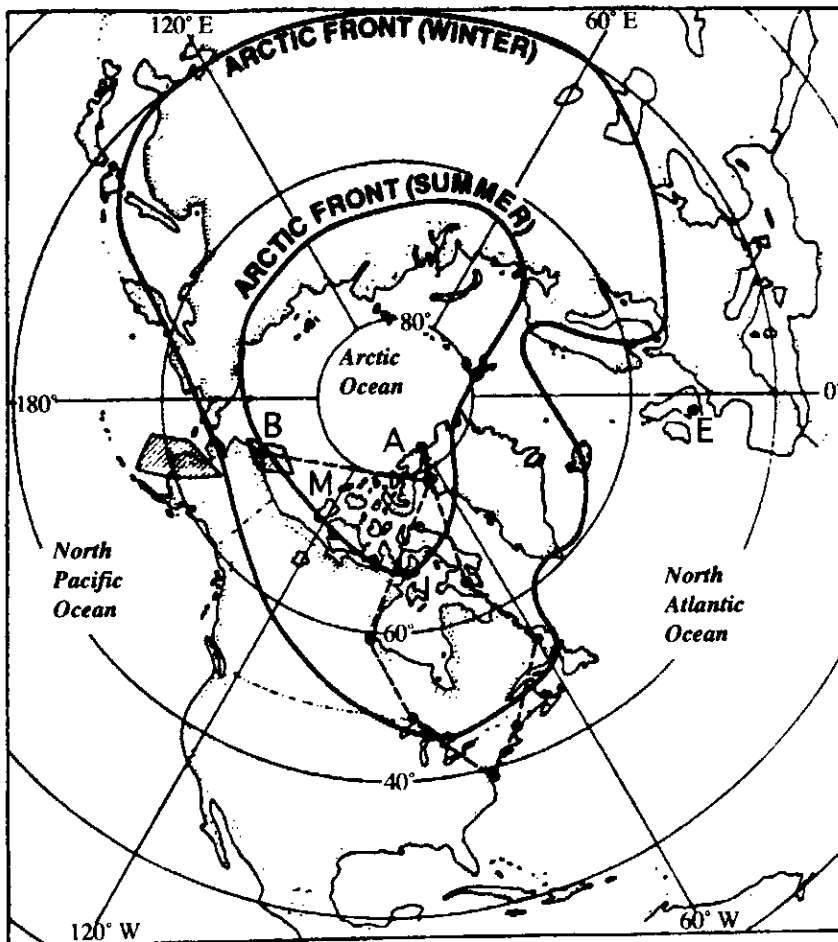
the contaminants in the lichens is the atmosphere. This is reasonable since lichens have no roots or vascular system and no cuticle on their outer surfaces. However, many lichen species are substrate-specific, implying a nutrient connection. This makes epiphytic lichens particularly useful since they apparently derive only structural support from their plant substrate. The high ability of lichens to intercept dry and wet deposition is related to their large surface area.

**SOURCE IDENTIFICATION AND APPORTIONMENT TECHNIQUES**

Tracers from particular source regions or industrial processes, including various metals with characteristic origins, have been used to document the dispersal of pollutants by atmospheric transport. In fact, long-range atmospheric transport may be the most important mode of global transport for a variety of trace sub-

stances and elements. Among the first to be used in the Arctic was a tracer system proposed by Rahn (1981), involving Mn/V ratios. Both Mn and V are emitted from anthropogenic sources; mostly coal and oil combustion. Based on measured ratios it was determined that industrial sources in Europe and the former Soviet Union were the major contributors to the arctic aerosol. Similar application of an additional group of elements (As, Se, Zn and In) confirmed the use of this technique and the conclusions previously derived. These elements are pollution derived, capable of long-range transport and easily measured.

Application of statistical methods, such as factor analysis, to data on element concentrations in the Greenland aerosol has shown that it may be composed of three to five statistically independent components, some natural and some anthropogenic (Heidam, 1986). They include two crustal components (containing loadings of Al, Si, Ti, Fe) and a marine component (Cl) accounting for 40 to 60% of the variance. Also present were a combustion component from very distant industrial areas (S, Br), an anthropogenic component likely originating in the Urals (Zn, Cu), and an engine exhaust component (Pb). Maenhaut *et al.* (1989) obtained a three-component solution for sources of aerosol in the Norwegian Arctic. They applied both absolute principal component analysis (APCA) and chemical mass balance (CMB) techniques. The first component was anthropogenic (S, Zn) but had some contribution from crustal sources (Al, Si, Mn, Fe). The second component was interpreted to be dominantly crustal, since elements were present in roughly crustal proportions, and the third component indicated a sea salt contribution (Na, Cl). Because of the difficulty encountered in separating the crustal from the pollution signatures, Maenhaut *et al.* (1989) attempted CMB source apportionment using a set of elemental signatures obtained by Lowenthal and Rahn (1985). It was determined that North American sources contributed less than 10% of the pollution at the Norwegian site, so these were excluded. Potential pollutant sources did include the United Kingdom, Western Europe, Eastern Europe and the former Soviet Union, although chemical signatures could not distinguish among the European sources. Nevertheless, it was concluded that 60% of the winter pollution was from sources in the former So-



**Figure 2** Seasonal variation in position of the arctic polar front is shown by the two solid lines. In winter the front extends south to include pollutant source regions in Eurasia and southern Canada. In summer it contracts to cover a much smaller area contained within the boundary defined by the Arctic Circle. Letters denote sampling stations for various atmospheric components: A-Alert; B-Barrow; E-England; I-Igloolik; M-Mould Bay. Shaded regions and dashed lines denote study areas and flight paths from NASA GTE-ABLE 3A (from Li *et al.*, 1993).

viet Union, while in summer this declined to 25%. Factor analysis was also applied to several years of data collected at three stations in the Canadian Arctic (Alert, Mould Bay and Igloolik). The results indicated the same three groupings: anthropogenic, crustal and sea salt. Barrie and Barrie (1990) reported principal components analysis (PCA) of Alert aerosols. They were the first to find a polar sunrise component related to gas-to-particle conversion. It consisted of a loading by sulphate, bromide and iodide.

Metals can also be measured in lichens. Their use in atmospheric deposition monitoring, particularly around point emission sources is well established (Nieboer and Richardson, 1981; Puckett, 1988; Nash and Gries, 1995a, b). Contaminant distribution patterns have also been studied in several Arctic-northern Taiga localities. The most extensive data set for a relatively pristine location is that of Puckett (1978) for the Northwest Territories. It included 45 sites throughout an area extending from Great Slave Lake north to northern Ellesmere Island and from the Mackenzie Valley to eastern Baffin Island. Twenty species of lichen and 20 different elements were involved, however, the study focussed on one widely distributed, green algal species of lichen. (It has been reported that cyanolichens in general may have higher concentrations of many elements (Tomassini *et al.*, 1976). While a few sites were affected by anthropogenic activities, none were impacted by major industrial development. Crustal enrichment factors (EF) were used to identify large, non-crustal components of metals in the lichens. Scandium was the main reference element used. Highest EF values (>100) were recorded for Sb, Cl, Pb and S. Cl and S were attributed in part to marine aerosol influences since higher values were found near the coasts, although long-range transport of S is also known to occur. High Pb EF values occurred primarily around small settlements and airports and likely originated from gasoline combustion.

The varying sources of sulphur contributed to the atmosphere show a wide range of  $\delta^{34}\text{S}$  values, making the isotopic composition of sulphate useful for identifying and apportioning contributions. Sulphur isotopic studies show the effect of prevailing winds in transport of atmospheric sulphur compounds both on synoptic (eastern North America) and local (Bonavista peninsula) scales. In eastern

North America, sulphur isotopic variation is limited, ranging from +2‰ to +5.5‰. These values reflect the significant contribution of fossil fuel combustion to the atmospheric sulphur burden. In Newfoundland, the picture is somewhat different. There is a considerable range in sulphur isotopic composition with coastal areas (+15‰) several per mil higher than inland localities (+10‰) due primarily to higher sea salt contributions (Wadleigh *et al.*, 1996). The lowest values (+7‰ to +8‰) (Jamieson, 1996; Wadleigh *et al.*, 1996; Jamieson and Wadleigh, 1995) are found in the urban centre of St. John's and surrounding major point sources.

Sulphur isotopes have been applied recently to elucidate the origin of arctic haze (Nriagu *et al.*, 1991).  $\delta^{34}\text{S}$  values for the haze average +5.5‰ in winter and 9‰ in summer (Fig. 3). The overall average is slightly higher than that of urban and rural areas of central and parts of eastern North America reported above. It is similar to averages reported for Newfoundland and maritime Canada, but the seasonal trend is reversed with higher values occurring in the summer months when sea salt and biogenic sources dominate sulphur in the arctic atmosphere. This evidence suggests that atmospheric sulphur in the Arctic has a different origin from that in southern Canada. Limited isotopic measurements on aerosols from European and Asian sources (determined from air mass back trajectory analysis) fall within the same range as the arctic winter samples, supporting previous studies identifying these areas as major source regions for the haze. More measurements are needed

of the isotopic composition of sulphur pollution from Eurasian aerosols.

Li and Barrie (1993) applied sulphur isotopic compositions and a multivariate statistical procedure (absolute principal component analysis) in combination with chemical data on archived samples to apportion biogenic, sea spray and anthropogenic sources of sulphur to the arctic aerosol. They determined that the biogenic contribution was 25-30% during June and August and <14% in other seasons. Sea salt contributions ranged between 1% and 8% over the sampling period. Anthropogenic sources contributed between 62% and 74% of the sulphate during the summer months and more at other times of the year.

Another technique that may be used to identify the source of a pollutant is the analysis of stable lead isotopes. Lead used as a gasoline additive comes from an ore body with an isotopic composition reflecting its geologic history. Since the relative amounts of the four stable isotopes of Pb remain unaltered by normal physical and chemical processes, by measuring their ratios in atmospheric aerosols it is possible to obtain information on their sources. Pb isotopic compositions were measured on aerosols collected at Alert and Mould Bay between November 1983 and May 1984 in an attempt to gain such specific source information (Sturges and Barrie, 1989; Hopper *et al.*, 1991). No temporal trends were observed for either station and the ratios all fell within a fairly narrow band. The mean ratio of  $^{206}\text{Pb}/^{207}\text{Pb}$  ( $1.16 \pm 0.01$ ) was closer to eastern European than to either Canadian (lower) or United States

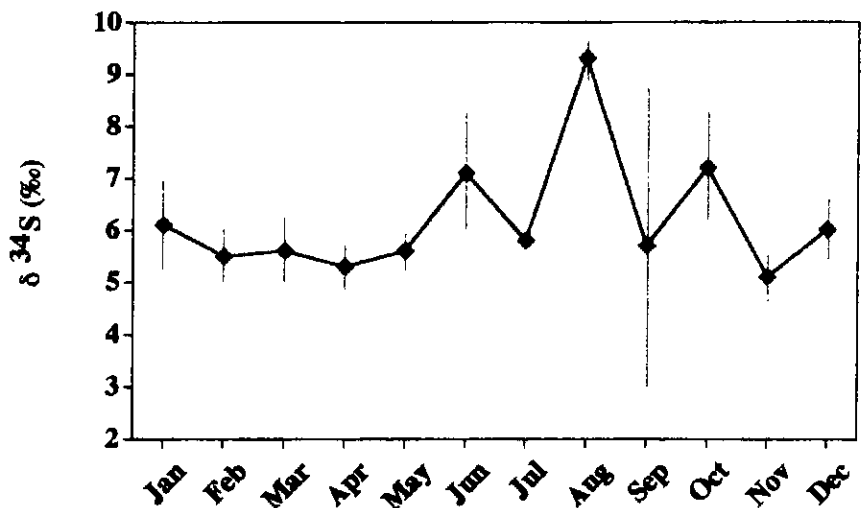


Figure 3 Monthly average sulphur isotopic composition of arctic sulphate aerosols collected at Alert, NWT. Vertical bars indicate the range of values (from Nriagu *et al.*, 1991).

(higher) averages, consistent with the suggestion that northern Eurasia is principal source area for arctic air pollution (Fig. 4). This type of analysis can also be carried out using lichen samples. Carignan and Gariepy (1995) used the isotopic composition of lead in epiphytic lichens to determine the sources of atmospheric lead emissions in southern Quebec.

One of the most comprehensive attempts at source apportionment was made by Barrie *et al.* (1992). They developed a five-compartment model to illustrate the state of knowledge of contaminant pathways into arctic northern systems. It consists of atmosphere, land (including freshwater), surface ocean, deep ocean and sediment reservoirs, and four types of pathways: 1) transport by air or water into a reservoir, 2) transformation within a reservoir, 3) sources within a reservoir and 4) exchange between reservoirs. The fluxes and pathways of acids are among the best understood within this framework, and they were utilized to estimate what fraction of total sulphur emissions are deposited within the Arctic. Apparently only  $\approx 12\%$  of the sulphur entering the Arctic is deposited there, the rest being transported back out of the region.

#### FUTURE WORK

Several studies have been reported in the literature dealing with aerosol chemistry in the Arctic, particularly in connection with the seasonal phenomenon of arctic haze. However, few studies have

examined arctic atmospheric composition utilizing lichens. The genera of most interest include *Alectoria*, *Bryoria*, *Cladonia* and *Hypogymnia*, which are reported in numerous locations throughout the Arctic. There is little or no fractionation of sulphur isotopes during plant metabolism, so lichens can preserve the isotopic signature of the atmosphere in which they grow. Recent work in Newfoundland has demonstrated that sulphur isotopic measurements made on *Alectoria sarmetosa*, a species of fruticose, epiphytic lichen, correlate well with measurements of precipitation sulphates (Wadleigh *et al.*, 1996). This provides an important link in the study of atmospheric contaminant measurements since it allows specific rather than relative comparisons to be made with direct sampling techniques. Analysis of trace metals in the lichens can help distinguish anthropogenic sources as well as offer specific information on long-range transport and deposition to the surface. There is still a need, however, to study the relationship between atmospheric concentration, deposition and lichen composition, especially for semivolatile compounds like Hg, organochlorines and PAHs.

Much of the concern surrounding arctic haze relates to its connection to the issue of global warming. It is thought to increase albedo, possibly counteracting some of the effects of higher concentrations of greenhouse gases. Lichens may be of use in resolving this issue as well. The algal component of all lichens photosynthesizes to provide energy for the fungal component. The carbon isotopic composition of the lichen may therefore be related to that of the atmospheric  $\text{CO}_2$  used during photosynthesis, which may in turn enable monitoring of this parameter.

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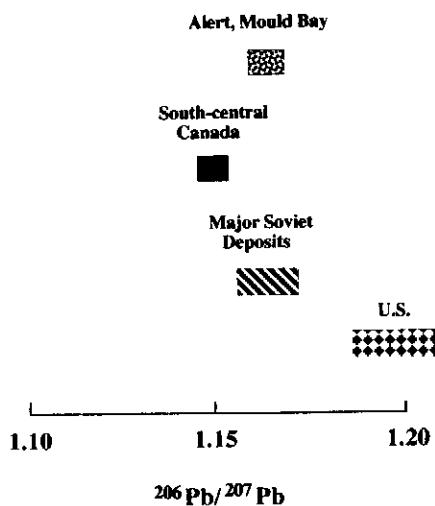


Figure 4 Stable lead isotopic compositions of arctic haze measured at Alert and Mould Bay, NWT compared to the range of values for potential source regions (from Sturges and Barrie, 1989).



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