

Acidifying Pollutants, Arctic Haze, and Acidification in the Arctic

The Arctic Haze Phenomenon

It has been more than 50 years since observations of a strange atmospheric haze, of unknown origin, were reported by pilots flying in the Canadian and Alaskan Arctic. Based on measurements at McCall Glacier in Alaska, Shaw and Wendler (1972) noted that the turbidity in the air reached its peak in spring. The first measurements of the vertical structure of the haze were made using an Alaskan “bush” airplane with a hand-held sunphotometer.

At that time the origin of the haze was uncertain and was attributed to ice crystals seeded by open leads in the ice or blowing dust from riverbeds. It was only through “chemical fingerprinting” of the haze that its primary anthropogenic (man-made) source in Eurasia was revealed. By the late 1970s the anthropogenic origin was clear but surprising, since it was widely believed that aerosols were generally not transported more than a few hundred kilometers from their source regions. Experts from Europe and America convened at the first Arctic Air Chemistry Symposium at Lillestrom, Norway, in 1978, and an informal measurement network was agreed upon. Data soon showed the direction of flow and the anthropogenic cloud of pollution. A combination of intensive field pro-

grams and long-term measurements extending over the past thirty years confirmed the early conclusions that the haze is anthropogenic and originated from Eurasia. It also became known that these atmospheric contaminants were transported to and trapped in the Arctic air mass during the winter and early spring.

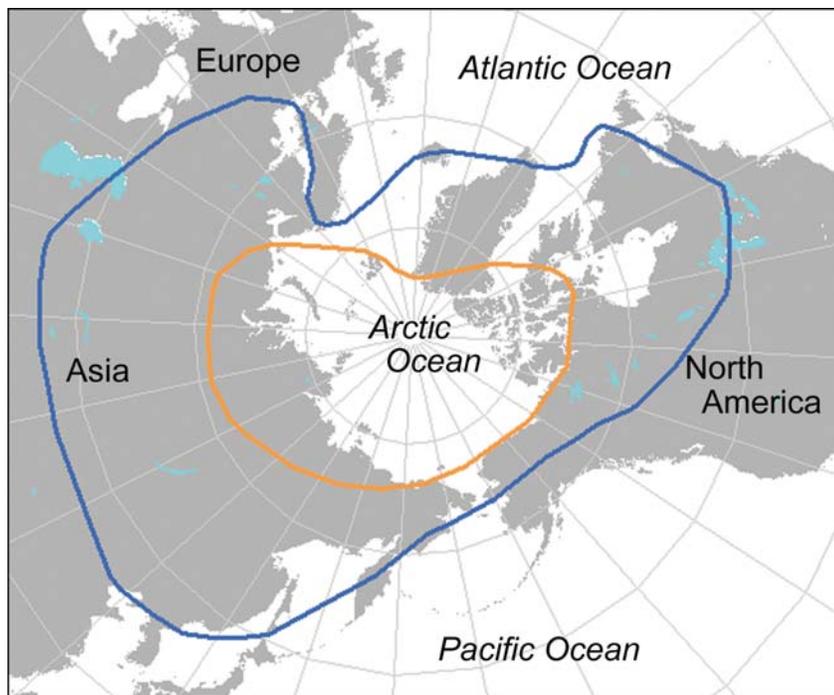
Arctic Haze has been the subject of more than three decades of study because of its potential to change the solar radiation balance of the Arctic, affect visibility, and provide a source of contaminants to Arctic ecosystems. The near-surface concentration of aerosols at most places in the Arctic is about an order of magnitude lower than those found at more polluted and industrialized locations. At the same time, however, the affected areas are much larger, and the affected ecosystems in the high Arctic are thought to be quite sensitive to gaseous and aerosol contamination.

The haze is composed of a varying mixture of sulfate, particulate organic matter (POM), and, to a lesser extent, ammonium, nitrate, dust, black carbon, and heavy metals. The identification of particular heavy metals allowed industrial sources to be identified. Particles within the haze are well aged, with a mass median diameter of 0.2 microns or less. This particle size range is very efficient at scattering solar radiation because the peak in the particle surface–area size distribution is near the maximum efficiency for Mie scattering. The haze also is weakly absorbing because of the presence of black carbon. These scattering and absorption effects lead to the well-documented reduction in Arctic atmospheric visibility (sometimes down to only a few kilometers or less). During transport from Eurasia to the Arctic, the pollutant-containing air masses have a high probability of reaching saturation and nucleating and precipitating clouds. Both the clouds and the Arctic Haze may also significantly affect climate because the haze weakens the reflectivity of the white snow and ice, lowering the albedo of the earth in the process.

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Soot covering a statue in Krakow, Poland, one of the source regions of Arctic Haze.





Range of the Arctic air mass in winter (January, blue) and summer (July, orange).

Several seasonally dependent mechanisms are thought to contribute to the formation of Arctic Haze:

- Strong surface-based temperature inversions form in the polar night, causing the atmosphere to stabilize.
- This cold and stable atmosphere inhibits turbulent transfer between atmospheric layers, and it also inhibits the formation of cloud systems and precipitation, the major removal pathway for particulates from the atmosphere.
- In addition, transport from the mid-latitudes to the Arctic intensifies during the winter and spring.

The combination of these factors results in the transport of precursor gases and particulates to the Arctic and the trapping of the pollutant haze for up to 15–30 days.

Aircraft and lidar measurements collected throughout the 1980s and 1990s revealed that the haze occurs primarily in the lowest 5 km of the atmosphere and peaks in the lowest 2 km. Throughout the haze season, the pollution layers are highly inhomogeneous, both vertically (tens of meters to 1 km thick) and spatially (20–200 km in horizontal extent).

Recent aircraft measurements of sulfate aerosol revealed how the haze develops its vertical structure between February and May (Scheuer et al. 2003). During early February, atmospheric sulfate aerosol is transported from cold regions in north-

ern Eurasia and accumulates in a 2-km-thick layer on the land and ocean surface. As the haze season progresses, transport from warmer regions in Eurasia (the source region of the haze) occurs at higher altitudes (up to at least 8 km). Since vertical mixing is prevented by the persistent Arctic low-level inversion, the haze layers remain stratified until spring. During early April, sulfate layers below 3 km begin to dissipate because of the beginning of solar heating and the resulting mixing near the surface. However, more stable isentropic transport (transport that follows constant temperature lines) continues at higher altitudes. By the end of May, both the lower- and higher-altitude sulfate enhancements are significantly decreased because of the continued break-up of the inversion and the return of rain and wet snow, which removes the haze from the atmosphere and deposits it to the ground.

Occurrence and Trends of Arctic Haze

Trends in Chemical Composition

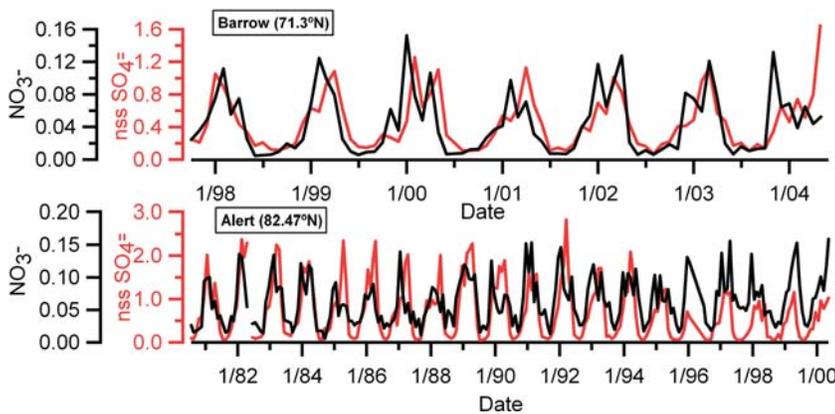
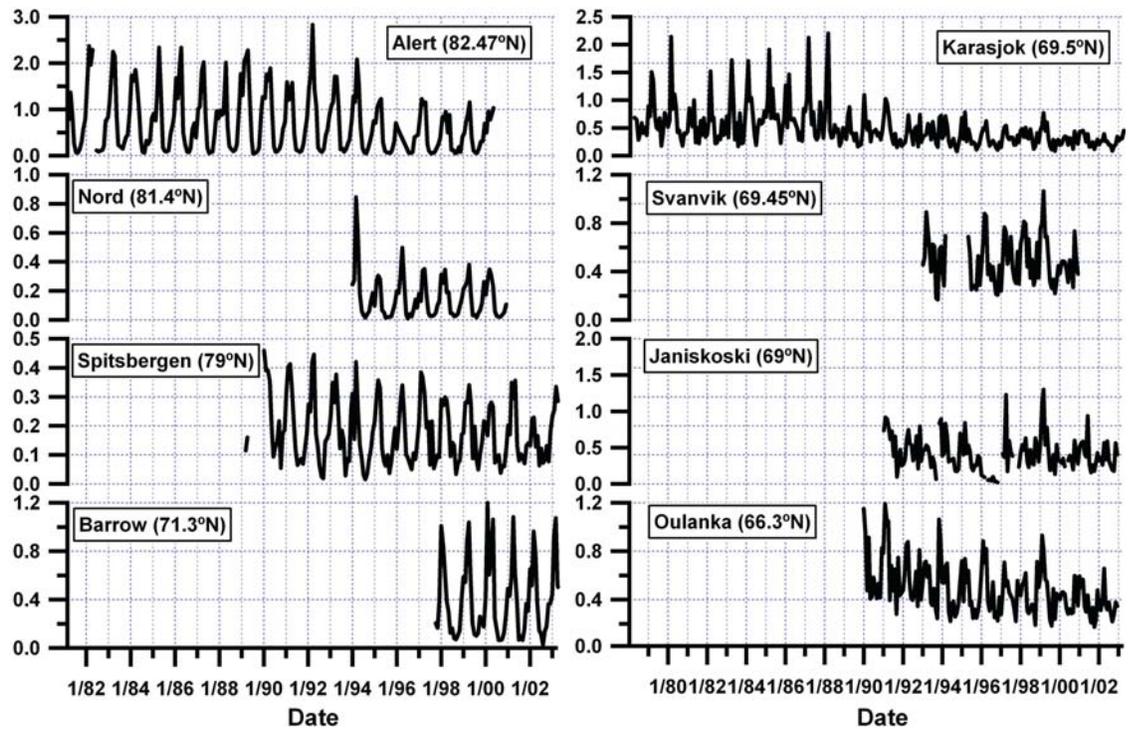
Arctic Haze is marked by a dramatic increase in the concentrations of several key particulate pollutants during winter. Stations where Arctic Haze is monitored include Alert in the Canadian Arctic (82.46°N), Station Nord in Greenland (81.4°N), Spitsbergen on the island of Svalbard (79°N), Barrow, Alaska (71.3°N), Karasjok (69.5°N) and Svanvik (69.45°N) in northern Norway, Oulanka in northern Finland (66.3°N), and Janiskoski (69°N) in western Russia.

Each site undergoes a similar winter/early spring increase in sulfate, with maximum concen-



Arctic Haze sampling station locations.

Time series of monthly averaged particulate sulfate concentrations in $\mu\text{g}/\text{m}^3$ for eight Arctic monitoring sites. The data were made available for Alert by the Canadian National Atmospheric Chemistry (NAtChem) Database and Analysis System, for Barrow by NOAA PMEL (Pacific Marine Environmental Laboratory; <https://saga.pmel.noaa.gov/data/>), and for the other stations by EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe; <http://www.emep.int/>).



Time series of monthly averaged particulate sulfate and nitrate concentrations in $\mu\text{g}/\text{m}^3$ for Barrow, Alaska, and Alert, Canada. The data were made available for Alert by the Canadian National Atmospheric Chemistry (NAtChem) Database and Analysis System and for Barrow by NOAA PMEL (<https://saga.pmel.noaa.gov/data/>).

trations reaching up to $2.5 \mu\text{g}/\text{m}^3$. Summertime monthly average concentrations are generally less than $0.1 \mu\text{g}/\text{m}^3$. Nss (non-sea-salt) sulfate makes up about 30% of the submicron mass during the haze season. The time series of particulate nitrate at Alert and Barrow show clear seasonal patterns for this chemical species. Maximum concentrations approach $0.15 \mu\text{g}/\text{m}^3$.

Other species sampled in the haze have their origins from biomass burning and dust from Eurasia (ammonium and nss potassium from biomass burning and magnesium and calcium from dust). The concentration of these particles in the haze reaches a maximum in the winter and spring.

Natural aerosol chemical components have seasonal cycles that are quite different from anthropogenic components. Sea salt is a natural

aerosol component that is transported to the North American Arctic from the North Pacific and the North Atlantic Oceans between November through February.

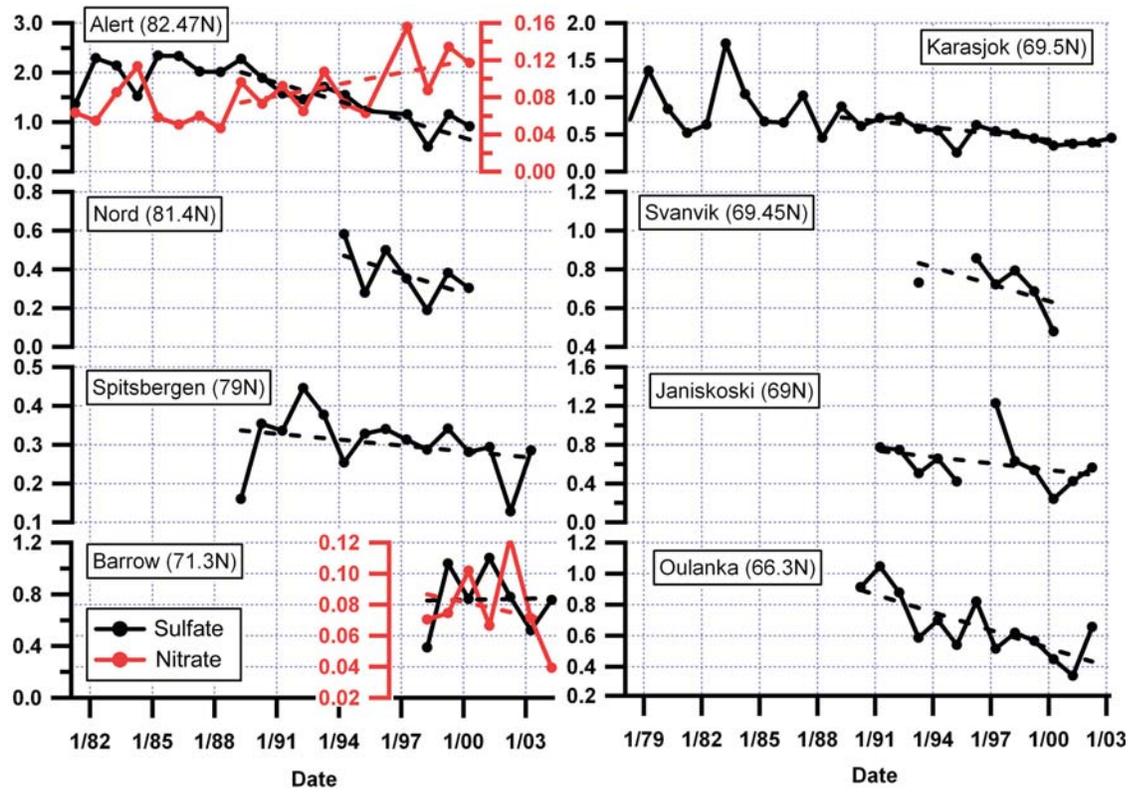
Another natural aerosol component is methane-sulfonic acid (MSA). Concentrations of MSA begin to increase in late June as the ice melts and recedes from the shoreline and phytoplankton productivity in surface waters begins. Dimethyl-sulfide that has been trapped under the ice is released to the atmosphere, where it oxidizes to form MSA.

A third aerosol component that has a natural source is particulate organic matter (POM), which makes up, on average, 22% of the total fine aerosol mass. POM reaches a maximum in the atmosphere during the summer, probably because of summer biogenic emissions and/or enhanced oxidation processes. There is a small increase in organic acids as early as February and March that may be an indication of photooxidation at polar sunrise.

The longest record of sulfate concentrations in the Arctic (1980 to present at Alert, Canada) revealed no change in sulfate concentrations during the 1980s. These stable concentrations are attributed to little change in emissions in the former Soviet Union between 1985 and 1990. Beginning in 1991, sulfate and other measured anthropogenic constituents (lead, zinc, copper,

Monthly averaged concentrations of sulfate and nitrate in $\mu\text{g}/\text{m}^3$ for April.

The dashed lines are linear fits to the data. The data were made available for Alert by the Canadian National Atmospheric Chemistry (NAtChem) Database and Analysis System, for Barrow by NOAA PMEL (<https://saga.pmel.noaa.gov/data/>), and for the other stations by EMEP (<http://www.emep.int/>).



Monthly averaged light scattering and light absorption at 550 nm by sub-10- μm aerosols at Barrow, Alaska, and black carbon mass concentration at Alert, Canada. The data were made available for Barrow by NOAA CMDL (Climate Monitoring and Diagnostics Laboratory) and for Alert by the Canadian National Atmospheric Chemistry (NAtChem) Database and Analysis System.

excess vanadium and manganese, ammonium, and nitrate) began to decline, suggesting that the reduction of industry in the early years of the new Eurasian republics had an effect in the Arctic. In fact, sulfate concentrations measured at Station Nord in northern Greenland and at several other sites in the Arctic decreased significantly throughout the 1990s, coinciding with a reduction in emissions from the former Soviet Union.

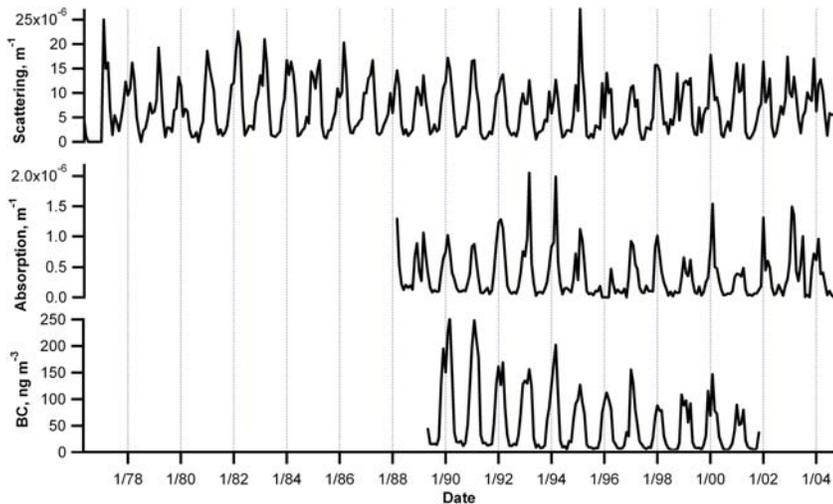
Based on a linear fit to monthly averaged April concentrations, the decrease ranges from 0.1 to

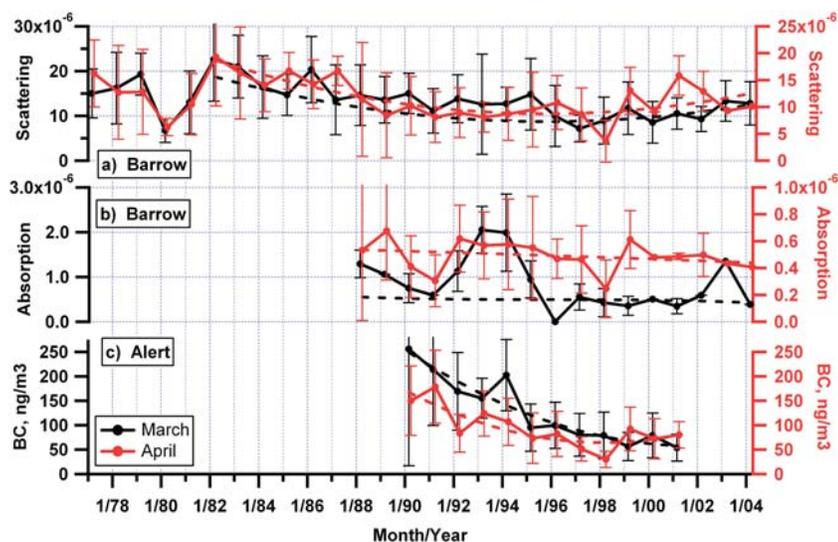
0.5% per year. In contrast, nitrate appears to be increasing at Alert at the rate of about 0.3% per year. The decoupling of the trends of nitrate and sulfate also are evident. Nitrate concentrations peak in early winter and then again in spring in Barrow, while sulfate concentrations do not.

Trends in Optical Properties

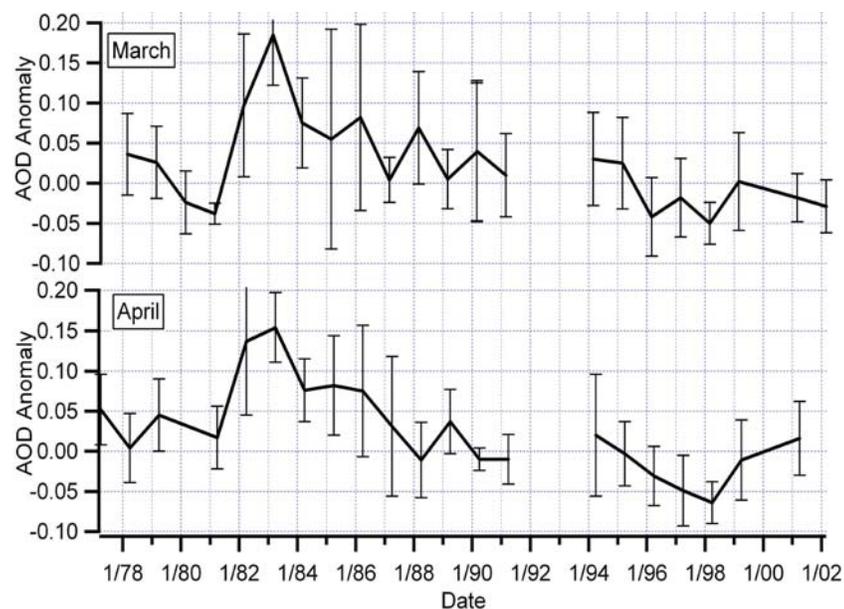
The seasonality and trends of Arctic Haze are clearly seen in time series data of light absorption and scattering by aerosols measured at the surface and in total column aerosol optical depth measurements.

Bodhaine and Dutton (1993) reported that aerosol scattering, optical depth measurements, and sulfate concentrations at Barrow and Alert were at a maximum in 1982, reducing twofold by 1992. The decrease was apparent during March and April, the usual maximum haze period. They suggested that the reduction in the output of pollution aerosols by Eurasia and stricter pollution controls in Western Europe caused the decrease in the haze. The decreases in aerosol scattering and optical depth at Barrow during this ten-year period are not equal to the known reductions of sulfate emissions, however, indicating that other factors such as changes in transport could have played a role.





Monthly averaged concentrations of light scattering and light absorption at 550 nm for sub-10- μm aerosol at Barrow, Alaska, and black carbon for Alert. The averages for March and April are shown. The dashed lines are third-order polynomial fits to the data. The vertical lines represent one standard deviation of the monthly mean. The data were made available for Barrow by NOAA CMDL and for Alert by the Canadian National Atmospheric Chemistry (NAAtChem) Database and Analysis System.



Monthly averaged aerosol optical depth anomalies at Barrow, Alaska, for March and April. The anomalies are relative to a base of non-volcanic years. The data from 1992 and 1993 were removed because of stratospheric aerosol influx from the Mount Pinatubo eruption in 1991. The vertical lines represent one standard deviation of the monthly mean. The data were made available by NOAA CMDL.

From 1992 through the late 1990s, light scattering at Barrow continued to decrease.

An update of the monthly averaged light scattering data analysis shows that, for the months of March and April, scattering increased from the late 1990s to 2004. This increase is not apparent in the March and April monthly averaged values of light absorption at Barrow. Sharma et al. (2004) reported a decrease of 56% in black carbon (the main light absorber in the Arctic atmosphere) during the winter and spring from 1989 to 2002 at Alert, Canada. A monthly average of the data for April suggests an increase in black carbon since 1998 at Alert.

An extension of the Barrow aerosol optical depth (AOD) data through 2002 shows a continued decrease through the late 1990s. Monthly averaged values of AOD anomalies (relative to a base of non-volcanic years) for March show a continued decline through 2002. However, the AOD anomalies for April indicate an increase between 1998 and 2001, where the currently available data record ends. In contrast to the Barrow trend through the 1990s, Herber et al. (2002) reported a slightly increasing trend in AOD (1% per year) at Koldewey station in Ny-Alesund, Spitzbergen, between 1991 and 1999.

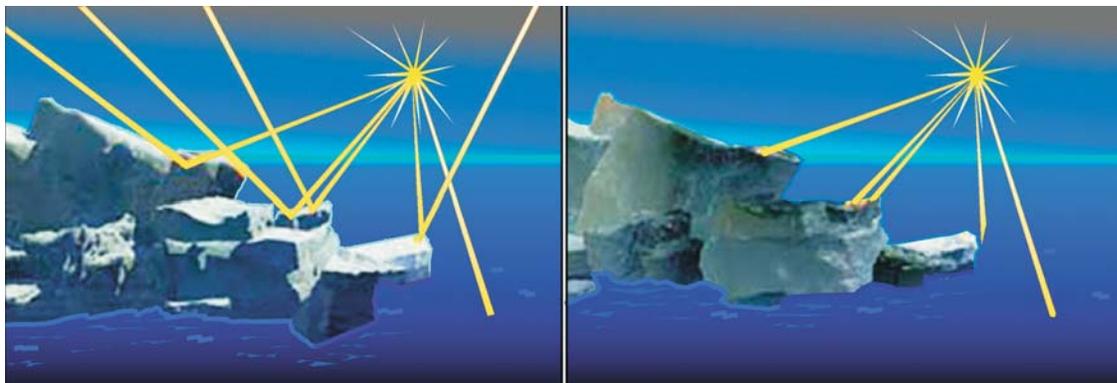
Effects of Aerosols on the Climate System in the Arctic

Direct Effect

The direct effect of aerosols on the radiation balance in the Arctic is due to the absorption and scattering of radiation by the aerosol. The Arctic is thought to be particularly sensitive to changes in radiative fluxes imposed by aerosols because of the small amount of solar energy normally absorbed in the polar regions. Arctic Haze is present as a layer of light-absorbing material over a highly reflective ice and snow surface.

Shaw and Stamnes (1980) first realized that the absorbing nature of Arctic Haze would have a significant impact on the energy balance of the Arctic. Several early calculations estimated that the diurnally averaged atmospheric warming due to the layer ranged between 2 and 20 W/m^2 . These estimates agreed with direct measurements from wideband sun photometers. Valero et al. (1989) measured heating rates of about 0.1–0.2 K/day during AGASP (Arctic Gas and Aerosol Sampling Program) II. The AASE (Airborne Arctic Stratospheric Expedition) II flights in the winter of 1992

Impact of soot deposited on snow and ice surfaces in the Arctic. Polar ice reflects light from the sun back to space (left panel). As the ice begins to melt, less light is reflected and more is absorbed by the oceans and surrounding land, leading to an increase in overall temperature and further melting. Darker, soot-covered ice reflects even less light and, thus, enhances the warming (right panel).



revealed soot-contaminated Arctic aerosols at altitudes of 1.5 km. Pueschel and Kinne (1995) calculated that this layer of aerosols could heat the earth-atmosphere system above surfaces of high solar albedo (ice and snow), even for single scattering albedos as high as 0.98. Hence, a modest amount of black carbon in the haze layers can result in a measurable contribution to diabatic heating.

MacCracken et al. (1986) estimated that the cooling of the surface because of absorption of solar radiation by the haze layers would be balanced by infrared emission from the atmosphere to the surface. The large reflection from the high-albedo ice and snow surface may enhance aerosol solar absorption. This aerosol-induced atmospheric heating would result in increased infrared emission from the atmosphere to the surface, producing surface cooling. During the dark winter, infrared emissions from the haze may heat the surface, but this amount of heating is expected to be small because the haze particles are predominantly in the submicron size range and therefore are an order of magnitude smaller than the characteristic wavelength of infrared radiation. Deliquescent sulfate salts, however, may cause the particles to grow and become cloud droplets or ice crystals, thereby enhancing their impact in the longwave. In addition, since the haze is present throughout the Arctic night, the integrated effect may modify the radiative budget. The vertical distribution of the absorbing haze layers does not affect the radiation budget at the top and bottom of the atmosphere but may impact atmospheric circulation and climate feedback processes.

Indirect Effects

The indirect effect of aerosols on radiative fluxes in the Arctic results from the impact aerosols have on the microphysical properties of

clouds. Aerosols modify cloud optical properties by changing the concentration, size, and phase of cloud droplets. An increase in the number of pollution aerosol particles that act as cloud condensation nuclei (CCN) will affect Arctic stratus and stratocumulus clouds by increasing the cloud droplet number concentration, which results in more radiation being reflected back to space. At the same time, cloud droplet size will decrease, reducing drizzle formation and increasing cloud coverage and lifetime. Garrett et al. (2004) showed that low-level Arctic clouds are highly sensitive to particles that undergo long-range transport during the winter and early spring. The sensitivity was detected as higher cloud droplet number concentrations and smaller cloud droplet effective radii compared to summertime clouds exposed to particles nucleated in the Arctic from local biogenic sources. In addition, Arctic stratus clouds appear to be more sensitive to pollutant particles than clouds outside of the Arctic. The most significant effect of the change in cloud properties caused by Arctic Haze may be on cloud emissivity. A decrease in droplet effective radius in these optically thin clouds will increase the infrared optical depth and thus the infrared emissivity. The result is expected to be an increase in downwelling infrared fluxes from the cloud and an increase in the rate of springtime snowpack melting.

Pollution aerosol within Arctic Haze also is thought to impact ice nucleation. Anthropogenic sulfate is a large component of the haze. Models estimate that aerosols containing sulfuric acid produce fewer ice nuclei than nearly insoluble aerosols. Measurements corroborate this finding. Borys (1989) reported that Arctic Haze aerosols had lower ice nuclei concentrations, a lower ice-nuclei-to-total-aerosol fraction, and slower ice nucleation rates than aerosols from the remote unpolluted troposphere. The reduction in ice nuclei leads to a decrease in the ice crystal number

concentration and an increase in the mean size of ice crystals. As a result, the sedimentation and precipitation rates of ice crystals increase, leading to an increase in the lower troposphere dehydration rate and a decrease in the downwelling infrared fluxes from the cloud. Girard et al. (2005) found that a cloud radiative forcing of -9 W/m^2 at Alert may occur locally as a result of the enhanced dehydration rate produced by sulfate aerosol. If this applies to much of the Arctic, it could explain the cooling tendency in the eastern high Arctic during winter.

Because of the combination of the static stability of the Arctic atmosphere, the persistence of low-level clouds, and the relatively long lifetime of aerosols during the haze season, the impact of aerosols on cloud microphysical and optical properties may be larger in the Arctic than elsewhere on earth.

Surface Albedo

Surface albedo affects the magnitude and sign of climate forcing by aerosols. Absorbing soot deposited on the surface via wet and dry deposition impacts the surface radiation budget by enhancing absorption of solar radiation at the ground and reducing the surface albedo. Hansen and Nazarenko (2004) have estimated that soot contamination of snow in the Arctic and the corresponding decrease in surface albedo yields a positive hemispheric radiative forcing of $+0.3 \text{ W/m}^2$. The resulting warming may lead to the melting of ice and may be contributing to earlier snowmelts on tundra in Siberia, Alaska, Canada, and Scandinavia.

Clearly, the radiative impacts of pollutant aerosols in the Arctic are complex. Complex feedbacks between aerosols, clouds, radiation, sea ice, and vertical and horizontal transport processes complicate the impact, as do potentially competing effects of direct and indirect forcing. As a result, the magnitude and sign of the forcing are not yet well understood for the Arctic.

Summary

Measurements of sulfate aerosol—a main constituent of Arctic Haze—and light scattering and extinction show that the amount of the haze impacting the Arctic was either nearly constant or decreasing between the 1980s and early 1990s. The updated trends in light scattering presented here show indications of an increase in the haze at Barrow, Alaska, since the late 1990s. There also is

evidence, although not as strong, of an increasing trend in light absorption during this same period at Barrow and in black carbon at Alert, Canada. Sulfate appears to still be declining at all sites except Barrow, where the trend is unclear. On the other hand, nitrate appears to be increasing at Alert and Barrow. Continued measurements coupled with chemical transport models are required to better define emerging trends and assess their causes.

Arctic Haze is generally understood to consist of anthropogenically generated material and has often been attributed to sources in central Eurasia. There may be, however, increasing amounts of material entering the Arctic from growing natural and anthropogenic sources in eastern Eurasia, particularly from China. Examples of Asian dust entering the Alaskan sector of the Arctic were documented as long ago as the mid-1970s. The rapid industrialization of China and increasing amounts of pollution being transported over long distances are likely to impact the Arctic. More research is required to document the contribution of this increasing source to Arctic Haze and to determine its impact on the Arctic.

Other key atmospheric species have a distinct seasonality in the Arctic. There is evidence of the enrichment of halogens in Arctic air masses in late winter and spring. Since these compounds tend to peak later in the year, it is thought that they are produced photochemically. More research is required to determine their sources (for example, anthropogenic, especially coal combustion, vs. marine), to investigate their numerous and complex chemical pathways, and to assess their environmental impacts. Of special note is iodine, which shows a bimodal seasonal behavior, peaking in both spring and autumn.

The direct radiative effect of Arctic Haze has been estimated with one-dimensional radiative transfer models, which find a warming in the atmosphere because of absorption of solar radiation and a concurrent cooling at the surface. These estimates are highly sensitive to the assumed properties of the aerosol in the haze. Despite the many research activities devoted to the characterization of Arctic Haze since the 1970s, measurements of Arctic aerosols are not extensive or well distributed in space or time, which limits the accuracy of the estimates of both the direct and indirect radiative forcing. Treffeisen et al. (2004) have designed an approach based on cluster analysis for integrating aircraft, ground-based, and long-term data sets for use in three-dimensional climate

models. The accurate evaluation of climate forcing by Arctic Haze requires such data sets coupled with three-dimensional climate models that consider both direct and indirect effects. In particular, three-dimensional models are required to assess the complex feedbacks between aerosols, clouds, radiation, sea ice, and dynamic transport and to quantify climate forcing caused by Arctic Haze.

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