ARCTIC HAZE: NATURAL OR POLLUTION?

A Progress Report and Renewal Proposal to the

Office of Naval Research

Arctic Program

August 1978

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and

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PII Redacted

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A124 914	3. RECIPIENT'S CATALOG NUMBER

4. TITLE *(and Subtitle)*
ARCTIC HAZE: NATURAL OR POLLUTION?

5. TYPE OF REPORT & PERIOD COVERED
Interim (7/77-7/78)

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
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8. CONTRACT OR GRANT NUMBER(s)
N00014-76-C-0435

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Graduate School of Oceanography
University of Rhode Island
Narragansett, Rhode Island 02882-1197

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Arctic Program Code 425 AR
Geophysics Division, Environ. Sci. Dept
Office of Naval Research
800 N. Quincy Street, Arlington, VA 22217

12. REPORT DATE
8/78

13. NUMBER OF PAGES
254

14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*

15. SECURITY CLASS. *(of this report)*
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

APPROVED FOR PUBLIC RELEASE, DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

DTIC
ELECTE
FEB 2 4 1983
S
H

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Arctic
aerosol
haze
snow
radiation
trace elements
desert dust

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

During summer 1977, an expanded air-sampling system was installed on a C117D at the Naval Arctic Research Laboratory, Barrow, Alaska, and five test flights were flown. Continued sampling of surface aerosol at Barrow confirmed the high concentrations ofpollution aerosol there during winter. Fairbanks shows smaller seasonal variations and intermediate concentrations. Inversions of spectra sun-photometer data were begun. The time evolution of aging aerosol was modelled. The Arctic Air-Sampling Network continued to grow. A major field program was held at Barrow and Fairbanks during spring 1978.

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S/N 0102-LF-014-6601

Unclass
SECURITY CLASSIF'

including filter and impactors, radiation measurements, and vertical [illegible] of turbidity. Elemental analysis of a series of desert soils as a function of particle size (for potential tracer purposes) was begun. An analytical technique for sulfate in Arctic aerosol was developed. The contrast in impressions on the Arctic environment offered by aerosol and snow was noted and explored.

Statement of Submission

The following progress report and renewal proposal, "Arctic Haze: Natural or Pollution?", is hereby submitted to the Office of Naval Research, Arctic Program, for consideration as a research contract. The proposal is complete except for the approval sheet from the University of Alaska, which should arrive within a week of the basic proposal.

This proposal is not being submitted to any other agency for financial support, although certain costs are to be shared with an existing grant from the National Science Foundation ("Climatically Important Properties of Arctic Haze", Division of Polar Programs).

ABSTRACT

A two-year program of research into chemical, physical, optical and meteorological aspects of Arctic haze and the general Arctic aerosol is planned, during which sources, transport, characteristics, environmental effects, and deposition of the Arctic aerosol will be studied. Particular emphasis will be placed on further evaluating the importance of midlatitude pollution as a source of Arctic haze aerosol. Continuous sampling of the surface aerosol at the existing Arctic and Arctic-related sites of Barrow, Fairbanks, Rhode Island, and New York City will continue. Continuous sampling will be initiated at Alert, NWT (Canada), Iceland, and western Ireland. In addition, samples from the Norwegian stations of Spitsbergen and Bear Island will continue to be received. All samples will be analyzed for trace elements, and most also for sulfate. This data will provide valuable information about the sources and transport of the Arctic aerosol. The spatial and temporal distributions of Arctic haze will be further investigated by a series of springtime survey programs based in Barrow and Greenland. Of particular interest will be the vertical distribution of the haze, the possible existence of a surface clear layer, and the Arctic-wide distribution of the haze. A Polaris photometer will be constructed and deployed at Barrow in winter 1978 to test for the existence of winter haze there. Detailed studies of the optical properties of Arctic haze will continue in Alaska, and inversion methods of deriving particle-size distributions will be further refined. Theoretical modeling of aerosol aging processes under Arctic conditions will continue. Trajectories of air masses from midlatitudes to the Arctic will be constructed using isobaric and isentropic techniques, as well as satellite data. A study of the amounts and characteristics of cloud-active aerosol particles in the Arctic will begin, with summer and winter field work in Alaska, Canada, the northeastern United States, Iceland, and Spitsbergen. An attempt will be made to deduce historical characteristics of Arctic haze by interviewing former weather officers of the Ptarmigan flights, and examining their photographs of the haze. The cooperative Arctic Air-Sampling Network will begin full-scale operation, with this project having partial or total responsibility for 6 or 7 of the sites. A conference on the Arctic aerosol will be held in September 1979 at the University of Rhode Island.

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I. Progress Report: July 1977 - July 1978

A. Highlights of Results

This year has been another productive one for our Arctic haze project. Our multi-disciplinary approach to the Arctic aerosol, involving chemistry, physics, optics, and meteorology, is finally yielding large dividends, the principal one of which is the emergence of a truly comprehensive picture of the Arctic aerosol. This picture, which contains a number of surprises, is perhaps the best way to summarize our results of this year. It can be stated roughly as follows:

Except for the sea, whose aerosol is confined to a shallow surface layer, the Arctic has virtually no aerosol sources of its own. The Arctic aerosol therefore reflects the effects of distant (primarily midlatitude) sources to a degree hitherto unknown in air chemistry. During the summer (May or June through August or September) the Arctic atmosphere is decoupled from the midlatitudes by the general circulation, i.e., the midlatitudes are in tropical air and separated from the Arctic by the polar front. Transport of midlatitude aerosol is sluggish and generally confined to the latitudes of emission. During summer, therefore, the Arctic atmosphere is remarkably clean and pure; it exhibits both low concentrations of aerosol and low turbidities. During winter, however, the midlatitudes are coupled to the Arctic meteorologically, because the polar front and the associated strong westerlies lie over or just south of the major source regions such as Europe and the northeast United States. Effluent from these sources is then carried rapidly westward and often northward. A much larger portion of this aerosol reaches the Arctic. Even though this is still only a very small fraction of the original emissions, it is very large compared to what the Arctic itself can produce. As a result, concentrations of the Arctic aerosol and its individual constituents increase during winter to 10 to 50 times their summer values (by far the largest winter-summer contrast ever documented, to our knowledge, for any region). This change takes place rapidly during November or December, and decays away during May or June, just the periods when the general circulation is also changing. The winter aerosol has a composition much more like pollution than does the summer aerosol. We feel that the most reasonable and simple interpretation of this data is that the winter aerosol is indeed aged pollution, for its absolute and relative concentrations are compatible with transport times of 10 to 20 days, residence times of about 3 days during transit, and dilution by factors of 2 to 4 along the way.

The winter is also the time when the Arctic atmosphere is the most turbid. Instrumental measurements of turbidity, which need a visible solar disk, show very high values during March and April. The most reliable visual observations, from seasoned Arctic scientists, indicate that the winter proper, i.e., January and February, is also a time of heavy haze, which is completely in accord with the general winter-long aerosol maximum that our ground stations are revealing. This Arctic haze now seems to be the unique result of a very unusual combination of sources, transport, aging of aerosol, and Arctic meteorological conditions: Polluted air masses in midlatitudes contain, in addition to the aerosol sulfate, several times more sulfur as gaseous sulfur dioxide. During transport to the Arctic this sulfur dioxide becomes oxidized to aerosol sulfate, which increases the relative concentration of sulfate in the aerosol by about an order of magnitude. The result is an unusually sulfate-rich aerosol where sulfate makes up roughly one-half the aerosol's mass. This sulfate is present mostly as sulfuric acid, which is highly hygroscopic and forms droplets which increase or decrease in size depending on the ambient relative humidity. The Arctic atmosphere, being so cold in winter, nearly always has a saturated or near-saturated layer extending from about 200 to 500 meters above the surface to roughly 1 to 1.5 km in elevation. The sulfate particles in these layers grow considerably in size, and create the well-known Arctic haze with unusually high turbidities. The combination of high sulfate concentrations and high and persistent relative humidities creates turbidities far in excess of what would be expected from "dry" aerosol alone. Thus, the anomalous turbidities of the Arctic seem to be nothing more than condensed water, of which there is an abundance even in the winter Arctic atmosphere.

This then accounts for what we have called the "diffuse" Arctic haze. It is not, however, the whole story. From time to time during the winter and spring, bands of Asian desert dust enter the Arctic atmosphere, being transported efficiently over the North Pacific and the Bering Strait. The appearance of these bands seems to be quite sporadic and variable from year to year; we observed them in 1976 but not at all this spring, even though there was much transport from Asia. Independent evidence suggests that the Asian dust storms of this spring seem not to have been transported effectively out over the Pacific.

Arctic haze seems to be really confined to the Arctic proper. Even at Fairbanks, only 800 km south of Barrow, the aerosol is very different. Haze concentrations are typically two times lower than at Barrow during spring; the haze seems to be nearly absent during winter. The Fairbanks aerosol is also less concentrated than that at Barrow, particularly for the pollution-derived elements. No major winter increase of aerosol is seen at Fairbanks; brief maxima at Fairbanks are, however, observed during winter or spring when the air flow is from the north, i.e., from the more polluted Arctic.

Most significantly, analyses of Arctic snows show no effect of this pollution aerosol. Rather, they give the impression that the Arctic is yet a pristine pure area, far removed from the influence of anthropogenic aerosol. This contrast between aerosol and snow is sure to generate controversy in the future; for the moment we take it to mean that snow is a poor indicator of the true state of the Arctic aerosol.

B. July 1977 field experiment at Barrow

During the last week of June and most of July 1977, Mr. R.D. Borys and Dr. L. Schütz of our program conducted a field experiment at NARL in Barrow, Alaska. This was a postponed version of the originally planned March 1977 experiment, which was to be a sequel to the highly successful spring 1976 experiment. Unfortunately, NARL's C117D was not available for aerosol sampling during spring 1977, and the experiment had to be rescheduled for July.

The main purpose of this summer experiment was to install a new and expanded air-sampling system on the C117D and test it with a series of actual flights. The installation process proved to be unexpectedly long and arduous, taking two people about three weeks. Because of time constraints, only 5 test flights could be performed during the final week of the experiment. Because most of these were multi-purpose flights (other NARL personnel needed the aircraft for one reason or another), and therefore were of less-than-optimum quality, they are to be regarded more as test samples than as having any real significance.

For the purposes of this report we can summarize the results of the July 1977 experiment as follows:

(1) Atmospheric turbidities were very low, in fact the lowest ever recorded at Barrow. Optical depths of 0.05 at 500 nm were reached. It is interesting to note that the hemispheric meteorological maps provide an immediate explanation for these low turbidities - July 1977 was marked by unusually low north-south exchange of air in the Northern Hemisphere, with the Arctic being strongly cut off from midlatitude air. During the second half of July the United States experienced a heat wave of major proportions, created by a retreat of the jet stream to the U.S.-Canadian border. In fact,

the polar front for that period formed an almost perfect circle around the globe, with nearly no waves on it. (Interestingly, a very similar situation occurred in the second half of June 1978, during which sulfate concentrations at Barrow decreased dramatically to extremely low concentrations.) This provides further evidence for our evolving view that air quality in the Arctic is closely related to midlatitude air and meridional exchange.

(2) Elemental concentrations in the aerosol were also quite low, although because of the compromise nature of the test flights nothing definitive can be said.

(3) A flight was made in the Prudhoe Bay area to determine whether the emissions there could be affecting air quality at Barrow. The results showed that V, Mn, and S could be detected in the plume at higher concentrations than in the surrounding air nearby, but still at much lower concentrations than those required to be seen at Barrow. V, and Mn, for example, had the same concentration at Prudhoe as they have in winter at Barrow, about 200 air miles away; S was at least four times lower than at Barrow in winter. Dilution of the Prudhoe plume during a trajectory of 200 miles must be at least a factor of 10 to 100; we therefore conclude that the Prudhoe plume does not measurably influence air quality at Barrow.

C. Surface aerosol sampling

Our program of continuous surface sampling of Arctic and Arctic-related aerosol, which was started in 1976 mainly to see whether Asian dust events could be detected at ground level in Barrow, has proved to have a significance far beyond this and has taken on a life of its own. The Arctic aerosol is emerging as an entity with its own unique characteristics, most of them unusual. The two most important features we have found so far are that the aerosol is markedly pollution-derived from midlatitudes and that it is much higher in concentration in winter than in summer. Neither of these two features was expected, and they are both controversial. The composition and behavior of the Barrow (and Spitsbergen) aerosol is completely consistent with major (pollution) sources in midlatitudes, travel times of 10-20 days (depending on season), and residence times of 2-3 days along the way. Europe and North America seem to be the main sources, with Japan and Asia occasionally contributing. Because of meteorological coupling of midlatitude and Arctic during winter and decoupling during summer, elemental concentrations in the Arctic aerosol are 10-50 times higher in winter than in summer, depending on the elements and its seasonal pattern of emission at the source. Interestingly, Fairbanks, only 800 km south of Barrow but in a sub-Arctic climatic regime, shows much smaller seasonal variations and intermediate aerosol concentrations. Evidently it is exposed to midlatitude aerosol more evenly the entire year than is Barrow.

As far as we know, the strong seasonal variations of the Arctic aerosol are unique in air chemistry. Other regions have much smaller variations, typically factors of three or less. The stong variations of the Arctic not only emphasize the dominant role that large-scale circulation plays in maintaining Arctic air chemistry, but also give a good idea of what "background" concentrations of aerosol for the Northern Hemisphere ought to be, namely what the Arctic has in summer.

We feel that there is much to be learned from a thorough study of Arctic air chemistry. To this end we will prepare a major summary article on our findings so far, which hopefully will be submitted to Nature in fall 1978. Our principal theses in this article will be (1) that available data on Arctic air chemistry suggest that it has many unusual features, and (2) that Arctic haze, the motivation for all these studies, seems to be a consequence of the peculiar meteorological conditions of the Arctic operating on the pollution-derived Arctic aerosol.

Within about a year we also hope to write a detailed article on our chemical aerosol data from these surface sites, particularly Barrow.

As the Arctic Air-Sampling Network comes more fully into operation over the next few years, we should get a much more complete picture of Arctic air chemistry, the forces controlling it, and its environmental effects.

D. Optical instruments and techniques

Instrument preparation and calibration. A series of optical instruments such as multi-wavelength sun photometers, angle-scanning sky photometers, coronameters, and diffuse radiation detectors, which are used to measure sky brightness, global radiation, and atmospheric transmission, were modified, tested, and calibrated in preparation for the 1978 spring campaign. The radiometric calibrations were referenced to radiation scales from the U.S. National Bureau of Standards and from the World Radiation Center, Davos, Switzerland.

New developments in Optical Inversion Theory. The objective of making the multi-wavelength optical measurements of sky and sun radiation is to be able to determine the size distribution and the column loading of the particles which make up Arctic haze. One wants to relate measured optical parameters (atmospheric extinction and the brightness and spectral distribution of the sky at different angles from the sun) to aerosol parameters, and in particular one wants to solve for the aerosol parameters. This problem is the reverse of usual optical theory, in which the scattered radiation field is calculated from a given distribution of scattering or absorbing particles.

The aerosol spectrum is recovered by "inverting" the usual optical scattering equations. The basic equation to be solved is a first order Freidbalm integral equation and its solution requires special theoretical treatment. The procedure which was developed to recover the aerosol distribution involves expanding an integral in the equation of the Mie scattering function into a set of linear equations which can then be inverted, at least in principle, by using matrix theory. A serious problem comes up, however, namely that the equations are poorly conditioned (almost linearly dependent) and the presence of measurement noise in the raw data causes the solution vector (the aerosol size spectrum) to become wildly unstable. This can be suppressed, and meaningful results can be obtained by using one of several strategies that have been developed. We used the so-called Twomey-Phillips method (Twomey, 1965; Twomey, 1977a).

The information about the aerosol size spectrum (the number of aerosols of radius r to r + dr in a column, as a function of particle radius r) that is contained in optical scattering or extinction measurements depends on what is measured. In optical scattering experiments, parameters such as the range of scattering angles used and the accuracy of the measurements and the number of specific scattering angles used determine whether one will be justified in solving for a complicated aerosol spectrum. The same is true for extinction experiments; if there is a great range of wavelength over which measurements are made, one will be able to extract more information than if measurements are made over a narrow region of the spectrum. Studies about the information content of optical experiments have occupied a great deal of our (GES) time this year, and the result has been the development of a new inversion scheme that uses <u>both</u> optical extinction (as a function of wavelength) <u>and</u> optical scattering (as a function of scattering angle). The new method has been programmed onto the University of Alaska's computer; modeling and testing have shown it to be successful.

An example of the inversion's predictions about an a priori specified aerosol size spectrum is shown in Figure I.D.1. The optical measurements were simulated with Mie theory for a given aerosol size distribution, then degraded with random noise (to simulate measurement errors), then used as input to the inversion routine. The degree of success can be evaluated

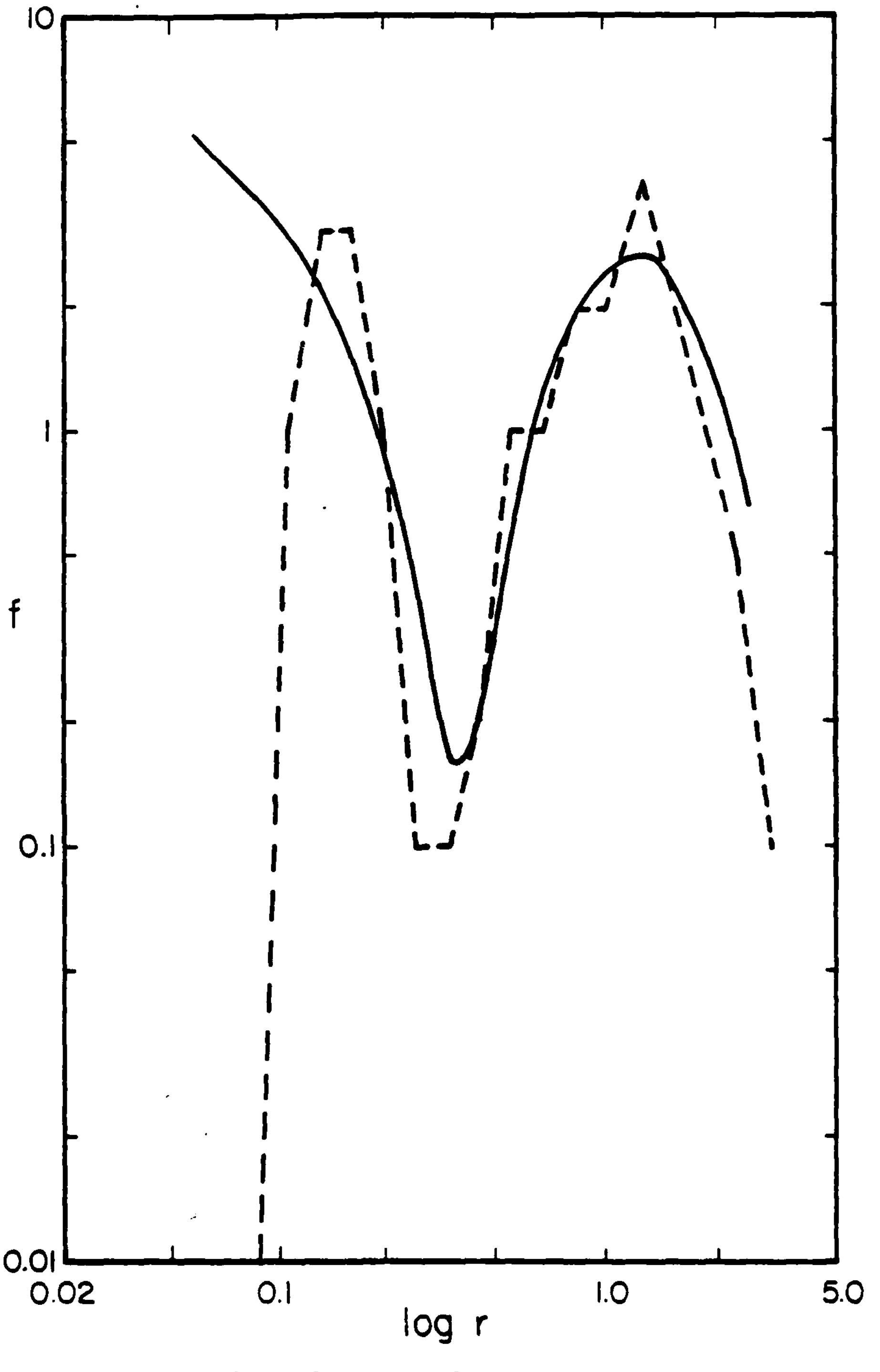

Figure I.D.1. Recovery of modeled aerosol size spectrum by constrained linear optical inversion. Optical extinction (at 8 wavelengths from 400 nm to 1000 nm) and optical scattering (at 10 angles from 1° to 30° and at $\lambda = 750$ nm) coefficients were calculated for the pre-specified aerosol size spectrum shown as the dotted line. The simulated "measurements" were degraded with 3.5% rms random noise, then inverted subject to the constraint of minimum second differences in the solution vector. The inverted result, or estimate, of the aerosol size spectrum is the solid line.

by comparing the given and predicted curves. The solution vector is smoothed somewhat, which would be expected to occur for a multi-mode spectrum such as that shown. Most real aerosol spectra are more smoothly varying than the one shown in Figure I.D.1; their recovery should be even better.

E. Modeling the time evolution of atmospheric aerosols

Because Arctic aerosols seem to be well aged both in summer and winter, we thought it would be of help in our interpretation of the aerosol size spectra we are obtaining to model the time evolution of aerosols over periods of a few days. The interpretation of an aged aerosol is not simple, because of the many processes that modify its size distribution and chemical composition during transport. For example, heterogeneous heteromolecular nucleation involving trace gases causes particle growth, and particle size varies due to condensation or evaporation of water vapor as the particles pass through high and low humidities. Removal processes for aerosol range from simple gravitational fallout or inertial impaction to complicated processes involving molecular or thermal diffusion or impaction to hydrometers and cloud droplets (Twomey, 1977b). Small particles collide and coagulate under Brownian motion to form larger particles.

In spite of the complexity, one can gain insight into aerosol evolution by modeling various possible growth and removal processes, then comparing predictions to observed aerosols. In this way one can at least get an idea of what the dominant aging processes might be.

Modeling the evolution of the aerosol size distribution also helps us interpret our optical measurements. An example is shown in Figure I.E.1., where wavelength-dependent optical thickness and sky brightness are shown at different times for an evolving aerosol that was introduced into the atmosphere on day 0. The three panels in this figure correspond to three different initial aerosol size-distribution functions of the Junge power-law type ($dn/d \ln r = c\, r^{-\nu}$) in the radius interval $2 \times 10^{-2}\mu m < r < 5\mu m$. In each case the amount of aerosol in a vertical column was originally taken

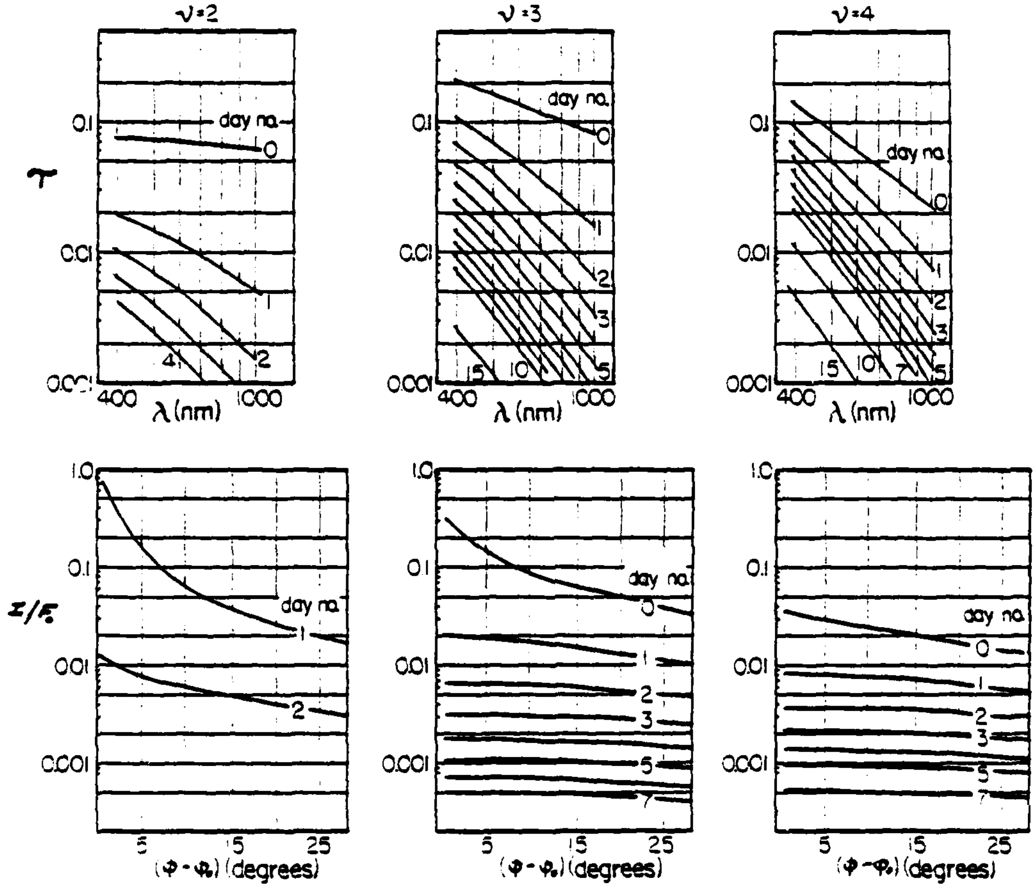

Figure I.E.1. Calculated optical extinction spectra (top) and optical scattering or sky brightness (bottom) for a lower tropospheric aerosol cloud evolving in time with the radius-dependent particle removal rates tabulated by Misaki et al. The initial ($t = 0$) aerosol cloud consisted of a one kilometer-thick column of air on aerosol mass loading of 50μg m^{-3} (5×10^{-6} g cm^{-2}). The aerosols clouds were assumed to consist of particles with mass density of 1 g cm^{-3}, and be distributed by size according to a Junge power law distribution function with $\nu = 2$ (left), $\nu = 3$ (middle); $\nu = 4$ (right) over the radius range $2 \times 10^{-6} < r < 5 \times 10^{-4}$ cm. The extinction spectrum steepens and the aureole gradient decreases as the cloud ages.

to be that corresponding to a homogeneous mass loading of $50\mu m^{-3}$ in a 1-km-thick column. The time-dependent aerosol removal rates for different particle sizes were taken from measurements of Misaki _et al_. (1975). It is seen in Figure I.E.1. that as the aerosol ages, the slope of the optical extinction spectrum steepens, and the gradient of the aureole intensity increases. These predictions can be understood qualitatively by realizing that as larger particles are preferentially removed, scattering and extinction become more dependent on smaller particles. Similar calculations are being performed for aerosols evolving in Arctic conditions, where alteration of the size distribution, hence changes in optical parameters, is very different (mainly because of decreased precipitation) from the rates measured by Misaki _et al_. (1975) over the midlatitude Pacific Ocean.

Ultimately, we will increase the comprehensiveness and complexity of our calculations. Thorough modeling of the time evolution of an aerosol will require that the processes listed in Table I.E.1. be treated.

Table I.E.1. Processes which can remove or modify atmospheric aerosols.

Dry Processes

1. Sedimentation.
2. Impaction through viscous surface layer
3. Brownian diffusion across laminar layer.
4. Coagulation.
5. Thermal diffusion.
6. Heteromolecular or homomolecular, heterogeneous or homogeneous nucleation involving gases and/or particles.

Wet Processes

1. Inertial impaction on hydrometeors.
2. Diffusive removal on hydrometeors.

Cloud Processes

1. Nucleation.
2. Diffusive attachment to cloud particles.

Larger-scale Processes

1. Dilution by eddy diffusion.
2. Vertical transport (convection, subsidence, sloping weather systems, etc.).

Miscellaneous

1. Electric charging, ion nucleation, etc.
2. Phoretic forces (ordered fluxes). Diffusiophoresis, thermophoresis.
3. Photochemical conversion or nucleation.

F. Korean Air-Sampling Program

The proposed air-sampling program at Kunsan Air Base, South Korea, to study the composition of the seasonal variations of Asian dust storms, has proven to be a major debacle. In November 1977 air-sampling equipment was shipped to the site via a commercial air-freight carrier (Emery). In December 1977 K. Rahn traveled to Kunsan Air Base to assemble the equipment, and discovered that it was not there. Only later, after Dr. Rahn had left South Korea, was a trace able to establish that the shipment had been delayed and was sitting at the Seoul airport. Since that time many phone calls and letters to the carrier have been unable to budge the equipment through Korean customs. This whole affair has been a major frustration and embarrassment to Dr. Rahn. At present we are still hoping to get the equipment to Kunsan Air Base in early fall 1978, but nothing seems certain.

The trip to Korea was not entirely wasted, however. Dr. Rahn was able to leave a Volz sun photometer there, which was used to record atmospheric trubidity from December 1977 through June 1978. While at the air base, Dr. Rahn interviewed a series of American weather observers and Korean and American pilots, and from them gained a great deal of practical knowledge about the characteristics and transport of Asian dust storms. This information will be summarized in a joint article with Prof. Akira Ono of Nagoya University, Japan, to be written during fall 1978 for Naval Research Reviews.

The Kunsan site continues to be important to us, and we will make every effort to see that it becomes operational during fall 1978.

G. Arctic Air-Sampling Network

Development of the cooperative Arctic Air-Sampling Network is proceeding smoothly and nearly on schedule. There are now six sites sampling the aerosol continuously, Spitsbergen and Bear Island (operated by the Norwegian Institute for Air Research), and Barrow, Fairbanks, New York City, and Rhode Island (operated by URI/UA). Trace-element analyses on all filters is being done by URI; NILU analyzes its samples for sulfate, nitrate, ammonia, and hydrogen ions, as well as for Pb and Cd. URI has just begun a program of sulfate analyses (see Section I.J.) on its filters.

Series of preliminary summer and winter samples were taken in northern and southern Greenland (Thule and Prins Christianssund) by the Danish Meteorological Institute, and are presently under analysis for trace elements at URI. Discussions are underway for sampling sites in western Ireland and Iceland. A Canadian site at Alert, NWT has been arranged. Trial sampling at sites in northern and southern Greenland will be carried out in summer 1978.

It now appears that the full network will begin operation in summer or fall 1979. At this time the Danish sites in Greenland, the Canadian Alert site, the western Ireland site, and possibly also the Icelandic site are expected to start up. Dr. B. Ottar of the Norwegian Institute for Air Research is negotiating with officials in the Soviet Union concerning their possible participation in the network. We do not expect them to join in the near future, however.

A technical meeting on the Arctic Network was held at the Danish National Agency of Environmental Protection's Air Pollution Laboratory, Roskilde, Denmark, on 6 January 1978, hosted by Dr. H. Flyger. Participating in the meeting, in addition to Dr. Flyger, were his colleague Dr. N.K. Heidam and Drs. Ottar and Rahn. At this meeting the basic principles of operation of the network were further defined and clarified, and future plans were laid. One future event of significance is a 3-day conference on the Arctic Aerosol, to be held at URI in September 1979. Details of this meeting are given in the Renewal Proposal section.

In connection with the Arctic Network, K. Rahn of URI circulates an "Arctic Newsletter" periodically, which contains current events related to reseach on the Arctic aerosol conducted at the several participating laboratories. Three editions have been issued so far.

A fuller write-up of the Arctic Network can be found in Section I.N.3., which is a preprint of an article to appear in the Arctic Bulletin of August 1978.

H. Spring 1978 campaign

During March and April 1978 we undertook another intensive study of the Alaskan aerosol. It was originally planned to focus this effort on the Barrow aerosol by using NARL's C117D aircraft which we had outfitted for air sampling the summer before, but because this aircraft was down for the entire spring, we divided our time between Barrow and Fairbanks.

The Fairbanks part of this study was based at the Geophysical Institute, and consisted mainly of various optical measurements. Instruments used included three sun photometers, a coronameter, an angle-scanning sky photometer, a diffuse radiation detector, and a halo camera. Measurement of the downwelling diffuse and global radiation at ten wavelengths was designed to infer the absorption coefficient (as opposed to the scattering extinction coefficient) of the haze; measurement of the sky brightness along the solar almucantar for scattering angles of 1° to 60° from the sun was designed to derive the vertically integrated aerosol size distribution with an inversion technique (discussed below and in Section I.D.). Experimental procedures with some of these instruments, and particularly their simultaneous use, are still being refined. In addition to the optical experments, filter samples and a series of double-stage impactor measurements were taken at Ester Dome. The double-stage impactor was on loan from the Mac-Planck-Institut für Chemie, Mainz, West Germany, and is used to measure the particle-size distribution of the surface aerosol.

The Barrow part of the spring campaign consisted of four vertical profiles of the aerosol (measured by a 10-wavelength sun photometer through an open aircraft window), a short series of intensive optical measurements (using a sun photometer, a diffuse radiation detector with shading ring, and a halo camera), double-stage impactor measurements, high-volume filter samples, and ice-nuclei measurements.

We feel that this spring campaign was a great success, in spite of the absence of the C117D. The vertical profiles of the Barrow aerosol have shown that the haze was composed of very fine particles (not desert dust this year), was very intense up to 1 to 2 km, and was associated with cold northern air rather than warmer southern air. The double-stage impactor samples strongly suggested that the haze was composed primarily of sulfate droplets, i.e., mostly water; this idea has been independently confirmed by Dr. E. Keith Bigg of Australia. Most importantly, the vertical profile of the haze showed a reasonable correlation with the relative humidity profile, which indicated that the haze was primarily condensation of water onto small hygroscopic aerosol particles. This idea, together with our very recent measurements on the sulfate content of the Barrow aerosol (reported in Section I.N.4.), have led us to an attractive explanation of the "diffuse" northern Arctic haze in terms of sulfate particles (derived from and transported from midlatitudes, via the Spitsbergen eastern Arctic pathway over the pole to Barrow) growing in size under high relative humidities during the Arctic winter. These important new ideas are discussed in detail in the discussion documents of Section I.N.

The results of the ice-nuclei determinations and daily filters are not yet available; they will be reported in the next progress report. The rest of this section describes in more detail the optical results of the spring campaign.

As in past years, the haze was strongest in northern Alaska, and it showed a great deal of variability, even on time scales as short as hours and, for coronagraphic records, as short as seconds! Generally, the major changes in the haze came and went of time scales of a few days.

Optical thickness of haze is twice as high at Barrow as at Fairbanks, and visual reports from locations in southern Alaska (Valdez, Anchorage) and in southeast Alaska (Juneau) support the hypothesis that the haze is generally heavier in northern Alaska. The haze blocks 25% of direct solar radiation at Barrow when the sun is 22° above the horizon. About half this radiation reappears in the form of diffuse radiation. Daily average optical thicknesses at Barrow and Fairbanks are shown in Figure I.H.1.

There are indications suggesting that the haze is richer in small particles ($r < 3 \times 10^{-5}$ cm) when the haze thickens. This information comes from the wavelength dependence of the optical extinction coefficient, shown as α in Figure I.H.1. An empirical relation between α and τ is shown in Figure I.H.2.; the interpretation of this relationship is not clear, but in general it would indicate that high turbidities are associated with a larger proportion of small particles.

The inverted aerosol size spectrum (Figure I.H.3. shows a typical example) shows tendencies toward bimodality, with peaks at about $r = 1.4 \times 10^{-5}$ cm and at $r = 1.5 \times 10^{-4}$ cm. A similar tendency has also been found by Keith Bigg for the Barrow aerosol. The sky-brightness scan from which Figure I.H.3. was derived is shown in Figure I.H.4.

Coronametric records (Shaw and Deehr, 1975) of sky brightness near the sun during haze episodes show a considerable amount of variation with time, which indicates unexpected horizontal inhomogeneities. Examples of these temporal variations are shown in Figure I.H.5. The "signal", actually the sky brightness at 1° from the sun, is due mainly to forward-scattered light from larger particles, especially particles larger than 1×10^{-4} cm. It thus seems that giant haze particles have a great natural variability. This may reflect the fact that larger particles tend to be lower in the troposphere because of

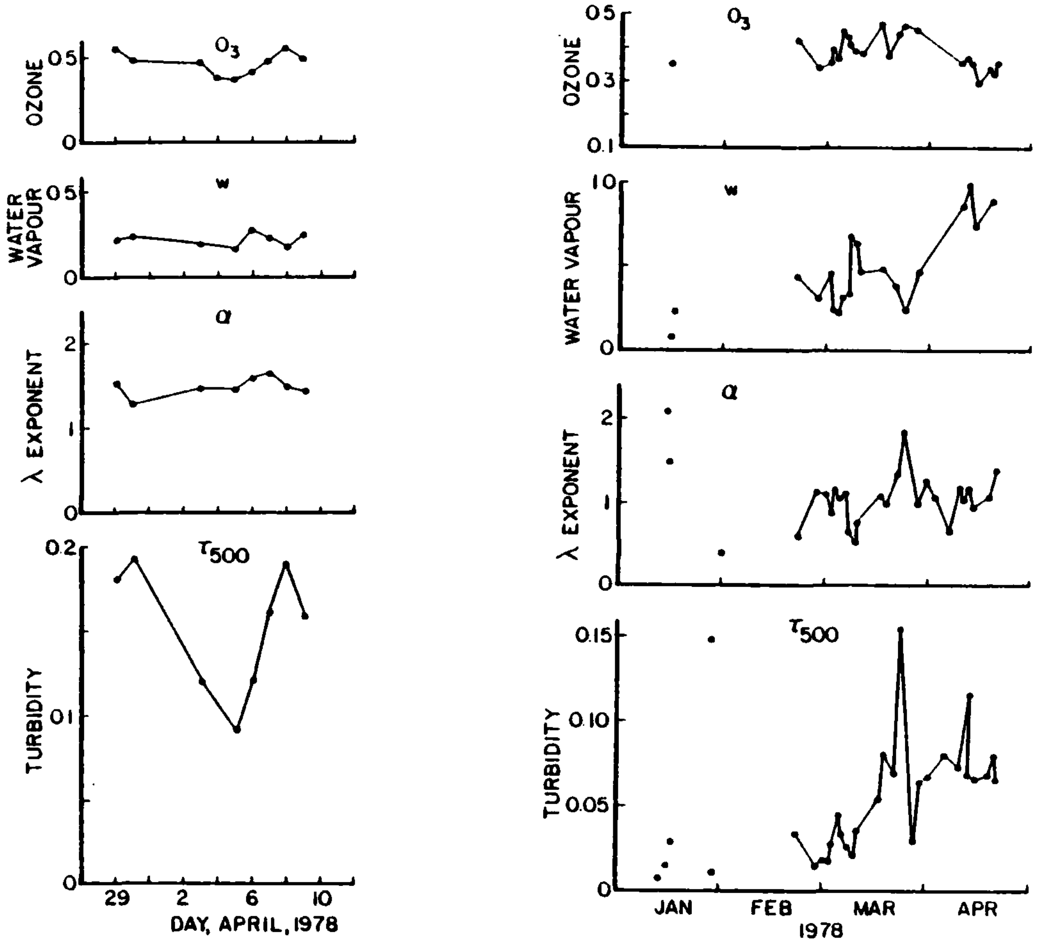

Figure I.H.1. Day average values of haze optical thickness at 500 nm wavelength, τ_{500}; precipitable water in g cm^{-2}, w; Angstrom wavelength coefficient, α and column ozone in column cm (STP), O_3. Left - Barrow (71.2°N). Right - Fairbanks (65°N).

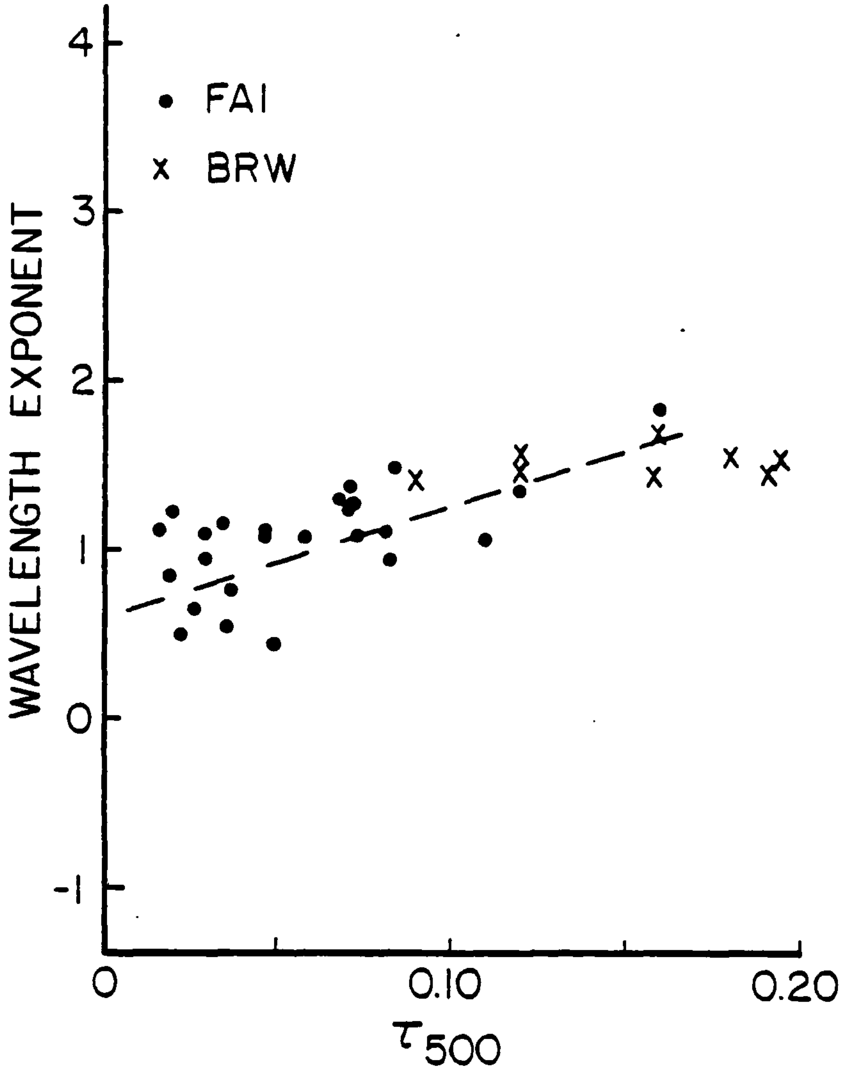

Figure I.H.2. Relation between haze optical thickness τ_{500} (500 nm wavelength) and the Ångstrom wavelength coefficient, α, (where $\frac{\tau_1}{\tau_2} = \left(\frac{\lambda_2}{\lambda_1}\right)^{\alpha}$) for spring haze, 1978.

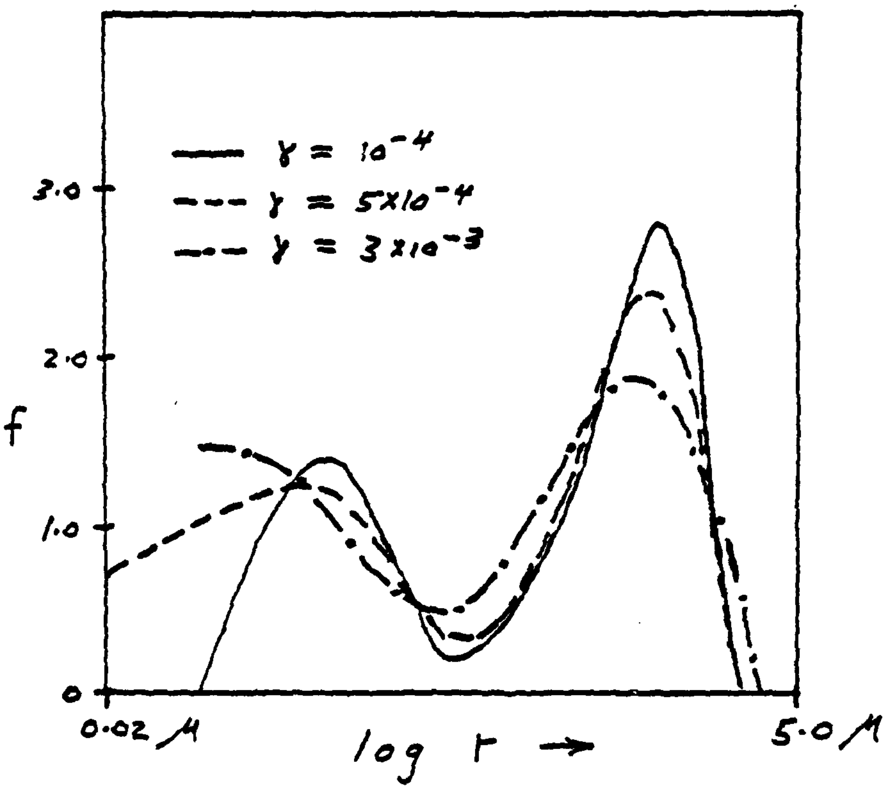

Figure I.H.3. Aerosol size spectrum factor (integrated through a vertical column) for April 11, 1978, during an episode of whitish diffuse haze at Fairbanks. The curves (estimates) were calculated by applying constrained linear inversion on optical scattering and extinction data, for 3 values of smoothing parameter. There is a tendency for bimodality at $r = 1.4 \times 10^{-5}$ and 1.5×10^{-4} cm. The aerosol size distribution estimate can be obtained by multiplying the curves by r^{-4}.

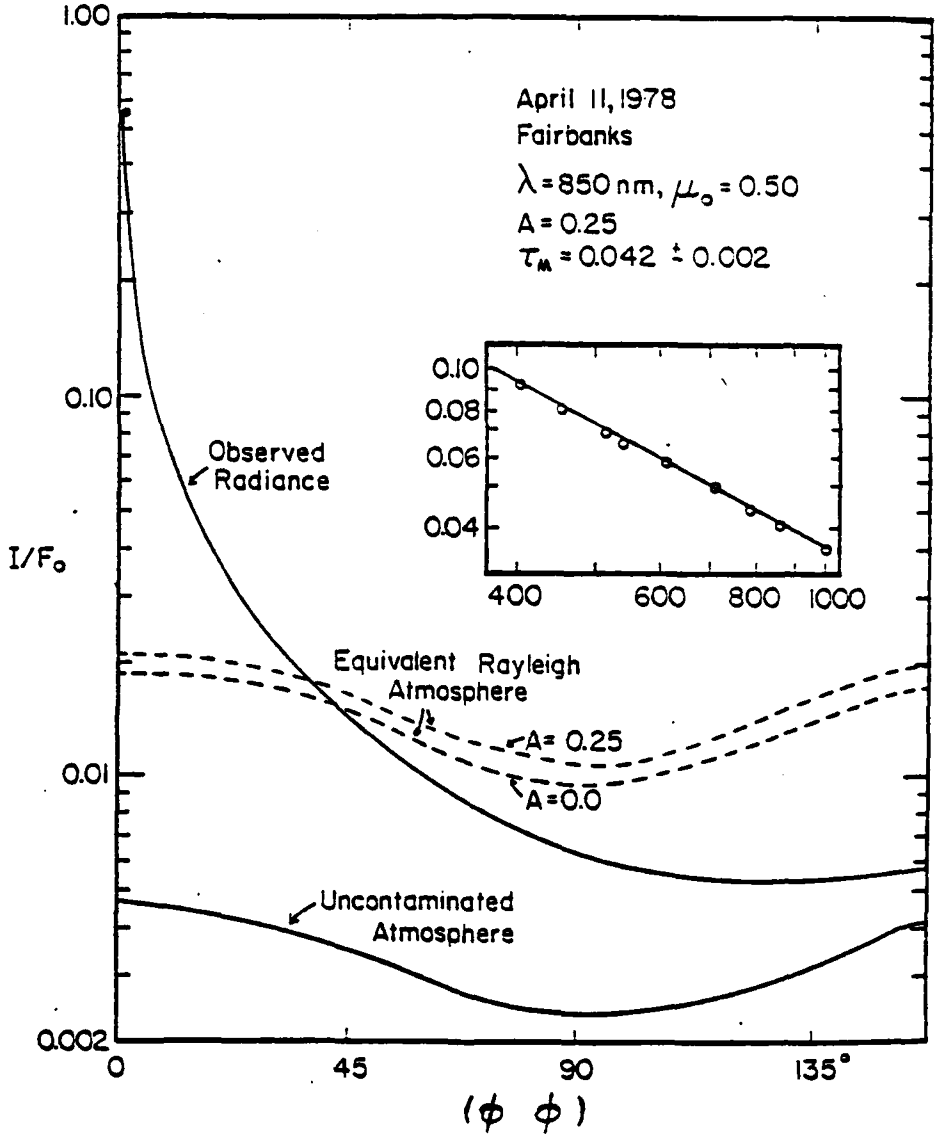

Figure I.H.4. Sky intensity (I/F_0) along the solar almucantar on April 11, 1978 near Fairbanks (500 nm wavelength) in units of stearadian^{-1}. The excess sky intensity due to haze scattering is seen by comparing with the calculated sky brightness curve (dotted) for a haze-free atmosphere. the enhancement in brightness close to the sun is caused by light diffracted by "large" haze particles.

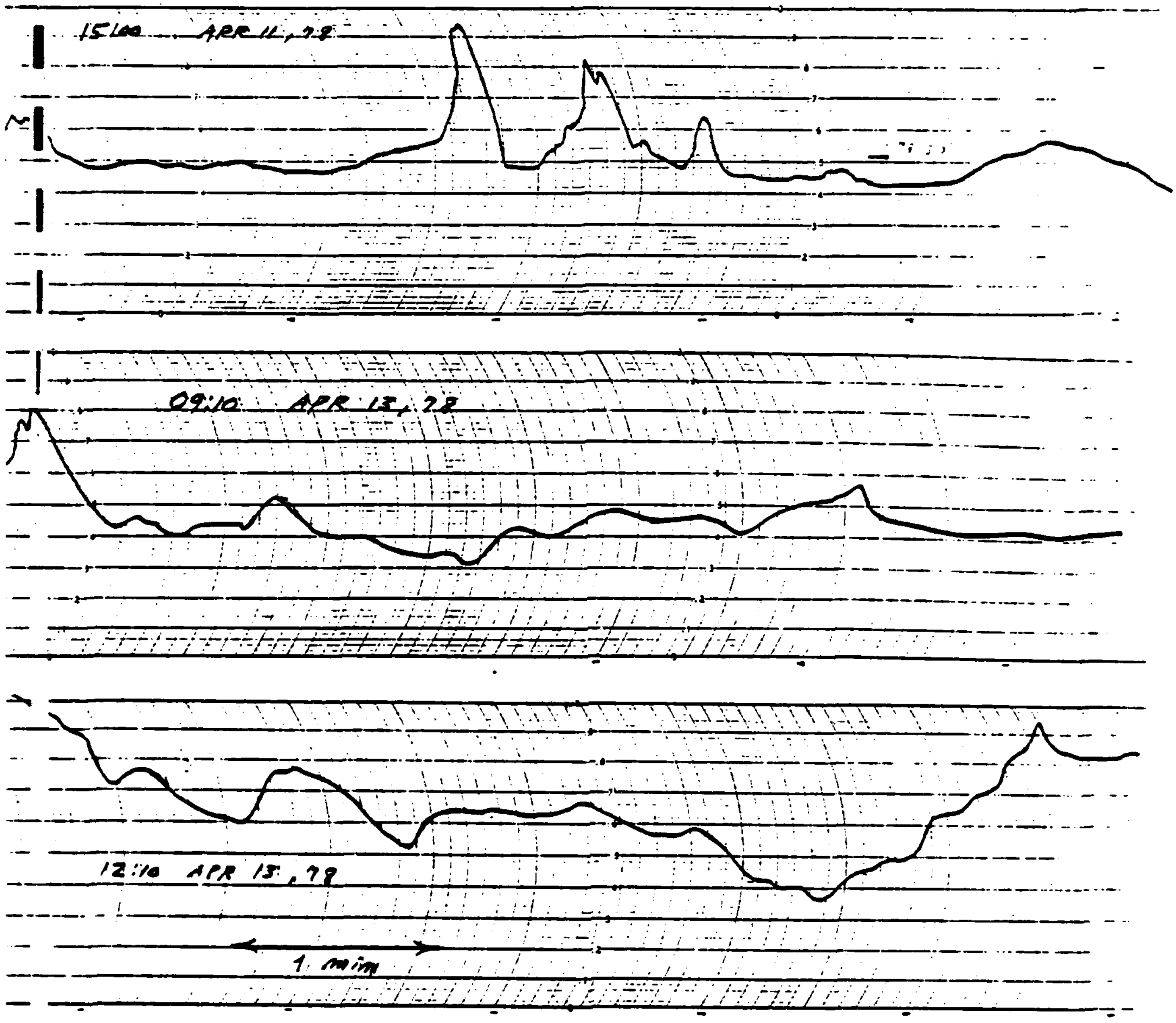

Figure I.H.5. Examples of sky brightness records at 1° from the sun (750 nm wavelength) during haze episodes. The fluctuations are caused by changing aerosols.

gravitational settling and are more variable because of higher turbulence in the low troposphere; it may also be associated with variations of pre-condensational growth of particles in nearly saturated layers.

Preliminary calculations from the diffuse radiation measurements indicate that the absorption coefficient for the haze is quite large, perhaps as large as $n_i = 0.05$ (where n_i is the imaginary component of the complex refractive index). This value is tentative, however.

I. Elemental analysis of desert soils as a function of particle size

During FY 78 Dr. Lothar W. Schütz of the Max-Planck-Institut für Chemie (MPI), Mainz, West Germany, completed his nine-month research visit at the Graduate School of Oceanography, University of Rhode Island. His principal project during these months was to use neutron activation analysis to determine the concentrations of 30-40 trace elements in size-fractionated desert soils from Africa and North America. This particular project was selected because it could be of use to both URI and MPI: MPI and Dr. Schütz have been involved for several years in the study of various aspects of deserts as potential sources of atmospheric aerosol, with emphasis on the Sahara Desert, which Dr. Schütz has visited and made the subject of his Master's and Ph.D. theses; our Arctic haze project has used the chemical composition of Alaskan aerosol of spring 1976 to determine that it was desert dust. Desert dust travels surprisingly long distances through the atmosphere, primarily because it is lifted to high elevations in the troposphere by intense thermal convection at the source, as opposed to, say, pollution aerosol which tends to remain at much lower levels near urban areas. As the great mobility of atmospheric aerosol becomes more and more recognized, more distant sources of aerosol like deserts will be discerned in remote aerosols from their detailed chemical composition. For this reason, MPI and URI decided to begin to build up a library of information about the chemical composition of various desert soils.

This task must be done as a function of particle size within the soils, however, because recent evidence has shown that neither elemental concentrations nor composition of desert soils is constant over particle size (Rahn *et al.*, 1976). We therefore decided to carry out this first investigation with several size fractions per soil sample.

The list of samples and fractions analyzed is shown in Table I.I.1 Each fraction contained particles over a radius range of about a factor of two. There were 11 samples from 5 locations in the Saharan and Great American Deserts. Wherever possible, samples were divided into 9 size fractions, by means of wet and dry sieving. All size fractionation was done at MPI before and during Dr. Schütz's stay at URI.

The Saharan soils from Libya were collected by Dr. Schütz (Schütz and Jaenicke, 1974); the Saharan soils from the Sudan were collected by Dr. S.A. Penkett of AERE Harwell, England (Penkett et al., 1977); the Arizona soil was collected outside Tucson by Mr. N. Korte, University of Arizona; and the Texas soil was collected by Dr. Dale Gillette of the National Center for Atmospheric Research, Boulder, Colorado.

Elemental compositions of the samples were determined by Dr. Schütz at URI, using facilities of the Rhode Island Nuclear Science Center. The accuracy of the analysis was checked by co-determination of elemental concentrations in four standard reference materials: JG-1 and JB-1 (Granite and Basalt from the Geological Survey of Japan, SRM 1571 (orchard leaves from the National Bureau of Standards), and SRM 1633 (flyash from the National Bureau of Standards).

The analytical procedure was as follows: A portion of each sample was weighed into a polyethylene vial and irradiated for 5 minutes in the RINSC swimming-pool nuclear reactor at a thermal-neutron flux of 4×10^{12} n cm^{-2} s^{-1}. After 15 minutes' cooling, its gamma radiation was counted for 1000 seconds on a Ge(Li) semiconductor detector connected to a 4196-channel analyzer, preceeded by a brief count of a co-irradiated Al flux monitor. From this count Dy, Ba, Ti, Sr, In, I, Br, Mn, Mg, Cu, Si, Na, V, Cl, Al, Ca, and S

Table I.I.1. Soil samples analyzed.

Radius µm	S-2	S-10	S-39	S-12	S-24	S-29	S-32/34	A	T	T-VII[1]	T-VIII[2]	FL	CTF-7
160-400	*	*	*	*	*	*	*	*	*	*	*	↑	↑
80-160	*	*	*	*	*	*	*	*	*	*	*	|	|
32-80	*	*	*	*	*	*	*	*	*	*	*	|	|
16-32	*	*	*	*	*	*	*	*	*	*	*	*	*
8-16	*	*	*	*	*	*	*	*	*	*	*	*	*
4-8	*	*	*	*	*	-	*	*	*	|	|	*	*
2-4	*	*	*	|	|	-	*	*	*	|	|	*	*
1-2	*	*	*	|	|	-	|	*	*	|	|	*	|
<1	*	*	*	↓	↓	-	↓	*	*	↓	↓	*	↓
Location	Camp Derj, Libya (Saharan rock desert)			Sebha Oasis, Libya (Saharan dune sands)				Arizona USA	Texas, USA			Sudan (Sahara)	

Arrows denote broader size ranges.

1) wet-sieved
2) dry-sieved

could be determined, subject to their relative abundances in the sample. A larger portion of the same sample was then weighed into another polyethylene vial, and together with a number of other similar samples, standards, and flux monitors, given a 7-hour irradiation in the same reactor at the same flux. These samples were then counted after 1 day for Sm, Mo, Cd, Au, Zn, Br, As, Sb, W, Ga, Eu, Na, K, and La; after 1 week for Sm, Au, Br, Sb, and La; and finally after 1 month for Ce, Lu, Se, Hg, Yb, Th, Cr, Hf, Ba, Nd, Ag, Zr, Cs, Ni, Tb, Sc, Rb, Fe, Co, Zn, Eu, and Sb. To date, the complete procedure has yielded useful data on roughly 30 elements per sample.

Because of the number of analyses in the project (between 300 and 4000 data points will eventually result), not all the calculations have been completed. In the rest of this section we summarize the results for one typical soil sample, as an indication of the main conclusions that are emerging.

Table I.I.2. gives the preliminary results from the Texas sample, expressed as ppm. The enrichment factors relative to Fe and crustal rock of Mason (1966) are given in Table I.G.3. There is a general trend of increasing elemental concentrations with decreasing particle size, with concentrations in the small range being 10 to 2 orders of magnitude higher than those in the largest size range. This was found to varying degrees in all samples except the two from the Sudan, which were cultivated land rather than deserts. For example, dune areas such as the Sebha Oasis in Libya (samples S-24 and S-29) had the largest increase of concentration, up to 3 decades. These samples consist of "blown-out" material, whose small particle-size fraction ($r < 16 \mu m$) has been almost completely removed

Table I.I.2. Elemental concentrations (ppm) in the Texas soil.

r,μm	<1	1-2	2-4	4-8	8-16	16-32	32-80	80-160	160-400
Na	3,250±100	3,800±100	4,800±100	5,800±100	7,100±100	8,300±100	1,130±50	130±5	70±5
K	21,000±1000	16,500±500	16,800±1000	15,500±1000	13,300±1000	15,500±1000	7,000±500	1,500±100	740±50
Sc	14.8±0.2	11.0±0.2	10.0±0.1	7.9±0.1	6.0±0.1	5.8±0.1	1.35±0.05	0.52±0.01	0.31±0.01
Cr	86±2	65±3	60±3	41±2	71±2	74±2	15±1	4.9±0.1	3.8±0.
Fe	46,000±1000	33,000±1000	31,000±1000	24,000±1000	20,000±1000	21,000±1000	5,600±100	2,200±100	1,440±100
Co	8.6±0.3	1.3±0.2	9.2±0.4	7.6±0.3	5.2±0.3	4.7±0.3	0.93±0.04	0.39±0.02	0.28±0.02
Ni	—	—	—	—	—	—	—	—	10±4
Zn	—	—	—	—	—	—	—	—	—
Ga	25±2	15±2	19±2	13±2	14±3	—	2.5±0.4	0.88±0.08	0.60±0.05
As	16±1	13±1	17±2	6±1	5±1	—	1.1±0.2	0.55±.05	0.36±.03
Se	—	3.5±1.6	3.8±1.3	—	—	—	—	—	—
Br	27±3	—	23±5	—	9±5	—	—	—	—
Rb	153±10	195±25	115±10	98±10	60±7	75±8	29±1	8.7±0.6	4.8±0.4
Mo	—	—	—	—	—	—	—	—	—
Ag	76±3	105±4	90±3	16±2	—	—	—	—	—
Cd	—	—	—	—	—	—	—	—	—
Sb	1.8±0.2	1.3±0.2	1.0±0.1	0.6±0.1	0.66±0.10	1.7±0.1	0.35±0.03	0.19±.01	0.12±.01
Cs	7.3±0.3	5.8±0.5	4.6±0.3	3.4±0.3	2.0±0.2	2.4±0.2	0.85±0.04	0.38±0.02	0.26±0.02
Ba	480±90	—	590±120	660±100	440±70	740±330	210±20	73±6	57±4
La	48±2	49±1	46±2	37±1	54±2	36±1	9.1±0.2	5.6±0.3	4.9±0.2
Ce	113±3	102±2	93±2	72±2	92±5	58±2	16±1	7.3±0.1	6.2±0.1
Nd	52±13	79±32	—	—	33±7	—	5.2±1.1	2.8±0.6	2.4±0.4
Sm	5.4±0.1	6.5±0.1	6.8±0.1	5.1±0.1	6.4±0.1	4.2±0.1	1.2±.1	0.60±.05	0.53±.03
Eu	1.1±0.1	1.4±0.1	1.3±0.1	1.1±0.1	1.1±0.1	0.75±0.15	0.27±0.03	0.11±.01	0.085±0.005
Tb	2.0±0.9	—	—	2.0±0.9	1.4±0.3	1.1±0.7	0.24±0.05	0.11±0.02	0.067±0.015
Lu	0.59±0.05	0.52±0.07	0.28±0.03	0.34±0.04	0.70±0.03	0.89±0.04	0.13±0.01	0.042±0.002	0.032±0.002
Hf	4.1±0.2	4.3±0.3	3.8±0.2	4.7±0.2	35±1	57±1	7.9±0.1	0.78±0.02	0.66±0.02
W	—	8.3±2.1	4.5±1.8	—	—	—	—	0.32±0.08	—
Au	0.29±0.02	0.37±0.01	0.12±0.01	0.06±0.01	—	0.01±0.001	—	0.002±0.002	0.004±0.003
Hg	58±2	—	8.4±1.6	1.85±0.65	—	—	—	—	—
Th	15±1	12.5±0.4	10.9±0.3	9.2±0.3	15±1	10±1	1.8±0.1	0.85±0.02	0.72±0.02

Table I.I.3. Enrichment factors (Fe, rock) for the Texas soil.

Radius,µm	<1	1-2	2-4	4-8	8-16	16-32	32-80	80-160	160-400
Na	0.12	0.20	0.27	0.43	0.63	0.70	0.36	0.10	0.09
Si	-	-	1.6	-	1.6	3.0	9.0	22	34
K	0.88	0.97	0.92	1.25	1.28	1.42	2.41	1.32	0.99
Sc	0.73	0.76	0.73	0.75	0.68	0.63	0.55	0.54	0.49
Ti	0.80	1.00	0.90	1.00	2.6	3.0	1.25	1.00	0.78
V	0.70	0.80	0.80	0.70	1.1	1.00	0.60	0.78	1.00
Cr	0.93	0.98	0.97	0.85	1.78	1.76	1.34	1.11	1.32
Fe	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Co	0.37	0.08	0.59	0.63	0.52	0.45	0.33	0.35	0.39
Ga	1.81	1.52	2.0	1.81	2.3	-	1.49	1.33	1.[illegible]
As	9.7	10.9	15.2	6.9	6.9	-	5.5	6.9	6.9
Se	-	106	122	-	-	-	-	-	-
Br	11.7	-	14.8	-	9.0	-	-	-	-
Rb	1.85	3.3	2.1	2.3	1.67	1.98	2.9	2.2	1.85
Ag	1180	2300	2100	480	-	-	-	-	-
Sb	9.8	9.8	8.1	6.2	8.2	20	1.6	22	21
Cs	2.6	2.9	2.5	2.4	1.67	1.90	2.5	2.9	3.0
Ba	1.23	-	2.2	3.2	2.6	4.2	4.4	3.9	4.7
La	1.74	2.5	2.5	2.6	4.5	2.9	2.7	4.2	5.7
Ce	2.05	2.6	2.5	2.5	3.8	2.3	2.4	2.8	3.6
Nd	2.02	4.3	-	-	3.0	-	1.66	2.3	3.0
Sm	0.98	1.64	1.83	1.77	2.7	1.67	1.79	2.3	3.1
Eu	1.00	1.77	1.75	1.91	2.3	1.49	2.0	2.1	2.5
Tb	2.42	-	-	4.6	3.9	2.9	2.4	2.8	2.6
Lu	1.28	1.58	0.90	1.42	3.5	4.2	2.3	1.91	2.2
Hf	1.49	2.2	2.0	3.3	29	45	24	5.9	7.0
W	-	8.4	4.8	-	-	-	-	4.8	-
Au	79	140	48	31	-	6.0	-	11.4	35
Hg	790	-	169	48	-	-	-	-	-
Th	2.3	2.6	2.4	2.7	5.2	3.3	2.2	2.7	3.5

by wind. A rock desert in Libya (samples S-2, S-10, and S-39) had a smaller concentration increase of roughly 1½ decades. These samples contained larger amounts of fine particles. The rock desert showed high rates of weathering (high frequency of sandstorms and dust devils) and high atmospheric turbidities. The Arizona sample had a moderate concentration pattern, with variations of less than about ½ decade. Finally, the Sudan samples had elemental concentrations which were essentially independent of particle size.

The size interval where the concentrations changed the most strongly was in general the sand range ($r > 30 \mu m$). Within the silt ($r = 1$ to $30 \mu m$) and clay ($r < 1 \mu m$) ranges the elemental concentrations were nearly constant. This is a very important feature of the results, because it is in these size ranges that the atmospheric aerosol is found. Progressive depletion of the larger desert-dust aerosol particles during transport of an air mass would not be predicted to greatly affect the composition of the aerosol. Observations of the Sahara plume confirm this (Rahn _et al._, 1976). Thus, chemical characterization of desert dust near its source should adequately represent it even after long-range transport.

It is interesting to note that Si has a concentration pattern which is nearly opposite to that of all the other elements. Whereas the other elements are constant in concentration throughout the clay and silt ranges, then decrease in the sand range, Si is constant throughout the clay and silt ranges, then increases strongly in the sand range. This seems to indicate that the SiO_2 of sand is the diluent of the other elements there. This explanation makes a great deal of sense, because of the well-known resistance of quartz to weathering. The Si/Al ratio, which has values of roughly 1-4 in the aerosol and 3-6 in bulk soil and rock, can be used as an indicator of the freshness of a crustal aerosol (Rahn, 1976). Out data provide a natural explanation for this, by showing that the Si/Al ratio is a strong function of particle size. For particle radii less than about 4-6μm the Si/Al ratio is close to that observed in the aerosol, but as particle size increases to 100μm it increases to values of 100 or more. These data show that Si, in spite of the commonly held view that it is the best reference element for calculation of aerosol-crust enrichment factors, is actually one of the riskiest, especially near sources of crustal aerosol.

From Table I.I.3. it can be seen that elemental enrichment factors generally have a maximum somewhere in the silt range. For some elements like Na this maximum is several times higher than the clay value, for others it is within a factor of two of the clay value. For some of the heavy metals such as As and Sb, there seems to be a moderate maximum of enrichment factor at the largest or smallest particles. Other elements, like Cs and Rb, have no discernable trend of enrichment factor with particle size.

Table I.I.3. is a particularly interesting one, for it goes a long way toward explaining a number of peculiar features of the composition of atmospheric aerosols which have been observed for 5-10 years but never properly understood. We now list a few of these features. A number of the "nonenriched" elements in the aerosol, such as Ba, the rare earths, Hf, and Th consistently show enrichment factors of about 2 relative to bulk crustal rock, both in the general aerosol and in the Sahara plume (Rahn, 1976a; Rahn _et al_., 1976). We have wondered for some time whether this was due to a particle-size effect within the soils from which the aerosol was derived, i.e., aerosol-crust fractionation, or whether it represented a bulk difference in composition between the parent soils and the crust as a whole. The Texas soil shows these same modest enrichments for the Si elements, but reveals clearly that they are essentially independent of particle size. This suggests that chemical weathering of the entire soil rather than selection of a narrow range of particle sizes by the wind is responsible for these enrichments. We have observed that Na, Sc, Co, and Mn are normally depleted in the aerosol relative to the crust; this is also confirmed by this data to be a property of the bulk soil. A number of heavy metals such as As, Ag, Sb, Au, and Hg, which normally have their major sources in materials other than desert soils, seem still to be enriched in areas where desert soils ought to be the main source of the aerosol. Table I.I.3. shows that these elements are enriched in the Texas soils by roughly 1 to 3 decades, in close agreement with aerosol observations (Rahn, 1976). Interestingly, these enrichements are nearly independent of particle size.

To show just how well the Texas soil agrees with the Sahara aerosol, which in turn agrees well with much of the world aerosol, especially for the nonenriched elements, we have constructed Table I.I.4. In this table we show the ranges of enrichment factor for the elements in the clay, silt, and sand ranges of the Texas soil. For comparison purposes the last column gives enrichment factors for the Sahara plume and the silt-clay ranges of the Texas aerosol.

In summary, then, this work is showing that many features of the atmospheric aerosol which deviate from the properties of the bulk crust seem to be explainable by a desert-soil precursor, in which the entire soil has been weathered. There seems to be less direct aerosol-soil fractionation than we had originally expected.

Table I.I.4. Texas enrichment factors in three size ranges compared to those of the Sahara plume.

Element	EF_{sand} (r >30 m)	EF_{silt} (1μm < r < 30μm)	EF_{clay} (r <1 m)	$EF_{Sahara\ plume}$
Na	0.1-0.4	0.2-0.7	0.1	0.14
Mg	0.5	0.5	0.7	0.8
Si	9-34	1.6-3.0	-	-
Cl	85	-	-	-
K	1.0-2.4	1.0-1.4	0.9	0.7
Ca	0.1	0.2	0.2	0.7
Sc	0.5	0.6-0.8	0.7	0.7
Ti	0.8-1.2	0.9-3.0	0.8	1.4
V	0.6-1.0	0.7-1.1	0.7	0.9
Cr	1.1-1.3	0.8-1.8	0.9	1.0
Mn	0.4	0.6	0.3	1.1
Fe	1.0	1.0	1.0	1.0
Co	0.3-0.4	0.4-0.6	0.4	0.5
Ga	1.4-1.5	1.5-2.3	1.8	1.9
As	5-7	6-15	10	8
Se	-	100-120	-	99
Br	-	9-15	12	-
Rb	2-3	1.7-3.3	1.8	1.0
Ag	-	500-2300	1200	23
Sb	15-22	6-20	10	6
Cs	2.5-3.0	1.7-2.9	2.6	1.4
Ba	4-5	2-4	1.2	2.3
La	3-5	2.5-4.5	1.7	1.8
Ce	2.4-3.6	2.5-3.8	2.0	1.8
Nd	1.7-3.0	3-4	2.0	-
Sm	1.8-3.1	1.6-2.7	1.0	1.7
Eu	2.0-2.5	1.5-2.3	1.0	1.7
Tb	2.4-2.8	2.9-4.6	2.4	2.0
Dy	2.7	3.7	1.5	1.7
Lu	1.9-2.3	0.9-4.2	1.3	1.4
Hf	6-24	2-45	1.5	2.0
W	∿5	5.8	-	2.5
Au	11-35	6-140	80	10
Hg	-	50-170	800	57
Th	2.2-3.5	2.4-5.2	2.3	1.9

J. Determination of sulfate concentrations in Arctic aerosols.

Perhaps the single most significant constituent of remote aerosols is sulfate. This soluble ion accounts for typically 50% of more of the mass of most aerosols in "background" regions, and should therefore be the starting point of investigations whose purpose is to understand the overall character of a particular aerosol rather than the individual trace elements within it. We, however, proceeded in the opposite fashion. Being of a multi-elemental background, we first investigated many of the minor elements in the Arctic aerosol.

In spring 1978 our attention was drawn strongly to sulfate by events described in Section I.F. As a result, we decided that the time had come to begin sulfate determinations in our laboratory. Dr. Richard J. McCaffrey, who has been associated with our Arctic haze project for the last year, developed an analytical technique for sulfate which uses ^{133}Ba tracer and existing, underutilized NaI(Tℓ) gamma-counting equipment which was readily available at the Rhode Island Nuclear Science Center, where we perform our neutron-activation analyses. This technique is now working very well, and is being systematically applied to all our filters from the past two years at Fairbanks and Barrow, as well as some from Rhode Island, New York and Colorado. The first results from Barrow are discussed in Section I.N.4. - they are already providing us with great insights into the processes which control the abundance and composition of the Arctic aerosol, namely mid-latitude sources and long-range transport.

Analytical procedure

From each 20x25 cm (8x10") Whatman No. 41 cellulose filter that is to be analyzed for sulfate, one or two 7/8"-diameter disks are removed and placed in the bottom of a 15-mℓ tapered polystyrene centrifuge tube, 1.5 mℓ of 0.05 N HCl wash solution is added, and the top is screwed on. Samples are usually processed in batches of about 30 with ten standards. The standards range from 20 to at least 400μg sulfate, and are usually run in duplicate. They can be prepared in either of two ways, found to be indistinguishable; namely, evaporating a solution of $(NH_4)_2SO_4$(1 mg $SO_4^=$/mℓ) spotted onto a Whatman No. 41 disk, or by pipetting directly into the centrifuge tube. Sufficient wash solution is added to standards to also give a volume of close to 1.5 mℓ. The 40 sealed tubes are inserted into a holder which is placed into boiling water and left ther for ½ hour, during which the sulfate is leached from the filters. Each tube is submerged only to the top of the leachate, so that refluxing can take place on the interior surfaces of the tube. This is important because there may be a positive pressure when the hot tubes are opened, and some of the liquid on the underside of the cap can be lost. When there is refluxing, the walls are washed down and, because this condensate is distilled water, any liquid lost upon opening the hot test tube will not contain appreciable sulfate. The tubes are lifted from the boiling water, and the filters are brought to the top of the test tube with a plastic hook. The hook is rinsed with a few drops of solution. This rinse and any solution remaining in the ½ mℓ micropipette are directed in such a way that the wash solution then flows over one side of the filter and back into the tube. Next, tweezers are used to hold the filter over the test tube mouth and the other side of the filter is also washed with ½ mℓ of wash solution. Drops hanging from the edges of the filter are removed by touching the side of the tube. Spotted standards are treated in the same way as samples. In the case of liquid standards, 1 mℓ of wash solution is simply added to attain the same final volume.

All 40 centrifuge tubes are placed back into the hot water bath in the rack, and left for about 10 minutes, during which time their temperature rises to about 95°C. Each tube is then taken out individually, and 1 mℓ of Ba-133 tracer solution (0.06 μC/mℓ, in a mixture of 5 mM $BaCl_2$ and 1.2×10^{-4} N HCl) is added. Each tube then contains 3.5 mℓ of liquid. The bath is turned off, and allowed to sit for at least two days, until the precipitate is properly formed. All tubes are then centrifuged for 3-4 minutes at about 1200 rpm. Using a micropipette aspirator, all but 0.1 mℓ of the liquid is drawn off, and fresh wash solution is added until the total volume is again 3.5 mℓ. The cycle of centrifuging, aspirating, and adding fresh wash solution is then repeated 3 more times, for a total of 4 cycles (we are presently experimenting with shortening this to 2 cycles). After the final centrifugation the wash wolution is removed without replacement and the tubes capped and counted for 1 to 10 minutes in a well-type NaI(Tℓ) gamma-ray detector coupled to a single-channel analyzer. The window is set wide enought to include all principal decay peaks of Ba-133. Blank filters are treated the same as exposed filters. A sample with 400 μg of sulfate will give roughly 60,000 cpm in our detector; blanks, which are usually indistinguishable from background, give about 1000 cpm.

The calibration curve of count rate vs. sulfate concentration is linear between 50 and 400 μg, and has a slightly negative intercept. The detection limit is about 25 μg sulfate. Most uncertainties seem to be less than 10%. For summer samples with very low sulfate concentrations, uncertainties can sometimes be higher than 10%. Two tests of replicate samples from the same filter, one heavily loaded and the other lightly loaded, showed coefficients of variation of less than 3% when replicates were analyzed in the same batch (Table I.J.1.). We are presently testing both the reliability of the sampling procedure (with two side-by-side setups) and the batch-to-batch variations of the analysis. Absolute accuracy of the analysis seems to be about 2%, as judged by the mean of two determinations on an EPA water standard.

Table I.J.1. Replication of the sulfate analysis, using 5 punches from each of two Barrow high-volume filters.

Sample	B-19	B-35
	2.56 μg $SO_4^=$ m^{-3}	0.416 μg $SO_4^=$ m^{-3}
	2.64	0.411
	2.65	0.408
	2.49	0.403
	2.55	0.429
$\overline{X} \pm \sigma(n) =$	2.58 ± 0.07(5)	0.413 ± 0.010 (5)
c.v.	2.6%	2.4%
	∿300 μg per punch	∿50 μg per punch

K. Alert, Northwest Territories sampling site

The Canadian Atmospheric Environment Service (AES), a branch of Environment Canada, had a representative at the April 1977 planning meeting of the Arctic Air-Sampling Network, and has since then expressed a strong interest in becoming an official part of this program. During this year we reached an agreement with them, through their contact man Dr. Leonard Barrie, on an AES/URI cooperative program at Alert, NWT, or possibly at an equivalent site. The station is basically theirs - AES has contracted with URI to supply them, at cost, with a pump-shelter combination for collection of high volume aerosol samples on 20x25 cm cellulose filters, similar to our sites in Barrow and Fairbanks. Because Alert is a Canadian military site, the AES will install the system and operate it. All the filters will, however, be sent to URI for chemical analysis.

The station was originally foreseen to have begun operation in summer 1978, but because of delays in evaluation of the site for possible simultaneous use as a WMO background monitoring site, we have been advised that sampling will begin in summer 1979.

The system has been constructed, calibrated, and tested at URI. As soon as it is inspected by Mr. Ken Petit of AES it will be shipped to their laboratories in Downsview, Ontario. We are looking forward with great anticipation to the operation of this station, because it is situated in such a different part of the Arctic from Barrow and Spitsbergen. The data generated from this site will have much to say about the degree of homogeneity of the Arctic aerosol.

L. Aerosol-snow chemical fractionation - A spinoff project

During FY78 our Arctic haze project spawned another one, on aerosol-snow chemical fractionation in the Arctic (and elsewhere). In December 1977 K. Rahn came upon a preprint of an article by Weiss et al. (recently published as Weiss et al., 1978) which used the trace-element composition of several modern and historic Arctic snows to conclude that the modern Arctic aerosol was exclusively natural in origin. Of greatest interest to us was a series of snows taken in February 1974 near Barrow, which showed natural (crustal) proportions for Al, V, and Mn. This was in direct contradiction to our aerosol analyses from the last two years at Barrow, which indicated that V was nearly 95% pollution-derived and Mn was about 75% pollution-derived, at least during the winter.

What made this turn of events so fascinating was that we had no reason to doubt the validity of either the snow data of Weiss et al. (they are one of the premier groups in trace-element analyses of snows) or our aerosol data (it is reproducible from year to year and from site to site in the Arctic). Having accepted both data sets, we were forced to conclude that Arctic snows and Arctic aerosols give quite opposite pictures of their environment - the former points toward the natural origin of trace elements in the Arctic whereas the latter shows that the very same elements are in fact pollution-derived.

Clearly, the direct evidence of the aerosol is more valid than the indirect evidence of the snows. But how can the snows be so misleading? We postulated that there must be major aerosol-snow chemical fractionation occurring regularly in the Arctic, and systematized our thoughts in a fairly detailed research proposal of URI to the Atmospheric Chemistry section of the National Science Foundation. Should this proposal be funded, and we hope that it will be as of 1 November 1978, our research into the Arctic aerosol will have closed the environmental loop by adding deposition to the previous topics of sources, transport, and characteristics.

The essence of this proposal is contained in Section I.M.5., which is the preprint of an article which we have submitted to *Nature* in response to the original article of Weiss *et al*., which we believe contains a number of errors.

M. Publications, August 1977-July 1978

During this year we have had 10 publications which have either been submitted, accepted, or which have appeared. They are listed below, roughly in order of decreasing importance. The first five, which are judged to be particularly relevant to the main points of this progress report, are reproduced here. Note that some of these publications were listed in last year's report, having changed in status in the inerim.

Rahn, K.A., R.D. Borys and G.E. Shaw, "The Asian source of Arctic haze bands", *Nature*, *268*, 713-715 (1977).

Rahn, K.A., R.D. Borys and G.E. Shaw, "Particulate air pollution in the Arctic: Large-scale occurrence and meteorological controls", *Proceedings of the 9th International Conference on Atmospheric Aerosols, Condensation and Ice Nuclei*, Galway, Ireland, 21-27 September 1977 (In press).

Rahn, K.A., "The Arctic Air-Sampling Network", *Arctic Bulletin* (In press).

Rahn, K.A., L. Schütz and R. Jaenicke, "The crustal component of background aerosols: its importance in interpreting heavy metal data", *Proceedings of the World Meteorological Organization Technical Conference on Atmospheric Pollution Measurement Techniques, (TECOMAP)*, Gothenburg, Sweden, 11-15 October 1976 (In press).

Rahn, K.A. and R.J. McCaffrey, "Low "natural" enrichment of elements in modern Arctic snow: Derived from fractionated pollution aerosol?" *Nature* (Submitted).

Walsh, P.R., K.A. Rahn and R.A. Duce, "Erroneous mass-size functions resulting from particle bounce-off in a high-volume cascade impactor", *Atmos. Env.* (In press).

Leaderer *et al.* "Summary of the New York Summer Aerosol Study (NYSAS)", *J. Air Poll. Control Assoc.*, *28*, 321-327 (1978).

Larssen, S. and K.A. Rahn, "Elemental concentrations of total suspended particulate matter in background areas in Scandinavia as a function of Northern Latitude." Discussion Paper No. R.3/COM.5, presented at Seminar on Fine Particles, Economic Commission for Europe, Villach, Austria, 17-22 October 1977. To appear in *Proceedings*.

Bernstein, D.M. and K.A. Rahn, "New York summer aerosol study: trace element concentration as a function of particle size", New York Academy of Sciences Monograph (Submitted).

Lioy, P.J., G.T. Wolff, K.A. Rahn, T.J. Kneip, D.M. Bernstein and M.T. Kleinman, Characterization of aerosols upwind of New York City. I. Aerosol composition", New York Academy of Sciences Monograph (Submitted).

I.M.1.

(Reprinted from Nature, Vol. 268, No. 5622, pp. 713–715, August 25, 1977)

The Asian source of Arctic haze bands

'ARCTIC haze' refers to turbid layers of air which are found regularly over the pack ice north of Alaska during periods of clear weather[1]. These layers are diffuse, hundreds to thousands of kilometres wide, 1–3 km thick, and can occur as single or multiple bands of different heights at nearly any level in the troposphere. They are invisible from the ground, but may limit horizontal and slant visibility within a layer to as little as 3–8 km. Their colour is grey–blue in the antisolar direction and reddish–brown in the solar direction, suggesting that they are true aerosol rather than ice crystals.

The initial, purely visual observation of Arctic haze were made more than 20 years ago. It was then forgotten about until 1972 when radiation measurements near Barrow, Alaska revealed unexpectedly high atmospheric turbidities, confirmed in 1974 (ref. 2). The anomalous turbidity was partly found in distinct layers at altitudes of only a few kilometres. About 40%, however, was above 4 km, the effective ceiling of the aircraft used.

The 1974 observations raised the question of possible anthropogenic origin of the haze, because rough trajectory analysis for a persistent haze period during March and April 1974 suggested that the air had passed over the north-eastern United States some days earlier. To check this possibility, we have used the chemical composition and morphology of the spring 1976 Arctic aerosol as indicators of its source, and concluded that it originated in the great Asian deserts. During April and May 1976 a series of 15 flights with a single-engine aircraft were made from the Naval Arctic Research Laboratory in Barrow, Alaska. Nine high-volume (90–360 m^3) samples of haze aerosol were collected on acid-washed 11-cm Whatman No. 41 cellulose filters. Nuclepore filter samples were taken concurrently for electron microscopy. Height of the haze layers was determined by a combination of visual observation, condensation-nucleus count, and turbidity profile.

The high-volume samples were subsequently analysed at the University of Rhode Island for a number of elements with short-lived nuclides by neutron activation, with results shown in Table 1. The month-long sampling period had very low elemental concentrations at the beginning, a strong maximum in the middle, followed by a sharp dropoff at the end. The high-concentration period coincided with visible haze bands, all of whose visual properties suggested Arctic haze. The bands did not come and go quickly; rather a single broad maximum of 6–13 days' duration was seen. During this period Al and Mn were increased in concentration relative to their initial and final values by over an order of magnitude, V by an order of magnitude, and Na and Ba by somewhat less than an order of magnitude.

The aerosol-crust enrichment factors (Table 1) for the elements

$$Ef_X(\text{Al, rock}) = (X/\text{Al})_{\text{aerosol}}/(X/\text{Al})_{\text{rock}}$$

showed similar trends of high values in the early samples which decreased smoothly to unity or lower with increasing haze aerosol. For V the trend was most marked; indeed of these elements V has the highest enrichments in cities (5–500 (ref. 3)). Taken together, the trends of these enrichment factors clearly indicated that the background aerosol was pollution-derived but that the haze aerosol itself was crustal, that is natural, just the opposite of what we had expected. Electron microscopy of the Nuclepore filters showed that angular crustal particles of diameter greater than roughly 0.4–0.8 μm are present in all samples, but with greatly increased numbers during the haze episode. In contrast, most particles smaller than 0.4–0.8 μm diameter were nearly spherical; their abundances were much less haze-dependent. Although we have studied only this one episode, we feel that it may well be typical, as discussed below.

The source of the crustal haze aerosol must be very strong to account for its high concentrations. It seems to be the great Takla Makan and Gobi deserts of eastern Asia. Upper-level constant-pressure charts indicate that our haze period was preceded by several days of intense air flow from these deserts to Alaska. Figure 1 shows the 700-mb isobaric trajectories for air arriving at Barrow before, during, and after the episode. Only episodic air had recently passed over the Asian deserts.

Several factors support the idea of an Asian source for Arctic haze. First, spring is the period of greatest dust storms in deserts. In our case, during nearly all of April 1976 the Asian deserts were filled with dust storms. Second, the composition of Arctic haze greatly resembles that of the Sahara aerosol (K. A. Rahn, L. Schütz, and R. Jaenicke, unpublished data). Third, flow patterns conducive to long-range transport from Asia to Alaska are strongest during the spring[4,5]. Fourth, the Asian deserts are farther north than the other deserts, lying mostly between 40° and 50° North as opposed to the more normal desert latitude of 20° to 30°. Fifth, the length of typical trajectories between Asia and Alaska (9,000–12,000 km) is not out of line with the well documented 6,000-km path for transport of Sahara dust to Barbados[6].

An Asian source for Arctic haze explains or confirms many previous observations such as:

Table 1 Elemental concentrations and enrichment factors for aircraft filter samples

Sample	AB	CD	E	F	G	IJ	KL	M	N
				Concentration [ng m^{-3} (ambient)]					
Al	10.0±0.9	17.0±1.0	35±2	34±2	91±5	240±10	203±10	240±10	14.7±1.7
V	0.035±0.006	0.148±0.010	0.126±0.012	0.094±0.010	0.22±0.02	0.40±0.03	0.37±0.02	0.40±0.04	0.0192±0.0100
Mn	0.146±0.012	0.36±0.02	0.59±0.04	1.58±0.03	1.55±0.08	3.0±0.2	3.1±0.2	3.4±0.2	0.21±0.02
Na	12±10	32±11	<30	21±16	47±27	58±15	37±11	37±30	<20
Ba	0.4±0.2	0.4±0.2	<0.8	<0.5	1.6±0.6	2.0±0.2	2.0±0.2	1.9±0.5	<0.5
				Enrichment factor (Al, rock)					
Al	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
V	2.1	5.2	2.2	1.66	1.46	1.00	1.10	1.00	0.79
Mn	1.25	1.81	1.44	1.46	1.46	1.07	1.31	1.21	1.22
Na	3.4	5.4	<2.5	1.77	1.48	0.69	0.52	0.44	<4
Ba	8	5	<4	<3	3.5	1.7	1.8	1.5	<6
Date	12, 13 April	14, 15 April	17 April	19 April	21 April	28, 29 April	30 April, 1 May	3 May	5 May
Volume (m^3)	249	341	149	176	110	309	365	88.7	108
Altitude (km)	3.3	2.0, 1.2	2.1	2.1	3.0	1.8, 2.3	2.1, 2.0	2.5 to 2.8	1.8

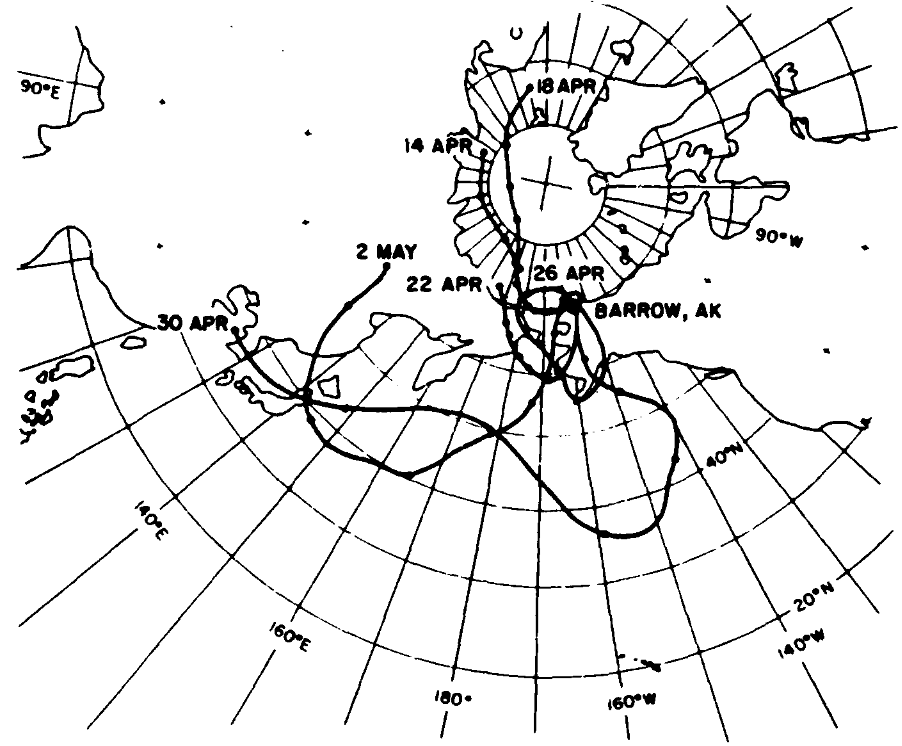

Fig. 1 700-mbar isobaric trajectories of air to Barrow. Numbers refer to date of arrival at Barrow. Solid circles each 24 hours along trajectory.

(1) Anomalously high turbidities over Barrow, especially during the spring[7] (flow patterns between Asia and Alaska appear to be common from November through May);

(2) The large size of the haze bands (see below);

(3) Previous haze events at Barrow (for example, the episode of March–April 1974 was preceded by a few days of strong flow from the Asian deserts);

(4) Previous measurements of anomalous turbidities over Fairbanks, Alaska. For example, 17–22 February 1976 was a whitish haze episode in Fairbanks which affected air at all levels and for which no explanation could be found. Visibilities were reduced from the normal 150 km to less than 30 km. Trajectory analysis now reveals that this air was also of Asian origin. Similar haze incidents with trajectories leading back to Asia seem to be a regular feature of the Fairbanks atmosphere during winter and spring;

(5) The accumulation of brownish insoluble deposits in the pack ice north of Barrow, which under examination with a light microscope seem to be continental dust (R. Paquette, personal communication). The mineralogy and possible sources of this dust have also been discussed[8];

(6) Anomalous ice-nucleus concentrations at College, Alaska, Blue Glacier, Washington, and Nagoya, Japan during February and March 1968, for which trajectory analysis showed eastern Asia to be the probable source[9];

(7) A case of abnormally high condensation nucleus concentrations at Barrow in March 1970[10], which was explained as pollution from Prudhoe Bay to the east but which may have originated from Asia because the large-scale flow for this period was from those deserts.

The mass of desert dust transported into the Arctic seems to be very great. For the five-day episode over Fairbanks discussed above, columnar mass loadings derived from radiation measurements showed values of about 45 mg m^{-2} (for aerosol density 2.5). For a point source in Asia and a dispersion angle of 5° (typical of volcanic plumes), the dust cloud would be 900 km wide at Alaska, or about the width of the state itself. (Indeed during this incident visibility was poor over the entire north half of the state.) Such a plume travelling at 80 km h^{-1} would carry 4,000 tons of dust into the Arctic per hour, or a half-million tons over the five-day episode. This is equivalent to skimming off a 0.2-μm layer from a $10° \times 10°$ desert.

Clearly, more detailed studies are needed to refine our ideas about this significant phenomenon. Also, possible climatic effects of such large amounts of aerosol in the Arctic should not be overlooked.

This work was supported by Office of Naval Research (contract N00014-76-C-0435). The cooperation of many staff members of the Naval Arctic Research Laboratory, Barrow, Alaska is gratefully acknowledged. Samples were chemically analysed using facilities of the Rhode Island Nuclear Science Center, Narragansett, Rhode Island.

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[1] Mitchell, M. *J. Atmos. Terr. Phys.* Special Supplement 195–211 (1956).
[2] Holmgren, B., Shaw, G. & Weller, G. *AIDJEX Bulletin* 27, 135–148 (1974).
[3] Rahn, K. A. *The chemical composition of the atmospheric aerosol* (University of Rhode Island Technical Report, 1976).
[4] Staff members of the section of Synoptic and Dynamic Meteorology, Institute of Geophysics and Meteorology, Academia Sinica, Peking. *Tellus* 9, 432–446 (1957); *ibid.* 10, 58–75 (1958).
[5] Jackson, M. L. *et al. Soil Sci.* 116, 135–145 (1973).
[6] Carlson, T. N. & Prospero, J. M. *J. appl. Meteor.* 11, 283–297 (1972).
[7] Shaw, G. E. *Tellus* 27, 39–49 (1975).
[8] Darby, D. A., Burckle, L. H. & Clark, D. L. *Earth planet. Sci. Lett.* 24, 166–172 (1974).
[9] Isono, K. *et al. Tellus*, 23, 40–59 (1971).
[10] Radke, L. F., Hobbs, P. V. & Pinnons, J. E. *J. appl. Meteor.* 15, 982–995 (1976).

Printed in Great Britain by Henry Ling Ltd., at the Dorset Press, Dorchester, Dorset

PARTICULATE AIR POLLUTION IN THE ARCTIC: LARGE-SCALE OCCURENCE AND METEOROLOGICAL CONTROLS

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BASIC DATA

A series of chemical analyses of the Barrow, Alaska surface aerosol beginning in September 1976 has revealed the routine presence of mid-latitude pollution aerosol there. Our best indicator of pollution aerosol is vanadium (V), although several other elements can also be used. Atmospheric vanadium has two major sources, (natural) crustal fragments and (pollution) combustion of residual (#6) oil (Zoller *et al.*, 1973; Duce and Hoffman, 1976). In remote continental areas crustal V dominates, but near urban areas pollution V dominates. Interestingly, pollution V is a good index of mid-latitude pollution aerosol, because the high viscosity of residual oil limits its use to temperate areas where it can easily be kept warm enough for handling. The lighter fuels which are burned in more northern latitudes contain insignificant vanadium (Hofstader *et al.*, 1976).

This paper is concerned with the noncrustal or "excess" vanadium in the aerosol, which is calculated from the total measured V by subtracting the crustal component (derived from the crustal reference element Al, measured simultaneously) as follows:

$$V_{excess} = V_{tot} - V_{crust} = V_{tot} - Al(V/Al)_{crust}. \qquad (1)$$

Excess V is then assumed to be completely pollution-derived.

The seasonal variations of excess V at locations ranging from temperate to Arctic show a striking similarity. Figure 1 (after Rahn *et al.*, 1977) shows monthly mean concentrations of excess V from New York City and Narragansett, Rhode Island (temperate areas); Skoganvarre, Norway (sub-Arctic); and Spitzbergen and Barrow, Alaska (Arctic). All five sites have winter maxima, usually in January. Temperate and sub-Arctic winter maxima are a few times higher than their summer minima (3-4 times higher for New York and Narragansett; 5-10 times for Skoganvarre), but for the Arctic the winter maximum is 30-40 times higher. Concentrations decrease with distance from the source areas as far as the Arctic, but remain constant in the Arctic - Spitzbergen and Barrow, on opposite sides of the Arctic, have essentially the same concentrations and trends.

Comparison of the individual samples from Barrow and northern Norway reveals another basic difference between the Arctic and the non-Arctic. Figure 2 shows weekly values of excess V for these two sites for September through March. At Barrow there was a sudden increase of about an order of magnitude during the first week of November (1976), followed by a slow but steady increase of another factor of 3 to 4. At Skoganvarre there was no such sudden increase, only a gradual increase to the January maximum. Futhermore, at Barrow the weekly variations are much less important than the seasonal variations, whereas at Skoganvarre the opposite holds true.

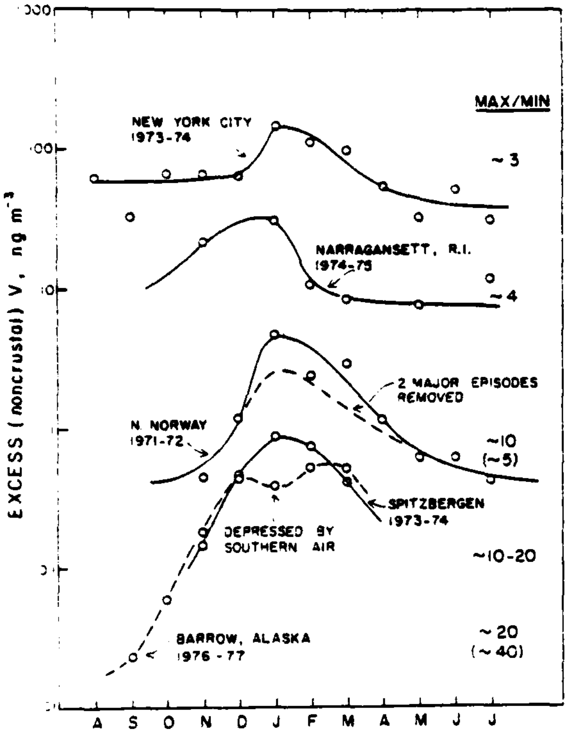

Fig. 1. Monthly mean concentrations of excess vanadium (after Rahn *et al.*, 1977).

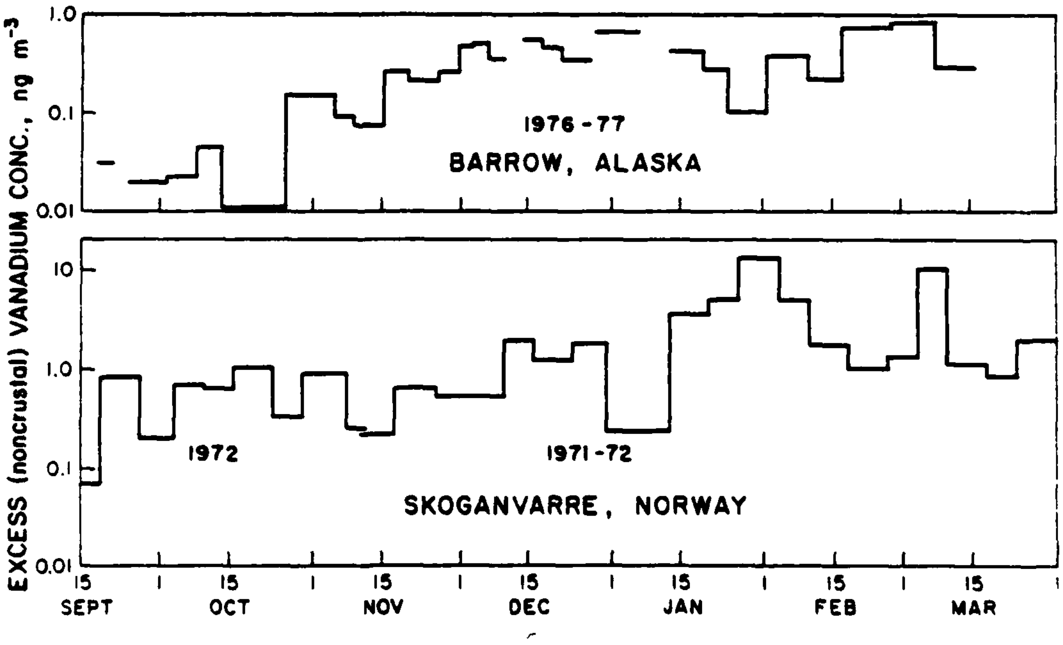

Fig. 2. Weekly concentrations of excess vanadium at Barrow and Skoganvarre.

THE INTERPRETATION

We believe that Figs. 1 and 2 can be explained meteorologically, by injection of pollution V in mid-latitudes followed by transport, together with dilution and removal, to the Arctic. We propose to consider the Northern Hemispheric troposphere as composed of "northern" and "southern" air masses separated by the polar front. Each of these air masses is assumed to be quasi-well-mixed. at least on the time scale of a month or two. (This is admittedly an over-simplification but is nevertheless useful). The polar front forms a very effective barrier to meridional mixing, so that during most of the year northern and southern air masses are quite different chemically, with most of the pollution aerosol constrained to the same side of the front as the sources. Because the highly industrialized countries of North America and Europe lie (not coincidentally) in the mid-latitude temperate regions over which the polar front swings from summer to winter, seasonal differences in pollution for remote high latitude regions can be quite large.

The polar front does not migrate steadily from its summer to its winter position, or vice versa. Rather, it moves southward in a big jump about mid-October and northward in early to mid-June (Yeh *et al.*, 1959). In 1976, as samples were being taken at Barrow, the southward jump over the northeastern United States occurred one to two weeks before the abrupt rise of pollution V was observed there. We feel that these phenomena were cause and effect, respectively. Before the shift the northeastern United States lay south of the front, with its pollution effluent generally confined to that side. After the shift, however, the polar front lay south of the northeastern United States, so that pollution aerosol could mix freely and rapidly to the north. Travel times to Barrow were probably only a few days. According to this picture one would not expect a similar abrupt increase of pollution V for northern Norway because it is much closer to the polar front at all times of the year than is Barrow. The fact that the polar front can swing erratically over northern Norway at any time of the year may explain the larger weekly variations and smaller seasonal variations of pollution V found there.

NUMERICAL CONFIRMATION OF THE INTERPRETATION

The actual winter/summer concentration ratios of vanadium in the Arctic appear to be compatible with values derived from a simple mathematical model of mid-latitude emission followed by transport, dilution, and removal. The winter/summer concentration ratio of a pollutant in the Arctic may be expressed as:

$$\frac{C_w}{C_s} = \frac{C_{ow}}{C_{os}} \cdot \frac{F'_w}{F'_s} \cdot \frac{R_w}{R_s} \cdot \frac{V_s}{V_w} \qquad (2)$$

where C_o is the source-area concentration of the pollutant; F' is the position effect of the polar front, which is a "leaky" barrier; R is the removal effect during transport to the Arctic; V is the dilution volume of northern air; and w and s refer to winter and summer, respectively. The value of C_{ow}/C_{os} appears to be 3-4 for vanadium (Figure 1). $R_w/R_s = \exp(-\lambda_w t_w)/\exp(-\lambda_s t_s)$ for a first-order removal rate, where λ is the rate constant and t is the age of the aerosol. Our best guess at present is that $\lambda_w/\lambda_s \approx 2$ and that $t_w/t_s \approx 1/2-1/3$. Thus R_w/R_s is approximately 0.4-1.0. V_s/V_w is about 1/2.

Thus the value of $[(C_{ow}/C_{os})(R_w/R_s)(V_s/V_w)]$ can range from about 0.6 to 2, or within a factor of two of unity. Thus in large measure these three terms cancel each other, and the value of C_w/C_s is determined primarily by F'_w/F'_s, to which we now pay special attention.

The position effect F'_w/F'_s of the "leaky" frontal barrier can be written as:

$$\frac{F'_w}{F'_s} = \frac{(E_n + E_m)(1-\ell) + \ell E_s}{E_n(1-\ell) + \ell(E_m + E_s)} \qquad (3)$$

where E_n, E_m, and E_s are the annual emission rates for areas north of the summer polar front, between summer and winter polar fronts, and south of the winter polar front, respectively. ℓ is the concentration of aerosol on one side of the barrier which has leaked across from unit concentration on the other side. As an example of the use of this equation, the table below shows values of E_n, E_m, E_s, and F'_w/F'_s calculated from two estimations of the polar front positions (Fig. 3, upper plot for the surface and lower plot for 500 mb) and annual commercial energy consumption for various countries in 1974 (United Nations, 1976), to which we assume pollution-aerosol emission is proportional.

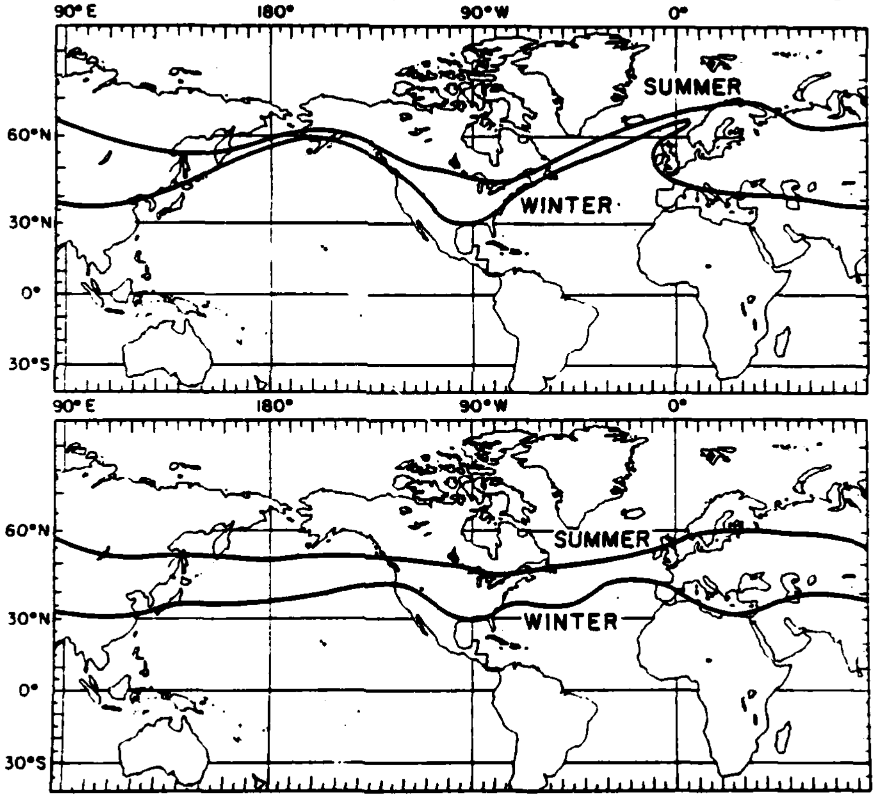

Fig. 3. Summer and winter positions of the surface (upper plot) and 500-mb (lower plot) polar fronts.

	Surface polar front	500-mb polar front
E_n	2%	8%
E_m	63%	75%
E_s	36%	18%
ℓ	0.03	0.03
F'_w/F'_s	13.1	7.7

The value of 0.03 for ℓ is based on data of Duce and Hoffman (1976). Note that the values of F'_w/F'_s are well below those observed for vanadium in the Arctic.

If now E_s and E_n are set equal to zero in Equation (3) (more appropriate to the case of vanadium, which comes overwhelmingly from mid-latitudes), then

$$F'_w/F'_s = (1-\ell)/\ell \approx 1/\ell \approx 33 \tag{4}$$

This is now completely compatible with the value of 30-40 actually observed at Barrow. Note that this result is independent of the details of the winter and summer positions of the polar front. This result also nicely confirms the idea that the concentration ratio across the polar front at a given time is analogous to the seasonal concentration ratio at an Arctic location (Rahn *et al.*, 1977).

Although further work will surely refine this model greatly, we believe that it is already adequate to fundamentally explain the seasonal patterns of vanadium abundance in the Arctic aerosol.

ACKNOWLEDGEMENTS

This research was supported by Office of Naval Research Contract N00014-76-C-0435. Barrow ground-level aerosol samples were taken as part of a cooperative investigation with NOAA at its GMCC clean-air observatory by NOAA personnel Emerson Wood and Roger Williams. Norway data were obtained while one of us (K.A.R.) was at the Institute of Nuclear Sciences, University of Ghent, which supported that work. Barrow samples were chemically analyzed using facilities of the Rhode Island Nuclear Science Center.

REFERENCES

Duce R.A. and Hoffman G.L. (1976) Atmospheric vanadium transport to the ocean. Atmos. Env. 10, 989-996.

Hofstader R.A., Milner O.I. and Runnels, J.H. (1976) Analysis of Petroleum for Trace Metals, Advances in Chemistry Series No. 156, American Chemical Society, Washington, D.C., p. 165.

Rahn K.A., Borys R.D., Shaw G.E. and Larssen S. (1977) Arctic-wide aerosol pollution. Science (submitted August 1977).

United Nations Report (1976) World Energy Supplies 1950-1974, Statistical Papers Series J, No. 19, United Nations, New York.

Yeh, T.-C., Dao S.Y. and Li M.-T. (1959) The abrupt change of circulation over the Northern Hemisphere during June and October, in: The Atmosphere and the Sea in Motion, Scientific Contributions to the Rossby Memorial Volume, ed. B. Bolin, The Rockefeller Institute Press, New York, pp. 249-267.

Zoller W.H., Gordon G.E., Gladney E.S. and Jones A.G. (1973) The sources and distribution of vanadium in the atmosphere, in: Trace Elements in the Environment, Advances in Chemistry Series, No. 123, American Chemical Society, Washington, D.C., pp. 31-47.

The Arctic Air-Sampling Network

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Prepared for submission to the
Arctic Bulletin
March 1978

The atmospheric chemistry of the Arctic has been studied very little. The Antarctic, in contrast, has been the subject of much greater study, perhaps because it is more remote.

There are several features of the Arctic which make its atmospheric nature quite different from that of the Antarctic. (1) The Arctic is located in the Northern Hemisphere, where 90% of the world's air pollution is emitted. Because of the relatively short lifetimes of pollution products, particularly aerosols, in the atmosphere relative to inter-hemispheric mixing times, these pollutants should be found primarily in the hemisphere of emission (Two notable exceptions in this regard are carbon dioxide and the Freons, which have atmospheric lifetimes greater than 10 years, and so can mix freely into both hemispheres before being removed). (2) Northern Hemispheric pollution sources are geographically closer to the Arctic than Southern Hemispheric sources are to the Antarctic, i.e., Northern Hemispheric sources are found at higher latitudes. (3) The "meteorological distance" between the Northern Hemispheric pollution sources and the Arctic is even shorter than the geographical distance would suggest, whereas for the Southern Hemisphere and the Antarctic the reverse is true. In the Northern Hemisphere the zonal alternation of land and water masses in mid-latitudes creates rather direct meridional transport paths to the Arctic, especially in winter. In the Southern Hemisphere, the predominance of water at mid-latitudes creates a much more zonal wind system; trajectories to Antarctica tend therefore to be longer and in a series of gradually contracting latitudinal circles. Thus air masses reaching the South Pole have been away from land for significantly longer periods than have air masses reaching the North Pole, and the aerosol is more aged. (4) The Arctic is essentially at sea level, which allows air masses from mid-latitudes to flow freely into it. The Antarctic, on the other hand, is fundamentally a high continent (1500-4000 meters elevation), which presents a barrier to poleward flow of temperate air masses. This causes continental aerosols reaching the South Pole to be still more aged than their Northern Hemispheric counterparts.

The above points suggest that the Arctic ought to have significantly greater concentrations of air-pollution products than the Antarctic should. Indeed, the few previous studies of Arctic air chemistry tend to confirm this picture. For example, Robinson and Robbins (1969) measured carbon monoxide concentrations on the ice cap of northern Greenland during July and August 1967, and observed a 2-day pulse of high concentrations which they were able to correlate with air-mass trajectories from the urbanized Great Lakes and New England areas of the United States. Scientists from the Danish Air Pollution Laboratory have observed aerosol layers over Greenland in which very high numbers of particles were found (Flyger _et al._; 1973; 1976). The writer observed a dramatic change in composition of the aerosol of Canada's Northwest Territories between summer and winter, with the winter aerosol being much more polluted (Rahn, 1971). Because of the remoteness of the area it was difficult to imagine local sources being responsible for this pollution. The OECD Programme on Long Range Transport of Air Pollutants has amply documented that southern Scandinavia (Latitude 55-65°N) has regular incursions of pollution-derived aerosols and gases from central Europe, which cause, among other effects, acid precipitation (OECD,1977) The writer has studied the aerosol of northern Norway (70°N), and observed strong pulses of concentrated pollution aerosol during the winter, presumably also from central Europe. Thus the Arctic, while in general a very clean region atmospherically, seems to be subject to major intrusions of pollution-laden air, particularly during the winter.

As a result of these first studies it slowly became apparent that proper study of Arctic air chemistry depended not only on investigation of atmospheric chemistry in situ, but also upon a systematic study of the sources, particularly the strong pollution sources just south of the Arctic borders. The best approach to this kind of study seemed to be a network of sampling sites extending from suspected source regions to the Arctic. Fortunately, in the most interesting region (between the Arctic and the industrialized areas of eastern North America and Europe) there is a "natural network" of islands (Greenland, Iceland, Spitsbergen, Jan Mayen, the Faroe Islands, the Shetland Islands, etc.) which would be suited to this purpose.

It also became clear that the Arctic was probably a much more complex region than the Antarctic, both atmospherically and politically. Strong sources nearby and a small number of preferred atmospheric pathways to the Arctic could work together to create quite large spatial and temporal variations of both gases and aerosols within the Arctic. Thus several stations would be required in order to properly characterize the entire Arctic. Further, because several countries border on the Arctic or possess islands suitable to the network, a large-scale study would have to be international and cooperative, preferably with each country maintaining near autonomy over its part of the total effort.

The direct beginnings of the Arctic cooperative study described here can be traced to a program of study of the Barrow aerosol performed by

Drs. K. Rahn (University of Rhode Island) and G. Shaw (University of Alaska) under a contract from the United States Office of Naval Research. This contract, for study of the sources and characteristics of Arctic haze started in 1976 and continues through the present. Among the first results were that much of the springtime Arctic haze results from large quantities of Asian desert dust being carried rather directly into the Arctic atmosphere, over a path length of some 15,000 km (Rahn et al., 1977). It was also found that the winter Barrow atmosphere contains easily detectable amounts of pollution aerosol which, because of its chemical makeup, must have come from mid-latitude sources, probably a combination of the northeastern United States and central Europe. At the moment it is suspected that the United States is the more effective source, even though it is farther removed from the Arctic than is Europe, because of more favorable flow patterns from North America. This hypothesis is, however, quite tentative and subject to revision as more data become available.

The point to be stressed from this Alaskan study is that both urban and desert sources of Arctic aerosol can contribute strongly to the Arctic aerosol in spite of their geographical remoteness from the Arctic. This supports the previous conclusion that study of suspected source regions is an integral part of Arctic air-chemistry research.

In October 1976 these new ideas were discussed in a conversation between the writer and Dr. B. Ottar of the Norwegian Institute for Air Research, also an enthusiastic proponent of Arctic air research and a past collaborator with Dr. Rahn. Dr. Ottar, who was very familiar with the various Scandinavian Arctic research programs and interests, noted that many of the ingredients of a potential Arctic network were in fact already in existence. For example, most of the Scandinavian countries already had programs of Arctic air research in operation. Those that didn't had a strong interest in beginning. Only leadership was needed to achieve a working network in the near future.

The writer approached ONR about assisting this network to come into being, and received a very favorable response from Dr. G. Leonard Johnson, project manager for the Arctic Haze contract. Dr. Johnson awarded Dr. Ottar a conference grant to co-sponsor a meeting in Norway of all parties interested in participating in the network. In April 1977 a 2-day meeting was held at the Norwegian Institute for Air Research in Lillestrøm, Norway. This meeting was hosted by Dr. Ottar and co-chaired by Drs. Ottar and Rahn. Twenty-eight delegates from 7 countries attended. A report of the conference is available from ONR Code 461, Arlington, VA 22217, U.S.A., under the title "Sources and Significance of Natural and Man-Made Aerosols in the Arctic". Four general objectives were agreed upon: (1) Verify and broaden existing evidence regarding composition, sources, transport and sinks of both pollution and natural aerosol to the Arctic; (2) Determine the possible climatic effects of this "imported" aerosol in the Arctic; (3) Determine 1977-1980 baseline air quality values for the Arctic; (4) Keep in mind a general concern for possible biological effects of this (pollution) aerosol entering the Arctic. A rough timetable for the future was proposed, with preliminary experiments during summer and winter 1977, evaluation of the results during 1977-78, and coordinated sampling and analysis projected to begin during summer 1978. An Arctic Newsletter was established, with the writer as Editor, to serve as the principal means of exchange of news and information between meetings. (Interested parties can be placed on the mailing list for the Newsletter by writing to K. Rahn).

Since the April 1977 meeting the Arctic Air-Sampling Network has progressed nicely. It now includes 13 stations, 6 of which are functioning continuously, 2 of which are functioning intermittently, and 5 of which are in various stages of planning. Data about these stations are presented in Table 1, and their locations are shown in Figure 1. Three of them are source-oriented (New York, Rhode Island, and South Korea), with the rest being Arctic or near-Arctic in nature. Four of these sites are direct results of this meeting (Spitsbergen (which had also been operated intermittently since 1973), Bear Island, North and South Greenland), while two others resulted indirectly from the meeting (New York and Rhode Island). Analyses being currently performed on the filters include sulfate, nitrate, and ammonium ions as well as about 30 trace elements. There are tentative plans to add three more Greenland sites in summer 1979 (Danish Air Pollution Laboratory, RISØ).

The philosophy of operation of the network is best summarized by the four principles of coordination outlined at a technical meeting held among the three most active groups (University of Rhode Island, Danish Air Pollution Laboratory, and Norwegian Institute of Air Research) in January 1978 in Roskilde, Denmark. These principles are: (1) Each participating institute must keep as independent a program as possible; (2) Preliminary data will be informally exchanged at the earliest possible moment via the Arctic Newsletter; (3) All groups must be ready to exchange samples, so that sampling and analytical techniques between groups can be compared; (4) Local authorities should operate stations on their own territory. It is hoped that by adherence to these principles a true Arctic cooperative effort can emerge, in which decentralization, availability of facilities to all groups, and commonness of programs

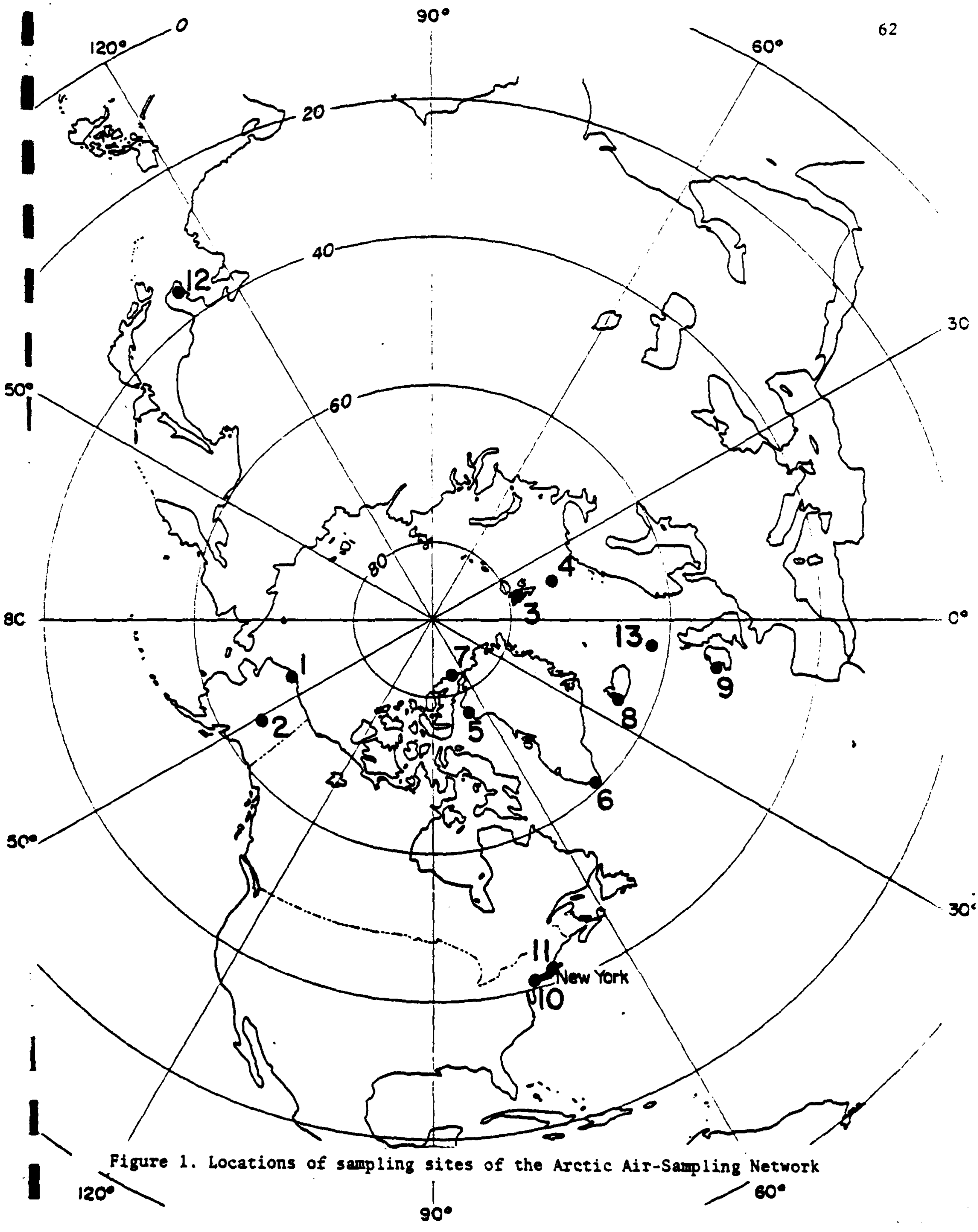

Figure 1. Locations of sampling sites of the Arctic Air-Sampling Network

Table 1. Sampling sites of the Arctic Air-Sampling Network

te No. gure 1)	Name	Responsible Agency or Institute	Country	Types of Samples Taken	Sampling Frequency	Analysis
				Arctic Sites		
1	Barrow, Alaska	URI/NOAA-GMCC	USA	Hi-vol cellulose filters; lo-vol glass-fiber filters	1-2 x weekly	Trace elements, total mass, sulfate
2	Fairbanks, Alaska	URI/UA	USA	Hi-vol cellulose filters; lo-vol glass-fiber filters	1-2 x weekly	Trace elements, total mass, sulfate
3	Ny Ålesund, Spitsbergen	NILU	Norway	Hi-vol cellulose filters	3 x weekly	Trace elements, sulfate
4	Bear Island	NILU	Norway	Hi-vol and lo-vol cellulose filters, KOH-impregnated filters	3 x weekly	Trace elements, sulfate, SO_2
5	Thule, Greenland	DMI	Denmark	Lo-vol cellulose filters	1-3 x weekly (preliminary winter & summer samples only)	Trace elements, total mass
6	Prins Christianssund, Greenland	DMI	Denmark	Lo-vol cellulose filters	Same as Thule	Trace elements, total mass
7	Alert, NWT, Canada	EC	Canada	Hi-vol cellulose filters	1-2 x weekly (to begin summer 1978)	Trace elements, sulfate
8	Iceland	IMH	Iceland	Hi-vol cellulose filters	1-2 x weekly (foreseen to begin fall 1978)	Trace elements, sulfate
				Arctic-related Sites		
9	W. Coast of Ireland (under consideration)	UCG	Ireland	Hi-vol cellulose filters	1-2 x weekly	Trace elements sulfate
10	New York City	URI/NYU	USA	Lo-vol cellulose filters	2 x weekly	Trace elements, sulfate
11	Narragansett, Rhode Island	URI	USA	Lo-vol cellulose filters	2 x weekly	Trace elements, sulfate
12	Kunsan Air Base South Korea	URI/30 WS, 10 DET	USA	Hi-vol cellulose filters	1-3 x weekly	Trace elements, sulfate
13	Faroe Islands	DAPL	Denmark	Lo-vol membrane filters, KOH-impregnated cellulose filters	Daily (to begin spring 1978)	Trace elements, sulfate, SO_2, total mass

bbreviations URI: University of Rhode Island; NOAA-GMCC: National Oceanic and Atmospheric Administration, Geophysical Monitoring for Climatic Change; UA: University of Alaska; NILU: Norwegian Institute for Air Research; DMI: Danish Meteorological Institute; EC: Environment Canada; IMH: Icelandic Ministry of Health; UCG: University College, Galway; NYU: New York University; 30 WS, 10 DET: 30th Weather Squadron, 10th Detachment; DAPL: Danish Air Pollution Laboratory, Ministry of Environment.

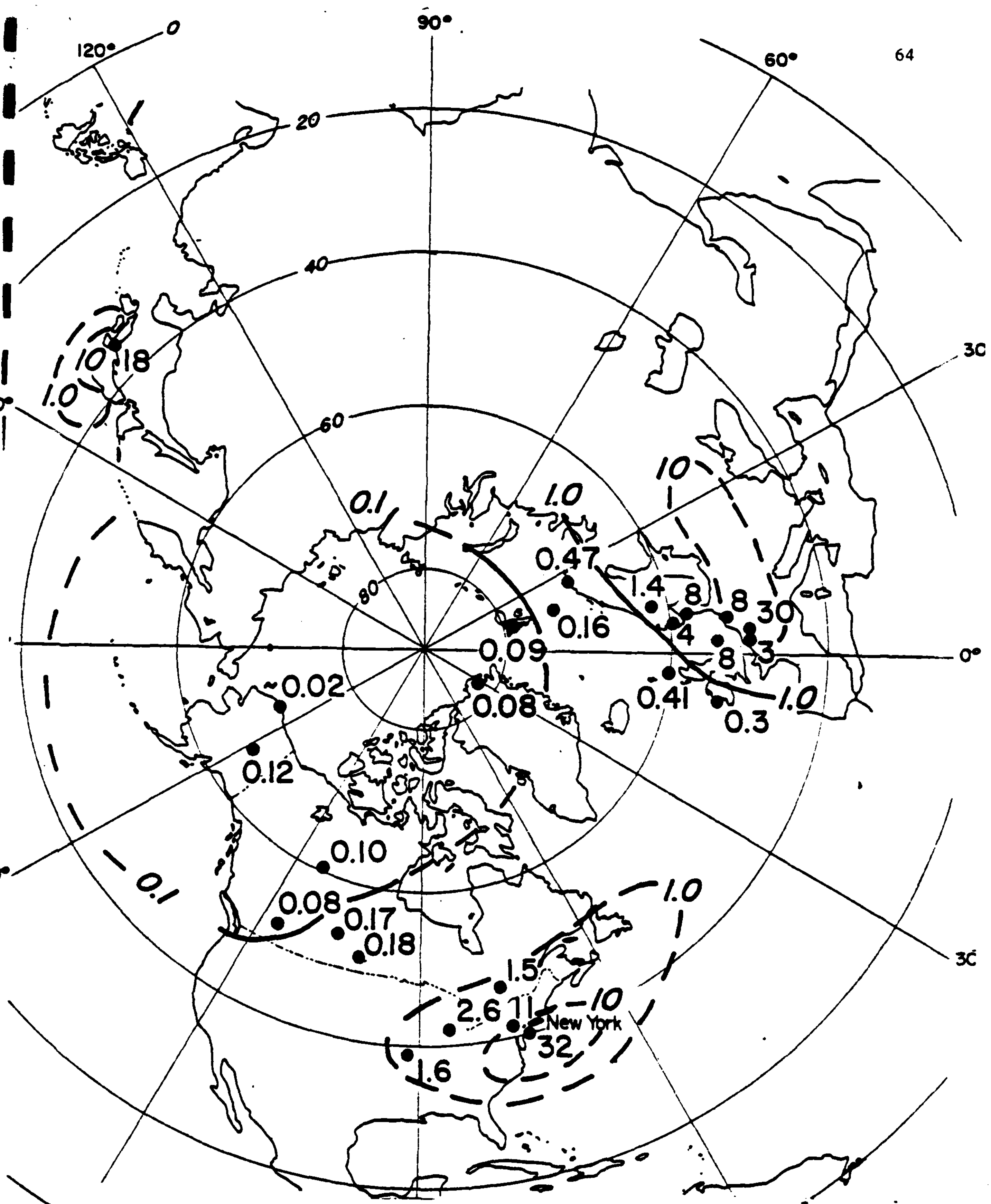

Figure 2. Summer concentrations of excess (noncrustal) vanadium, ng m^{-3}.

can be combined into an integrated scientific effort greater than any of the individual institutions could produce.

A second technical meeting will be held at the University of Rhode Island in January 1979, at which time further results and plans for the network will be discussed in detail. Then in September 1979 a second general conference on the Arctic aerosol is planned, also to be held at the University of Rhode Island.

As a first example of the kind of information that will be available from the Arctic Network, Figure 2 shows a sort of "pollution map" of the northern half of the Northern Hemisphere. The values plotted are concentrations of "excess", or noncrustal vanadium, which to the best of our knowledge comes overwhelmingly from combustion of fossil fuels, particularly the heavy #6 residual oil. Because residual oil is burned in temperate climates, excess vanadium in the Arctic seems to be a very reliable indicator of long-range transport of aerosol. Most of the Arctic data of this figure were taken in summer 1977 as part of the Arctic Network. The more southerly data, except for New York and the Shetland Islands, were compiled from other studies in other years, but should represent typical summer conditions. One interesting feature of this map is that the "pole of minimum concentrations" does not correspond with the North Geographical Pole. Rather, it is shifted away from the strong source areas, in the general direction of Alaska and extreme eastern Siberia. Barrow seems to be at the center of this region. The other interesting feature of this map is the existence of a rather braod area where concentrations of excess vanadium are within a factor of two of 0.1 ng/m^{-3}. This might be considered the "background region" for vanadium in the atmosphere.

Clearly, much more data are needed before anything definite can be stated about the large-scale air quality in the Arctic. In particular, the half of the Arctic which borders on the USSR has no sites. But the Arctic Network is already giving us a valuable first impression of Arctic air quality that would not otherwise be available.

References

Flyger H., Hansen K., Megaw W.J. and Cox L.C. (1973) The background level of the summer tropospheric aerosol over Greenland and the North Atlantic Ocean. J. Appl. Meteor. 12, 161-174.

Flyger H., Heidam N.Z., Hansen K., Megaw W.J., Walther E.G. and Hogan A.W. (1976) Aerosol Sci. 7, 103.

OECD (1977) The OECD Programme on Long Range Transport of Air Pollutants. Measurements and Findings. Organization for Economic Co-Operation and Development, Paris.

Rahn K.A., Borys R.D. and Shaw G.E. (1977) "The Asian source of Arctic haze bands", Nature 268, 713-715.

Rahn K.A. (1971) Sources of trace elements in aerosols - An approach to clean air. Ph.D. Thesis, University of Michigan, Department of Atmospheric and Oceanic Science, 309 pp.

Robinson E. and Robbins R.C. (1969) Atmospheric CO concentrations on the Greenland ice cap. J. Geophys. Res. 74, 1968-1973.

The Crustal Component of Background Aerosols: Its Importance in Interpreting Heavy Metal Data

K. A. Rahn, L. Schütz, and R. Jaenicke

INTRODUCTION

Crustal material is nearly ubiquitous in the tropospheric aerosol, and forms a baseline composition against which the abundances of many elements can be evaluated. During the last several years of multi-elemental analysis of aerosols in regions varying from urban to highly remote, it has consistently been found useful to relate elements of the aerosol to the crust via an aerosol-crust enrichment factor, defined for an element X as:

$$EF_X = (\text{Conc X/Conc REF})_{\text{AEROSOL}}/(\text{Conc X/Conc REF})_{\text{CRUST}}$$

where REF is a crustal reference element and CRUST is a crustal reference material. Typically one-half of the elements of the aerosol are in crustal proportions; in high-dust or remote continental regions this figure may be considerably higher. In certain circumstances even heavy metals such as Pb, Zn, Cr, Mn, Ba, Ni, W, Mo, Sb, As, etc., may have an overwhelmingly crustal origin, which can easily be completely overlooked unless one or more crustal reference elements are co-determined. It is thus the principal thesis of this paper that measurement of heavy metals alone in the background aerosol is not enough; they must be accompanied by determination of at least one crustal reference element, subsequent calculation of aerosol-crust enrichment factors, and proper interpretation of this information. If these steps are not followed, serious errors in interpretation of elemental concentration data can easily occur, as illustrated by the following examples.

First Example: This example concerns Cr, but could equally well be any number of other elements. Two measurements of its concentration in the widely separated remote areas of Novaya Zemlya [1], an Arctic Island, and the southern North Atlantic Ocean [2] gave nearly identical concentrations of 0.3 to 0.4 ng m^{-3}, as shown in Table 1.

Table 1. CONCENTRATIONS AND ENRICHMENT FACTORS IN THE AEROSOLS OF NOVAYA ZEMLYA AND THE NORTH ATLANTIC

	Novaya Zemlya		North Atlantic	
	Concentration ng m^{-3}	EF(Fe, rock)	Concentration ng m^{-3}	EF(Fe, rock)
Cr	0.34	40	0.39	0.39
Fe	4.3	1.0	500	1.0

In both of these sets of samples Fe was also measured, however, and when aerosol-crust enrichment factors for Cr are calculated according to the above formula using Fe as a reference element and average crustal rock [3] as reference material it is immediately seen that the value at Novaya Zemlya (40) is approximately 100 times higher than the value over the Atlantic (0.4). In other words, Cr in the North Atlantic aerosol is crustal in origin, whereas that over Novaya Zemlya is not.

Second Example: The next example is from a recent study of the Arctic aerosol over northern Alaska [4]. During a series of aircraft flights in the vicinity of Barrow, Alaska during April and May 1976, high-volume filter samples of the aerosol aloft were taken and analyzed for several trace elements by neutron activation. Here we will be concerned with the results for only two of these, V and Al. [illegible] is now well known that V is a very sensitive indicator element for air pollutio[illegible] c is released into the atmosphere in large quantities by the combustion of fuel oi[illegible] particularly in the northeastern United States and Europe [5]. In these regions the V concentrations are very much higher than in lower-latitude cities or remote regions. Table 2 shows the V and Al concentrations in the aerosol over Barrow during April and May 1976, as well as the V enrichment factors relative to Al and crustal rock.

Table 2. CONCENTRATIONS, ENRICHMENT FACTORS IN THE ALASKAN ARCTIC AEROSOL

Date	V, ng m^{-3}	Al, ng m^{-3}	EF_V(Al, rock)
12-13 April 1976	0.035	10	2.1
14-15 April 1976	0.148	17	5.2
17 April 1976	0.126	35	2.2
19 April 1976	0.094	34	1.7
21 April 1976	0.22	91	1.5
28-29 April 1976	0.40	240	1.0
30 April-1 May 1976	0.37	203	1.1
3 May 1976	0.40	240	1.0
5 May 1976	0.0192	15	0.8

There was a gradual increase in V concentration through the initial samples, followed by a sharp maximum in the middle few samples, and terminated by an abrupt dropoff to the original concentration in the last sample. If considered alone, the high V concentrations of the middle samples would suggest that they were somehow pollution-derived. In fact, just the opposite is true. Aluminum also increased in concentration in the middle samples, and to a larger extent than did the V. The V enrichment factors were therefore highest in the early, low-concentration samples and decreased to essentially unity in the subsequent high-concentration samples. Thus when Al is considered it becomes evident that the high levels of V were purely crustal, i.e. natural in origin rather than pollution-derived.

Third Example: The last example illustrates how simple calculation of enrichment factors may not be enough; they themselves must be properly interpreted. In a recent study of Sahara dust in the Northeast Trades region of the North Atlantic Ocean some 40 elements were determined in a suite of 7 filter samples taken in the strong Sahara plume [6]. Among these elements were As, Sb, and Fe, the average concentrations for which in the 7 samples are shown in Table 3. Values of the enrichment factors (relative to Fe and rock) for As and Sb were 8 and 6, respectively, as also shown in this table.

Table 3. CONCENTRATIONS AND ENRICHMENT FACTORS IN SAHARA DUSTS AND SOILS

Element	7 Sahara Dust Samples		3 Sahara Soils ($r < 16$ μm)	
	Concentration ng m^{-3}	EF(Fe, rock)	Concentration ppm	EF(Fe, rock)
As	1.20	8.0	6.5-6.6	3.8-5.1
Sb	0.096	5.8	0.66-0.83	3.6-6.8
Fe	4160	1.00	36,000-48,000	1.00

Taken alone, these high values might suggest that both As and Sb in Sahara aerosol have some additional source besides the Sahara itself, i.e. are considerably enriched. But analysis of 3 Saharan soils showed that the fraction with radius smaller than 16 μm, from which the aerosol would be drawn, had enrichment factors of 4 to 5 and 4 to 7 for As and Sb, respectively, thus indicating that these elements were indeed very close to crustal abundances in the aerosol. In fact, As and Sb in average soils have enrichment factors (relative to Fe and rock) of approximately 4 and 10 to 50, respectively. Further evidence that soils are enriched in these elements relative to rock comes from a compilation of enrichment factors from all regions of the world [7], which shows that the enrichment factor of Sb in high-dust regions seems to settle down at no lower than about 3 to 4.

The above examples should suffice to make the point clear that even in remote areas the crustal component of many metals of interest may play a major role in explaining their abundances. Unfortunately, however, we do not yet know how to properly evaluate this crustal component to the desired accuracy. The broad outlines of how to do it are clear enough, but substantial uncertainty still persists regarding details. Because the fundamental process of generation of crustal aerosol is simply not very well understood, several different crustal reference elements and reference materials are presently in use by various research groups. The meaning of such enrichment factors is often unclear; furthermore those from one publication often cannot be directly compared with those from another publication because they have been calculated differently. The rest of this paper summarizes the various reference elements and reference materials currently used in calculating enrichment factors, then briefly attempts to choose the best of them and ends by proposing a direction for future research which should help to improve our understanding of the nature and composition of crustal aerosol.

REFERENCE ELEMENTS

The reference element for enrichment-factor calculations can in principle be Si, Fe, Al, Ti, Sc, the rare-earth elements (REE), Th, etc., i.e. any of those elements which consistently occur in crustal proportions in the atmospheric aerosol. For a detailed review of this subject, see Rahn [7]. The ideal reference element would be determinable by a number of analytical techniques, be a major element in the crust, have a minimum of pollution sources, and not be easily contaminated during sampling. Of the possible elements, Si, Fe, Al, Sc, and Ti have actually been used or are being used as reference elements. Each of these elements has its own set of advantages and disadvantages, as follows.

Si, which in principle is the most unambiguous crustal reference element, is only difficultly determinable in the aerosol. Fe is a fine reference element in many remote areas, but has major pollution sources in cities, the influence of which may extend into remote areas far downwind. Ti, a heretofore largely unrecognized candidate for reference element, is also difficulty determinable but otherwise excellently suited. Sc has the disadvantage of being a minor element (22 ppm in rock, 7 ppm in soil), so that it could be expected to have more local variations than a major element like Fe or Al, although its actual abundance in the aerosol is very consistent. It is determined mostly by neutron activation. The REE and Th also have the disadvantage of having small concentrations (0.5 to 60 ppm for REE, 7 ppm for Th), but otherwise seem to have few specific pollution sources.

Perhaps the best reference element at present is Al. It is a major element in the crust, is determinable by a variety of analytical techniques, and has markedly smaller pollution sources in cities than does Fe, for example. It is, however, subject to some contamination during sampling, by common objects made of Al such as ladders, pipes, screens, etc. Some sampling equipment, e.g. the Andersen cascade impactor, is made of Al and may contaminate the samples during prolonged usage in the field. Overall, though, these disadvantages are far outweighed by the advantages of Al, and it is currently the most used reference element.

REFERENCE MATERIALS

Crustal reference materials which have been used include average and local soil and rock. Currently the most popular choice is average rock, for which several compositions are available [3, 8, 9, 10]. Three important aspects of choosing a reference material are (1) rock vs soil, (2) local vs average, and the newer (3) bulk vs fraction. These are discussed below.

Rock vs Soil: A number of publications have chosen soil as reference material, using two major sources of data for average composition [11, 12]. The problem with this approach is purely practical - average soil data are still lacking several important elements such as Ag, In, Sb, W, and the rare earths, elements which are routinely determined in urban aerosols and often in remote aerosols as well. When soils are used as reference material, data for these elements must be borrowed from one of the estimates of average crustal rock. For consistency's sake alone, rock is to be preferred over soil because the former's trace-element data is much more complete.

On the other hand, soil is clearly a much more realistic reference material than is rock. For one thing, 93% of the continents are covered by soils. Soils are obviously much more easily wind-eroded than is rock, and so will preferentially enter the atmosphere. Even deserts are highly weathered chemically in spite of their lack of water. Furthermore, relative abundances of at least Na, Mg, and Sc in the aerosol are low relative to rock and seem to need a soil component to explain them [7]. The great dust storms of the world, which are one of the major mechanisms of injecting crustal material into the atmosphere, occur over deserts and arid lands which are covered by soils. There would thus seem to be little objection to the idea that soils are the proper reference material.

Local vs Average: Most calculations of enrichment factors are done using average crust. This has the advantage of providing a common base for enrichment calculations, so that enrichment factors from different aerosol samples can be immediately intercompared. Occasionally, however, local soils or rocks have been used as reference material. This approach has the advantage of relating a certain fraction of the local aerosol more precisely to the crust directly below it, but suffers some major disadvantages as well. First, this approach is limited to those cases where detailed trace-element data on local crust is available, which are few in number relative to the total number of locations used as air-sampling sites. Second and more fundamental, the extent to which a single local reference material is a valid concept is not at all clear. Different size ranges within the crustal aerosol have different lifetimes in the atmosphere and will have blown in from greatly different distances. Thus the crustal aerosol at a given site will represent a mixture of sources with perhaps different chemical compositions, the larger particles originating closer to the site and the smaller particles coming from farther away. Nevertheless, the use of local reference materials when available may be quite useful. Perhaps a reasonable compromise approach to the question of local vs average would be to always cite enrichment factors relative to average crust, so that these may be immediately compared with those of other workers, and then if local enrichment factors are available to list them additionally, but in no case should local enrichment factors be presented alone.

Is there in fact any truly valid single average reference material for crustal aerosols found at different points over the globe? Weathering under different climatic conditions may create significant large-scale differences in resultant soils. Should this be the case, concentration ratios of, say, an element to aluminum in large-scale regional reference materials may vary by a certain factor. At present it is not yet clear what the magnitude of such a factor would be, although there is certain evidence [7] that it may be in the range of 2 or so.

Bulk vs Fraction: Recent parallel research of Gillette et al. [13-19] and Schütz and Jaenicke [20, 2.] on the physical aspects of generation of soil aerosol from arid and desert areas have yielded remarkably similar results concerning the particle-size distributions of parent soil and derived aerosol. In great contrast to the parent soils, which have most of their mass between radii of roughly 20 to 200 μm, the aerosols derived from them have most of their mass between radii of roughly 1 and 10 μm. Thus there is essentially no overlap between mass ranges of soil and aerosol, i.e. a major physical fractionation has occurred in the generation of crustal aerosol, with the aerosol appearing in a size range where only negligible soil mass exists. It thus follows that to the extent that soils have a size-dependent composition, their bulk composition may not truly reflect the 1-to-10-μm precursor of soil-derived aerosol. A major improvement in the use of soils as crustal reference material will come after an investigation of their size dependence of chemical composition; if a strong dependence is found, the composition of the appropriate subregion can be chosen rather than the bulk composition.

The only data presently available on the multi-elemental composition of soils as a function of particle size is that of Rahn et al. [6] for the several Libyan Sahara soils reported earlier [21], and these were only analyzed in two size fractions. Much more data is needed for various size fractions of different soils before the composition of the true crustal-aerosol precursor can be synthesized.

There are, however, a number of indications that the chemical composition of the crustal aerosol differs measurably from its bulk-soil precursor. This is equivalent to a particle-size dependence of composition within the soil; it is also equivalent to a crust-air fractionation of soil material during generation of crustal aerosol. First, the Si/Al ratio in the aerosol is approximately 30 to 50% lower than in bulk crustal rocks and soils [22]. Second, the data of Rahn et al. [6] for Sahara soils show clearly that certain elements, particularly the REE, Hf, and Th, are very concentratable in the $r < 16$ μm fraction of these soils. By contrast, the transition metals are only moderately concentratable, and the Group I and II metals and a few heavy metals are the least concentratable. Some of the heavy metals, e.g. As and Sb, while not very concentratable, are present at higher-than-expected concentrations in all particle size ranges of the soils. Crustal aerosol from these soils would thus be enriched in the REE, Hf, Th, and some heavy metals relative to average crustal rock. Such enrichments have been noted above for the Sahara aerosol [6], and seem to be a general feature of the world aerosol as well [7]. Determination of the true crustal-aerosol precursor will ultimately require analysis of soils by size fraction, laboratory wind-tunnel experiments with these same soils, and probably also more extensive chemical analysis of natural crustal aerosols such as those produced by arid regions with and without the presence of dust storms.

SUMMARY

Important as the calculation of crustal enrichment factors is, there is presently no agreement about best reference element or reference material. The best practical crustal reference element seems to be Al, although a number of others are satisfactory. The best crustal reference material would seem to be the 1-10 μm fraction of soils or some subfraction thereof. Unfortunately, little is known about the extent to which this material may differ in composition from bulk soils. It is also not yet clear whether this material is sufficiently homogeneous globally to allow the meaningful use of a single average composition, which for simplicity's sake would be highly desirable.

Acknowledgements: The authors wish to acknowledge valuable discussions with Mr. Norman Pattenden and Dr. Stuart Penkett of AERE Harwell and Dr. Dale A. Gillette of NCAR, Boulder, Colorado. This research was supported by NSF grants GA-31918 and ATM75-23725, ONR contract N00014-76-C-0435, and the Max-Planck-Gesellschaft of West Germany.

REFERENCES

[1] Egorov V.V., Zhigalovskaya T.N. and Malakhov S.G. (1970) Microelement content of surface air above the continent and the ocean. J. Geophys. Res. 75, 3650.

[2] Dudey N.D., Ross L.E. and Noshkin V.E. (1969) Application of activation analysis and Ge(Li) detection techniques for the determination of stable elements in marine aerosols. In: Modern Trends in Activation Analysis, J.R. DeVoe, P.D. LaFleur, eds., Nat. Bureau of Stds. Special Publication 312, Vol. I, pp. 55-61.

[3] Mason B. (1966) Principles of Geochemistry, 3rd ed., Wiley and Sons, Inc., New York.

[4] Rahn K.A., Borys R.D. and Shaw G.E. (in preparation) Asian desert dust over Alaska.

[5] Zoller W.H., Gordon G.E., Gladney E.S. and Jones A.G. (1973) The sources and distribution of vanadium in the atmosphere. In: Trace Elements in the Environment, Advances in Chemistry Series, No. 123, American Chemical Society, Washington, D.C. pp. 31-47.

[6] Rahn K.A., Schütz L. and Jaenicke R. (in preparation) Elemental composition of Sahara aerosol and Sahara soil.

[7] Rahn K.A. (1976) The chemical composition of the atmospheric aerosol. Univ. of Rhode Island Technical Report, 265 pp.

[8] Taylor S.R. (1964) Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28, 1273-1285.

[9] Wedepohl K.H. (1971) Geochemistry, Holt, Rinehart, and Winston, Inc., New York, p. 65.

[10] Turekian K.K. (1971) Elements, geochemical distribution of. In: McGraw-Hill Encyclopedia of Science and Technology, 3rd Edition, Vol. 4, pp. 627-630.

[11] Vinogradov A.P. (1959) The Geochemistry of Rare and Dispersed Chemical Elements in Soils, 2nd Ed., Consultants Bureau, Inc., New York.

[12] Bowen H.J.M. (1966) Trace Elements in Biochemistry. Academic Press, New York.

[13] Gillette D.A., Blifford I.H. Jr. and Fenster C.R. (1972) Measurements of aerosol size distributions and vertical fluxes of aerosols on land subject to wind erosion. J. Appl. Meteor. 11, 977-987.

[14] Gillette D.A. (1974) On the production of soil wind erosion aerosols having the potential for long range transport. J. Rech. Atmos. 8, 735-744.

[15] Gillette D.A., Blifford I.H. Jr. and Fryrear D.W. (1974) The influence of wind velocity on the size distributions of aerosols generated by the wind erosion of soils. J. Geophys. Res. 79, 4068-4075.

[16] Gillette D. and Goodwin P.A. (1974) Microscale transport of sand-sized soil aggregates eroded by wind. J. Geophys. Res. 79, 4080-4084.

[17] Gillette D. and Walker T. (1975) Characteristics of airborne particles produced by wind erosion of sandy soil, high plains of West Texas. National Center for Atmospheric Research (Boulder, Colo.) and Department of Geology, Univ. of Colorado (Boulder, Colo.), personal communication.

[18] Gillette D.A. (1976) Production of fine dust by wind erosion of soil: Effect of wind and soil texture. In: Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants (1974), Symposium Proceedings, CONF-740921, NTIS, U.S. Dept. of Commerce, Springfield, VA 22161, pp. 591-609.

[19] Patterson E.M., Gillette D.A. and Grams G.W. (1976) The relation between visibility and the size-number distribution of airborne soil particles. J. Appl. Meteor. 15,470-478.

[20] Schütz L. (1971) Messung der Grossenverteilung von Luftgetragenem Staub und Bodenmaterial in der Libyschen Saharah. M.S. dissertation, Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz, W. Germany.

[21] Schütz L. and Jaenicke R. (1974) Particle number and mass distributions above 10^{-4} cm radius in sand and aerosol of the Sahara Desert. J. Appl. Meteor. 13, 863-870.

[22] Rahn K.A. (1976) Silicon and aluminum in atmospheric aerosols: Crust-air fractionation? Atmos. Environ. 10, 597-601.

Low "natural" enrichment of elements in Arctic snow: Derived from fractionated pollution aerosol?

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Prepared for submission as a Letter to Nature
8 August 1978

In a recent Letter to Nature [1], Weiss et al. interpreted the abundances of trace elements in modern and historical polar snows according to the following logic: (1) There are two broad classes of elements present in snow - nonenriched, nonvolatile Al, V, Mn, Mg, and Ca and enriched, volatile Zn, Cd, Hg, S, Cu, As, Se, and Sb. (2) The nonenriched elements in snow are deemed natural (crustal) in origin because they have crustal ratios and are uniformly distributed in the snow. (3) The enriched elements in snow are deemed natural because they are uniformly distributed in snow, have modern enrichments similar to historical enrichments, and can be emitted to the atmosphere by a number of natural processes such as volcanism. (4) The trace-element compositions of Arctic snow and Arctic aerosol are the same or nearly so. (This step was assumed but not stated.) (5) Hence, the composition (and enrichments calculated from it) of both modern and historical Arctic aerosols is natural.

We agree with Weiss et al. that the historical evidence, as summarized in their Table 2, does indeed argue strongly for natural enrichments in modern polar snows. We differ with them, however, in a number of important respects. We have new direct evidence that the modern Arctic aerosol is significantly pollution-derived (at least during winter), that its composition differs from that of Arctic snow because of systematic aerosol-snow fractionation (with the pollution component being attenuated in snow), and consequently, that the trace-element enrichments of snow (hence even the low enrichments of Arctic snows) are not necessarily completely natural. In the rest of this Letter we present and discuss this new data.

Since September 1976 we have been collecting continuous filter samples of the Barrow, Alaska surface aerosol. The full results will be published soon; here we consider only a small portion of the first year's data. Table 1 gives winter mean concentrations and aerosol-crust enrichment factors for several elements during winter 1976-77. For comparison we also present corresponding data for the snows of Weiss et al., which were collected in February 1974 near Barrow. A great contrast in composition between aerosol and snow is apparent: enrichment factors for Na, Mg, V, Mn, Zn, Cd, and possibly also Hg are up to an order of magnitude higher in the aerosol than in the snow. For Na and Mg much of the discrepancy is because our aerosol samples were taken closer to the sea than the snow samples of Weiss et al. were; for other elements the discrepancy must have a different cause. For V, Zn, and Cd the difference between snow and aerosol is roughly an order of magnitude, but for Mn it is less than a factor of two. For Zn, Cd, and Mn the differences are quantitative only - Zn and Cd are enriched in both media whereas Mn is essentially nonenriched in both media. But V has a qualitative difference - it is enriched in the aerosol but essentially nonenriched in the snow.

We interpret the Barrow aerosol data to mean that the aerosol is significantly pollution-derived, probably from the midlatitudes. Our reasons for this are the following: (1) Pollution aerosol also contains enriched V, Mn, Zn, Cd, and Hg[3]. (2) Natural aerosols, to the best of our knowledge, do not contain enriched V and Mn. V, for example, is enriched primarily due to midlatitude combustion of residual oils[4]. (3) The nonmarine aerosol at Barrow has a strong winter maximum, with typical winter/summer concentration ratios of 10 for sulfate, 20 for noncrustal Mn, and 50 for noncrustal V. Large-scale circulation patterns couple the Arctic to the mid-latitudes during winter but decouple them during summer[5]. (4) The winter composition is much closer to that of pollution aerosol than is the summer

Table 1. Arctic Alaskan aerosol vs. snow

Element	Aerosol[a] Concentration, ng m^{-3}	EF^{c}_{crust}	Snow[b] Concentration, $\mu g\ \ell^{-1}$	EF^{c}_{crust}
Na	910	95	68	7.5
Mg	160	23	41	6.1
Al	27	1.0	26	1.0
Ca	50[d]	4.1	57	4.9
V	0.62	13.6	0.086	2.0
Mn	1.07	3.3	0.62	2.0
Zn	14.8[d]	630	1.12	50
Cd	0.37[d]	5500	0.047[d]	730
Hg	<0.4[d]	<15,000	0.0055[d]	210

[a] Mean of December 1976 - April 1977 samples from Barrow, Alaska.

[b] From reference 1, 28-224 km south of Barrow, Alaska, 15 February 1974.

[c] For element X, $EF_{crust} = (X/Al)_{aerosol}/(X/Al)_{rock}$, where the rock composition is that of reference 2.

[d] Estimated from incomplete series of measurements.

composition. (5) Both absolute and relative elemental concentrations in the aerosol are consistent with travel times of 10-15 days from mid-latitudes, as well as residence times of about 3 days and dilution of the polluted air mass by factors of 2-3 during transit.

Several possible objections to our data and interpretation can be raised and refuted: (1) The aerosol was contaminated locally. All samples during this first year were taken in the clean sector only, so that local influences were eliminated. Samples deliberately taken in the contaminated sector, which included Barrow and the Naval Arctic Research Laboratory, showed little or no change for most elements. (2) Snow and aerosol were not from the same site. Remote areas like the Arctic should have broadly uniform aerosols because of the absence of local sources. We have confirmed this with data from Spitsbergen[6], Bear Island[7], northern Norway[3], Fairbanks, the Northwest Territories of Canada[8], and the non-Arctic Shetland Islands[9] and western Ireland[10], all of which have similar patterns of enrichment. (3) Snow and aerosol were not collected in the same year. In addition to our continuous samples from the winters of 1976-77 and 1977-78, we have a few samples from the winters of 1974-75 and 1975-76. All four of these sets agree closely with one another. They also answer the objection that we may be concluding too much from a single year. (4) Surface aerosol may differ from aerosol aloft, from which the snow was derived. Two sets of samples from spring 1976 show no major differences between the surface aerosol and that at 2-3 km. During strong transport of Asian desert dust to Alaska[11], however, the aerosol aloft may be temporarily more crustal than that at the surface. This probably has little effect on snow composition, though, because most of the Barrow snow falls before the dust appears in the spring.

We are thus presented with two diametrically opposed pictures of the modern Arctic environment: the snow which indicates a natural character and the aerosol which indicates the presence of pollution. Because we have no reason to doubt the correctness of either set of data, we are forced to conclude that these two phases of the environment can co-exist with quite different compositions, i.e., there is great chemical fractionation across the aerosol-snow "interface". In fact, Junge[12] recently warned of this possibility.

A scatter diagram of enrichment factors in Barrow snow vs. Barrow aerosol (Figure 1) reveals that aerosol-snow fractionation varies regularly with enrichment factor. Elements enriched in the aerosol by factors of greater than about 10 are depleted in the snow by roughly an order of magnitude relative to the nonenriched (crustal) elements. Because the enriched elements are associated with smaller aerosol particles and the nonenriched elements with larger particles [3], aerosol-snow fractionation would appear to be a particle-size-dependent process, with larger particles preferentially incorporated into snow. One obvious mechanism for this is ice nucleation on clay-mineral particles, which are both large and crustal. Indeed, Kumai [13-16] has found that the majority of ice crystals from polar regions contain clay particles as central nuclei. Other possible mechanisms include below-cloud scavenging, dry deposition, and crustal aerosol aloft. At present it is not possible to assess quantitatively the relative importance of these mechanisms. Whatever the mechanism, though, it now seems clear that Arctic aerosol and snow are quite different in composition, with the snow being representative of the larger-sized aerosol particles, and not of the submicron (pollution) fraction. Because the temporal and spatial

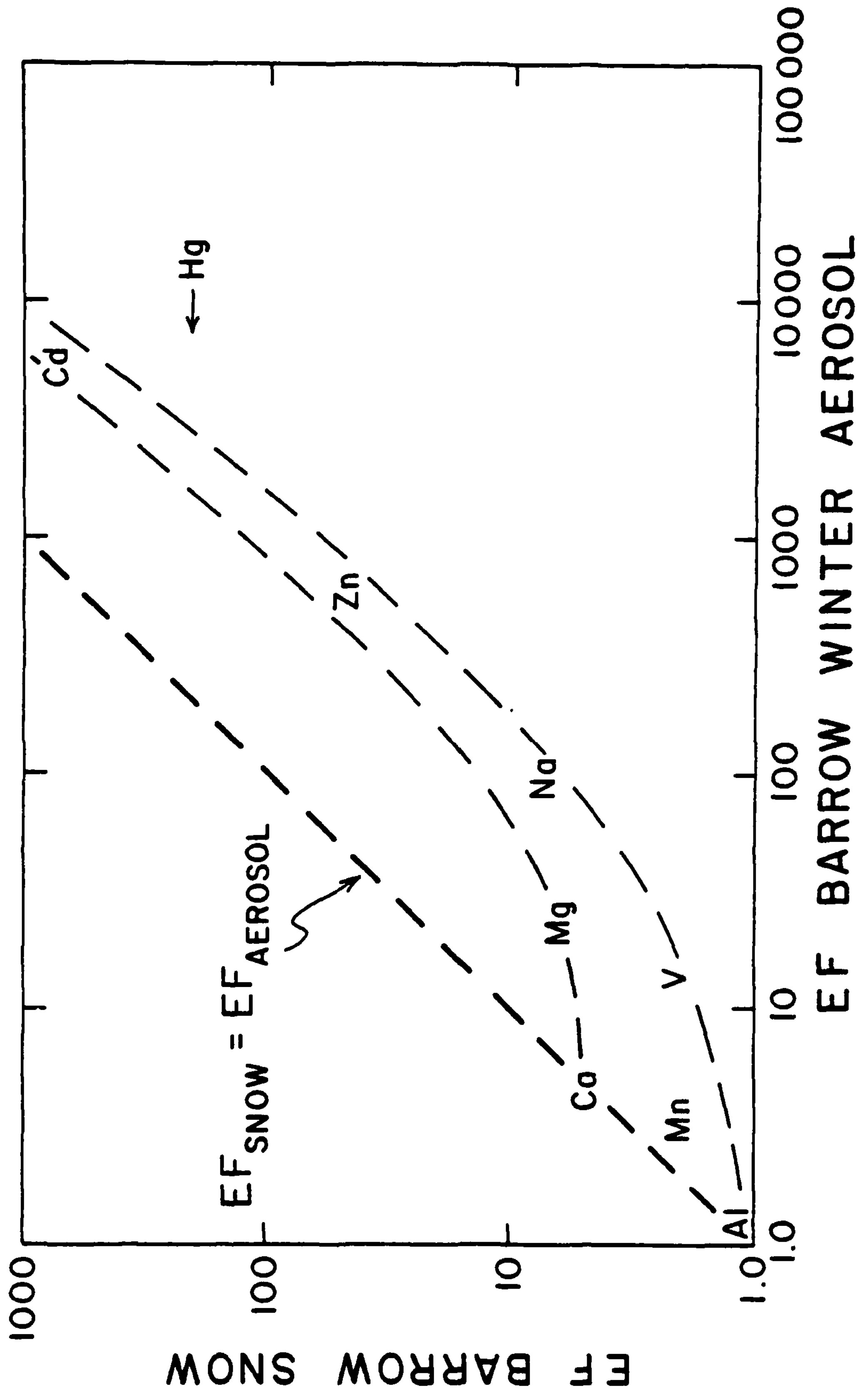

Figure 1. Enrichement factors in Arctic Alaskan aerosol and snow.

variations of these aerosol-snow differences are so imperfectly known at present, inferring the nature of an aerosol directly from snow, such as was done by Weiss et al. from their Table 2, is of very uncertain validity and may give results which are both imprecise and misleading.

This work was supported by the Office of Naval Research (Contract N00014-76-C-0435). Barrow aerosol samples were collected as part of a cooperative program with the NOAA GMCC program, using equipment designed and constructed by R.D. Borys. The cooperation of staff members of the GMCC Clean-Air Observatory and the Naval Arctic Research Laboratory in Barrow, Alaska is gratefully acknowledged. Samples were chemically analyzed at the Rhode Island Nuclear Science Center, Narragansett, Rhode Island, with assistance from R.D. Borys and T.J. Conway. Helpful discussions with G.E. Shaw are acknowledged.

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References

1. Weiss, H.V., Herron, M.M., and Langway, C.C. Jr. Nature 274, 352-353 (1978).

2. Mason, B. Principles of Geochemistry, 3rd ed., Wiley and Sons, Inc., New York (1966).

3. Rahn, K.A. The chemical composition of the atmospheric aerosol (University of Rhode Island Technical Report, 1976).

4. Zoller, W.H., Gordon, G.E., Gladney, E.S., and Jones, A.G. In: Trace Elements in the Environment, Advances in Chemistry Series, No. 123, American Chemical Society, Washington, D.C., pp. 31-47 (1973).

5. Rahn, K.A., Borys, R.D., and Shaw, G.E. In: Proceedings of the 9th International Conference on Atmospheric Aerosols, Condensation and Ice Nuclei, Galway, Ireland, 21-27 September 1977 (In press).

6. Larssen, S., Norwegian Institute for Air Research (personal communication).

7. Rahn, K.A., Conway, T.J., and Larssen, S. (Unpublished data).

8. Rahn, K.A. Sources of Trace Elements in Aerosols - An Approach to Clean Air (Ph.D. Thesis, University of Michigan, 1971).

9. Cawse, P.A. A survey of atmospheric trace elements in the U.K. (1972-73) (AERE Harwell Report R 7669) H.M. Stationery Office, London (1974).

10. Schütz, L., Max-Planck-Institut für Chemie, Mainz (Unpublished data).

11. Rahn, K.A., Borys, R.D., and Shaw, G.E. Nature 268, 713-715 (1977).

12. Junge, C.E. In: Isotopes and Impurities in Snow and Ice - Symposium - Isotopes and Impuretés dans les Neiges et Glaces (Proceedings of the Grenoble Symposium August/September 1975; Actes du Colloque de Grenoble, août/septembre 1975); IAHS Publ. No. 118, 63-77 (1977).

13. Kumai, M. Geofisica pura e applicata 36, 169-181 (1957).

14. Kumai, M. J. Meteor. 18, 139-150 (1961).

15. Kumai, M. J. Atmos. Sci. 33, 833-841 (1976).

16. Kumai, M. and Francis, K.E. J. Atmos. Sci. 19, 474-481 (1962).

N. Internal discussion documents

During this year we have become more and more impressed with the difficulties of communicating thoughts and ideas within a research group located in Rhode Island, Colorado, and Alaska. This spring we began an experiment of writing down our thoughts as discussion documents, so that the other branches of the group could examine them in concrete form. This approach has been quite successful, and we will continue it. The first five discussion documents are reproduced here.

What is Arctic haze?

Discussion document prepared by

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8 June 1978

General type of Arctic haze

Characteristics

Same as "diffuse" haze of 1st half of spring 1976 experiment; see Péwé paper.

Associated with "clean" atmosphere, i.e., low concentrations of elements in the aerosol, also no strong narrow bands of dust or other specific aerosols.

High τ (0.1-0.3), high α (1.3 ± 0.3).

Explanation

Submicron droplets formed by condensation of water vapor onto hygroscopic nuclei (aerosol particles), followed by limited growth.

Sulfate should be dominant constituent, probably as sulfuric acid.

Special types of Arctic haze

Characteristics

Occur sporadically during the winter half-year.

Possibly other seasons as well.

Few times per year (considerable uncertainty here).

Well-defined narrow bands at specific elevations.

Best example so far: "Banded" haze of 2nd half of spring 1976 experiment; see Péwé paper.

A second possible case: Band at 8,000-12,000 ft. during flight 1, spring 1978 (No RH maximum but high β and high α). Composition unknown.

High aerosol concentrations in narrow layers.

Transport of specific aerosols to the Arctic.

Composition and other properties of these bands may vary considerably, depending on the specific source.

Evidence for the general case

Evidence for submicron-sized particles

Mitchell (1956): Radius of haze particles $\leq 1 \mu m$, based on coloration and lack of ice-crystal optical effects.

High α (1.3) of spring 1978.

Very broad solar aureole - spring 1978.

Particle-size distributions (from double-stage impactor and optical measurements) suggest sufficient submicron particles to dominate optical effects. (N.B. Impactor data from surface clear layer, not in strongest haze).

Color effects (brownish cast in solar direction, grayish in antisolar direction) suggest narrow range of submicron particles.

Evidence for droplet/RH/condensation/hygroscopic nuclei explanation

Droplets/RH/condensation

Direct	Droplets observed in abundance on double-stage impactor slides.
Direct	Keith Bigg: Surprisingly large fraction of Barrow spring aerosol (1977) is sulfuric-acid droplets.
Direct	Association of haze aerosol with high RH (80-100%) in the vertical profiles of spring 1978
Indirect	Pure water droplets can be supercooled to -38°C at radius $\approx$ 1 µm, and to still lower temperatures if radii are smaller and/or solutions are impure.
Indirect	Association of turbidity with low temperatures (high RH's?) during spring 1978 at Barrow.
Indirect	General association of turbidity with high RH's at other places (see "Water vapor" document).
Indirect	Water needed to account for all the Barrow haze - individual constituents of the aerosol are not enough.
Indirect	Smooth progression of haze into clouds, especially near Prudhoe Bay in spring 1978 (This same effect is seen in many locations, and is particularly marked near summer cumulus clouds).
Indirect	Similarity between Arctic haze and Toronoto brown haze, which seems to be of water droplets.
Indirect	Existence of clear layer at surface, where RH $\leq$ 80%.

Hygroscopic nuclei

Indirect	Critical RH $\gtrsim$ 80% from the vertical profiles - same values as the deliquescence point of many hygroscopic aerosol particles.

Indirect Most remote aerosols are approximately 50% water-soluble, the majority of which is sulfate.

Indirect Relatively high sulfate concentration at Barrow during spring 1977:

SO_4	0.5 - 1.0 $\mu g\ m^{-3}$	
Soil	0.35 "	
Sea salt	1.3 "	
Other pollutants	0.1 "	
Total	2.0 - 2.5 $\mu g\ m^{-3}$	($SO_4^=$ is 25 to 40% of total)

Evidence against the general case

Indirect No icing of aircraft flying in Arctic haze (Mitchell, 1956).

Possible reasons:

a) Sulfuric-acid solutions have too low a freezing point. Not so. 20% H_2SO_4 lowers freezing point by 13.6°C, about the same as 20% NaCl (16.5°C).

b) Droplet mass too small to notice any icing. Mass concentration in Arctic haze $\leq 100\ \mu g\ m^{-3}$, or about 10^4 times lower than liquid water concentrations in clouds.

c) Submicron haze particles deflected by surface layer of aircraft, whereas much larger cloud droplets can penetrate the surface skin.

The actual explanation for lack of icing is probably a combination of (b) and (c).

Alternative explanations for the general case

(1) Asian desert dust

But α too high in general case.

Asian dust not present during first half of spring 1976 experiment.

(2) Stratospheric sulfate

Could be. Even at minimum concentration (between volcanic eruptions), sulfate concentrations in the Junge layer are a few tenths $\mu g\ m^{-3}$ (STP), which is large enough to explain the surface concentrations at Barrow, assuming that the Junge layer reaches the surface without being diluted. Probabilities are very much against this, however. There must be some stratospheric sulfate at Barrow during the spring, because spring is only a bit after the ^{7}Be maximum of February observed at Barrow by HASL.

(3) Particles formed locally by the reaction O_3(stratospheric) + light + (?)

Surface O_3 has a broad minimum of concentration ast Barrow from April through August. If light plus O_3 are needed for this reaction, its maximum production would probably be in summer.
[Note: at Barrow the annual cycles of surface O_3 and ^{7}Be are roughly similar, both having broad winter maxima. ^{7}Be tends to peak in February, O_3 in December (variable). Therefore stratospheric O_3 is likely to be present in winter (winter O_3 may also have a long-range transport component).]

Evidence against a stratospheric origin of O_3:

Vertical profiles of O_3 in spring 1978 showed a constant mixing ratio up to nearly 5 km. This would not be expected with subsidence from above.

Evidence against reaction of O_3 to form aerosols:

(a) No obvious correlation between day-to-day values of O_3 and turbidity (only 2 days' data, though)

(b) No correlation between O_3 and haze on the vertical profiles. O_3 was constant, whereas the aerosol varied widely (10X). The O_3 concentration was low enough (30 ppb = 50 $\mu g\ m^{-3}$, about the same as the highest values for the aerosol) so that it should have varied if it were being used up in formation of the aerosol.

Note 1: If O_3 reacts to form particles in the absence of light, Arctic haze should have a broad winter maximum, not a spring maximum.

Note 2: This explanation requires high concentrations of Aitken nuclei in the haze. In fact, Aitken counts are very low near Barrow during spring. Neither the double-stage impactor nor the sun photometer can tell us now whether the

Aitken nuclei are abmornally high, because (a) DSI data all from clear layer, not thickest haze, (2) sensitivity of photometer to Aitken nuclei is low.

(3) <u>Organics (terpenes?)</u>

Concentrations almost certainly are not high enough to account for the haze. Surface aerosol a few μg m^{-3}. Three rough determinations of total organic carbon gave $\approx$0.5 μg m^{-3}. Haze may be 50 μg m^{-3}.

Note: Atmospheric circulation to the surface of the Arctic during winter is most interesting. Winter is just the time of broad maxima of stratospheric air <u>and</u> mid-latitude polluted air.

Comments on Alaskan Haze

by

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23 June 1978

This is a first draft of a discussion document by GES to complement "What is Arctic haze?" by KAR. During fall 1978 these two documents will be revised into a single one.

Facts about the haze

1. Its Alaska-wide, strongest in the north and extends out over the pack ice. We don't know how extensive the haze is over the Arctic, so for the moment I'll call it Alaska haze.

2. The haze always comes in spring. Perhaps there are small events in winter or late fall, but they are visually uninteresting.

3. The haze is usually diffuse. It is whitish and it is a high haze, indicating either long-range transport or in situ production at 500-700 mb level.

4. The diffuse haze consists almost entirely of sulfate particulates; mostly hydrated sulfuric acid droplets, but sometimes $(NH_4)_2SO_4$. (From K. Bigg)

5. The spring occurrence coincides with a strong maximum of total ozone in the Arctic, but there is evidence at the same time of a depletion of surface ozone.

6. Spring is the time when the sun's radiation becomes significant in the Arctic after the polar night.

7. Spring is the time when significant areas of open water begin to appear.

8. The size distribution of the haze is bi-modal, it has been derived by optical inversion and also Keith Bigg has derived essentially the same information from impactor studies. The modal radii are at $r = 0.1\mu$ and $r \cong 1\mu$. There are few particles with $r \lesssim 0.05\mu$! This indicates that the haze is aged. Same aerosols are found at Mauna Loa and at other clean-air sites.

9. The meridional index at 700 mb and 500 mb (an indication of meridional transport by eddies) peaks in the spring and in the fall.

10. Back trajectory analyses at 700 mb (isobaric, not isentropic) for mean monthly weather conditions shows the most extreme southern excursions occur in spring. The corresponding excursions in fall are not dramatic. The back trajectories run down the Bering Straits, then veer westward down the sub-polar jet and graze the northern islands of Japan.

11. The haze is associated with general air subsidence and with an anticyclone NE of Barrow. There has always been clear weather over northern and central Alaska during the haze. When clouds appear the haze always decreases in intensity for one or two days afterward.

12. The haze is slightly absorbing. Keith Bigg says he finds occasional industrial aerosol mixed in with the sulfates, they sometimes seem to be particles of flyash - these could be responsible for the slight absorption. ${}_0n^1$ activation also indicates a pollution component.

13. Alaskan haze introduces a net heating of the earth-atmosphere system over areas covered with ice or snow. I estimate the temperature change in a radiative equilibrium situation to be about 1°C.

14. The stratospheric aerosol layer varies, but it seems to vary independently of the variations in Alaskan haze (stratospheric aerosol has been studied from Fairbanks with twilight spectrophotometry).

15. There were reports this spring from Reeves Aleutian pilots of haze north of the Aleutian Island Arc.

16. Perhaps an associated fact: Radioactive tracers from bomb debris show high concentrations at relatively low altitudes (8 km) over the poles in spring. This indicates poleward transport and enhancement.

17. Another associated fact: The Arctic is a desert. Annual precipitation at 80-90°N is 120 mm/yr; 70-80°N, 185 mm/yr, (compare with rainfall at 40-50°N, 907 mm/yr). The precipitable water vapor is: 80-90°N, 4.9 mm; 70-80°N, 6.1 mm, (compare with 40-50°N, 15.2 mm). The precipitation efficiency is 6.7% at 80-90°N and 16.3% at 40-50°N.

18. The average radius of particulates changes with altitude, becoming smaller with increasing altitude (inferred from sun photometry).

19. There is evidence from ${}_0n^1$ activation) that banded, dark and slightly colored haze is crustal; this type of haze does not occur as frequently as the diffuse haze in the Arctic.

20. The haze vertical profile contains "structure", especially at altitudes below the peak of the diffuse distribution. One often finds blowing snow or ice crystals in a 50-200 m-thick layer just above the surface, and above this, thin regions of enhancements or depletion in the vertical profile. There is sometimes a depletion and sometimes an enhancement in the saturated layer at the top of the boundary layer; usually at about 500 m altitude.

21. The Aitken count normally increases upward from the surface, but only reaches $\sim$100-200 cm^{-3}.

Speculations on the origin of the haze

One can invoke the following possibilities for haze origin:

1. Particles injected downward from convergent flow from the stratosphere.

2. Particles forming *in situ* at 500-700 mb from homogeneous heteromolecular nucleation of trace gases.

3. Particles transported to the Arctic:
   a. Gobi dust transported in the sub-polar jet.
   b. Particles transported from Japanese industrial sources.
   c. SO_2 from Sudbury Nickel refinery in Ontario (very unlikely).
   d. Pollution from Europe.

4. "Local" pollution:
    a. Loess from deposits on the north slope of the Brooks Range or blowing in from loess deposits in interior Alaska or in the Alaska Range.
    b. Wind-blown sand from exposed river bed cuts on the North Slope.
    c. Vapors from open leads in the pack ice.
    d. Particulates from Prudhoe oil fields.
5. Secondary effects:
    a. Localized particle growth to optical size range in layers of high humidity.
    b. The possibility of photochemistry associated with the appearance of the sun.
    c. The possibility of enhanced nucleation or enhanced chemical reactions due to high ozone concentrations.
    d. Association with dynamics of stratospheric warmings (that occur in mid-winter and spring).
6. Cosmic dust.
7. Volcanic activity in Aleutians.
8. Di-methyl sulfide from oceans?

<u>Comments on haze transport and haze evolution</u>

In this brief document it is just not possible to explain in detail the complexities associated with haze evolution, but extensive theoretical work that I've done these last few months is converging to a point where quantitative statements can be made about the relative importance of the source mechanisms suggested above. I've been considering the following processes that act in the atmosphere to change, form or remove particulates:

1. Gravitational fallout ($r > 10^{-3}$ cm).
2. Impaction to the surface in the turbulent boundary layer ($r > 10^{-4}$ cm).
3. Diffusion across the 0.5 mm-thick laminar surface layer ($r < 10^{-5}$ cm).
4. Thermal diffusion across thermoclines in the atmosphere ($r < 10^{-7}\mu$).
5. Diffusion of particles to cloud drops or ice crystals ($r < 10^{-5}$cm).
6. Impaction of particles on ice crystals or cloud droplets ($r > 10^{-4}$cm).
7. Nucleation to form ice crystals or cloud droplets ($r > 10^{-5}$ cm).

8. Humidity growth.

9. Coagulation of particles under Brownian motion ($r < 10^{-6}$ cm).

10. Meridional convergent-flow concentration of incoming cosmic dust particulates ($r > 10^{-5}$ cm). Occurs in summer mainly.

11. Nucleation of particles from trace gases ($r < 10^{-7}$ cm):

    a. nucleation on ions,
    b. homogeneous-homomolecular nucleation,
    c. homogeneous-heteromolecular nucleation,
    d. heterogeneous-heteromolecular nucleation.

12. Photochemical reactions involving excited singlet oxygen, SO_2 and sunlight.

13. Atmospheric large-scale diffusion of SO_2 gas.

Interpretation of Alaskan haze

The year-after-year occurrence of diffuse haze in Arctic Alaska during the same few months (March-early May) suggests that there is a dominant mechanism at work that causes the haze. This dominant mechanism is not obvious. But more than anything else, it seems to me that one must look for something "different" going on in the atmosphere in spring. Fortunately, in Alaska, there is quite a lot of symmetry between spring and fall for many atmospheric physical and dynamical processes and since we find the haze only in spring this allows us to immediately exclude many of the processes that were suggested in the "speculations" we listed. There are two observations that seem to be really unique to spring-time in Alaska:

1. The mean monthly isobaric back trajectories at the 700 mb level (from Barrow) undergo maximum southerly excursion in spring. This suggests that the haze is coming from Japan, China or perhaps from an oceanic source (di-methyl sulfide?).

2. Atmospheric ozone (and also NH_3 according to Tom Gosink) concentration undergoes a strong spring-time peak. This indicates strong transport to the polar regions, at least in the lower stratosphere (8-10 km).

   I believe, further, that other "key" facts about the haze are:

3. The haze is "high", sometimes being entirely above the peak flying elevation of a Cessna (12,000 ft.), but often "peaking" at 700 mb. This suggests long-range transport.

4. Precipitation and clouds are lower in spring (especially April) than at any other time of the year, although fall sometimes also has spells of clear weather. The atmosphere in the Arctic is stable.

5. Twilight probing shows that the stratosphere is the "cleanest" that it has been for years, yet Alaskan haze was strong in spring 1978. Alaskan haze seems to be unassociated with stratospheric turbidity.

6. The back-air trajectories go southward, to about latitude 45°, then westward along the high velocity sub-polar jet. Transport of gases or particles in the lower sub-polar jet from Asiatic sources would be rapid (about 4 days).

7. Calculations indicate that ice crystals and clouds would efficiently scavenge particulates. We see this in low (500 m) layers of depletion after clouds form, then dissipate. On the other hand, when humidity increases in a layer, particles grow to the optical range sizes and form visual layers.

8. Calculation also indicates that the depletion of particles with $r \lesssim 10^{-5}$ cm is due to coagulation. The implication is that the particles are at least a "few days" old.

As a working hypothesis that comes out of the above comments, I suggest that the diffuse haze has its origin in Asia. Its composition $(NH_4)_2\ SO_2$, flyash, etc.), suggests a pollution source from Japanese industrial regions. The biggest problem seems to be to explain how the particles or sulphur gases could travel along the northern fringe of the Aleutian cyclone without being washed out. Obviously our sampling work will have to start moving in the direction of the Aleutian Islands.

Suggestions for future investigations

1. Keith Bigg has demonstrated an extremely useful (in my opinion) method to determine the composition of the haze. The method involves transmission electron microscopy on particles collected with a small impactor. Although details won't be listed here, the method can be used to identify the presence of individual sulfate particles and to separate ammonia compouds from sulfuric acid droplets. A great advantage of the method is that particles can be collected in short time intervals (10 min. to 30 min.) and thus it could be (and has been) used to determine composition and size distribution at individual "points" in the haze. We are currently implementing this technique in Alaska, but it ought to be realized that in no way will the method replace ${}_0n^1$ activation studies - it supplements ${}_0n^1$ activation. I suggest that this method be adopted in our future studies.

2. The horizontal extent of the haze ought to be investigated more than it has been. I suggest making flights down the Aleutian Chain with continuous sampling of Aitken counts and SO_2 and O_3 concentrations. Particles should be sampled for ${}_0n^1$ activation studies and for transmission electron microscopy.

3. Daily flights, made from Barrow, have provided and could continue to provide useful information on the vertical structure of the haze and its relation to meteorological parameters. It would be useful to supplement optical and chemical work with Aitken counts and humidity profiles (with a frost-point hygrometer?). A Knollenberg probe could provide useful information, but I can think of better ways to spend money. Perhaps the NCAR Electra could be made available for a week?

4. The particle size spectrum has been estimated, apparently quite accurately, by inverting optical extinction and optical scattering measurements. This work needs to be continued at Fairbanks and Barrow.

5. Isentropic back trajectories would be very useful to have, but I'm not certain how to do them. Does someone have a computer routine to do isentropic trajectories?

6. It would be useful to conduct more experiments on the size distribution of the Aitken particles. Work is underway in Alaska on the Nuclepore filtering method, we already have built a very sensitive Aitken counter and we may try our hand at constructing a diffusion-battery to go along with it. Incidentally, the recovery of an aerosol size distribution function from a diffusion-battery can be done by inversion using exactly the same computer routines that we've developed for inverting optical data.

7. URI's snow sampling project and "wet chemical" methods to identify ions should, in my opinion, be emphasized.

8. Can we encourage NOAA to move a lidar to Barrow? The lidar is built, tested and ready to go. Ron Fegley is keen to bring the instrument to Barrow for at least one spring season. Let's encourage Kirby Hanson or Lester Machta to put priority on this.

Evidence for a link between Arctic haze and water vapor

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First revision, 21 July 1978

Introduction

It has recently been impressed on me, primarily by a spring 1978 field trip to Alaska, that Arctic haze may have strong links with relative humidity. In fact, it is entirely possible that relative humidity (in combination with omnipresent hygroscopic particles) is the dominant force creating Arctic haze. In view of the fact that this idea is a major departure from those we have held in the past, I have decided to summarize my new thoughts on paper. This document is only preliminary, and will surely be heavily revised in the future. It is intended to serve as a focal point for further discussion, and is being circulated to participants in the Arctic haze project, as well as interested ONR personnel. All comments are most welcome.

Hygroscopic particles in the atmosphere

The atmosphere is full of hygroscopic particles (those which take up water vapor from the air at relative humidities well below 100%), even in the most remote regions. (To a first approximation, all water soluble substances in the aerosol may be considered hygroscopic, so that the greater the mass fraction of the aerosol which is soluble, the more hygroscopic the aerosol is.) Cadle et al. (1968), for example, have detected sulfate particles, presumably sulfuric acid, at various sites near McMurdo Station in Antarctica. More than 50% of the particles studied were sulfates. Fenn et al.(1963) found that about 40% of the aerosol mass at Camp Century, Greenland, consisted of sulfate particles. The Junge layer of the stratosphere consists of sulfate particles of various types (Bigg et al, 1970, for example). Nearer the surface, sea-salt fragments such as sodium chloride and calcium sulfate abound over the oceans and somewhat inland. Winkler (1974) showed that about 60% of the mass of near-surface European aerosols was water-soluble. For rural aerosols with relatively low anthropogenic influence, 70% of the mass was water-soluble. Approximately one-half of this soluble fraction was considered to be ammonium sulfate and other simple salts. The relative composition of the soluble fraction was nearly the same at three different sampling sites in Europe. The solubility of the aerosol seemed to increase with decreasing radius, reaching a value of nearly 80% for the 0.1-0.3 μm fraction, the smallest size range investigated by Winkler.

To the best of our knowledge, solubility experiments similar to those of Winkler (1974) have not been performed on aerosols of remote regions, particularly the Arctic. But it can be safely assumed that Arctic aerosols are at least 50% water-soluble, based on the above-mentioned data for sulfates.

Growth of hygroscopic particles with relative humidity

There are two ways in which soluble aerosol particles respond to relative humidity. Because the Köhler curves for soluble particles (growth curves as a function of relative humidity) pass through a maximum at slight supersaturations, soluble particles may undergo limited growth in unsaturated conditions or "unlimited" growth when the supersaturations exceed some "critical" value. In the former case growth typically stops around a radius of a few tenths of a micrometer; in the latter case the droplets may reach radii of 5 to 20 μm, and become genuine cloud droplets. To the extent to which Arctic haze may be considered droplets, all available evidence suggests that the droplets are submicron-sized, hence are products of restricted growth. For this reason, the rest of this document will be limited to consideration of possible formation and growth of Arctic haze droplets at relative humidities below 100%.

With such a large portion of aerosols being water-soluble, they should respond sensitively to the water-vapor content of the atmosphere. Available data bear this out. Junge (1952a,b) first measured the growth of particles in continental air as a function of relative humidity, and found that particles began to grow at 70% relative humidity. Jiusto (1967) calculated that soluble aerosol particles should increase in radius by about a factor of two under humid but unsaturated conditions. Winkler carried out an extensive study of the growth of natural and artificial aerosols, both pure and mixed, with relative humidity (Winkler, 1969; Winkler and Junge, 1971; Winkler and Junge, 1972; and Winkler, 1973). Typical of his results were the findings that giant particles absorbed more water than large particles, and that German aerosols at 90% relative humidity contained approximately double their dry mass. R. Charlson's group at the University of Washington has also actively studied humidity effects on growth and optical scattering of the aerosol (Charlson et al., 1969; Pueschel et al., 1969; and Covert et al., 1972, for example).

Effect of growth of hygroscopic particles on atmospheric turbidity

There are several specific lines of evidence that turbidity and atmospheric moisture are related: (1) Flowers et al. (1969), in a report of 6 years of data from the former United States Volz sun-photometer network, have demonstrated that there is a general summertime maximum of turbidity, with mean values approximately double those of winter. At a given site, polar or Arctic air masses had characteristically lower values of turbidity than did tropical air masses. For this they offered two possible explanations, namely that the tropical air masses carried more particulate matter than did the more northern air masses, or that the higher water-vapor contents of the tropical air masses caused the scattering particles to grow in size, and hence to scatter more light. (2) Vickers and Munn (1977) showed a strong effect of relative humidity on haze frequency in Canada. (3) Lundgren and Cooper (1969) also found that visibility decreased as relative humidity increased for Lewistown and State College, Pennsylvania, and Riverside, California. (4) We have found that the characteristic summer hazes of Narragansett, Rhode Island, depend strongly on relative humidity. Figure 1 shows the relation between turbidity at 500 nm and relative humidity during summer 1978. These measurements were taken near the shore of Narragansett Bay, about 10 km from the Atlantic Ocean proper. Notice the rapid increase of turbidity for relative humidities above about 65 to 70%. (5) The most massive, systematic body of information on the relation between relative humidity and various optical properties of the aerosol is found in the Russian literature, the only reference to which we have come across in western literature on the aerosol is in a review of atmospheric haze by Germogenova _et al_. (1970). The many Russian articles on relative humidity and haze are well summarized through 1967 in an article by Rosenberg (1967). Three quotations from this article speak for themselves: "Atmospheric turbidity is always related to a condensation process and is due almost exclusively to particles with a water (or ice) envelope, the size of which increases with the relative humidity and is the basic, but not the only, factor determining the optical characteristics of the atmosphere"; "The condensation process becomes optically perceptible as soon as the

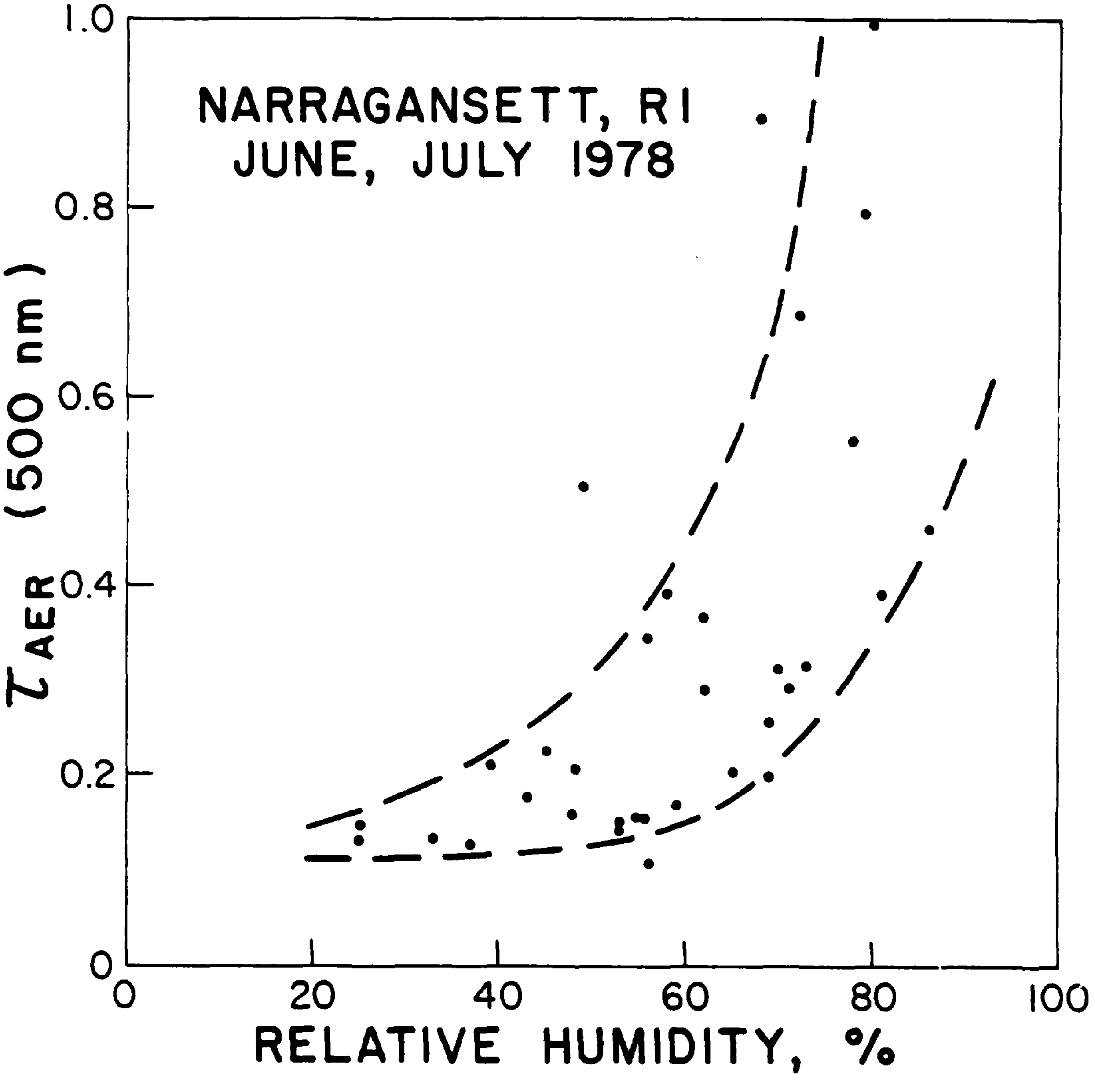

Figure 1. Turbidity vs. relative humidity at Narragansett, Rhode Island, summer 1978.

humidity w = 35% and - first slowly, then more rapidly - increases progressively with a rise in w"; "A direct relation is obtained between relative humidity and the optical characteristics of an atmospheric aerosol; at a given humidity, the range of variation of the relevant quantities is fully determined." For a list of other Russian references on the subject, see Rosenberg (1967).

Other pieces of evidence for the effect of atmospheric humidity include: (6) the high turbidities of the tropics relative to mid-latitudes, and (7) the positive correlation between τ_{500} and absolute humidity at Fairbanks from January through April 1978 (note here that this correlation is valid on a long-term basis - the day-to-day changes seem to be inversely-correlated).

Arctic haze as viewed all over the North Slope during spring 1978 was a most impressive phenomenon. It was brown to the eye and extremely intense. The sun photometer gave optical depths of 0.1 to 0.25, which was at least twice as high as in Fairbanks that spring, and higher than in Narragansett, Rhode Island during spring. In fact, one of the major problems that we have had to deal with in interpreting this haze was that there was too much of it to be explained simply in terms of aerosol content. For example, Barrow had considerably higher haze conentrations than did Rhode Island during winter, but had concentrations of dry aerosol 10-20 times lower than in Rhode Island. Every component of the Barrow aerosol which we have measured, including sulfate is at least several times lower than in the northeastern United States, and normally an order of magnitude lower or more. We know of no component of the dry Barrow aerosol which could be sufficiently abundant to cause the high haze concentrations there.

On the other hand, there is plenty of water in the Arctic atmosphere to increase the conentrations of aerosol. Even at -50°C there is more than 50,000 $\mu g\ m^{-3}$ water vapor in equilibrium with liquid water in the surface atmosphere, as opposed to less than 10 $\mu g\ m^{-3}$ of aerosol proper. Even with low relative humidities at the coldest possible temperatures in the Arctic, there is a great excess of water vapor over aerosol; thus aerosol growth should never be vapor-limited.

The haze of spring 1978 was a low-temperature haze, that is, it was associated with colder rather than warmer air. This effect was clear-cut (see Figure 2), and quite different from the spring of 1976, when only a poor correlation with temperature was seen. In 1976 there were at least two types of haze, a coarse-particle desert-dust haze from the south and a fine-particle haze from both north and south. This spring, however, the optical measurements showed only a fine-particle haze, presumably from only a singe source or source type because of its well-defined inverse correlation with temperature.

There may have been at least two mechanisms operating, singly or together, to create the observed temperature dependence of the 1978 haze: a direct effect (via relative humidity, for example) and an indirect effect (where temperature signifies the origin and presumably also the aerosol loading of the air mass.) These two effects might be imprecisely called "wet" and "dry", respectively. Until this spring, our interpretations of Arctic haze had been "dry", in the sense that the effect of water vapor had not been explicitly considered. Rather, we sought to explain the haze in terms of various strong sources of aerosol such as deserts or polluted urban areas. It is the dual thesis of this document that (a) such attempts have failed, i.e., that they have not demonstrated the presence of sufficient

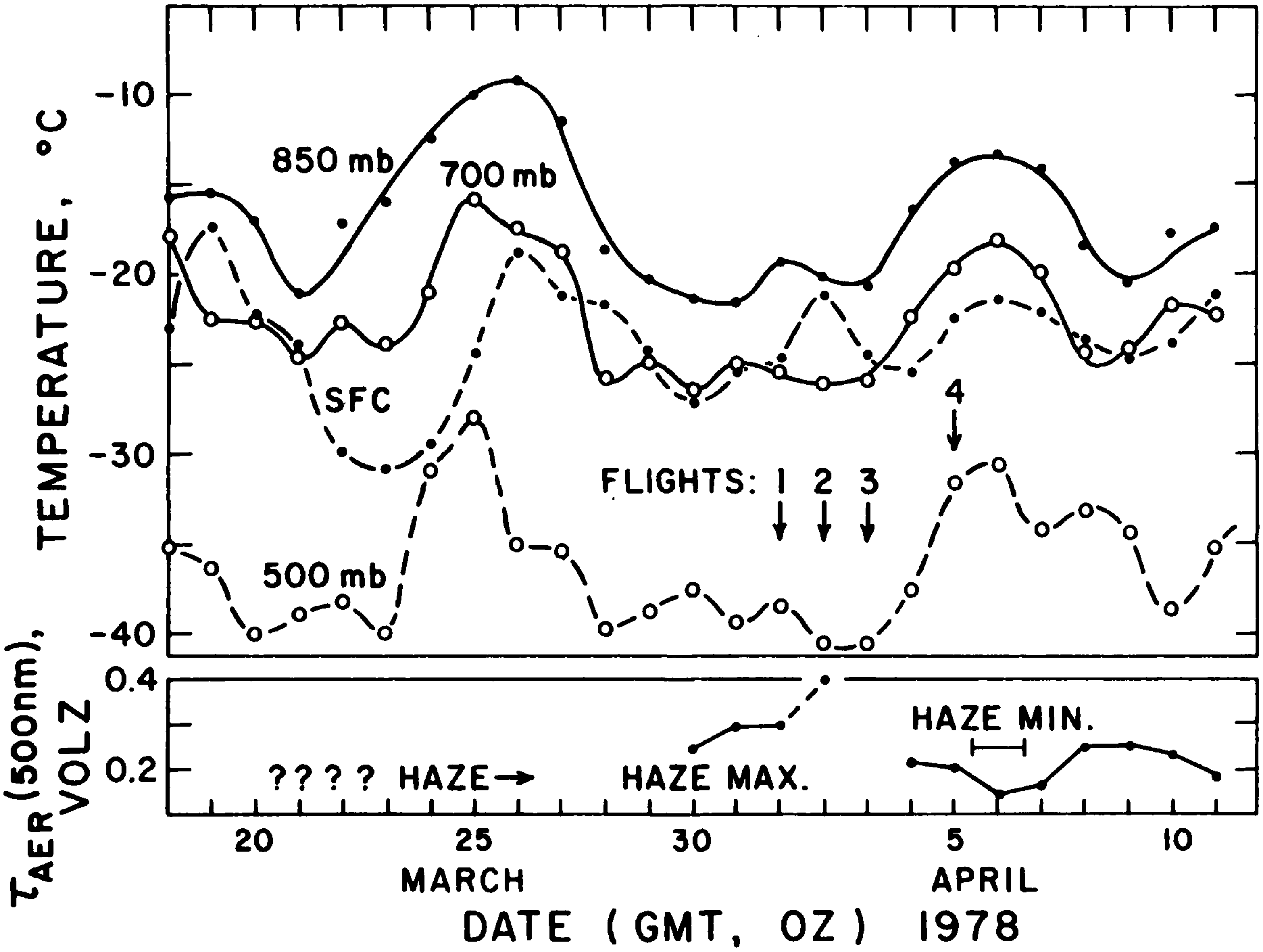

Figure 2. Trends of temperature and turbidity at Barrow, March and April 1978.

dry aerosol to account for the haze, and (b) that the 1978 data point toward a relative-humidity effect. It is my opinion that we must now consider liquid aerosols very seriously.

Because in practice the intensity of a given haze will depend on both the relative-humidity and particle-loading effects (most likely as a linear combination of the two, as opposed to later stages of cloud formation when the much larger cloud droplets compete for a limited supply of water vapor), it is of interest to learn just how the haze intensity would vary with each of these parameters individually. The particle-loading effect should be directly proportional to the number of hygroscopic particles (mostly submicron sulfates) present per unit volume of Arctic air, at least for unsaturated conditions. On the other hand, available evidence is that haze depends on relative humidity in a nonlinear way, increasing slowly for relative humidities below about 50%, then more rapidly above this figure, then very rapidly as the humidity exceeds 60 to 70% (Rosenberg, 1967; Covert _et_ _al_., 1972; Winkler and Junge, 1972). Marine aerosols have somewhat more abrupt increases than continental aerosols (Winkler and Junge, 1972). Thus, the combined relative-humidity and particle-loading effect on Arctic haze should be nonlinear.

What is the relative importance of the direct (relative-humidity) vs. the indirect (air-mass or particle-loading) effects on Arctic haze? The air-mass effect could be quite large in principle, because Barrow (and Alaska as a whole) is a great meeting ground for air masses of vastly different origin. This can be seen from any map of climatological zones, which shows that there is an unusually strong transition in climate from north to south across Alaska. The air masses associated with these climatic regimes vary correspondingly, with cold and dry northern air masses from over the pole bordering on warm and moist southern air masses from the Pacific Ocean. Only a slight shift in the boundary between these air masses is enough to radically change the air over Alaska, and, one might presume, the chemistry and abundance of the associated aerosol as well. We have in fact found such a difference for vanadium, our primary indicator of pollution aerosol, which has about double the concentration in northern air masses at Barrow that it has in southern air masses there. On the other hand, sulfate, by far the most abundant pollution product in the Arctic aerosol, has nearly the same concentrations in Euro-American air at Barrow as it has in Asian-derived air there. Thus, the large-scale origin of wintertime Arctic air would seem to play only a small role in its haze intensity.

In support of the relative importance of the direct (relative-humidity) effect on Arctic haze are the vertical profiles of the haze aerosol as recorded by our 4 spring 1978 airplane flights, versus the vertical profiles of relative humidity as recorded by the NOAA radiosondes from Barrow. These profiles are given here as Figures 3 through 6. Figures 3 and 4 show the aerosol optical depth τ (a vertically integrated measure of aerosol) versus height; Figures 5 and 6 show the optical extinction coefficient β (the derivative of τ with respect to height) versus height. The correlation between haze and relative humidity is seen better with β than with τ, because β and relative humidity refer to conditions at a point, whereas τ is a vertically integrated parameter. For the first three flights, which were during a cold, high-haze period (see Figure 2), the greatest haze was found below about 1 km, a region which was saturated or near-saturated with water vapor. By contrast, the fourth flight, which was

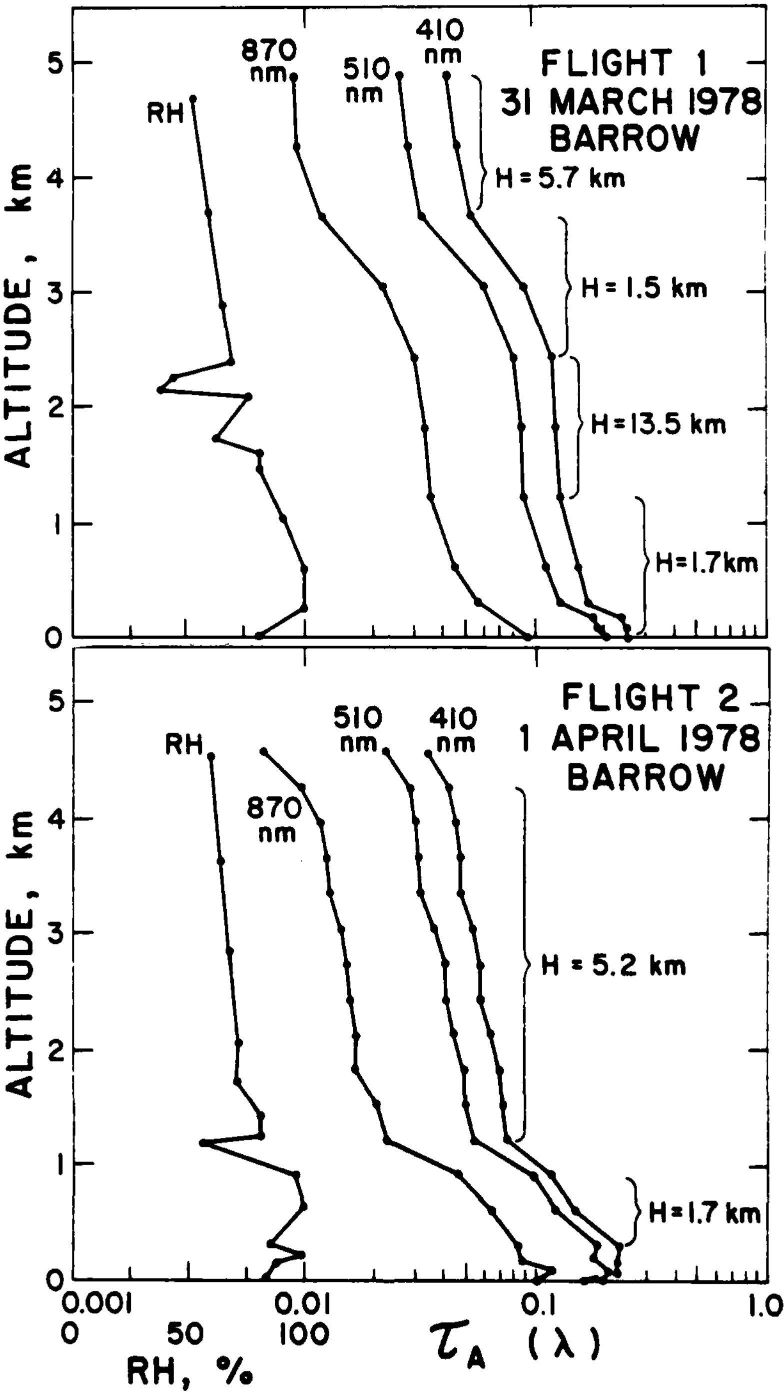

Figure 3. Vertical profiles of optical depth and relative humidity.

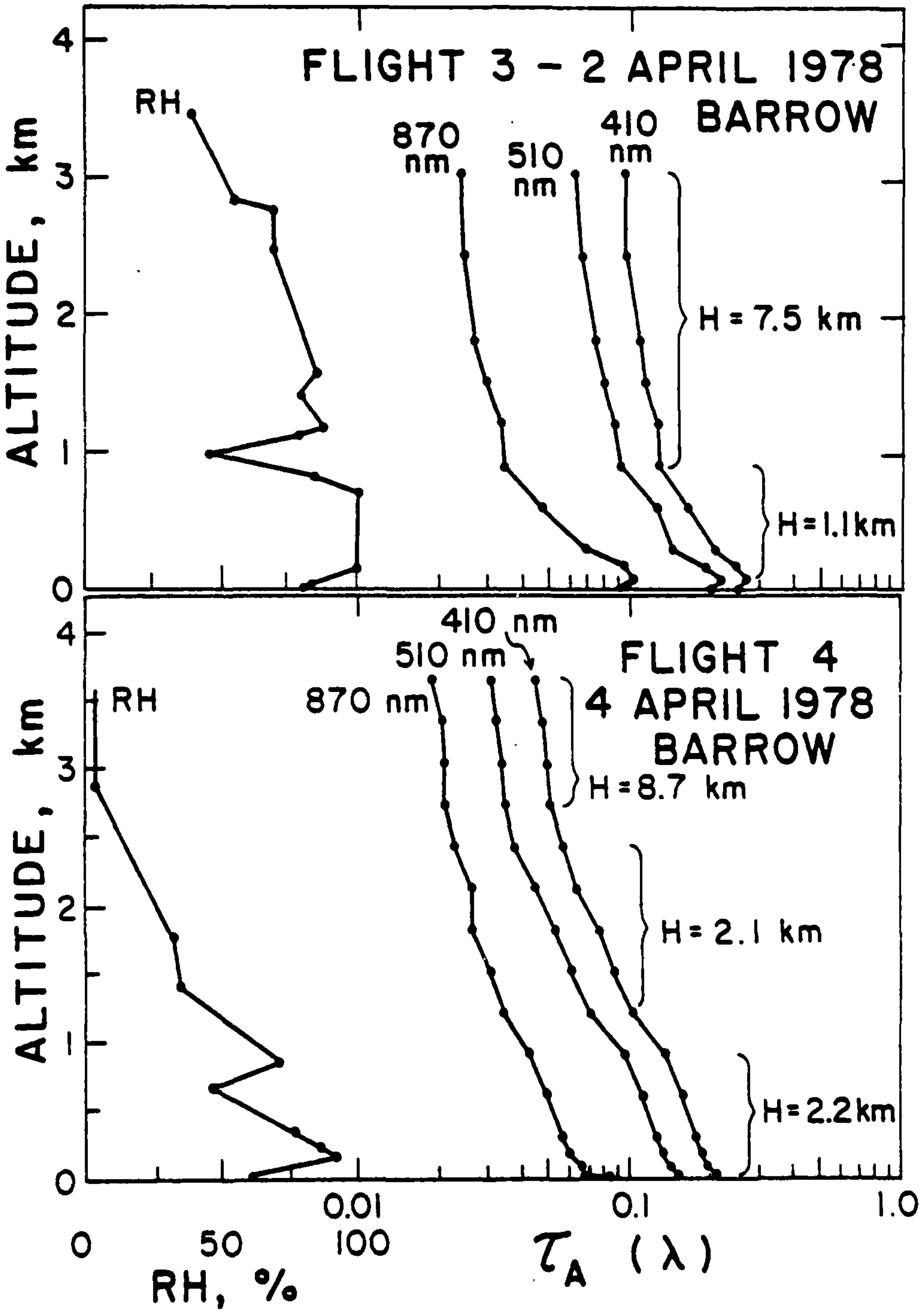

Figure 4. Vertical profiles of optical depth and relative humidity.

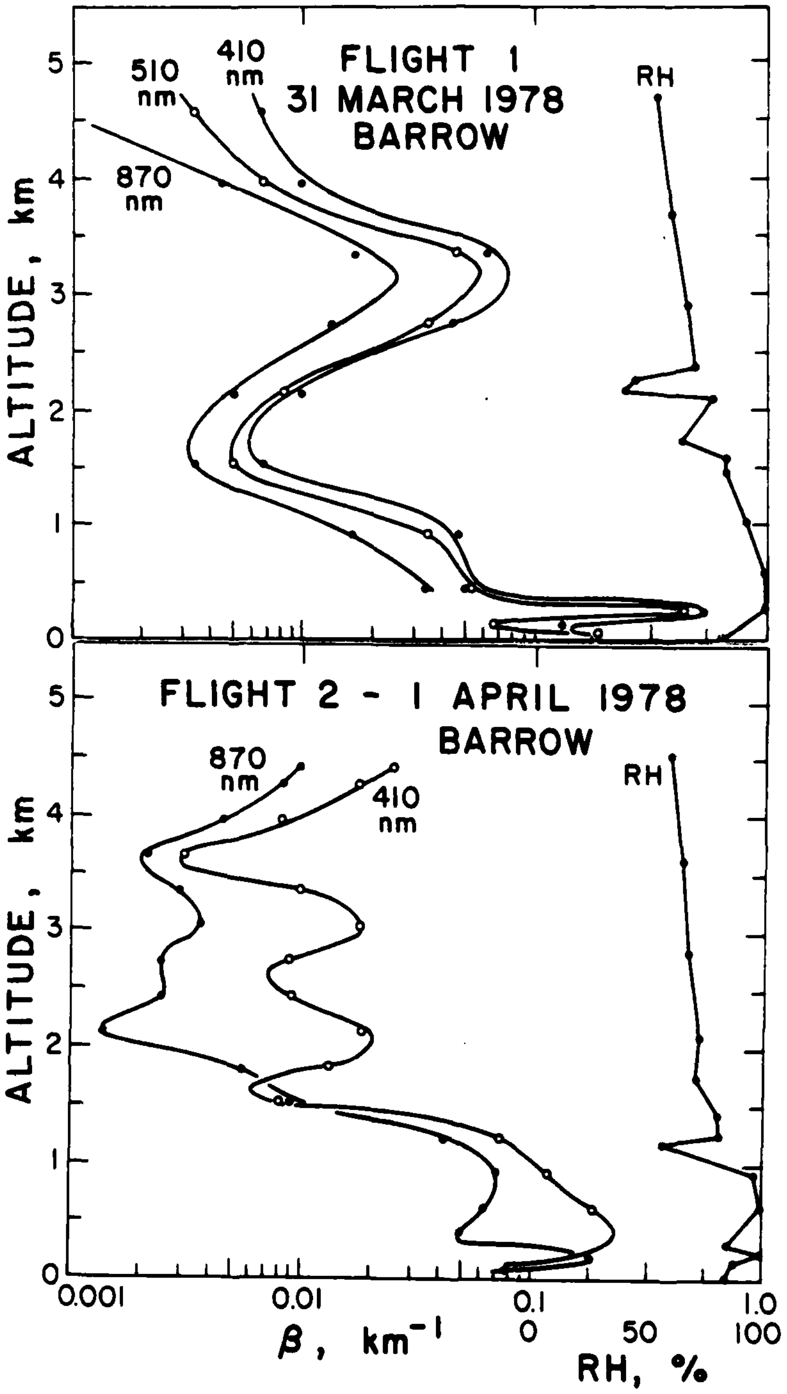

Figure 5. Vertical profiles of extinction coefficient and relative humidity.

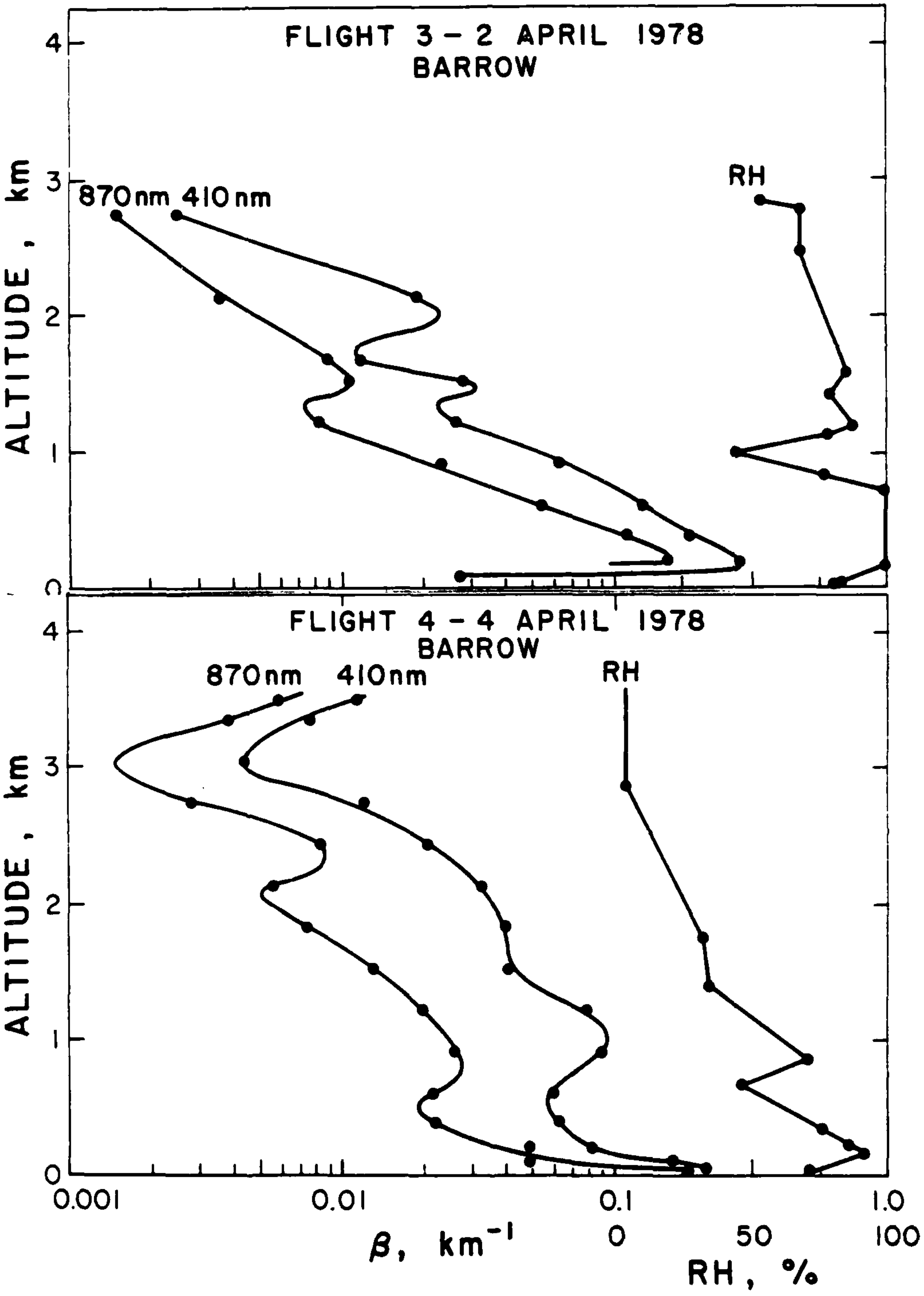

Figure 6. Vertical profiles of extinction coefficient and relative humidity.

during a much warmer period, showed no saturated layer and no strong haze layer below 1 km. Further, the atmosphere above 1 km often showed signs of a quite detailed response to the relative humidity profile.

The information in Figures 5 and 6 can be used to effectively demonstrate the link between Arctic haze and relative humidity, at least in a semi-quantitative way. We have taken the data from elevations up to 1.2 km (4000 ft) from all 4 flights and plotted a scatter diagram of β vs. relative humidity, as shown in Figure 7. A regular pattern is seen, with β's falling within a well-defined envelope. This pattern is very similar to those presented by Rosenberg (1967) for various optical properties of haze as a function of relative humidity. In our mind, this plot is sufficient to prove that a real, albeit not precise, correlation between relative humidity and haze exists. Much of the scatter of this plot is surely attributable to variation in sulfate concentration, which is not accounted for either in this plot or in those of Rosenberg (1967). Note that the relative humidity where the rapid increase of β begins is about 75 to 85%, well within the range of normal values.

The direct, or relative-humidity, hypothesis is further supported by the fact that the Alaskan atmosphere does not lack hygroscopic particles during spring. At both Barrow and Fairbanks during spring 1978 every double-stage impactor sample showed an abundance of small, clear, usually colorless, spheres, which presumably were water droplets formed around a hygroscopic nucleus. Only those droplets having radii near 1 μm were specifically identifiable under the light microscope, and they accounted for most of the particles in this size range. Because the size distributions obtained from the double-stage impactor (and from the Nuclepore filter samples of spring 1976) suggested that these particles were in the

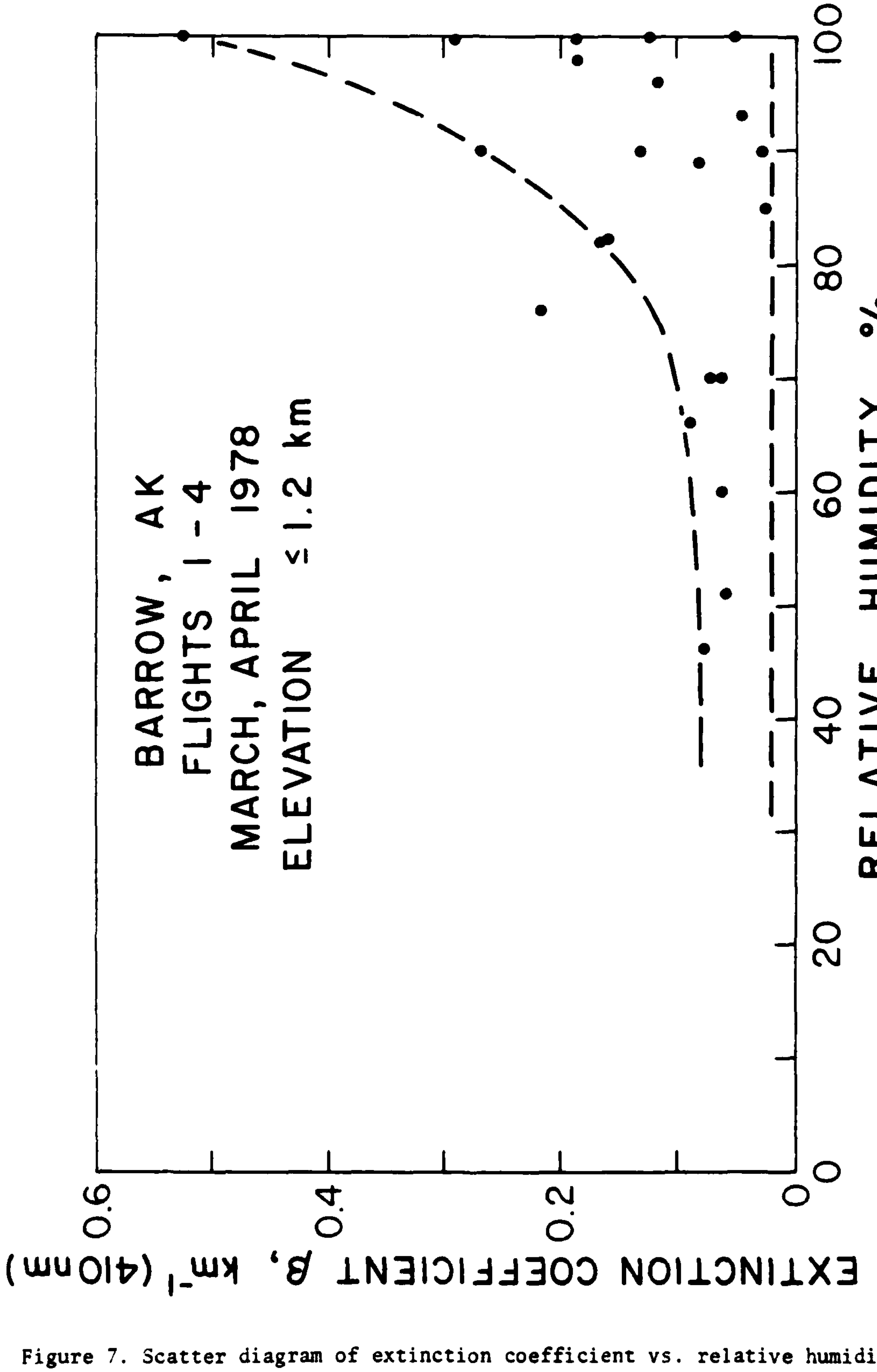

Figure 7. Scatter diagram of extinction coefficient vs. relative humidity, spring 1978 flights at Barrow.

upper end of a distribution centered at much smaller radii, probably at radius 0.1 to 0.3 μm, we felt that the smaller particles were also water droplets. We guessed that these droplets were most likely sulfuric acid, primarily because this substance always exists as droplets, whereas other sulfates crystallize to solids at low relative humidities. Independently, Dr. E. Keith Bigg of Australia has recently concluded that a large portion of the particles in the Barrow surface atmosphere during winter and spring 1976-77 were sulfuric acid. Interestingly, Covert _et al_. (1972) have shown that sulfuric acid droplets are already growing in size by relative humidities of 20%, and that they grow rapidly in size at relative humidities greater than about 80 to 85%, although there is no sharp deliquescence point such as there is for NaCl, for example, at a relative humidity of about 70%. Incidentally, this figure of 80 to 85% is in close qualitative agreement with our empirical estimates of 75 to 85% for the "critical" relative humidity for Arctic haze (based on Figure 7).

At this point a caveat must be inserted. It now appears that our ground-based measurements with the double-stage impactor might not be completely representative of true haze conditions. We have found evidence (detailed in the "clear layer" document) that the surface layer at Barrow (approximately the lowest 200 m) is anomalously clear and dry. Surface relative humidities were typically 80%, just about the point at which many soluble and hygroscopic particles should begin to decrease greatly in size. Thus, we did not observe the maximum growth of hygroscopic particles. Extinction coefficients (Figures 4 and 5) had values several times higher a few hundred meters above the surface than at the surface. Thus all our particle-size distributions determined with the double-stage impactor refer to a relatively dry aerosol, <u>not</u> the haze aerosol proper. There might well be a maximum in the size or mass distribution within the haze, perhaps near radius 0.3 μm as found for the Toronto thin-layer hazes (see below), that we would have missed entirely. For this reason, our size distributions derived from the double-stage impactor must not be considered representative of the haze aerosol. Size distributions derived by inversion of the sun-photometer data and other optical measurements should be more reliable, because the haze aerosol accounted for most of the optical thickness of the Barrow aerosol. Clearly, one of the highest priorities for future work will have to be direct determination of the particle-size distributions of the haze aerosol within the strongest haze layers.

If the Arctic haze of spring 1978 was really dominated by sulfate droplets grown in size by relative humidities near 100%, one would expect the water added to these particles to have been concentrated in the size range between radii 0.1 and 1 μm, because the parent (sulfate) particles appeared to be near 0.1 μm in radius, and because Jiusto (1967) has calculated that hygroscopic particles increase in radius by about a factor of two in humid but unsaturated conditions. Thus a maximum in the size distribution somewhere near radius 0.3 μm might be created similar to what Megaw (1977) has reported for the brown thin-layer haze near Toronto. Two things about such a size distribution would be worth noting: (a) A particle maximum near radius 0.3 μm would be just in the optically active size range, so that nearly the maximum optical effect (maximum haze) could be obtained from a given amount of aerosol mass, and (b) The narrowness of the resulting size distribution would be such that it would tend to produce a haze of a specific color, as opposed to the normal urban hazes whose whitish coloration is produced by much broader size distributions. In fact, Arctic haze of spring 1978 was distinctly brownish in color, which we have managed to capture on a number of our slides.

Other observations (by us and others) explained by water hazes

There are a few other observations, both by us and by others, which are nicely explained by the hypothesis of Arctic haze being basically a water-droplet haze: (1) The smooth progression of thick haze into thin clouds. This was occasionally observed over the North Slope in spring 1978, especially near Prudhoe Bay, which at the time was about 10 degrees F cooler than Barrow, and therefore probably had a higher mean relative humidity. (2) A droplet haze could also help explain why Arctic haze is limited to the Arctic. The low temperatures there during winter create the necessary high relative humidities, the low nucleus concentrations are actually favorable to the observation of this haze because they are adequate for its formation but low enough to prevent obscuration of the haze by "white" scattering by aerosol between the haze and the observer, and lastly the Arctic pack ice, contrary to what is generally assumed, is an abundant source of water vapor to the atmosphere during the winter. In fact, the Arctic would seem to be the ideal location for this type of haze to form: it is sufficiently cold, clean and wet. (3) A humidity-dependent haze could also explain the rapid changes in the haze structure over Barrow, observed from day to day on our flights. All that would be needed would be a change in the relative humidity between values of greater than and lesser than about 80%, which is relatively easy to accomplish in the atmosphere. From this standpoint a change in air mass would not necessarily be required to change the degree of haze. Alternatively, a change of air mass with accompanying change in degree of pollution could also change the haze. As noted above, air masses of very different character meet over Alaska. In fact, the Brooks Range is the approximate boundary between the more polluted northern air and the less polluted southern air, at least during winter. (4) Droplet hazes could also explain how they can so easily reach the tropopause in the Arctic: All that is needed is a high relative humidity and some hygroscopic particles, both of which can easily be attained in the upper troposphere. Because of the "cold trap" for water vapor at the tropopause, one would not expect droplet hazes to be common in the lower stratosphere, but in the vicinity of breaks in the tropopause they might be expected to occur. There is at least one report in the literature of a sighting of a stratospheric haze layer (Scorer, 1975). (5) The droplet hypothesis can also explain the large horizontal dimensions of the haze bands (hundreds to thousands of kilometers). The lower figures are typical of synoptic systems in the atmosphere, and the upper figures approach the dimensions of the Arctic itself. Given a generally cold Arctic during the winter, individual colder or warmer air masses could create greater or lesser hazes on the synoptic scale, while the Arctic as a whole was hazy. Recall that the hygroscopic particles which form the droplets are probably distributed over the entire Arctic at all times during the winter, and are probably everywhere in the troposphere. (6) Flyger _et al_. (1973, 1976) have observed similar haze bands over Greenland, another Arctic location. (7) There is a striking similarity between Arctic haze and the thin-layer brown haze occasionally observed in the vicinity of Toronto, for which Megaw (1977) advances a droplet explanation. The Toronto haze is brown, occurs at a height of several hundred to 1000 m, has a thickness of 50 to 100 m, is observed mainly during July and August, appears to be mainly composed of droplets of mean radius about 0.3 μm, and is associated with a layer of high relative humidity (60 to 85%), overlain by a subsidence inversion. It appears not to be brown because of NO_2, which has low concentrations both inside and outside the layer. Megaw posits that the coloration comes from the droplets themselves, specifically from their narrow size distribution and peak in the blue end of the optical range.

(8) A related observation is that of the existence of large concentrations of very small cloud droplets in clouds and fogs. Junge (1963) cited several examples of cloud-droplet distributions taken down into the submicron range (traditional impaction methods could only capture droplets larger than radius about 3 μm), all of which showed highest concentrations at the lower limit of detection. In one case, a bimodal distribution was found in an orographic cloud on top of Mt. Washington. By comparing this distribution with calculated spectra for similar conditions, Junge proposed that the fine-particle cloud-droplet mode represented "nonactivated but grown" nuclei, and that the larger-sized peak represented the "real droplets of condensed water". Concerning fogs, he cited the cases of "thick" London fogs (many fine droplets) routinely progressing to "thin" fogs (fewer but coarser droplets). I suggest that Arctic haze may be very similar to the "thick" fogs or the fine-particle mode of cloud droplets, but of a lesser intensity because of the smaller concentrations of nuclei and water vapor in the Arctic. Perhaps the simplest analogy would be to what is loosely termed "precondensation", the state of the atmosphere under near-saturated conditions before clouds have formed, rather like the edge of a cloud.

This then is the droplet/relative-humidity hypothesis for Arctic haze. At the moment it seems to be a potentially powerful one, and represents a major departure from our previous approaches. It is by no means complete - it needs much further work and refinement. Several interesting questions remain, such as (1) The relative importance of particle supply and relative humidity in determining the intensity of the haze, (2) Natural vs. anthropogenic sources of the hygroscopic particles, (3) Why more of the droplets don't grow to cloud-droplet sizes, (4) Actual size distributions of the aerosol in the haze, and (5) Whether there is haze throughout the winter as well as during spring. (Should we develop a moon-photometer to answer this one? Glenn Shaw says it is possible.)

Perhaps the most significant implication of this droplet hypothesis for the future of our work is that it forces us to focus on the principal constituent of the aerosol, namely sulfate, an area in which we have little experience. Work with sulfate will likely bring us into very close contact with the large survey projects on sulfate such as the former OECD and present EMEP European projects, as well as the American MAP3S and SURE studies. The Arctic Air-Sampling Network will be an obvious candidate for pursuing our sulfate studies in cooperation with these other networks.

As a final note, I recognize that this document may have a disturbing and unsettling effect on those of us who have become comfortable with the Asian-dust interpretation of Arctic haze. I too have been greatly affected by the realization that Arctic haze in general may be something quite different than what we have imagined. New evidence, however, compels us to consider the droplet explanation seriously, and its ramifications as well. As an attempt to put our current views of the old and new in perspective, Glenn Shaw and I have prepared a summary of what we think are the true sources and formation mechanisms for Arctic haze. Honest opinions are welcomed from one and all on any aspect of Arctic haze.

References

Bigg E.K., Ono A. and Thompson W.J. (1970 Aerosols at altitudes between 20 and 37 km. Tellus 22, 550-563.

Bulrich K. (1964) Scattered radiation in the atmosphere and the natural aerosol. Advances in Geophysics 10, Academic Press, New York, pp. 101-257.

Cadle R.D., Fischer W.H., Frank E.R. and Lodge J.P. Jr. (1968) Particles in the Antarctic atmosphere. J. Atmos. Sci. 25, 100-103.

Charlson R.J., Pueschel R.F. and Ahlquist N.C. (1969) Proc. 7th Conf. on Condensation and Ice Nuclei, Prague and Vienna 1969, pp. 292-298.

Covert D.S., Charlson R.J. and Ahlquist N.C. (1972) A study of the relationship of the chemical composition and humidity to light scattering by aerosols. J. Appl. Meteor. 11, 968-976.

Fenn R.W., Gerber H.E. and Wasshausen D. (1963) Measurements of the sulphur and ammonium component of the Arctic aerosol of the Greenland icecap. J. Atm. Sci. 20, 466-468.

Flowers E.C., McCormick R.A. and Kurfis K.R. (1969) Atmospheric turbidity over the United States, 1961-1966. J. Appl. Meteor. 8, 955-962.

Flyger H., Hansen K., Megaw W.J. and Cox L.C. (1973) The background level of the summer tropospheric aerosol over Greenland and the North Atlantic Ocean. J. Appl. Meteor. 12, 161-174.

Flyger H., Heidam N.Z., Hansen K., Megaw W.J., Walther E.G. and Hogan A.W. (1976) Aerosol Sci. 7, 103.

Germogenova O.A., Friend J.P. and Sacco A.M. (1970) Atmospheric haze: A review. Final Report, Environmental Health Service Contract Nos. CAPA-6-68(1-68), CPA22-69-29. Bolt Beranek and Newman Inc., Cambridge, Mass. Available as PB 192 102 from NTIS, Springfield, VA, 22151.

Juisto J.E. (1967) Nucleation factors in the development of clouds. Ph.D. Thesis, Pennsylvania State University.

Junge C. (1952a) Ann. Met. 5, 1-55 Beiheft.

Junge C. (1952b) Ber. des dt. Wetterd., US Zone 38, 264-267.

Junge C.E. (1963) Air Chemistry and Radioactivity. Academic Press, New York, 382 pp.

Lundgren D.A. and Cooper D.W. (1969) Effect of humidity on light-scattering methods of measuring particle conentration. J. Air Poll. Control Assoc. 19, 243-247.

Megaw W.J. (1977) Thin layer brown haze. J. Aer. Sci. 8, 21-29.

Pueschel R.F., Charlson R.J. and Ahlquist N.C. (1969) On the anomalous deliquescence of sea spray aerosols. J. Appl. Meteor. 8, 995-998.

Rosenberg G.V. (1967) The properties of an atmospheric aerosol from optical data. Izv., Atmos. Oceanic Phys. 3, 936-949(Russian); 545-552 (English).

Scorer W.H. (1975) Haze in the stratosphere. Nature 258, 134.

Vickers G.G. and Munn R.E. (1977) A Canadian haze climatology. Climatic Change 1, 97-103.

Winkler P. (1969) Untersuchungen über das Grossenwachstum natürlicher Aerosolteilchen mit der relativen Feuchte nach einer Wägemethode. Ann. Meteor. 4, 134-137.

Winkler P and Junge C.E. (1971) Comments on "Anomalous Deliquescence of Sea Spray Aerosols" J. App. Meteor. 10, 159-163.

Winkler P. and Junge C. (1972) The growth of atmospheric aerosol particles as a function of the relative humidity. I. Method and measurements at different locations. J. Rech. Atmos. 6, 617-638.

Winkler P. (1973) The growth of atmospheric particles as a function of the relative humidity. II. Improved concept of mixed nuclei. Aer. Sci. 4, 373-387.

Winkler P. (1974) Die relative Zusammensetzung des atmosphärischen Aerosols in Stoffgruppen. Meteorol. Rdsch. 27, 129-136.

I.N.3.

On the existence of a clear surface layer over Arctic snows and ice

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First revision, 20 July 1978

The clear layer

During the period 28 March through 10 April 1978 Glenn Shaw, Tom Conway, and I performed a chemical, physical, optical and meteorological study of Arctic haze in and around Barrow, Alaska. Arctic haze was very intense at that time, with aerosol optical depths at the surface routinely reaching or exceeding 0.2, a value more often associated with medium-sized mid-latitude cities than with the Arctic. A series of four flights through the haze, during which the vertical profiles of the aerosol were measured with a 10-wavelength sun-photometer, revealed that much of the haze was concentrated below 1 km, usually in the form of a single thick optically-dense layer. The results of these four flights are displayed in Figures 1-4.

Figures 1 and 2 are vertical profiles of the aerosol optical depth τ at three wavelengths. The aerosol optical depth is a measure of the vertically-integrated aerosol through the entire atmosphere, and is directly related to the readout of the sun photometer, which measures the darkening of the solar disk by aerosol. A more meaningful quantity for this discussion is the aerosol optical extinction coefficient β, the derivative of the optical depth with respect to height. It represents the "vertical density" of the aerosol, and corresponds roughly to what one sees when looking horizontally. For example, large extinction coefficients in a restricted vertical layer correspond to a visibly dark haze band. The extinction coefficients for the four flights are plotted in Figures 3 and 4. In all 4 figures the vertical profile of relative humidity is also plotted, as derived from the temperature and dew-point depression values of the NOAA radiosondes from Barrow.

The sun photometer measurements from the first three flights suggested the presence of a shallow clear layer at the surface, of thickness 100 to 300 m.

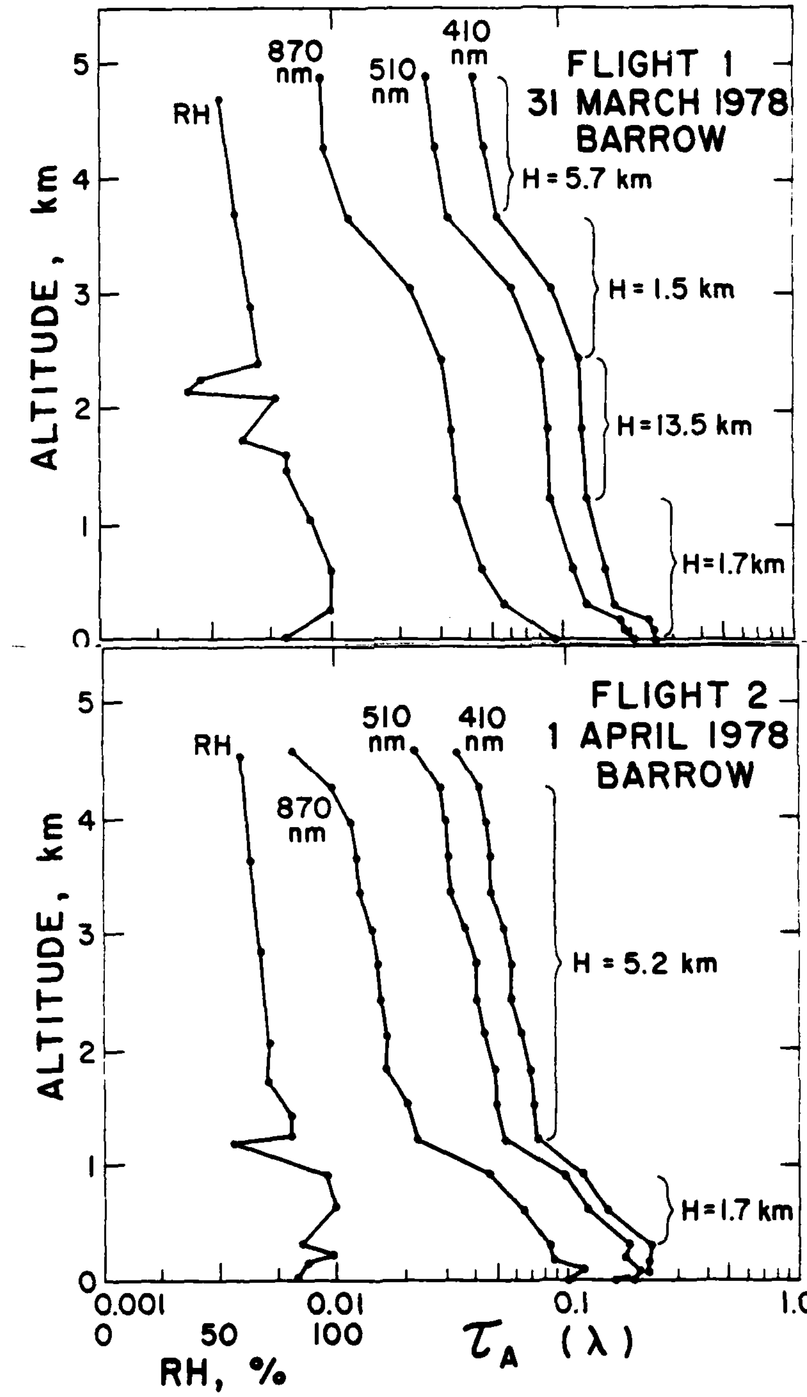

Figure 1. Vertical profiles of optical depth and relative humidity.

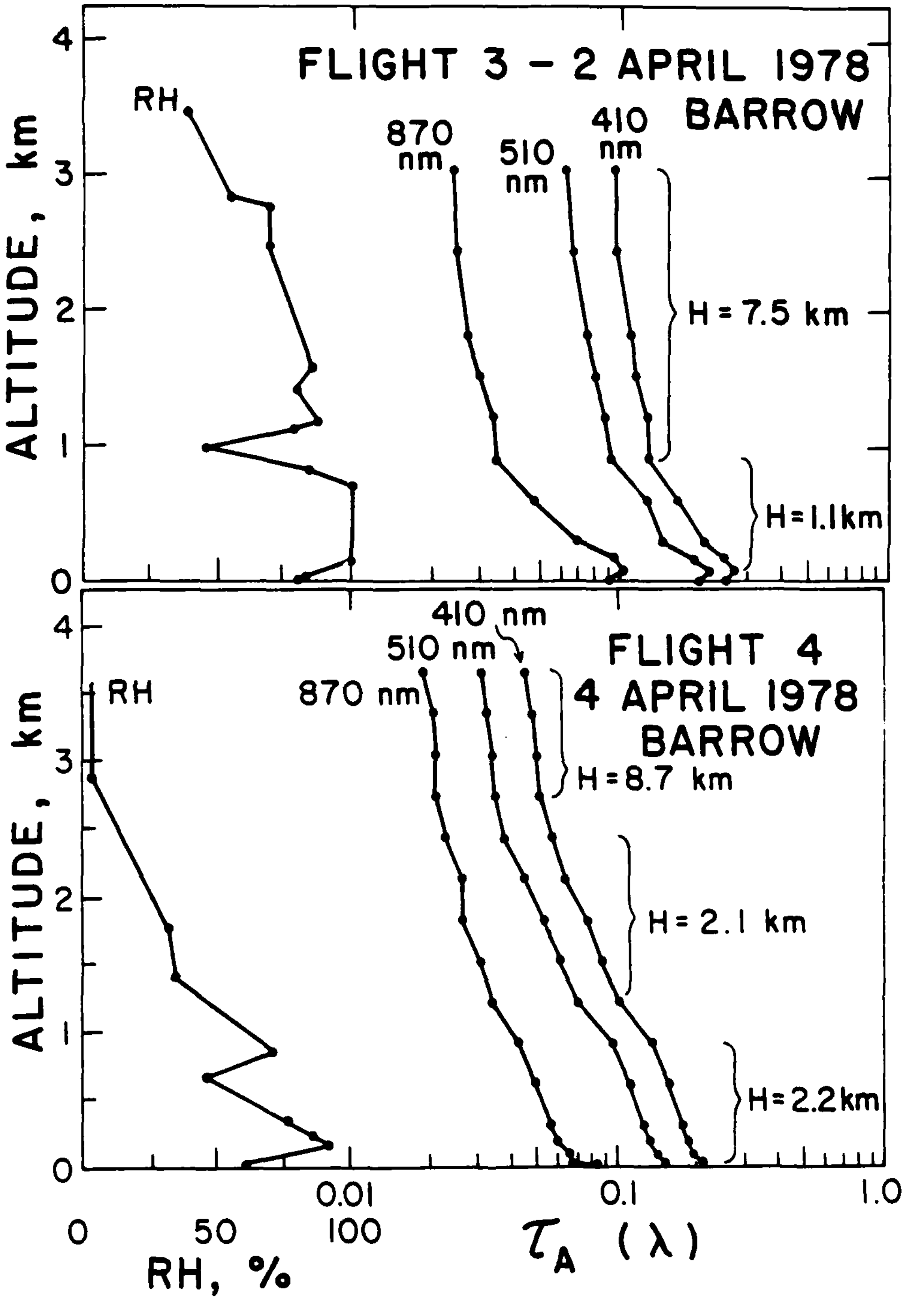

Figure 2. Vertical profiles of optical depth and relative humidity.

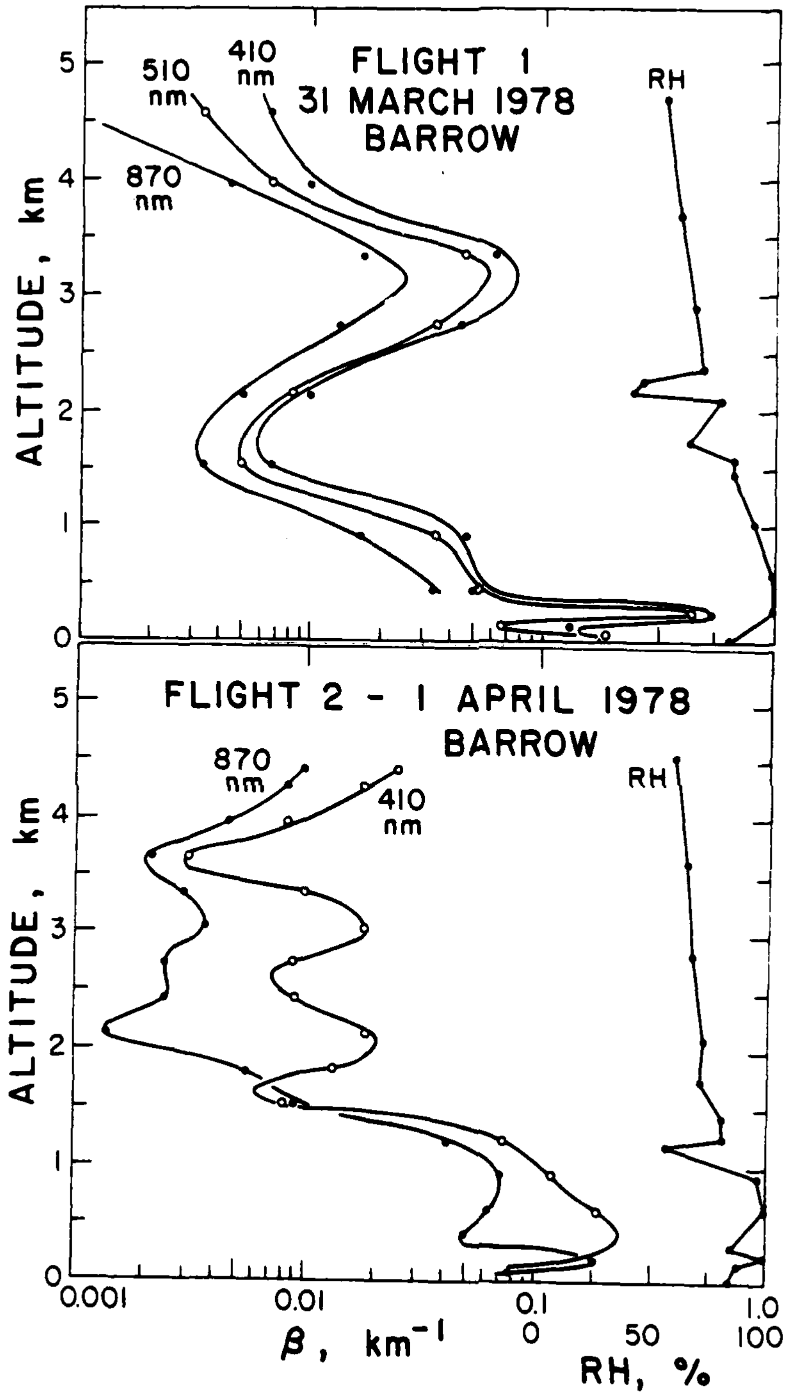

Figure 3. Vertical profiles of extinction coefficient and relative humidity.

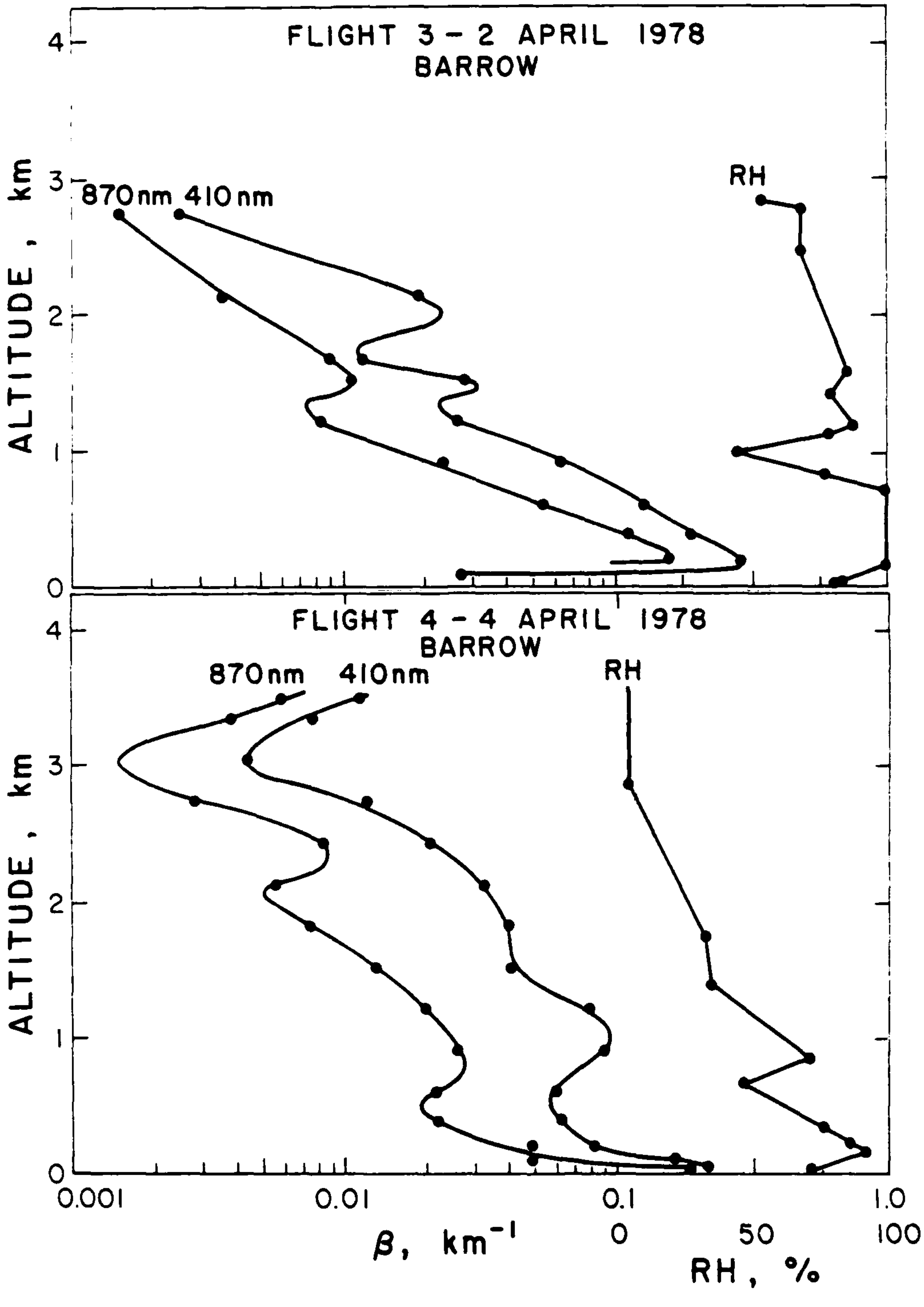

Figure 4. Vertical profiles of extinction coefficient and relative humidity.

No such layer was seen on the fourth flight, perhaps because conditions were quite different from the first flights (much warmer temperatures, much less haze in general, and no deep haze layer at the surface). Because of the difficulties of documenting the existence of such a shallow layer so close to the ground (horizontal inhomogeneities of the haze are likely to be largest near the surface, and the vertical measurements show only very small differences because the levels of measurement are spaced so closely), indications of a layer on only a single flight would not constitute strong evidence and would likely have been discarded In our case, however, appearance of the layer in three of four flights lent credibility to its existence.

As a first idea of the clarity of this layer, rough calculations showed that the extinction coefficient was 7-10 times lower in the clear layer for short wavelengths than it was just above in the haze, and about 3 times clearer at long wavelengths. These figures are averages of data with considerable scatter, however. On flight 2, for instance, the layer between 200 and 300 m showed no measureable extinction coefficient, and on flights 2 and 3 the layer between the surface and 100 m showed negative extinction. Considering the small differences in large numbers that we were attempting to measure, one can only say that the clear layer was at times very clear.

We discovered this clear layer quite by accident. We were not aware of it visually, for reasons to be discussed below. We first "noticed" it well after we had left Barrow and were plotting up the flight data in Fairbanks. The only reason we were able to detect it instrumentally was that we chose to take turbidity readings at four levels within the first 100 ft, as opposed to every thousand feet thereafter. The reason for such close spacing of readings in the lower thousand feet had nothing to do with a clear layer, for at the time we suspected nothing. Rather, it followed from the general principle that the atmosphere changes most rapidly near the ground. Micrometeorological studies, for example, space their sensors logarithmically upwards from ground level. It seems that the only time the eye can notice the clear layer is when on flies upwards or downwards through it rather quickly, such as during takeoff in a commercial jetliner. In fact, after we had posited the existence of a clear layer, we came across notes I had made as Tom Conway and I left Barrow on a Wien Boeing 737 flight of 10 April 1978. I observed a clear layer near the surface, above which a haze layer extended with only a single break to above 20,000 feet (6000 m). I noted this and promptly forgot it, because I was not attuned to the regular occurrences and possible significance of clear layers at the surface.

There are a number of other pieces of evidence for the existence of a clear layer: (1) Much smaller ground-level optical scattering by the aerosol at Barrow in spring (Porch _et_ _al_., 1970; data taken in March 1970 with an integrating scattering nephelometer) than that extrapolated to ground level from a series of aircraft measurements (Shaw, 1975; data taken in April 1972 with a sun photometer). When both sets of data are calculated as extinction coefficients, the surface values from the nephelometer are 10 to 30 times smaller than those from the sun photometer, either those from aloft or those extrapolated to the surface. As pointed out by Shaw (1975), part of the discrepancy may be due to the nephelometer missing some forward-scattered radiation, or else cleaner air in March 1970 than in April 1972. Additionally, though, the discrepancy is consistent with an Arctic clear layer. (2) Glenn Shaw's recollections of a sharp horizon coupled with high overall turbidity in springtime at Barrow. This was mentioned during a conversation long before we had formalized the idea of an Arctic clear layer, and is consistent with the notion that the data of (1) represented a clear layer rather than an instrumental artifact exclusively. (3) A comment by Dr. Norbert Untersteiner of ONR on the proposed clear layer: "Everyone who has flown a lot in the Arctic has seen it, but apparently not wondered about it." (4) An unpublished study by Dr. Lewis Grant of Colorado State University of a similar phenomenon in the Rockies of western Colorado, west of the continental divide. According to Grant, long continuous mountain ridges throughout this region will have a cap cloud, but will never have fog on the top of the ridge. Similarly placed isolated peaks, however, will always have cap clouds and fog. This phenomenon was observed repeatedly during several years and at many ridge-top meteorological stations. The stations on long ridges never rimed; those on isolated peaks rimed. Grant believes that warm moist Pacific air masses coming into contact with the Rockies of western Colorado are meeting land surface for the first time after crossing the Pacific Coast. The longer contact time with the cold surface snows afforded this air by ridge systems, as opposed to isolated peaks where the air at the peak itself was striking land for the first time, was presumably enough to remove large amounts of water vapor before the air reached the crest of the ridge. The lower relative humidities thus inhibited condensational growth of aerosol particles to cloud-droplet size, and produced a clear layer. The magnitude of this removal effect can be seen by some calculations of Grant: The frost rate onto 1 m^2 plastic sheets laid out on these ridges, extrapolated to the number of days per year that Pacific air could be expected, gave values of up to 30% of the annual snowfall.

All in all we feel that it is remarkable that there is a clear layer over snow in Colorado that seems to have its origin in exactly the same mechanism that we have proposed for the Arctic clear layer. Furthermore, Grant's calculations show that vapor deposition through a clear layer can be considerable, so that the layer may be established quickly, maintained easily, and perhaps simultaneously depleted in particles.

As mentioned above, the surface clear layer is not apparent to an observer at the surface. We suggest the following reasons: (1) The untrained observer expects clean air in the Arctic, and therefore sees nothing amiss when the visibility is good and the seeing is "crisp". (2) The trained observer, on the other hand, is always scanning the sky for Arctic haze. We considered ourselves trained observers, and spent a lot of time watching the Barrow sky for signs of haze, because we were familiar with past reports of how nearly impossible it is to observe from the ground. Looking back on it, it seems that we were inevitably looking well above the horizon, for reasons unknown. Perhaps it was that we knew that Arctic haze could be found to great elevations in the atmosphere, perhaps it was a reaction to frequent blowing snow, or perhaps we simply didn't bother with the horizon because we "knew" from our flight experience that it wouldn't be sharp anyway. It might also have been because we spent a good deal of our time in camp where the buildings interfered with the horizon. Whatever the reason, even if we had known to look for the clear layer we probably wouldn't have been able to see it, for at least two reasons: (a) There are no high objects in the Arctic near Barrow (and in the Arctic in general) which can be used to evaluate visibilities at the surface vs. those aloft in the way that, say, the mountains of the Alaska Range can be used from the Geophysical Institute in Fairbanks, and (b) Just as it is very difficult or impossible to see a haze layer from below (because you always have to look through it at a high angle, whereas at or above it you can always find a sufficiently low angle to make it stand out), it is difficult to see a clear layer from below, which is what a surface observer of a surface-based clear layer is trying to do, and (c) Spotting a clear layer against a hazy background may be even harder than spotting a haze layer against a clear background, and demands much more stringent conditions.

Explanation of the clear layer

The existence of the clear layer is best explained in conjunction with reasons for the existence of the haze layers just above it. The next paragraphs will therefore summarize our current thoughts about the causes of the dense Arctic haze over Barrow during spring. A much fuller explanation of Arctic haze is provided in a separate document entitled "Evidence for a link between Arctic haze and water vapor", which has just been circulated by K. Rahn.

Our current picture of Arctic haze is that, while it may have diverse causes, the main one is probably uptake of water vapor by hygroscopic aerosol particles under humid but unsaturated conditions, specifically relative humidities between 80% and 100%. There are several pieces of evidence in favor of this hypothesis. First is the general principle that "Atmospheric turbidity is always related to a condensation process and is due almost exclusively to particles with a water (or ice) envelope, the size of which increases with the relative humidity and is the basic, but not the only, factor determining the optical characteristics of the atmosphere" (Rosenberg, 1967). Two others are concerned directly or indirectly with relative humidity and haze at Barrow: The inverse correlation between temperature and haze while we were there, and the direct correlation between relative humidity and haze during the four vertical profiles shown in Figures 1-4. The combination of high haze and low temperatures can be interpreted as either a direct effect of cold on an air mass, or as an indirect effect of different air masses, namely cold air from the north being more polluted than warm air from the south. We now lean to ward the former, direct interpretation, that cold temperatures produce relative humidities greater than some "critical" range, above which hygroscopic particles in the air take up large amounts of moisture. They do not, however, grow into full-fledged cloud droplets. Instead, their growth is arrested at radii of a few tenths of a micrometer. There is some precedent for this kind of explanation, both from earlier measurements of droplets in fogs and clouds, and in more recent data from the Toronto brown thin-layer hazes (Megaw, 1977). The critical relative humidity can be roughly estimated at 80 to 85% from the vertical profiles, that is, above these relative humidities the haze rapidly becomes intense, below this range little haze is seen. This break point of relative humidity agrees reasonably well with those determined in other studies of the aerosol, both in the laboratory and in the free atmosphere (Covert *et al.*, 1972; Rosenberg, 1967; Winkler and Junge, 1972). Our measurements with the double-stage impactor, during which particles are captured on glass microscope slides and observed under the light microscope, have shown that there is an abundance of hygroscopic particles in the Arctic atmosphere during spring, which appear as tiny (submicron) droplets. E. Keith Bigg of Australia has identified these particles as sulfuric acid droplets.

We thus envision Arctic haze as a water droplet phenomenon, probably a sulfuric-acid haze. Because of the generality of the processes involved in its formation, we expect that it should be found all over the Arctic, which seems to be the case.

One of the most reproducible features of the atmospheric soundings from Barrow during the spring is the presence of a layer of reduced relative humidity near the surface. While we were at Barrow this spring the surface air had a dewpoint depression of between 2 and 5 degrees Celsius. This layer was typically overlain by a saturated or near-saturated layer. We now identify these upper and lower layers with the hazy and clear layers, respectively. It is most interesting, and perhaps one of the great coincidences that we have found in the Arctic so far, that the upper limit of the relative humidity at the surface is just about 80%, the critical value for haze formation. In other words, surface relative humidities can't get quite high enough for haze to form. Figure 5 shows the sequence of surface relative humidities for parts of March and April 1978 at Barrow. Values ranged from 63% to 83%, with a mean of 73 ± 7%.

We propose that the explanation for the low relative humidities of the clear layer is that water vapor there is generally in contact with the surface and is therefore at or near equilibrium with snow and ice rather than with liquid water. Because the vapor pressure of ice at temperatures below freezing is always less than that of liquid water at the same temperature, relative humidities less than 100% would be expected in the clear layer. In actual fact, calculated and observed relative humidities agreed quite well, with predicted values being a weak positive function of the temperature and varying from 74% to 84%, only half the range of the observed values, and having a mean of 79 ± 3%. Interestingly, the actual values

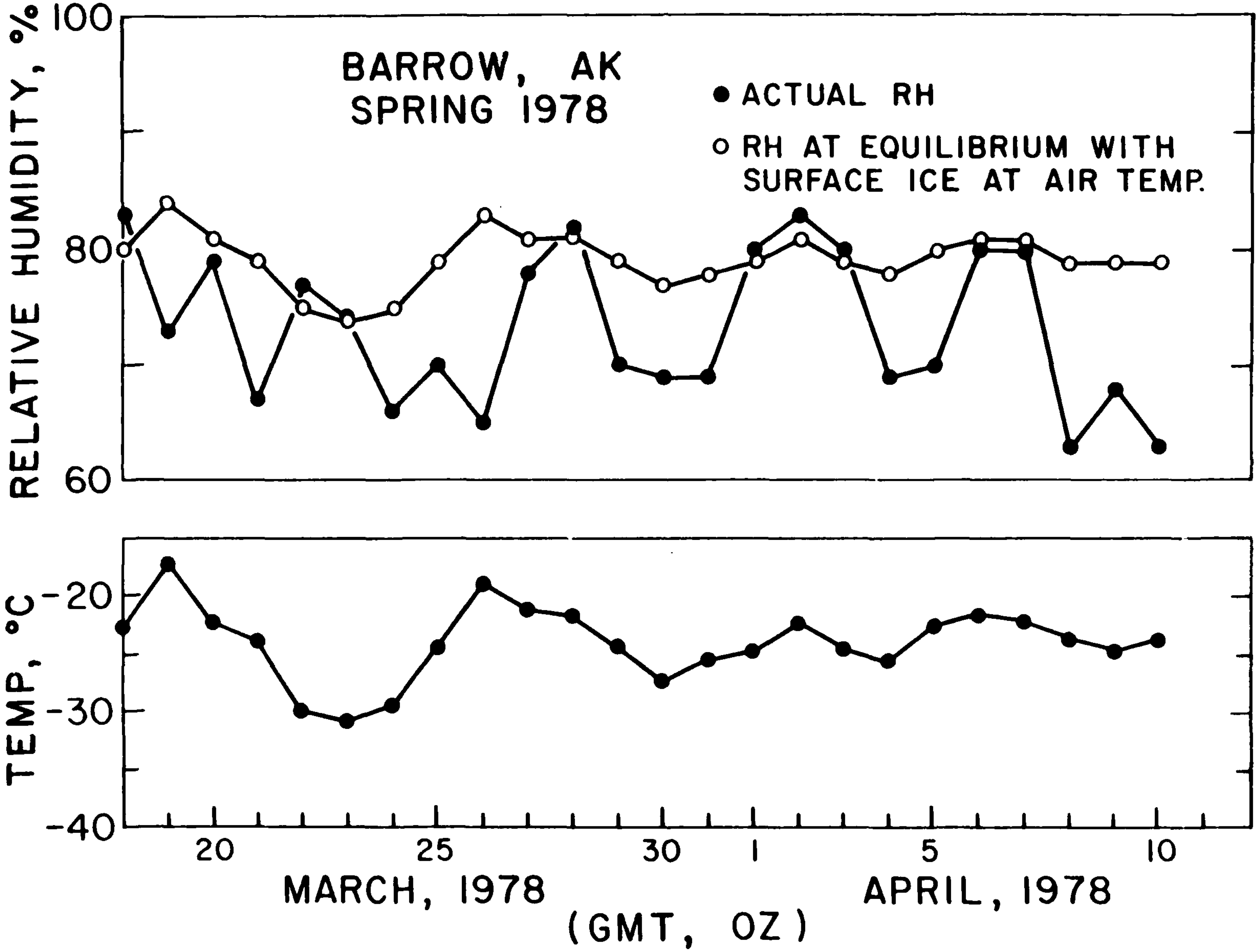

Figure 5. [illegible] actual relative humidities vs. those calculated from equilibrium with ice, Barrow, Alaska, spring 1978.

seem either to be essentially at the predicted values or about 10 percentage points below, but seldom at intermediate values. At the moment we have no explanation for this "switched on - switched off" behavior. All in all, the idea of snow-vapor equilibrium comes surprisingly close (6%) to explaining the actual relative humidities.

The clarity of the surface layer may be some combination of two possible explanations: Hygroscopic particles kept small by the low relative humidities or actual "cold-trap" removal of particles from the layer. According to the first explanation, which almost certainly is operative, surface relative humidities are always at or below the value of about 80% needed to initiate rapid growth of the particles. Because the majority of the particles before they have taken up water are small enough to be at the lower end of the optically active range, they exert a greatly reduced optical effect on the surface layer, thus keep it clear. According to the second explanation, particles may be removed by any number of cold-trap mechanisms, including thermal diffusion to the snow surface, phoretic forces (being swept out by the current of water-vapor molecules), and scavenging by diamond dust (clear-sky sprecipitation). At present we have no idea of the relative importance of these three mechanisms, or even whether other mechanisms could be important. Both Kumai (personal communication) and Hogan (1975) have reported that diamond dust seems to be a very efficient scavenger of aerosol particles, and so we tend to give this mechanism credence. But we simply do not know about the others.

There is some precedent for the idea of a cold-trap mechanism for removing particles in the surface layer of polar regions. Hogan (1975) stated that he found the surface layer over both the South Pole and Greenland to be deficient in particles. He speculated that the surface may be a cold-trap for them, but was not able to establish any particular mechanism(s) responsible.

Implications of a clear layer in the Arctic

The existence of a clear surface layer in the Arctic has several important implications. The most obvious of these is the navigational one, both for visual and instrumental flight. The haze seems to consist primarily of fine droplets, whose primary interaction with radiation is in the visible, near-ultraviolet, and near infra-red. For aircraft flight, the important point is that visibilities aloft are considerably worse than at the surface. Aloft, for example, the horizon is totally obscured. Luckily, however, vertical visibility is nearly unimpeded, and we know of no cases where conditions similar to a whiteout resulted solely from Arctic haze. Instruments which depend on radiation in or near the visible may operate considerably better within the clear layer than within the haze aloft.

Second, we are coming to believe that the surface clear layer has been an unrecognized major factor in hindering ground-based perception of the presence of Arctic haze. As mentioned earlier, it is well known that inhabitants of the Arctic are unaware that they are surrounded by haze. The reason normally given for this is the difficulty of observing a layer from its lower extremity or below. We believe that the clear layer has an additional effect which must be considered, namely that the good surface visibilities convince observers that there is no haze at all present. We have reviewed our surface slides from the spring 1978 Barrow trip, and find generally excellent visibilities. From this kind of evidence alone, one would never guess that there was heavy haze aloft.

The third implication of a surface clear layer concerned the representativeness of physical and chemical measurements taken within the layer. In the flat Arctic, surface-based measurements are far more common than measurements from aircraft or balloons. The NOAA GMCC site in Barrow, where data are taken between elevations of 2 and 20 meters, is typical. For understanding Arctic haze, or any other phenomenon affected by relative humidity, measurements in near the surface may be very nonrepresentative. For other chemical and physical measurements, such as nucleus counts or chemical data on the aerosol, the degree of nonrepresentativeness of the surface layer will depend on the extent of particle deficiency within the layer. At present we are not at all sure how effectively particles are removed from the surface layer. This is one of the prime features of the layer which must be investigated. Should the effect be significant, the interpretation of measurements by NOAA and by URI at their GMCC site would be affected.

Future studies of the clear layer

First and foremost, any future study of the Arctic clear layer should document its existence better than we in our hindsight were able to do this spring. In short, were our measurements, being based on only four flights, a fluke? We think not, but this must be conclusively demonstrated before any detailed programs can be planned. The implications of an Arctic-wide clear layer are great enough that it should be definitely followed up.

If the clear layer is shown to exist, a number of its important features could then be investigated. These include: (1) Its frequency of occurrence, particularly during the winter and spring; (2) Its seasonal occurrence (the seasonal occurrence of Arctic haze in general, a question which we have not yet adequately answered, could also receive an impetus from a detailed study of the clear layer, because measurements of both phenomena would be closely linked); (3) Better measurements of the height of the clear layer. This spring we took data in the lowest layer at elevations of 300, 600, and 1000 feet. At the time these seemed unnecessarily closely spaced relative to Arctic haze as a whole, but relative to the Arctic clear layer they are now seen as being much too far apart. The precision of Glenn Shaw's sun photometers is such that we could make measurements each 100 feet, or perhaps at even smaller intervals. The height of the clear layer is surely one of its most important properties; (4) The various meteorological, chemical, and physical factors controlling the clear layer. Factors which come to mind here include relative humidity, particle concentration and composition, surface temperature, (Is there for example a threshold temperature for formation of the clear layer?), and "age" of the clear near-surface layer of air (i.e., is there a certain time required for a fresh air mass to reach equilibrium with the snow surface before a clear layer is formed?); (5) The extent of the clear layer and its degree of homogeneity (Is it found over the entire Arctic Basin? Is it found only over or near the pack ice, or does it extend far inland as well?); (6) Various internal properties of the layer, such as the amount and chemical composition of its aerosols (Important for estimating the columnar loading of various constituents of the aerosol from surface measurements alone) - these measurements must be made in conjunction with more extensive vertical profiles of the aerosol above the clear layer; optical properties such as the wavelength dependence of the aerosol extinction coefficient; physical properties such as the particle-size distribution of the aerosol and how it changes, if at all, through the clear layer; and (7) Whether particles of various sizes are being removed from the clear layer by some cold-trap effect, and if so, what the mechanism or mechanisms are.

There are two other points of interest relative to the existence of a clear layer that refer more to effects on other processes than to specific properties of the layer: Modification of snow falling through the layer and modification of fallen snow by thermal cleansing of the layer. Concerning the first of these points, Arctic snows form not too far above the clear layer. If a major part of their descent to the ground is within the clear layer, and this layer is particle-deficient, one may conclude that below-cloud scavenging of particles might not be as significant as it would be otherwise. At the moment the relative contributions of nucleation and scavenging to the trace-element composition of Arctic snows is very much an open question. A clear layer would tend to make one weight the effect of scavenging less than otherwise. Concerning the second point, a thermally-cleansed surface layer would force one to consider the effects of dry deposition in the Arctic more seriously than otherwise, whereas a surface layer cleansed by clear-sky precipitation would force one to add this mechanism to the traditional list of nucleation, in-cloud scavenging, below-cloud scavenging (of flakes which originated in the cloud aloft), and dry deposition.

Needs for future work

A study of the Arctic clear layer should not be undertaken lightly, especially after its existence has been documented and its detailed characteristics are to be determined. Several requirements come immediately to mind: (1) A reliable aircraft for the vertical soundings. This aircraft should be large enough to accomodate our filter-and impactor-sampling system for chemical measurements on the aerosol, and should have the range to travel the entire

Arctic. It should be available for several years, so that a single sampling system could be used for the duration of the experiment. Building new systems for aerosol sampling wastes much time, as we have learned in Barrow; (2) A state-of-the-art sun photometer for the detailed measurements in the first kilometer of the atmosphere. Glenn Shaw is able to provide such equipment, and is the best in the world at it. For measurements during winter, a moon photometer might be considered, which Glenn could also build; (3) Good particle-counting equipment for determination of particle-size distributions of the aerosol as a function of height within and above the clear layer. There is need for development of simple, rugged and reliable particle counters for use in many remote locations. Perhaps a clear-layer project could be a stimulus in this direction. Glenn is presently working on one such system, which will be field-tested next spring; (4) Some sort of instrument for determining horizontal visibility (a nephelometer that can fly?); (5) Accurate temperature and humidity probes for the aircraft, which will likely be flying in regions where radiosondes are not sent up (temperature probes are no problem, but humidity probes might be. I understand that the EG & G humidity probe is the best one); (6) And, of course, support to get and keep the personnel necessary to operate this kind of challenging program.

A fringe benefit of all this would be a windfall of new data on Arctic haze. So far in our Arctic haze program we have extracted the maximum information from the minimum data. A coherent series of well-instrumented flights in various parts of the Arctic could do wonders to improve our understanding of not only the clear layer, but also of Arctic haze in general.

References

Covert D.S., Charlson R.J. and Ahlquist N.C. (1972) A study of the relationship of the chemical composition and humidity to light scattering by aerosols. J. Appl. Meteor. 11, 968-976.

Hogan A.W. (1975) Antarctic aerosols. J. Appl. Meteor. 14, 550-559.

Megaw W.J. (1977) Thin layer brown haze. J. Aer. Sci. 8, 21-29.

Porch W.M., Charlson R.J. and Radke L.F. (1970) Atmospheric aerosols: Does a background level exist? Science 170, 315-317.

Rosenberg G.V. (1967) The properties of an atmospheric aerosol from optical data. Izv., Atmos. Oceanic Phys. 3, 936-949 (Russian); 545-552 (English).

Shaw G.E. (1975) The vertical distribution of tropospheric aerosols at Barrow, Alaska. Tellus 27, 39-49.

Winkler P. and Junge C. (1972) The growth of atmospheric aerosol particles as a function of the relative humidity. I. Method and measurements at different locations. J. Rech. Atmos. 6, 617-638.

Sulfate in the Barrow atmosphere
- A discussion document

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First draft, 15 July 1978

Introduction

There are several reasons to be interested in sulfate in the Barrow atmosphere: (1) Sulfate is normally a major, perhaps the major constituent of remote aerosols. It often accounts for about 50% of their mass. For this reason, understanding the aerosol of remote regions is largely equivalent to understanding the sulfate component. Our Arctic haze project is long overdue for a study of sulfate, because for the first 2½ years we have concentrated on other trace elements. (2) In the spring of 1976 and again in the spring of 1978 we observed large numbers of submicron spherical droplets in the Barrow aerosol, both at the surface and up to elevations of nearly 4 km, which we suspected but could not prove were sulfuric acid droplets. Microprobe analysis of these droplets from some of the 1976 flights showed that they were rich in sulfur. In 1976 they accounted for roughly 25 to 75% of the aerosol's mass, and in 1978 our impressions were similar even though we do not yet have precise figures. (3) Dr. E.K. Bigg of Australia has recently positively identified these droplets, which he has also observed in the Barrow surface atmosphere during spring, as sulfuric acid. According to him, they represent a large percentage of the Barrow aerosol's mass. (4) During the spring 1978 Arctic haze field experiment at Barrow, we observed a good correlation between relative humidity and intensity of the haze, which we have come to attribute to the formation of droplets on hygroscopic aerosol particles, probably sulfates. For reasons not yet completely clear, the initial condensation is followed by only limited growth of the droplets, so that they remain within the optically-active (submicron) size range of the aerosol. This was confirmed by the sun-photometer readings, which showed the mean particle size of the haze to be very small.

All these reasons together suggest that sulfate is a very important chemical constitutent of the Barrow aeorsol, and that its abundance, seasonal variation, and atmospheric behavior may well be the key to understanding Arctic haze. We have therefore embarked upon a program of determining sulfate concentrations in the Barrow aerosol, the preliminary results of which are significant enough to form the basis of this document.

Sampling

Since September 1976 we have been taking nearly continuous aerosol samples at NOAA's GMCC clean-air sampling site in Barrow, as part of a cooperative program with them. Typical sample durations are one week or less. The aerosol is collected on a 20 x 25 cm (8 x 10 in) Whatman No. 41 cellulose filter, through which air is drawn by a high-volume vacuum pump. Portions of these filters have been used for trace element analyses, but because of the large filter size, about $^3/4$ or more remains for other analyses. We are presently analyzing all these filters for sulfate, using the method described below. Only about 4-8 cm^2 are needed for this, so that the majority of the filter still remains for future analyses.

Analytical technique

Dr. Richard J. McCaffrey of our laboratory has recently developed an analytical technique for determination of sulfate which uses Ba-133 tracer and gamma counting. This technique will be described in detail elsewhere. Briefly, the sulfate is leached from the filters in boiling water, then a small quantity of Ba-133 is added to the solution, and $^{133}BaSO_4$ is allowed to precipitate over a period of 2-3 days. At the end of this period the precipitate is found completely on the walls of the plastic test tube in which the precipitation occurred. The excess Ba-133 is carefully removed, and the gamma radiation of the test tube and precipitate are counted in a well-type (NaI(Tl) scintillation crystal attached to a single-channel analyzer. A standard calibration curve is constructed between about 20 and 400 μg of sulfate. The curve is usually linear to below 50 μg, and we estimate the detection limit to be in the vicinity of 30 μg sulfate. This is comparable to other techniques where $BaSO_4$ is precipitated, such as turbidimetry. The detection limit is apparently determined by the solubility of $BaSO_4$ rather than by the mechanics of the precipitation process itself or any incomplete collection of the small amounts of precipitate. The accuracy of the technique has been tested with an EPA standard sulfate solution, and found to be within 2% for a mean of two determinations. We estimate the uncertainty of the analysis to be better than 10% for winter samples, when concentrations of sulfate are high, and about 15-20% for the much lower summer period. The total uncertainty of the final result, which includes uncertainties in sampling and subdivision of the filter, is probably a few percent higher.

Seasonal cycle of sulfate in the Barrow atmosphere

This document is concerned with the first 40 samples from Barrow that have been analyzed for sulfate. They represent the 13-month period from September 1976 to October 1977. Dates and results are shown in Table 1, both for total and nonmarine (excess) sulfate. The marine component was calculated from the Na concentrations of the same filters, which had been previously determined by neutron activation analysis. The ratio of sulfate to Na in bulk seawater was taken to be 0.25, and no sea-aerosol fractionation was assumed, in accord with the laboratory experiments of Gravenhorst (1978).

Table 1. Total and nonmarine (excess) sulfate concentrations at Barrow, Alaska, September 1976 - September 1977.

Filter	Dates	Total sulfate, $\mu g\ m^{-3}$	Nonmarine (excess) sulfate $\mu g\ m^{-3}$
1	18-21 Sept. 1976	0.14	0.07
2	24 Sept. - 2 Oct.	0.32	0.18
3	2-8 Oct.	0.68	0.45
4	8-13 Oct.	0.76	0.58
5	13-26 Oct.	0.55	0.25
6	26 Oct. - 5 Nov.	1.01	0.89
7	5-9 Nov.	1.06	0.30
8	9-15 Nov.	0.69	0.58
9	15-20 Nov.	1.03	0.85
10	20-26 Nov.	0.98	0.75
11	26-30 Nov.	1.25	0.39
12	30 Nov.-3 Dec.	1.43	1.34
13	3-6 Dec.	1.44	1.39
14	6-10 Dec.	1.38	1.35
15	13-17 Dec.	1.71	1.49
16	17-21 Dec.	1.72	1.68
17	21-27 Dec.	1.42	1.12
18	27 Dec. - 6 Jan. 1977	1.43	1.12
19	6-12 Jan.	2.17	1.71
20	12-19 Jan.	1.31	0.97
21	19-24 Jan.	1.33	1.18
22	24 Jan. - 1 Feb.	1.33	0.94
23	1-9 Feb.	1.66	1.36
24	9-16 Feb.	0.97	0.90
25	16-26 Feb.	1.17	0.68
26	26 Feb. - 7 Mar.	2.05	1.96
27	7-15 Mar.	1.35	1.28
28	15 Mar. - 1 Apr.	1.02	0.92
29	1-21 Apr.	1.36	1.25
30	21-27 Apr.	1.36	1.31
31	28 Apr. - 7 May	1.21	1.17
32	7-16 May	0.82	0.81
33	16 May - 3 June	ND	ND
34	26 Jul. - 13 Aug.	0.04(?)	0.03
35	13-23 Aug.	0.56	0.38
36	23 Aug. - 12 Sept.	0.36	0.12
37	12-20 Sept.	0.18	0.08
38	20-24 Sept.	0.19	0.13
39	24-28 Sept.	0.22	0.05
40	28 Sept. - 3 Oct.	0.26	0.21

For most of the rest of this document, the sulfate referred to at Barrow will be the nonmarine component only. The reason for this is that marine sulfate is quite uninteresting atmospherically - it is in the giant (optically inactive) size range, and is limited to the marine inversion layer, which during the Arctic winter is roughly 0.5 km or less in elevation. Excess sulfate, on the other hand, is found throughout the atmosphere, is largely submicron-sized, differs chemically from marine sulfate, and appears to have a nonmarine origin. Its concentration, even near an ocean, is usually greater than marine sulfate, and because of its small particle size, is composed of many more particles, hence exerts greater optical effects.

The nonmarine sulfate of Table 1 shows two markedly different seasonal regimes, summer and winter. In summer (June through September) its concentration is low, about 0.1 to 0.15 $\mu g\ m^{-3}$. In winter (December through April) its concentration is much higher, approximately 1.1 $\mu g\ m^{-3}$. Our winter data are much more complete than our summer data, and it is remarkable how constant the sulfate concentration is during this period. From 30 November 1976 through 7 May 1977 the 20 samples had a range of only 0.68 to 1.96 $\mu g\ m^{-3}$, an unweighed mean of 1.26 $\mu g\ m^{-3}$, and a coefficient of variation of only 24%. By contrast, the coefficients of variation of some other elements for that same period were 83 % for Na, 46% for Al, and 70% for noncrustal V. This low coefficient of variation for sulfate becomes even more remarkable when it is realized that it is only about 10% greater than the variation attributable to analysis and subdivision of the filter. Thus winter sulfate at Barrow must be considered all but constant.

Why should this be? One possible reason is its type of origin. As will be shown later in this document, available evidence indicates that 90% or more of the nonmarine sulfate at Barrow is secondary in origin, which here means that it has been converted from SO_2 after leaving major regional pollution sources such as Europe or the northeastern United States. This idea is only tentative, however, and needs to be confirmed.

The seasonal variations of several constituents of the aerosol are shown in Figure 1. Note the great similarity of pattern between V, Mn, and sulfate, and to a lesser extent Al, ^{7}Be, and surface ozone. All have broad winter maxima from November or December through April or May, with varying amplitudes. Vanadium has the largest amplitude, a factor of 25 to 50. It is followed by Mn with a factor of 20, excess sulfate with a factor of 10, ^{7}Be (derived from the stratosphere) with a factor of 6, Al with a factor of 4, and ozone with a factor of 2. Factors of 5 to 10 appear to be the most common, based on incomplete evidence for other elements. Some other properties of the Barrow atmosphere not shown here, including turbidity and darkening of the filters by the aerosol, also have a winter or spring maximum a few times greater than the summer minimum. The repeated occurrence of this winter maximum indicates to us that it is the prime feature of the Barrow aerosol.

This winter maximum of aerosol appears to be attributable to long-range transport from mid-latitudes, as evidenced by the abundance of vanadium, a pollutant which is preferentially emitted by combustion of petroleum in mid-latitudes during winter. Certain meteorological aspects of this transport have been discussed elsewhere (Rahn _et_ _al_., 1977b). Basically, the seasonal differences in transport stem from vigorous general circulation and coupling of mid-latitude sources to the Arctic during winter, versus weaker general circulation and decoupling of mid-latitude sources from the Arctic during summer. This interpretation is reinforced by Rn-222 data from

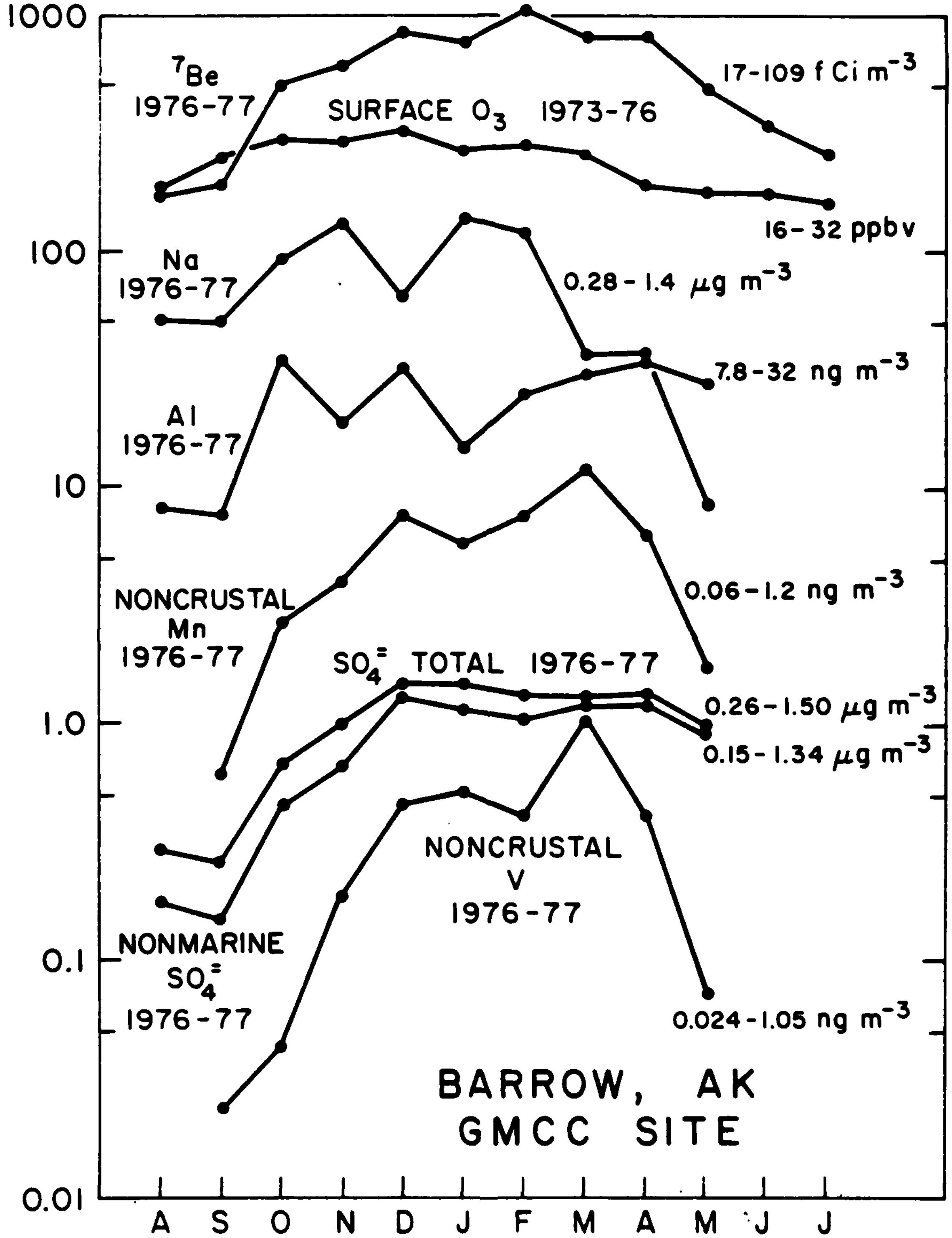

Figure 1. Monthly mean concentrations of various gaseous and particulate constituents of the Barrow atmosphere.

Spitsbergen (Wilkniss et al., 1975), which show markedly reduced travel times from continents during winter. We can therefore conclude with confidence that the Barrow sulfate is of mid-latitude origin, at least during winter.

A larger question follows almost immediately: Because so much of present-day mid-latitude aerosol (and sulfur) is pollution-derived during winter, how much of the Barrow winter sulfate is also pollution-derived? This is equivalent to asking how much of the Barrow aerosol in general, and probably also how much of the Arctic haze, is pollution-derived. The rest of this document will address this most important question in detail. It is our considered opinion that the present data strongly support but do not prove a pollution origin of Barrow sulfate in winter, and probably also in summer.

To address this question, it is most efficient to survey the sulfate data systematically.

Overall composition of the Barrow aerosol

Perhaps the most striking feature of the sulfate concentrations is how high they are. Table 2 compares the abundance of sulfate with other major constituents of the Barrow aerosol. At the surface, where sea-salt is abundant, nonmarine sulfate accounts for about one-quarter of the aerosol. To get an estimate of the corresponding figure for the aerosol above the marine inversion layer, we have derived rough figures for the submicron component of the aerosol, which should simulate the aerosol aloft. Under these conditions more than 50% of the aerosol is sulfate, which is more in line with figures for other remote areas. Notes 5 and 6 of this table are derived from our spring 1976 study (Rahn et al., 1977a); note 7 follows from the presence of sea-salt in the giant ($r > 1$ μm) size range of the aerosol.

Table 2. Composition of Barrow aerosol, December 1976 - February 1977.

Constituent	Concentration, µg m^{-3}
Surface aerosol	
Sulfate (nonmarine)[1]	1.2 (24%)
Soil[2]	0.3
Sea salt[3]	3.3
Nonsulfate pollutants[4]	0.2
TOTAL	5.0
Submicron component ∿ aerosol aloft	
Sulfate (nonmarine)[5]	∿0.8 (57%)
Soil[6]	∿0.1
Sea salt[7]	∿0.3
Nonsulfate pollutants[8]	∿0.2
TOTAL	∿1.4

1) $\text{Total sulfate} - \left(\frac{SO_4^{=}}{Na}\right)_{\text{seawater}} \times Na_{\text{aer}} = 1.43\mu g\ m^{-3} - 0.25(1.06\mu g\ m^{-3})$

2) $\left(\frac{10^6}{Al_{\text{rock}},\text{ppm}}\right) \times Al_{\text{aer}},\mu g\ m^{-3} = \left(\frac{10^6}{81,300}\right) \times 0.024\mu g\ m^{-3}$

3) $\left(\frac{10^6}{Na_{\text{seawater}},\text{ppm}}\right) \times Na_{\text{aerosol}},\ \mu g\ m^{-3} = \left(\frac{10^6}{324,000}\right) \times 1.06\mu g\ m^{-3}$

4) $\frac{\text{Submicron NYC winter aerosol}}{V_{NYC}(\text{assumed submicron})} \times V_{\text{Barrow}} = \frac{40\mu g\ m^{-3}}{100 \times 10^{-3}\mu g\ m^{-3}} \times 0.47 \times 10^{-3}\mu g\ m^{-3}$

5) Two-thirds nonmarine sulfate assumed submicron.

6) One-third soil aerosol assumed submicron.

7) One-tenth sea-salt aerosol assumed submicron.

8) All submicron (see note 4).

"Too much" sulfate at Barrow

We now begin a series of calculations which attempt to account for the high sulfate concentrations at Barrow in terms of various sources. Involved in this are concentrations of SO_2, sulfate, and vanadium from a variety of areas. All data used in the following calculations are shown in Table 3, together with the appropriate references. It must be emphasized at this point that many of these data are not accurately known. The basic problem is that we have had to use regional data, which are poorly established relative to urban data. But we believe that these estimates are generally better than factors of two, and often much better than that. Subsequent calculations bear this out.

Let us first attempt to account for the sulfate at Barrow in a straightforward way from a series of known aerosol sources. This attempt is shown in Table 4. We consider sea-salt, volcanoes, the stratosphere, the biosphere, and pollution sulfate (as it exists in source regions). All calculations have been performed for the winter period of December through February. For this period in 1976-77 the total sulfate in the Barrow surface aerosol was 1.43 $\mu g\ m^{-3}$. The sea-salt component, derived from Na, was 0.27 $\mu g\ m^{-3}$, or 19% of the total. The volcanic contribution has been set at 5% of the fossil-fuel sulfur component (expressed as sulfate), in accord with current estimates of the global sulfur cycle (see Bolin and Charlson (1976), for example), and is thus negligible in this first approximation. The stratospheric component is harder to evaluate, but also turns out to be negligible: We used concentrations of ^7Be (generated by cosmic rays in the stratosphere, where it becomes attached to aerosols and serves as an excellent indicator of stratospheric aerosol in the troposphere) in surface air at Barrow

Table 3. Concentrations of atmospheric sulfur and vanadium in various areas.

Constituent	Season	Concentration unit	New York City	Northeastern United States	United Kingdom	Europe	Northern Norway	Spitsbergen	Barrow
SO_2	Winter	$\mu g\ m^{-3}$	$\underline{69}$ (43^{b}x1.61^{a})	$\underline{16}$ (10^{e}x1.61^{a})	$\underline{16}$ (10^{h}x1.61^{a})	$\underline{32}$ (20^{h}x1.61^{a})	-	-	-
SO_2	Summer	$\mu g\ m^{-3}$	$\underline{34}$ (43^{b}x0.8^{a})	$\underline{8}$ (10^{e}x0.8^{a})	$\underline{8}$ (10^{h}x0.8^{a})	$\underline{16}$ (20^{h}x0.8^{a})	-	-	-
SO_2	Annual	$\mu g\ m^{-3}$	$\underline{43}^{b}$	$\underline{10}^{e}$	$\underline{10}^{h}$	$\underline{20}^{h}$	-	-	-
$SO_4^{=}$	Winter	$\mu g\ m^{-3}$	$\underline{11}^{c}$ ($9.8=8.9^{b}$x1.1^{a})	$\underline{6}^{f}$ (5.5^{c})	$\underline{3.4}$ (4^{h}x0.86^{f})	$\underline{6}$ (7^{h}x0.86^{f})	$\underline{3.2}^{\ell}$	$\underline{1.99}^{m}$	$\underline{1.43}^{n}$
$SO_4^{=}$	Summer	$\mu g\ m^{-3}$	$\underline{10.3}$ (8.9^{b}x1.16^{a})	$\underline{9}^{f}$	$\underline{5.1}$ (4^{h}x1.29^{f})	$\underline{9}$ (7^{h}x1.29^{f})	-	-	$\sim\underline{0.3}^{n}$
$SO_4^{=}$	Annual	$\mu g\ m^{-3}$	$\underline{8.9}^{b}$	$\underline{7}^{f}$ (8.1^{e})	$\underline{4}^{h}$	$\underline{7}^{h}$	-	-	$\sim\underline{0.9}^{n}$
V(noncrustal)	Winter	$ng\ m^{-3}$	$\underline{103}^{d}$	$\underline{21.7}^{g}$	$\underline{21}$ (14^{i}x1.51^{j})	$\underline{23}$ (15^{k}x1.51^{j})	$\underline{3.3}^{\ell}$	$\underline{0.63}^{m}$	$\underline{0.47}^{n}$
V(noncrustal)	Summer	$ng\ m^{-3}$	$\underline{48}^{d}$	$\underline{9.7}^{g}$	$\underline{9.4}$ (14^{i}x0.67^{j})	$\underline{10}$ (15^{k}x0.67^{j})	-	-	$\sim\underline{0.02}^{n}$
V(noncrustal)	Annual	$ng\ m^{-3}$	$\underline{67}^{d}$	$\underline{14.3}^{g}$	$\underline{14}^{i}$	$\underline{15}^{k}$	-	-	$\sim\underline{0.27}^{n}$

a) Lynn et al. (1975), data of 1972

b) Hidy et al. (1978), data of 1974-75.

c) R. Tanner, pers. comm.; data of 1977.

d) Eisenbud and Kneip (1975), data of 1972-74.

e) Altschuller (1973), data from 1968 - ~1972.

f) Hitchcock (1976), data from 1965 - 70.

g) 1974-77

h) Ottar (1978), data from 1974.

i) Cawse (1974), data from 1972-73.

j) From NE USA; data, this table.

k) Hoste et al. (1974), data from 1973.

ℓ) Data from 1971-72.

m) B. Ottar, pers. comm.; data from 1973-74.

n) Data from 1976-77.

Table 4. Calculated sources of sulfate aerosol for Barrow winter aerosol, December 1976 - February 1977

Component of sulfate	Concentration, $\mu g\ m^{-3}$
TOTAL	1.43
Sea-salt[1]	0.27(19%)
Volcanic[2]	∿0
Stratospheric[3]	0.005
Biogenic[4]	∿0
"Primary" pollution[5]	0.10 - 0.13 (7 - 9%)
SUBTOTAL	0.38 - 0.41 (23 - 29%
Unaccounted for	1.02 - 1.05 (71 - 73%)

1) $\frac{SO_4^=}{Na}$ seawater $\times\ Na_{aer} = 0.25 \times 1.06\mu g\ m^{-3}$

2) 5% of fossil-fuel sulfate emissions - negligible for this first approximation.

3) $\frac{{}^7Be_{Barrow}}{{}^7Be_{\text{lower polar stratosphere}}} \times SO^=_{4\,\text{lower polar stratosphere}} = \frac{80f\ Ci\ m^{-3}}{8000f\ Ci\ m^{-3}} \times 0.53 \times 10^{-3}\mu g\ m^{-3}$

4) Figure in dispute - should be very low in Arctic during winter.

5) $\left(\frac{SO_4^=}{V}\right)_{source} \times V_{Barrow}$

Europe - U.K.: $(0.21\times10^3) \times (0.47\times10^{-3})\mu g\ m^{-3}$

NE USA: $\frac{6\mu g\ m^{-3}}{0.022\mu g\ m^{-3}} \times 0.47\times10^{-3}\mu g\ m^{-3}$

(recent data from Environmental Measurements Laboratory, 1978) during winter and in the lower stratosphere at 70° North Latitutde (Rama (1963), October 1959-June 1960). The surface/stratosphere concentration ratio is about 1/100, which interestingly is nearly the same as one can derive for ozone, using surface data from the Barrow GMCC site (Hanson (1976), concentration 30 ppb, during December through February of 1973-76) and the lower stratosphere (Junge (1963), 60° North Latitude, spring, 15 km altitude, concentration 2 ppm). When this factor is multiplied by the concentration of sulfate in the lower Arctic stratosphere (value of 0.53 $\mu g\ m^{-3}$ derived from Lazrus and Gandrud (1974), spring 1971-73 (no winter data available), elevation 12-13 km), the stratospheric component of the Barrow surface sulfate is clearly seen to be negligible.

Evaluation of the biogenic contribution is not obvious. The actual emissions of biogenic (reduced) sulfur compounds to the atmosphere is very poorly known. Hitchcock (1976) has estimated the global emissions of S from decomposing plant tissue to be $2\text{-}5\times10^6\ T\ y^{-1}$, which is very small compared to current emissions of SO_2-S of about $60\times10^6\ T\ y^{-1}$ (Bolin and Charlson (1976), for example). Biogenic releases from anoxic marshes and mud flats are much harder to evaluate, however, and published estimates are very uncertain indeed. They are usually a difference term needed to make the global sulfur cycle balance. Published estimates of this quantity range from about 30 to $300\times10^6\ T\ y^{-1}$, with the more recent estimates being toward lower figures as the sulfur cycle comes more nearly into balance (see table in Rodhe, 1978). In our view, these difference figures are so uncertain as to render them all but worthless. For the moment we neglect biogenic sulfur altogether. The high Arctic in winter is probably as good a place and time as there is in the world to do this. Later, however, it will be shown that biogenic emissions can be included in the SO_2 and sulfate figures from pollution source regions, so that they are not altogether neglected.

The last contributor to Barrow sulfate that we consider is "primary" pollution, that is, the sulfate that exists in regional source areas before the air masses move out toward the Arctic. This figure was derived by multiplying the ratio of sulfate to vanadium in the source regions of the northeasted United States and Europe/U.K. by the vanadium concentration at Barrow.

The result of these calculations is that sea salt would appear to be the largest contributor to sulfate at Barrow (19%), followed by "primary" pollution (7-9%). All other sources are negligible. Most significantly, some 71 to 73% of the sulfate is left unexplained by this approach - thus there is "too much" sulfate at Barrow.

This excess of sulfate at Barrow relative to what can be accounted for by primary aerosol sources can be seen better by a plot of $SO_4^=/V$ ratios in regions ranging from cities to the Arctic, as shown in Figure 2. The points on this plot are arranged from left to right as they would fall along an imaginary trajectory beginning at New York City, passing northeastward to Europe, thence northward to Spitsbergen and Barrow. This corresponds very roughly to increasing "Arctic character" of the sites, or increasing remoteness from strong urban "point sources" of pollution aerosols and gases. One sees immediately two main features of this plot, that the $SO_4^=/V$ ratio varies over more than an order of magnitude, and that it increases regularly with remoteness. New York City has the lowest ratio of all, followed by the regional sources of the northeastern United States, the United Kingdom, and

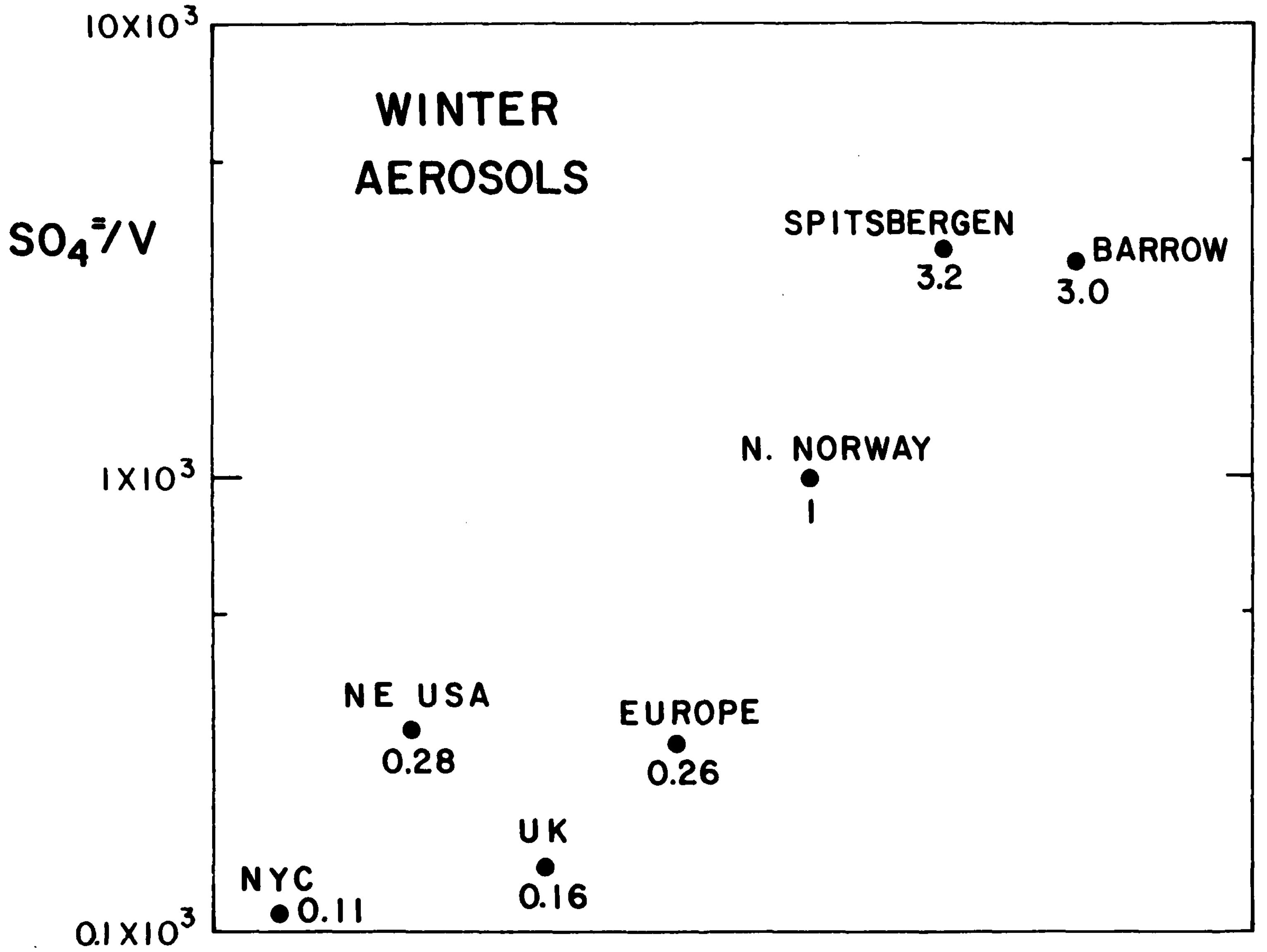

Figure 2. Ratios of sulfate to noncrustal vanadium in the northeast United States, Europe, Norway, and the Arctic.

Europe with ratios between 1.5 and 2.5 times higher. These are followed by sub-Arctic northern Norway, with a ratio about 4 times higher still, and then by the Arctic Spitsbergen and Barrow, with essentially identical ratios about 3 times higher than the sub-Arctic . Thus there is an orderly progression of values from the cities to the Arctic, in regular steps depending on distance and climate.

It is logical to interpret the regularity of this figure to mean that something is slowly and steadily adding to the sulfate in the aerosol as it travels toward the Arctic. The obvious agent is SO_2 being converted to sulfate on a time scale of days. The rest of this document will explore this possibility in some detail, and will conclude that it is indeed the most likely explanation. Both the time scale for oxidation and the available SO_2 will be proven to be adequate to explain the changes in ratio.

One final remark before proceeding: The similarity of ratios between Barrow and Spitsbergen seems to us to be a very important fact. It suggests that the air chemistry on both sides of the Arctic is basically similar, which lends a generality to our concentrated studies of the Barrow aerosol that they would not otherwise have. This is confirmed by a more detailed comparison of data between Barrow and Spitsbergen, which we have not yet completed but which is already quite convincing. We are rapidly coming to believe that air quality of the Arctic is quite similar from site to site, at least during winter.

The Barrow-Spitsbergen similarity also suggests that if the Barrow aerosol is indeed derived from the Spitsbergen aerosol by further transport, changes between these two locations must be small relative to what transpired before the aerosol reached either of them. There are at least two possible reasons for this: (1) Most of the SO_2 has been converted to sulfate or removed well before mid-latitude air reaches the Arctic, as we show below; (2) Reaction and/or removal rates may be considerably slower inside the Arctic than outside it. Glenn Shaw was the first in our group to advance this latter idea, which seems to be confirmed by various recent evidence. For example, the writer and R. McCaffrey have recently estimated, on the basis of trace-element concentrations in snow and aerosol from Barrow, that residence times there ought to be several times longer than in mid-latitudes.

We now investigate how much SO_2 can be converted to sulfate during typical transport times to the Arctic, and how much this can affect the observed $SO_4^=/V$ ratio.

Conversion of SO_2 to sulfate

Consider a regionally-polluted mid-latitude air mass which is a potential source of Arctic aerosol. While still within its source region it contains characteristic concentrations of SO_2 and sulfate, as well as a host of other trace elements in the aerosol which we shall neglect for the moment. Imagine this air mass being advected away from the source, out over a cleaner region, typically the ocean, which is not emitting SO_2 or submicron sulfate. As the air mass ages, three major transformation processes will occur: SO_2 will be removed (directly at the surface as well as in precipitation) with a characteristic rate constant $k_{wd\ SO_2}$, SO_2 will be oxidized to sulfate (both photochemically and catalytically in droplets) with a rate constant $k_{ox\ SO_2}$, and the sulfate (both "primary" and secondary) will be removed by precipitation (dry removal of sulfate can generally be neglected) with a rate constant k_p. Of course, any rigorous treatment of the SO_2/sulfate equilibrium during aging will assign individual rate constants to the wet and dry removal and oxidation of SO_2 and treat each of the four processes separately, but this seems beyond both our present requirements and the reliability of the data available for our calculations. What we do here is a first step only, to demonstrate that sulfur in the Arctic must be seriously considered to be pollution-derived; we do not, however, claim finality of results.

Thus, the controlling equations for SO_2 and sulfate are:

$$\frac{d(SO_2)}{dt} = -k_{wd\ SO_2}(SO_2) - k_{ox\ SO_2}(SO_2) \qquad (1)$$

and

$$\frac{d(SO_4^=)}{dt} = -k_p(SO_4^=) + 1.5k_{ox\ SO_2}(SO_2)\ . \qquad (2)$$

The solutions are:

$$(SO_2) = (SO_2)_o\ e^{-(k_{wd\ SO_2} + k_{ox\ SO_2})t} \qquad (3)$$

and

$$(SO_4^=) = e^{-k_p t}\left((SO_4^=)_o + \frac{1.5k_{ox\ SO_2}(SO_2)_o}{A}[1 - e^{-At}]\right) \qquad (4)$$

where $A = k_{wd\ SO_2} + k_{ox\ SO_2} - k_p$.

Alternatively:

$$\left[\frac{SO_2}{SO_4^=}\right] = \frac{\left[\frac{SO_2}{SO_4^=}\right]_o e^{-At}}{1 + \left[\frac{SO_2}{SO_4^=}\right]_o \frac{1.5k_{ox\ SO_2}}{A}[1 - e^{-At}]} \qquad (5)$$

where the subscript o refers to the state of the air mass as it leaves the source region, i.e., at time 0 for our calculations. The limit of the expression for large t is zero, for A > 0.

In order to demonstrate the factor of change of the $SO_2/SO_4^=$ ratio $[(SO_2/SO_4^=)/(SO_2/SO_4^=)_0]$ in the most general terms, we have made up a large table (Table 5) for aging times up to 20 days and for a variety of intial values of the various rate constants and $SO_2/SO_4^=$ ratios. In this and subsequent tables the rate constants have been expressed as their reciprocals, i.e., residence or turnover times, which are easier to get a feel for. Because these parameters will be used over and over again in the rest of this document, we now present a brief discussion of how they were chosen.

Residence time for dry removal of sulfur SO_2 are generally estimated to be some days. Typical recent estimates are 1.16 d for Europe (Eliassen, 1978), 2.5 d for Europe (Rodhe, 1978), and 4 d for the Europe/U.K. region (Garland, 1978). We have chosen the estimate of Garland of 4 d as the best value, because he was the only author to specifically consider remote-area conditions.

Residence times for wet removal of SO_2 vary hugely. Some writers contend that the relatively great solubility of SO_2 in water should make wet removal a major mechanism. Others, however, contend equally strongly that the acidity of rain drops will decrease this solubility to the point where it is of no consequence. Three examples will point up the uncertainties here: Eliassen (1978) estimates a residence time for wet removal of SO_2 in Europe to be 0.29 d; Garland (1978) claims that in the free atmosphere it is long enough to be negligible relative to dry removal of SO_2; Rodhe takes an intermediate estimate of 4.2 d for Europe. For the reason given above, we have used Garland's (1978) estimate, and neglect wet removal of SO_2. More properly stated, we take the combined residence time for wet and dry removal of SO_2 to have a best value of 4 d; we have used values of 3,4, and 5 in our calculations.

Table 5.

Change of $SO_2/SO_4^=$ ratio starting from urban regional sources.

$[(SO_2/SO_4^=)/(SO_2/SO_4^=)_o]$

$\tau_{wd}\ SO_2$,d	3 →									→								→
$\tau_{ox}\ SO_2$,d	3 →									→4								→
τ_p,d	2	2	2	3	3	3	4	4	4	2	2	2	3	3	3	4	4	4
$(SO_2/SO_4^=)_o$	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4
t = 5d	0.16	0.20	0.30	0.09	0.11	0.13	0.06	0.08	0.10	0.26	0.32	0.37	0.14	0.18	0.22	0.10	0.13	0.16
10d	0.06	0.06	0.07	0.01	0.02	0.02	0.007	0.009	0.01	0.12	0.14	0.16	0.03	0.04	0.05	0.02	0.02	0.03
15d	0.02	0.03	0.03	0.003	0.003	0.004	8×10^{-4}	0.001	0.001	0.07	0.08	0.08	0.01	0.01	0.01	0.003	0.004	0.005
20d	0.01	0.01	0.01	5×10^{-4}	6×10^{-4}	7×10^{-4}	1×10^{-4}	1×10^{-4}	2×10^{-4}	0.04	0.05	0.05	0.003	0.003	0.004	6×10^{-4}	8×10^{-4}	9×10^{-4}
$\tau_{wd}\ SO_2$,d	3 →									→4								→
$\tau_{ox}\ SO_2$,d	5 →									→3								→
τ_p,d	2	2	2	3	3	3	4	4	4	2	2	2	3	3	3	4	4	4
$(SO_2/SO_4^=)_o$	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4
t = 5d	0.36	0.45	0.52	0.19	0.25	0.31	0.13	0.19	0.23	0.22	0.26	0.29	0.12	0.15	0.17	0.09	0.11	0.13
10d	0.20	0.23	0.26	0.06	0.08	0.09	0.03	0.04	0.05	0.10	0.11	0.12	0.03	0.04	0.04	0.01	0.02	0.02
15d	0.13	0.15	0.16	0.02	0.03	0.03	0.007	0.009	0.01	0.05	0.06	0.06	0.008	0.01	0.01	0.003	0.003	0.004
20d	0.10	0.11	0.11	0.007	0.009	0.01	0.002	0.002	0.003	0.03	0.04	0.04	0.002	0.003	0.003	5×10^{-4}	6×10^{-4}	7×10^{-4}
$\tau_{wd}\ SO_2$,d	4 →									→								→
$\tau_{ox}\ SO_2$,d	4 →									→5								→
τ_p,d	2	2	2	3	3	3	4	4	4	2	2	2	3	3	3	4	4	4
$(SO_2/SO_4^=)_o$	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4
t = 5d	0.34	0.42	0.47	0.19	0.25	0.29	0.14	0.18	0.22	0.47	0.58	0.66	0.26	0.34	0.40	0.19	0.25	0.31
10d	0.21	0.23	0.25	0.07	0.08	0.09	0.03	0.04	0.05	0.34	0.38	0.40	0.11	0.14	0.15	0.06	0.08	0.09
15d	0.15	0.16	0.17	0.03	0.03	0.04	0.01	0.01	0.01	0.27	0.29	0.30	0.06	0.07	0.07	0.02	0.03	0.03
20d	0.11	0.12	0.13	0.01	0.01	0.01	0.003	0.003	0.004	0.24	0.25	0.26	0.03	0.03	0.04	0.007	0.009	0.01

Table 5.
Change of $SO_2/SO_4^=$ ratio starting from urban regional sources (p.2)

$[(SO_2/SO_4^=)/(SO_2/SO_4^=)_o]$

τ_{wd} SO_2,d	5 →																	→
τ_{ox} SO_2,d	3 →									4 →								→
τ_p,d	2	2	2	3	3	3	4	4	4	2	2	2	3	3	3	4	4	4
$(SO_2/SO_4^=)_o$	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4
t = 5d	0.26	0.30	0.33	0.14	0.18	0.20	0.10	0.13	0.15	0.41	0.49	0.54	0.23	0.29	0.33	0.17	0.22	0.26
10d	0.14	0.15	0.16	0.04	0.05	0.06	0.02	0.03	0.03	0.28	0.31	0.32	0.10	0.11	0.13	0.05	0.06	0.07
15d	0.09	0.09	0.10	0.01	0.02	0.02	0.005	0.006	0.007	0.23	0.24	0.25	0.05	0.06	0.06	0.02	0.02	0.02
20d	0.06	0.07	0.07	0.005	0.006	0.007	0.001	0.002	0.002	0.20	0.20	0.21	0.02	0.03	0.03	0.006	0.008	0.009

τ_{wd} SO_2,d	5 →								→
τ_{ox} SO_2,d	5 →								→
τ_p,d	2	2	2	3	3	3	4	4	4
$(SO_2/SO_4^=)_o$	1	2	4	1	2	4	1	2	4
t = 5d	0.56	0.67	0.75	0.31	0.40	0.47	0.23	0.30	0.36
10d	0.44	0.48	0.50	0.16	0.19	0.21	0.09	0.11	0.12
15d	0.39	0.41	0.42	0.10	0.11	0.12	0.04	0.05	0.05
20d	0.37	0.38	0.38	0.06	0.07	0.07	0.02	0.02	0.02

Estimates of oxidation times for SO_2 also show very wide ranges. Homogeneous (photochemical) oxidation of SO_2 in urban atmospheres has been calculated to have residence times of 0.2 to 2 d (Eggleton and Cox, 1978; Calvert et al., 1978). Residence times from homogeneous oxidation in nonurban atmospheres have been calculated to be 2 to 4 d in summer and 4 to 42 d in winter (Eggleton and Cox, 1978; Calvert et al., 1978). Heterogeneous oxidation has been measured with residence times from 130 minutes to 100 hours in power-plant plumes (Flyger et al., 1978; Pueschel and Van Valin, 1978; Lusis and Weibe, 1976), and as short as 1000 sec (Beilke and Gravenhorst, 1978) for more general urban conditions. Actual observations of total oxidation rates of SO_2 in nonurban atmospheres have a much narrower spread of values, however. Recently reported values include 4.2 d for the North Sea in September and October (Smith and Hunt, 1978), 3.3 d annual mean for Europe (Rodhe, 1978), 3.3 d annual mean for Europe (Eliassen, 1978), 5.8 d annual mean for Europe (Eliassen and Saltbones, 1975), 2.9 d for air masses traveling from the U.K. to the Faroe Islands in February (Prahm et al., 1976), and 11.6 d annual mean for Europe (Fisher, 1978). The mean of all but the last estimate is 3.9 ± 1.2 d; we have therefore taken 4 d as our best estimate and used 3, 4, and 5 in our calculations.

Sulfate has been estimated to have an annual mean residence time in Europe with respect to wet removal of 2.9 d (Eliassen, 1978) and 3.3 d (Rodhe, 1978). We have, however, previously derived a somewhat shorter residence time for vanadium crossing the Atlantic of nearer 2 d, and for this reason together with the fact that we are primarily concerned with transport to the Arctic in the prevailing westerlies, which are quite rainy, we originally chose a best value of 2 d. Subsequently, however, this value produced an instability in our calculations (described below), and so was revised to 2.5 d, which was then closer to the measurements for Europe.

The various values of the $SO_2/SO_4^=$ ratio used in our calculations can be derived from Table 3. It has been very difficult for us to derive values for this ratio with which we could feel comfortable, primarily because of the lack of good regional SO_2 data and the tendency of agencies to report annual means rather than monthly or seasonal values. For this reason we have used values of 1, 2, and 4 in Tables 5 and 6, and where the exact value was of greater significance we have made up special tables (Tables 9

Table 5 shows that most of the SO_2 has been lost or transformed about 5 d travel from the regional sources. By this time the $SO_2/SO_4^=$ ratio has decreased to typically 0.1 to 0.3, as opposed to 1 to 4 at the source. Subsequent travel produces still lower ratios. In other words, the biggest changes in the aerosol occur before it reaches the Arctic. After this, there is little SO_2 left to be converted to sulfate. These predictions are in good agreement with published $SO_2/SO_4^=$ ratios of 0.17 to 0.43 for the Faroe Islands during February (Prahm _et_ _al_., 1976).

Unfortunately, no data on SO_2 in the Arctic exist, to our knowledge. This is a deficiency that should be remedied as soon as possible. The $SO_2/SO_4^=$ ratio of an air mass is a clear indicator of the aging time it has had since its last exposure to strong sources of SO_2.

Effect of SO_2 conversion of $SO_4^=/V$ ratio of an aging air mass

The effect of conversion of SO_2 to sulfate on the $SO_4^=/V$ ratio of an aging air mass, which has been postulated above as the most likely explanation for the changes shown in Figure 2, is not obvious from Table 5, because removal of the original vanadium during transport is not taken into account. To remdey this, let us treat this case specifically.

Consider a regionally polluted mid-latitude air mass transported toward the Arctic. As before, SO_2 is removed and oxidized at characteristic rates, and sulfate is removed with a rate constant k_p. This time, however, vanadium will be removed with the same rate constant k_p. The equations for transformation are then Equations (1) and (2), plus

$$\frac{d(V)}{dt} = -k_p(V) \tag{6}$$

The solutions for (SO_2) and $(SO_4^=)$ are the same as before, in Equations (3) and (4). the solution for (V) is:

$$(V) = (V)_o\, e^{-k_p t} \tag{7}$$

The $SO_4^=/V$ ratio is then:

$$\frac{\left(\frac{SO_4^=}{V}\right)}{\left(\frac{SO_4^=}{V}\right)_o} = 1 + \frac{1.5k_{ox\ SO_2}\left(\frac{SO_2}{SO_4^=}\right)_o}{A}\left[1 - e^{-At}\right] \tag{8}$$

As opposed to the behavior of Equation (5), the right side of Equation (8) does have a well-defined limit for large t, provided A is positive. This limit is:

$$\lim_{t \to \infty} 1 + \left\{\frac{1.5k_{ox\ SO_2}\left(\frac{SO_2}{SO_4^=}\right)_o}{A}\left[1 - e^{-At}\right]\right\} = 1 + \frac{1.5k_{ox\ SO_2}\left(\frac{SO_2}{SO_4^=}\right)_o}{(k_{wd\ SO_2} + k_{ox\ SO_2} - k_p)} \tag{9}$$

Equation (9) is useful because it reveals that the change in the $SO_4^=$ ratio should be most sensitive to $\tau_{ox\ SO_2}$ and to $(SO_2/SO_4^=)_o$, which is confirmed by numerical calculation.

The various values of Equation (8) are shown in Table 6, for times up to 20 d, as well as for the limit of large times. Table 6 is a particularly important one for the consideration of sulfate in the Arctic. The values of $(SO_2/SO_4^=)_o$ of 1, 2, and 4 correspond respectively to approximate conditions during summer in the NE USA, winter in the NE USA and summer in Europe/U.K., and winter in Europe/U.K. By estimating transit times from these sources to the Arctic it is possible to survey the results in this table and compare them to the factors of increase actually observed (in Figure 2, for instance), and thereby get an idea of whether conversion of SO_2 to sulfate has any prospect of explaining the observed increased $SO_4^=/V$ ratios in the Arctic. If it can, then Table 6 can be used to get some idea of which values of the various parameters are most reasonable. As an example of how this can be carried out, we have underlined the various factors of increase expected for the winter situation, when $(SO_2/SO_4^=)_o$ and travel times from the NE USA are about 2 and 10 d, respectively, and corresponding values for Europe/U.K. are about 4 and 5 d. The observed factor of increase of $(SO_4^=/V)$ between mid-latitude sources and the Arctic is about 8, which becomes somewhat lower when the marine sulfate of the Arctic is subtracted. Table 6 shows that satisfactory factors of increase are obtained for $\tau_{wd\ SO_2}$'s of 3 to 5 d, $\tau_{ox\ SO_2}$'s of 3 to 5 d, and τ_p's of 2 to 3 d. This is an excellent agreement with our best values of 4, 4, and 2.5 d given earlier. We consider that this agreement is very strong evidence, albeit circumstantial, that the conversion of pollution SO_2 to sulfate does indeed explain the increased sulfate $SO_4^=/V$ ratios in the Arctic.

Closer inspection of Table 6 reveals that certain combinations of parameters have no limits given. This is because the A's for these values

Table 6.

Factor of change of $SO_4^=/V$ ratios in polluted air masses during transport.

$\tau_{wd}\ SO_2$,d	3 →																	
$\tau_{ox}\ SO_2$,d	3 →									4 →								
τ_p,d	2	2	2	3	3	3	4	4	4	2	2	2	3	3	3	4	4	4
$(SO_2/SO_4)_o$	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4
t = 1d	1.46	1.92	2.84	1.43	1.85	2.70	1.41	1.82	2.64	1.36	1.72	2.44	1.33	1.66	2.33	1.32	1.64	2.28
2d	1.85	2.70	4.40	1.73	2.46	3.92	1.68	2.36	3.73	1.69	2.38	3.76	1.59	2.18	3.36	1.55	2.09	3.19
3d	2.18	3.36	5.72	1.95	2.90	4.79	1.86	2.71	4.45	2.00	2.99	4.98	1.79	2.58	4.17	1.71	2.42	3.84
4d	2.46	3.92	6.84	2.10	3.21	5.42	1.98	2.95	4.93	2.28	3.55	6.10	1.95	2.90	4.79	1.83	2.66	4.31
5d	2.70	4.39	7.78	2.22	3.43	5.87	2.06	3.10	5.25	2.53	4.07	7.13	2.07	3.14	5.28	1.91	2.83	4.65
6d	2.90	4.79	8.59	2.30	3.59	6.19	2.12	3.20	5.46	2.77	4.54	8.08	2.17	3.33	5.66	1.97	2.95	4.89
7d	3.07	5.13	9.26	2.35	3.71	6.42	2.15	3.27	5.60	2.99	4.98	8.96	2.24	3.48	5.96	2.02	3.03	5.06
8d	3.21	5.42	9.84	2.40	3.79	6.58	2.17	3.31	5.69	3.19	5.38	9.76	2.30	3.59	6.19	2.05	3.09	5.19
9d	3.33	5.66	10.32	2.43	3.85	6.70	2.19	3.34	5.76	3.37	5.75	10.50	2.34	3.68	6.37	2.07	3.14	5.28
10d	3.43	5.87	10.73	2.45	3.89	6.79	2.20	3.36	5.80	3.54	6.09	11.18	2.38	3.75	6.51	2.08	3.17	5.34
15d	3.75	6.51	12.01	2.49	3.98	6.96	2.22	3.40	5.87	4.21	7.42	13.84	2.46	3.93	6.86	2.12	3.23	5.47
20d	3.89	6.79	12.57	2.50	4.00	6.99	2.22	3.40	5.88	4.65	8.30	15.60	2.49	3.98	6.96	2.12	3.25	5.49
Limit	4.00	7.00	13.00	2.50	4.00	7.00	2.20	3.40	5.80	5.50	10.00	19.00	2.50	4.00	7.00	2.13	3.25	5.50
$\tau_{wd}\ SO_2$,d	3 →									4 →								
$\tau_{ox}\ SO_2$,d	5 →									3 →								
τ_p,d	2	2	2	3	3	3	4	4	4	2	2	2	3	3	3	4	4	4
$(SO_2/SO_4)_o$	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4
t = 1d	1.30	1.59	2.18	1.27	1.54	2.09	1.26	1.52	2.04	1.48	1.96	2.94	1.44	1.88	2.77	1.43	1.85	2.70
2d	1.58	2.16	3.32	1.49	1.99	2.98	1.46	1.92	2.83	1.92	2.84	4.68	1.79	2.57	4.15	1.73	2.46	3.92
3d	1.86	2.71	4.43	1.68	2.35	3.71	1.61	2.21	3.43	2.33	3.65	6.31	2.06	3.11	5.22	1.95	2.90	4.79
4d	2.12	3.25	5.49	1.83	2.65	4.30	1.72	2.44	3.87	2.70	4.40	7.80	2.26	3.53	6.06	2.10	3.21	5.42
5d	2.38	3.76	6.53	1.95	2.90	4.79	1.80	2.60	4.21	3.04	5.09	9.18	2.43	3.85	6.71	2.22	3.43	5.87
6d	2.63	4.26	7.53	2.05	3.10	5.19	1.87	2.73	4.46	3.36	5.72	10.44	2.55	4.11	7.21	2.30	3.59	6.19
7d	2.87	4.75	8.49	2.13	3.26	5.52	1.91	2.83	4.65	3.65	6.30	11.61	2.65	4.30	7.61	2.35	3.71	6.42
8d	3.11	5.21	9.43	2.20	3.39	5.79	1.95	2.90	4.80	3.92	6.84	12.68	2.73	4.46	7.92	2.40	3.79	6.58
9d	3.33	5.67	10.33	2.25	3.50	6.01	1.98	2.95	4.90	4.17	7.33	13.66	2.79	4.58	8.16	2.43	3.85	6.70
10d	3.55	6.10	11.20	2.30	3.59	6.19	2.00	2.99	4.99	4.39	7.78	14.57	2.84	4.67	8.34	2.45	3.89	6.79
15d	4.54	8.08	15.16	2.43	3.85	6.70	2.04	3.09	5.17	5.28	9.56	18.12	2.95	4.91	8.81	2.49	3.98	6.96
20d	5.38	9.76	18.52	2.47	3.95	6.89	2.06	3.11	5.22	5.87	10.73	20.47	2.99	4.97	8.95	2.50	4.00	6.99
Limit	10.00	19.00	37.00	2.50	4.00	7.00	2.06	3.12	5.24	7.00	13.00	25.00	3.00	5.00	9.00	2.50	4.00	7.00

Table 6.

Factor of change of $SO_4^{=}/V$ ratios in polluted air masses during transport (p.2)

τ_{wd} SO_2,d	4 →									→								
τ_{ox} SO_2,d	4 →									5 →								
τ_p,d	2	2	2	3	3	3	4	4	4	2	2	2	3	3	3	4	4	4
$(SO_2/SO_4)_o$	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4
t = 1d	1.38	1.75	2.50	1.35	1.69	2.38	1.33	1.66	2.33	1.31	1.62	2.23	1.28	1.57	2.13	1.27	1.54	2.09
2d	1.75	2.50	4.01	1.64	2.28	3.55	1.59	2.18	3.36	1.63	2.26	2.52	1.54	2.07	3.14	1.49	1.99	2.98
3d	2.13	3.26	5.52	1.89	2.77	4.54	1.79	2.58	4.17	1.97	2.94	4.88	1.76	2.52	4.04	1.68	2.35	3.71
4d	2.51	4.02	7.03	2.09	3.19	5.38	1.95	2.90	4.79	2.33	3.66	6.31	1.96	2.92	4.84	1.83	2.65	4.30
5d	2.89	4.77	8.55	2.27	3.54	6.09	2.07	3.14	5.28	2.70	4.41	7.82	2.14	3.27	5.55	1.95	2.90	4.79
6d	3.27	5.53	10.07	2.42	3.84	6.69	2.17	3.33	5.66	3.10	5.20	9.40	2.29	3.59	6.18	2.05	3.10	5.19
7d	3.65	6.30	11.59	2.55	4.10	7.20	2.24	3.48	5.96	3.51	6.03	11.06	2.44	3.87	6.74	2.13	3.26	5.52
8d	4.03	7.06	13.12	2.66	4.31	7.63	2.30	3.59	6.19	3.95	6.90	12.80	2.56	4.12	7.24	2.20	3.39	5.79
9d	4.41	7.83	14.65	2.75	4.50	7.99	2.34	3.68	6.37	4.41	7.82	14.64	2.67	4.34	7.69	2.25	3.50	6.01
10d	4.80	8.60	16.19	2.83	4.65	8.30	2.38	3.75	6.51	4.89	8.78	16.57	2.77	4.54	8.08	2.30	3.59	6.19
15d	6.73	12.46	23.93	3.07	5.13	9.26	2.46	3.93	6.86	7.70	14.40	27.81	3.12	5.25	9.50	2.43	3.85	6.70
20d	8.69	16.38	31.77	3.17	5.34	9.68	2.49	3.98	6.96	11.31	21.62	42.24	3.32	5.64	10.29	2.47	3.95	6.89
Limit	-	-	-	3.25	5.50	10.00	2.50	4.00	7.00	-	-	-	3.57	6.14	11.29	2.50	4.00	7.00

Table 6.

Factor of change of $SO_4^=/V$ ratios in polluted air masses during transport, (p.3)

$\tau_{wd}\ SO_2$,d	5																	
$\tau_{ox}\ SO_2$,d	3									4								
τ_p,d	2	2	2	3	3	3	4	4	4	2	2	2	3	3	3	4	4	4
$(SO_2/SO_4)_o$	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4	1	2	4
t = 1d	1.49	1.98	2.97	1.45	1.91	2.81	1.44	1.87	2.74	1.38	1.77	2.54	1.35	1.71	2.42	1.34	1.68	2.36
2d	1.97	2.93	4.87	1.82	2.65	4.30	1.76	2.53	4.05	1.79	2.58	4.16	1.67	2.34	3.68	1.62	2.24	3.47
3d	2.43	3.85	6.71	2.13	3.26	5.51	2.01	3.02	5.04	2.21	3.43	5.86	1.95	2.90	4.80	1.85	2.69	4.38
4d	2.87	4.74	8.49	2.38	3.75	6.51	2.20	3.39	5.79	2.66	4.32	7.64	2.20	3.40	5.79	2.03	3.07	5.13
5d	3.30	5.61	10.21	2.58	4.16	7.32	2.34	3.67	6.35	3.13	5.26	9.52	2.42	3.84	6.68	2.19	3.37	5.74
6d	3.72	6.44	11.88	2.75	4.49	7.99	2.44	3.88	6.77	3.62	6.25	11.50	2.62	4.24	7.47	2.31	3.62	6.24
7d	4.12	7.24	13.49	2.88	4.77	8.53	2.52	4.04	7.09	4.14	7.29	13.57	2.79	4.59	8.18	2.41	3.83	6.65
8d	4.51	8.02	15.04	3.00	4.99	8.98	2.58	4.16	7.33	4.69	8.38	15.75	2.95	4.90	8.80	2.50	3.99	6.99
9d	4.89	8.78	16.55	3.09	5.17	9.35	2.63	4.25	7.51	5.26	9.52	18.05	3.09	5.18	9.36	2.57	4.13	7.26
10d	5.25	9.50	18.01	3.16	5.32	9.65	2.66	4.32	7.64	5.87	10.73	20.46	3.21	5.43	9.85	2.62	4.24	7.48
15d	6.90	12.80	24.61	3.38	5.75	10.50	2.74	4.48	7.96	9.38	17.76	34.51	3.66	6.31	11.62	2.78	4.56	8.13
20d	8.30	15.60	30.19	3.45	5.91	10.82	2.76	4.52	8.03	13.89	26.77	52.55	3.90	6.81	12.61	2.84	4.68	8.36
Limit	16.00	31.00	61.00	3.50	6.00	11.00	2.76	4.53	8.06	-	-	-	4.21	7.43	13.86	2.88	4.75	8.50

$\tau_{wd}\ SO_2$,d	5								
$\tau_{ox}\ SO_2$,d	5								
τ_p,d	2	2	2	3	3	3	4	4	4
$(SO_2/SO_4)_o$	1	2	4	1	2	4	1	2	4
t = 1d	1.24	1.47	1.94	1.29	1.58	2.16	1.28	1.56	2.11
2d	1.38	1.76	2.52	1.56	2.12	3.25	1.52	2.04	3.07
3d	1.47	1.93	2.86	1.82	2.63	4.26	1.72	2.45	3.90
4d	1.52	2.04	3.08	2.05	3.11	5.21	1.90	2.80	4.61
5d	1.55	2.10	3.20	2.28	3.55	6.10	2.06	3.11	5.22
6d	1.57	2.14	3.28	2.48	3.97	6.93	2.19	3.37	5.75
7d	1.58	2.16	3.33	2.68	4.36	7.71	2.30	3.60	6.20
8d	1.59	2.18	3.36	2.86	4.72	8.44	2.40	3.80	6.59
9d	1.59	2.19	3.37	3.03	5.06	9.12	2.48	3.96	6.93
10d	1.60	2.19	3.38	3.19	5.38	9.76	2.55	4.11	7.21
15d	1.60	2.20	3.40	3.84	6.69	12.38	2.79	4.58	8.16
20d	1.60	2.20	3.40	4.31	7.63	14.26	2.90	4.80	8.60
Limit	-	-	-	5.50	10.00	19.00	3.00	5.00	9.00

are negative or zero, in which cases limits cannot be formalized. There does indeed seem to be no limit when A is zero, but when it is negative a limit may sometimes exist. Unfortunately, one of these cases, where $\tau_{wd\ SO_2} = \tau_{ox\ SO_2} = 4d$ and $\tau_p = 2d$ is quite significant, because it is very close to our best guess for the parameters. As noted above, it was originally our best guess until the discovery of this instability, which clearly does not correspond to the observed situation. For this reason, our best guess for τ_p was changed from 2 to 2.5 d.

All things considered, we feel that it is remarkable that such a simple model into which uncertain estimates are placed should predict the observations so closely. We interpret this as confirmation that we are on the right track in our explanation of sulfate in the Arctic as being pollution-derived.

Now that conversion of SO_2 seems to be a reasonable explanation for the high sulfate concentrations at Barrow, it is of interest to revise the source inventory for winter sulfate at Barrow previously presented in Table 4. The revised data are presented in Table 7. The sea-salt, stratospheric and biogenic components are the same as before, except that it is now understood that certain biogenic emissions are included in the regional "pollution" figure. The big change is in the pollution-derived sulfate, which now includes a secondary component. Factors of increase for the sulfate were derived from Equation (8) and the best estimates of the various parameters, exact values of which can be found in Table 9. In contrast to Table 4, pollution sulfate now accounts for 58-67% of the total at Barrow. Volcanic sulfate was set at 5% of the pollution value, and accounts for about 3% of the total. When the five components are added, 80 to 90% of the sulfate is explained, in contrast to the 23 to 29% of Table 4. If it is assumed that

Table 7. Revised source inventory for winter sulfate at Barrow.

Component of sulfate		Concentration, μg m^{-3}
TOTAL		1.43
Sea-salt		0.27 (19%)
Stratospheric		0.00
Biogenic		~ 0
Pollution[1] (primary & secondary)	USA (10d)	0.96 } (58-67%)
	Europe & U.K. (5d)	0.83
Volcanic (5% of pollution)		0.04-0.05
SUBTOTAL		1.15-1.29 (80-90%)

[1] $\frac{SO_4^=}{V}$ source x Factor of increase by oxidation of SO_2 (Table 6) x $V_{BRW\ winter}$, μg m^{-3}

$[\tau_{wd}\ SO_2 = \tau_{ox}\ SO_2 = 4d;\ \tau_p = 2.5d;\ (SO_2/SO_4^=)_o = \{ {2.67\ USA \atop 5.0\ Europe}]$

sea-salt sulfate is the only component in the giant range, then pollution sulfate accounts for 72 to 83% of the submicron (excess) sulfate.

Estimating the $SO_4^=/V$ ratio in the Arctic from global emissions

So far in this document we have shown that conversion of SO_2 to sulfate in polluted air masses can account satisfactorily for the high sulfate of Arctic aerosols, assuming that all the noncrustal vanadium there is pollution-derived and taking either Europe or the northeastern United States as source regions. It is interesting to examine an alternate approach to the $SO_4^=/V$ ratio, namely global emissions of SO_2 and V, followed by partial conversion of SO_2 to $SO_4^=$. This approach is completely independent of our previous approach, which depends on the properties of each particular source region under consideration.

To do this, assume an annual global pollution emission for SO_2 and for V. Imagine both the SO_2 and V to be injected into the same air mass, which then ages for t days on its way to the Arctic. The equations of transformation are the same as before, except for an additional constraint that $(SO_4^=)_o = 0$. The predicted $(SO_4^=/V)$ ratio at time t is then:

$$\left(\frac{SO_4^=}{V}\right) = \left(\frac{1.5SO_2}{V}\right)_o \left\{\frac{k_{ox}\ SO_2}{A}\ \left[1 - e^{-At}\right]\right\} \qquad (10)$$

where the term $(1.5\ SO_2/V)_o$ represents the ratio of globally emitted S and V, with S being expressed as sulfate. The term in brackets on the right side then represents the change in ratio of observed $SO_4^=/V$ relative to what it would be at the source, had all the emitted SO_2 been instantly converted to sulfate. This factor is convenient to use in calculations, because the product of it and the globally emitted ratio (with SO_2 converted to sulfate) predicts what the observed $SO_4^=/V$ ratio should be.

This term in brackets also has a limit:

$$\lim_{t \to \infty} \frac{k_{ox\ SO_2}}{(k_{wd\ SO_2} + k_{ox\ SO_2} - k_p)} [1 - e^{-(k_{wd\ SO_2} + k_{ox\ SO_2} - k_p)t}] = \frac{k_{ox\ SO_2}}{(k_{wd\ SO_2} + k_{ox\ SO_2} - k_p)} \qquad (11)$$

provided of course that $A = k_{wd\ SO_2} + k_{ox\ SO_2} - k_p$ is positive.

As before, Table 8 give values for the bracketed term in Equation (10) and the limit in Equation (11) for various combinations of different residence times. This table is considerably simpler than Tables 5 and 6, because the initial value of $(SO_2/SO_4^=)$ is always zero. Values for travel times of 5 and 10 days, which are what we assume for winter transport from Europe and the northeastern United States, respectively, are underlined. Note that they are much smaller than the factors of change listed in Table 6.

The global emissions of SO_2 and V from pollution sources give a ratio which is quite close to that actually observed in the Arctic. Hence, when this figure is multiplied by the relatively small factors of change in Table 8, the predicted $(SO_4^=/V)$ ratios for the Arctic (from generalized global emissions) are very close to the observed ratios. This can be seen as follows: The current range of estimates of pollution emissions of SO_2 is 100 to 160×10^6 T y^{-1} (Bolin and Charlson, 1976; Kellogg et al., 1972; Friend, 1973; Peterson and Junge, 1971). Of these, we somewhat arbitrarily chose the value of Peterson and Junge (1971) as being the most reliable;

Table 8.
Factor of change of $SO_4^=/V$, starting from global emission of SO_2 and V.

τ_{wd} SO_2,d	3									4								
τ_{ox} SO_2,d	3			4			5			3			4			5		
τ_p,d	2	3	4	2	3	4	2	3	4	2	3	4	2	3	4	2	3	4
t = 1d	0.31	0.28	0.27	0.24	0.22	0.21	0.20	0.18	0.17	0.32	0.29	0.28	0.25	0.23	0.22	0.21	0.19	0.18
2d	0.57	0.49	0.45	0.46	0.39	0.37	0.39	0.33	0.31	0.61	0.52	0.49	0.50	0.43	0.39	0.42	0.36	0.33
3d	0.79	0.63	0.57	0.66	0.53	0.48	0.57	0.45	0.40	0.88	0.70	0.63	0.75	0.59	0.53	0.65	0.51	0.45
4d	0.97	0.74	0.65	0.85	0.63	0.56	0.75	0.55	0.48	1.13	0.84	0.74	1.00	0.73	0.63	0.89	0.64	0.55
5d	1.13	0.82	0.70	1.02	0.71	0.61	0.92	0.63	0.53	1.36	0.95	0.81	1.24	0.85	0.71	1.14	0.76	0.63
6d	1.26	0.87	0.73	1.18	0.78	0.65	1.09	0.70	0.58	1.57	1.04	0.86	1.49	0.95	0.78	1.40	0.86	0.70
7d	1.38	0.91	0.76	1.33	0.83	0.68	1.25	0.75	0.61	1.77	1.10	0.90	1.73	1.03	0.83	1.68	0.96	0.75
8d	1.47	0.94	0.77	1.46	0.86	0.70	1.40	0.80	0.63	1.95	1.15	0.93	1.98	1.10	0.86	1.97	1.04	0.80
9d	1.55	0.96	0.78	1.58	0.89	0.72	1.56	0.83	0.65	2.11	1.19	0.95	2.23	1.17	0.89	2.27	1.11	0.83
10d	1.62	0.97	0.79	1.70	0.92	0.73	1.70	0.86	0.66	2.26	1.22	0.96	2.47	1.22	0.92	2.59	1.18	0.86
15d	1.84	1.00	0.80	2.14	0.98	0.75	2.36	0.95	0.70	2.85	1.30	0.99	3.68	1.38	0.98	4.47	1.42	0.95
20d	1.93	1.01	0.80	2.43	0.99	0.76	2.92	0.98	0.70	3.24	1.32	1.00	4.88	1.45	0.99	6.87	1.55	0.98
Limit	2.00	1.00	0.80	3.00	1.00	0.75	6.00	1.00	0.71	4.00	1.33	1.00	100.5	1.50	1.00	-	1.71	1.00

τ_{wd} SO_2 ,d	5								
τ_{ox} SO_2 ,d	3			4			5		
τ_p,d	2	3	4	2	3	4	2	3	4
t = 1d	0.33	0.30	0.29	0.26	0.24	0.23	0.21	0.19	0.19
2d	0.64	0.55	0.51	0.53	0.45	0.41	0.44	0.37	0.35
3d	0.95	0.75	0.67	0.81	0.63	0.56	0.70	0.54	0.48
4d	1.25	0.92	0.80	1.11	0.80	0.69	0.98	0.70	0.60
5d	1.54	10.5	0.89	1.42	0.95	0.79	1.30	0.85	0.70
6d	1.81	1.16	0.96	1.75	1.08	0.87	1.64	0.99	0.79
7d	2.08	1.26	1.01	2.10	1.20	0.94	2.03	1.12	0.87
8d	2.34	1.33	1.05	2.46	1.30	1.00	2.45	1.24	0.93
9d	2.59	1.39	1.08	2.84	1.39	1.04	2.92	1.35	0.99
10d	2.83	1.44	1.11	3.24	1.48	1.08	3.44	1.46	1.04
15d	3.93	1.58	1.16	5.59	1.77	1.19	6.96	1.90	1.19
20d	4.87	1.64	1.17	8.59	1.94	1.23	12.78	2.21	1.27
Limit	10.00	1.67	1.18	-	2.14	1.25	-	3.00	1.33

it also happens to be the highest, and so may best represent the emissions of the late 1970's. The pollution emission of V is almost exclusively from combustion of petroleum (Zoller et al., 1973). World consumption of petroleum in 1976 was 2.87×10^9 T, which when multiplied by a mean V content of 50 ppm and a mean emission factor of 0.5 (both figures proposed by Zoller et al., 1973) give a global emission of 7.18×10^4 T y^{-1} of V. Thus the globally produced ratio of S (as sulfate) to V is $1.5(160 \times 10^6$ T$)/7.18 \times 10^4$ T, or 3.34×10^3. This figure is within 10% of the Arctic ratio for $SO_4^=/V$, and, as noted above, when multiplied by the relatively small figures of Table 8 will not change significantly.

Thus we reach the important conclusion that both global pollution emissions and extrapolation of the properties of specific polluted mid-latitude air masses can explain, within experimental uncertainties, the observed $SO_4^=/V$ ratios in the Arctic. This of course does not constitute hard proof, but it is strongly suggestive.

It is enlightening to see just how far the logic and calculations of this document can be pressed. To do this, we have refined the two types of above calculations, using the best values of the various parameters. Tables 9 and 10 show best values of the calculated factors of change of Tables 6 and 8, respectively. The new results have been summarized for winter conditions and summer conditions in Figures 3 and 4, respectively. On these diagrams the abscissa has no meaning - it is merely a convenient way of spreading out the data points. In the lower left of each diagram the $SO_4^=/V$ ratio is plotted for the source conditions. From this, an arrow points upward, representing the increase of the ratio for the stated number of days of travel, as calculated from Table 9. The arrow terminates

Table 9. Best values of change of $SO_4^=/V$ ratios in polluted air masses during transport.

τ_{wd} SO_2,d	4 ⟶			
τ_{ox} SO_2,d	4 ⟶			
τ_p,d	2.5 ⟶			
$(SO_2/SO_4^=)_o$	1.14	2.67	1.7	5.0
t = 1d	1.41	1.95	1.61	2.78
2d	1.77	2.81	2.16	4.40
3d	2.11	3.60	2.65	5.86
4d	2.41	4.30	3.10	7.18
5d	2.68	4.94	3.51	8.38
6d	2.93	5.52	3.88	9.46
7d	3.15	6.04	4.21	10.44
8d	3.35	6.51	4.51	11.33
9d	3.54	6.94	4.78	12.13
10d	3.70	7.33	5.03	12.85
15d	4.32	8.78	5.95	15.57
20d	4.70	9.66	6.51	17.21
Limit	5.28	11.01	7.38	19.75
	*	**	***	****

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*Northeastern United States in summer

**Northeastern United States in winter

***Europe & U.K. in summer

****Europe & U.K. in winter

Table 10. Best values of change of $SO_4^=/V$ ratios, starting from global emissions of SO_2 and V.

$\tau_{wd\ SO_2}$,d	4
$\tau_{ox\ SO_2}$,d	4
τ_p,d	2.5
t = 1d	0.24
2d	0.45
3d	0.65
4d	0.82
5d	0.98
6d	1.13
7d	1.26
8d	1.38
9d	1.48
10d	1.58
15d	1.94
20d	2.16
Limit	2.50

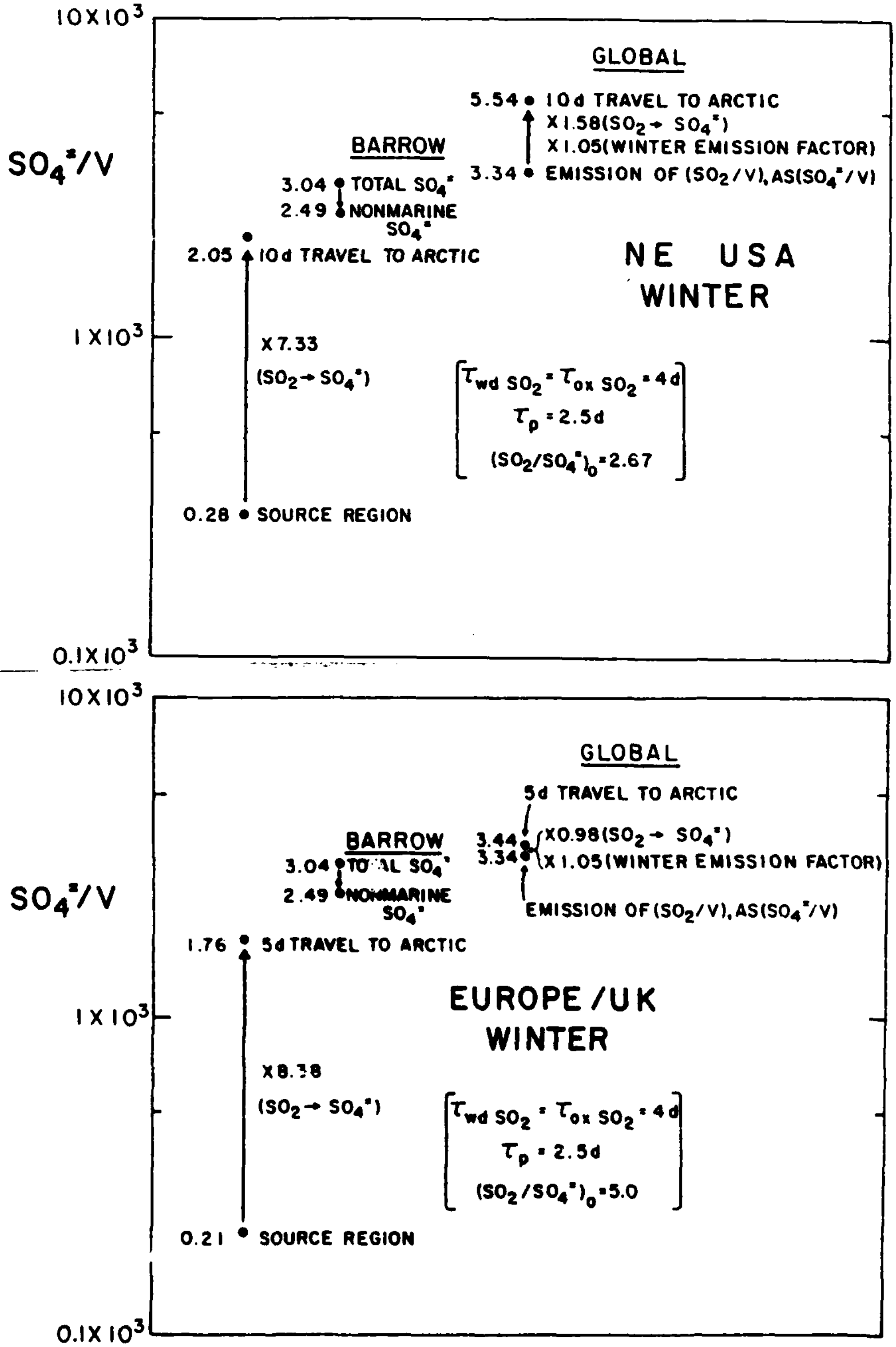


Figure 3. Derivation of Arctic winter ratios of sulfate to noncrustal vanadium from ratios of suspected sources.

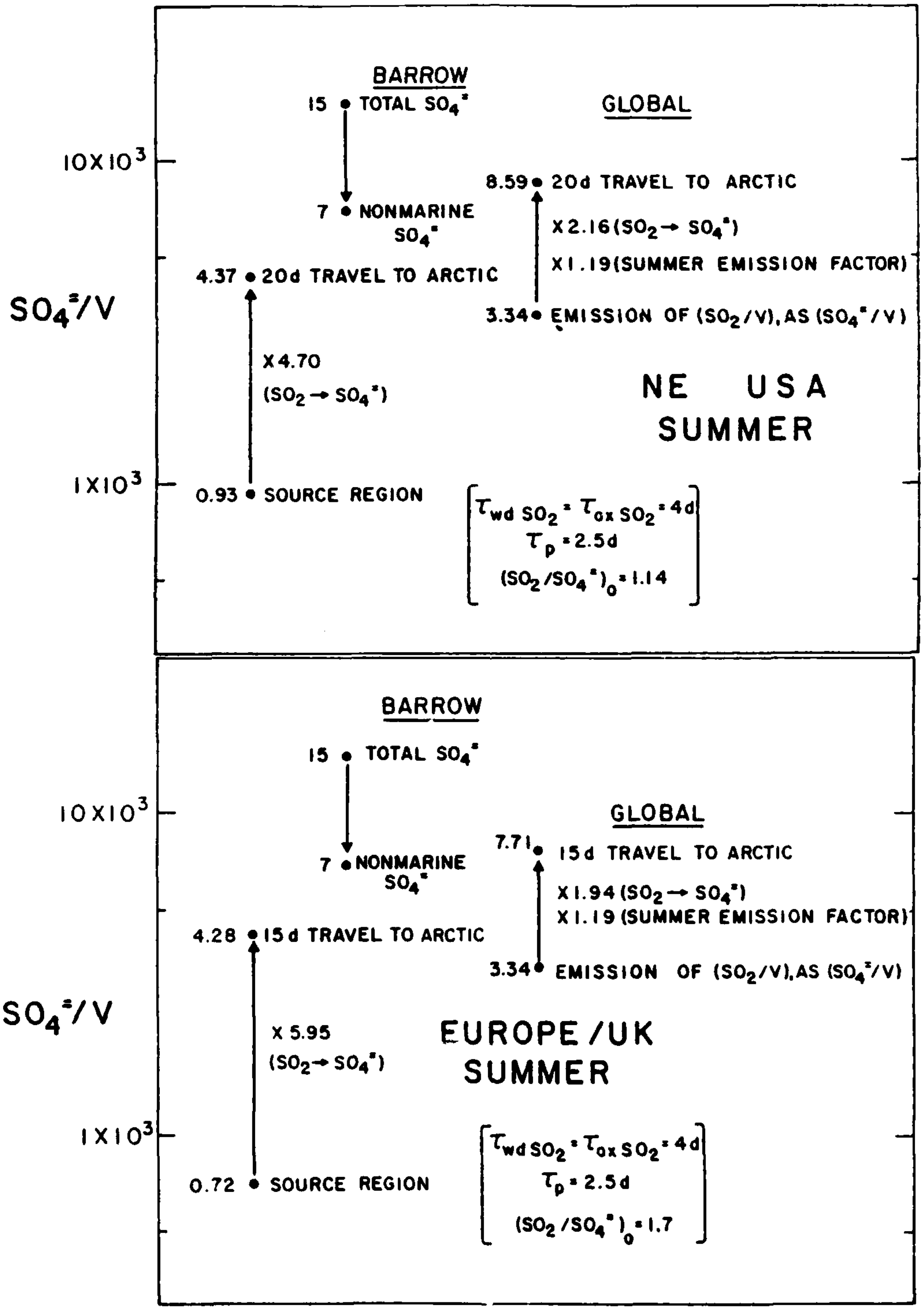


Figure 4. Derivation of Arctic summer ratios of sulfate to noncrustal vanadium from ratios of suspected sources.

at the final calculated value of the ratio. To the right of this terminus are values of the observed $SO_4^=/V$ ratio at Barrow in winter or summer, given for both total sulfate and nonmarine sulfate. The value for nonmarine sulfate is the one to which the two other estimates of these plots should be compared. On the far right of the plot appear the global estimates of $SO_4^=/V$, calculated both for annual mean direct emissions (with all SO_2 expressed as sulfate) and for aged seasonal emissions (derived from the global mean emission by multiplication by a seasonal emission factor and by an aging factor from Table 10). Again, the terminus of the arrow represents the final value.

The most striking feature of Figure 3 is how close both estimates of the $SO_4^=/V$ ratio come to the observed value. Considering all the uncertainties involved, for both types of estimates from both Europe/U.K. and the northeastern United States to come within a factor of about two is remarkable. One is tempted to ascribe this agreement to sheer chance, but we feel that this is not necessarily so, because the various parameters were very carefully chosen. The Europe/U.K. case seems to fit the data better than does the northeastern United States case, but this may not be a significant difference. The net effect of these two plots is to advance a very strong argument for the control of pollution gases and aerosol on the Arctic aerosol, and presumably also on Arctic haze.

We close this document with a discussion of Figure 4, for the summer period. Until now we have generally neglected the summer conditions, because we do not have as many reliable samples from summer as from winter, and because the concentrations of both vanadium and excess sulfate at Barrow are low enough to make the analysis less reliable than in winter. Furthermore, there is always the temptation, when confronted with an element whose concentration is an order of magnitude higher in winter than in summer, to confidently ascribe its winter origin to mid-latitude pollution, but to hedge about its summer origin because at those low concentrations, under conditions of weakened meridional circulation, other sources could easily come into play. Nevertheless, for completeness' sake we have attempted summer calculations, with the surprisingly good results of Figure 4. The summer $SO_4^=/V$ ratio at Barrow, which is 7×10^3 rather than the 2.5×10^3 of winter, is again explained to well within a factor of two by transport and aging of mid-latitude pollution aerosol. In fact, the agreement between calculation and observation seems better in summer than in winter. Interestingly, Europe/U.K. again seems to fit the observations better than the northeastern United States. Note that for these calculations the transport time from mid-latitudes was set at 10 days longer than in winter. This figure was derived from an unpublished analysis of various data for Barrow and Spitsbergen by the writer, which suggest that summer transport times to the Arctic are roughly 12 days longer than winter times.

Summary

The net result of our study of sulfate at Barrow has been to reinforce the notion that the pollution effect on the Arctic aerosol is a major one, and in fact may dominate all others. None of the logic or calculations advanced in support of this hypothesis are sufficient to prove it; rather they prove that it cannot be excluded from consideration.

We propose, therefore, that the pollution origin of the Arctic aerosol be seriously considered, and that a series of specific experiments be planned to test this idea further. The obvious vehicle for these experiments is the Arctic Air-Sampling Network, a cooperative venture between laboratories in several countries which is presently being started (Rahn, 1978).

It has long been said that the Arctic is a unique area. Our study of the Arctic aerosol confirms this notion. We know of no other remote area whose aerosol seems to be so dominated by imported aerosol, so much of which is ascribable to pollution sources. In view of the effect of the Arctic on the climate of the Northern Hemisphere, and because the Arctic aerosol may well play a role in the establishment of the Arctic climate, we feel that a more detailed study of the Arctic aerosol, its sources and modes of transport are more than justified.

One further note: Each new step in our knowledge of Arctic and Antarctic aerosols serves to increase our understanding of just how great the contrast between them is. This document proposes that the Arctic aerosol is mainly pollution-derived. The Antarctic aerosol, study of which has so far been limited mainly to the South Pole, is now seen to be mainly stratospheric (Maenhaut et al., 1978), and presumably natural. This is due to the combined effect of a number of factors, including the high elevation of the South Pole (3000 m), the much longer path lengths between continents and pole in the Southern Hemisphere than in the Northern Hemisphere, and the relatively small pollution emission in the Southern Hemisphere (10% of the world total). On balance, then, the Arctic, rather than the Antarctic, is thus emerging as the place where the large-scale effect of human activity on remote atmospheres can already be observed, monitored, and studied.

References

Altschuller A.P. (1973) Atmospheric sulfur dioxide and sulfate. Distribution of concentration at urban and nonurban sites in the United States. Environ. Sci. Technol. 7, 709-712.

Beilke S. and Gravenhorst G. (1978) Heterogeneous SO_2 - oxidation in the droplet phase. Atmos. Environ. 12, 231-239.

Bolin B. and Charlson R.J. (1976) On the role of the tropospheric sulfur cycle in the shortwave radiative climate of the earth. Ambio 5, 47-54.

Calvert J.G., Su F., Bottenheim J.W. and Strausz O.P. (1978) Mechanism of the homogenous oxidation of sulfur dioxide in the troposphere. Atmos. Environ. 12, 197-226.

Cawse P.A. (1974) A survey of atmospheric trace elements in the U.K. (1972-73). AERE Harwell Report R 7669. H.M. Stationery Office, London, 84pp.

Eggleton A.E.J. and Cox R.A. (1978) Homogeneous oxidation of sulphur compounds in the atmosphere. Atmos. Environ. 12, 227-230.

Eisenbud M. and Kneip T.J. (1975) Trace metals in urban aerosols. Research Project 117, Final Report - New York University, New York City, New York, 418 pp.

Eliassen A. (1978) The OECD study of long range transport of air pollutants: Long range transport modelling. Atmos. Environ. 12, 479-487.

Eliassen A. and Saltbones J. (1975) Decay and transformation rates of SO_2 as estimated from emission data, trajectories and measured air concentrations. Atmos. Environ. 9, 425-429.

Fisher B.E.A. (1978) The calculation of long term sulphur deposition in Europe. Atmos. Environ. 12, 489-501.

Flyger H., Lewin E., Thomsen E.L., Fenger J., Lyck E. and Gryning S.E. (1978) Airborne investigations of SO_2 oxidation in the plumes from power stations. Atmos. Environ. 12, 295-296.

Friend J.P. (1973) The global sulfur cycle. In: Chemistry of the Lower Atmosphere, Ed. S.I. Rasool, pp. 177-201. Plenum Press, New York.

Garland J.A. (1978) Dry and wet removal of sulphur from the atmosphere. Atmos. Environ. 12, 349-362.

Gravenhorst G. (1978) Maritime sulfate over the North Atlantic. Atmos. Environ. 12, 707-713.

Hanson K. (1976) Geophysical Monitoring for Climatic Change. No. 5. Summary Report 1976. NOAA Environmental Research Laboratories, Boulder, Colorado, 110 pp.

Hidy G.M., Mueller P.K. and Tong E.Y. (1978) Spatial and temporal distributions of airborne sulfate in parts of the United States. Atmos. Environ. 12, 735-752.

Hitchcock D.R. (1976) Microbiological contributions to the atmospheric load of particulate sulfate. In: Environmental Biogeochemistry, Volume I, ed. J.O. Nriagu, Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, pp. 351-367.

Hoste J., Dams R.,Block C.,Demuynck M. and Heindryckx R. (1974) Study of National Air Pollution by Combustion, Final Report 1974. Part I: Inorganic composition of airborne particulate matter. Instituut voor Nucleaire Wetenschappen, Rijksuiversiteit Gent, Belgium, 348 pp.

Junge C.E. (1963) Air Chemistry and Radioactivity. Academic Press, New York, 382 pp.

Kellogg W.W., Cadle R.D. , Allen E.R., Lazrus A.L. and Martell E.A. (1972) The sulfur cycle. Science 175, 587-596.

Lazrus A.L. and Gandrud B.W. (1974) Stratopsheric sulfate aerosol. J. Geophys. Res. 79, 3424-3431.

Lusis M.A. and Weibe H.A. (1976) The rate of oxidation of sulfur dioxide in the plume of a nickel smelter stack. Atmos. Environ. 10, 793-798.

Lynn D.A., Epstein B.S. and Wilcox C.K. (1975) Analysis of New York City Sulfate Data. Final Report EPA Contr. 68-02-1337, Task 10. GCA Corp., Bedford, Mass. 76 pp.

Maenhaut W.R., Zoller W.H. and Duce R.A. (1978) Concentration and size distribution of trace elements in the South Pole atmosphere. Unpublished manuscript.

Ottar B. (1978) An assessment of the OECD study on Long Range Transport of Air pollutants (LRTAP). Atmos. Environ. 12, 445-454.

Peterson J.T. and Junge C.E. (1971) Sources of particulate matter in the atmosphere. In: Man's Impact on the Climate, eds. W.H. Matthews, W.W. Kellogg, and G.D. Robinson, MIT Press, Cambridge, Mass., pp. 310-320.

Prahm L.P., Torp U. and Steen R.M. (1976) Deposition and transformation rates of sulfur oxides during atmospheric transport over the Atlantic. Tellus 28, 355-372.

Pueschel R.F. and Van Valin C.C. (1978) Cloud nucleus formation in a power plant plume. Atmos. Environ. 12, 307-312.

Rahn K.A. (1978) The Arctic Air-Sampling Network. Arctic Bull. (In press).

Rahn K.A., Borys R.D. and Shaw G.E. (1977a) Asian desert dust over Alaska: Anatomy of an Arctic haze episode. In: Proceedings of the AAAS Symposium "Desert Dust: Origin, Characteristics, and Effect on Man", Denver, 22-23 February 1977. (In press).

Rahn K.A., Borys R.D. and Shaw G.E. (1977b) Particulate air pollution in the Arctic: Large-scale occurrence and meteorological controls. In: Proceedings of the 9th International Conference on Atmospheric Aerosols, Condensation and Ice Nuclei, Galway, Ireland, 21-27 September 1977 (In press).

Rama (1963) Atmospheric circulation from observations of natural radioactivity. J. Geophys. Res. 68, 3861-3866.

Rodhe H. (1978) Budgets and turn-over times of atmospheric sulfur compounds. Atmos. Environ. 12, 671-680.

Smith F.B. and Hunt R.D. (1978) Meteorological aspects of the transport of pollution over long distances. Atmos. Environ. 12, 461-477.

Wilkniss P.E., Swinnerton J.W., Bressan D.J., Lamontagne R.A. and Larson R.E. (1975) CO, CCl_4, Freon-11, CH_4 and Rn-222 concentrations at low altitudes over the Arctic Ocean in Januay 1974. J. Atmos. Sci. 32, 158-162.

Zoller W.H., Gordon G.E., Gladney E.S. and Jones A.G. (1973) The sources and distribution of vanadium in the atmosphere. In: Trace Elements in the Environment, Advances in Chemistry Series, No. 123, American Chemical Society, Washington, D.C., pp. 31-47.

II. Renewal proposal: 1 October 1978 through 30 September 1980

A. Introduction and rationale

During FY 78 we have made important advances in our understanding of Arctic haze. Our new ideas are expounded in detail in the Progress Report section of this document; in this section it suffices merely to state that Arctic haze is now seen as a result of transport of sulfate-rich aerosol from midlatitudes to the Arctic during winter. The combination of hygroscopic sulfuric acid droplets and the high relative humidities of the lower Arctic winter troposphere creates a sulfate-based water haze which can have very high turbidities relative to the amount of "dry" parent aerosol. The near-absence of haze during the summer is attributable to the meteorological decoupling of midlatitutdes and Arctic.

In spite of these improvements in our understanding of Arctic haze, much still remains to be done, both in the short and long term. For example, we do not yet know for sure how much of the haze can be ascribed to pollution aerosol. Of the pollution component, we do not know how much comes from Europe, from North America, Japan, etc. We would like to know what the effect of the haze is on the northern environment by deposition (Are Alaska's lakes being acidified, for example?), by direct interaction with solar radiation (Is there a temperature increase associated with the haze that could cause the pack ice to melt a little earlier in the spring, or decrease the intensity of the general circulation by decreasing the temperature contrast between equator and pole?), or by a perturbation of cloud and/or precipitation formation. In a related vein, what might be the effects of increasing northern development and population on the northern environment? Can Arctic haze be significantly increased in the near future by any of the planned development in the relatively small Arctic? These and many other questions are of great interest.

We feel that our time during the next two years can be best spent by systematically attempting to fill in the various holes that remain in our knowledge of Arctic haze and the Arctic aerosol in general. As in the past, we propose to perform a combination of optical, chemical, physical, and meteorological studies of the Arctic atmosphere and its aerosol. A series of optical measurements of the Arctic aerosol will be made, and from these results the particle size distribution will be deduced by an inversion technique. Numerical modeling of the time evolution of the Arctic aerosol will be continued. An expanded network of ground-based aerosol-sampling stations will be methodically used to collect data on the chemical composition of the Arctic aerosol and its degree of temporal and spatial uniformity. A series of meteorological analyses will aid us in delineating features of the principal pathways of aerosol transport from midlatitudes to the Arctic which are being revealed by these ground stations. Counts of ice nuclei and cloud-condensation nuclei, which control formation of clouds and precipitation, will be taken at a number of the ground stations during summer and winter. The spatial and vertical distribution of the haze and the possible existence of a surface clear layer will be studied by survey campaigns in both Alaska and Greenland in spring 1979. The critical question of whether there is winter Arctic haze will be addressed by a series of flights at Barrow during December 1978, during which both visual and photographic observations will be made. To answer this question in more detail, we will attempt to obtain a Polaris photometer to determine optical depths at Barrow during the polar night. In an attempt to learn more about the past appearance and strength of Arctic haze, a series of interviews with retired weather officers who flew the Ptarmigan weather reconaissance missions over the Arctic Ocean will be conducted. In September 1979 a conference on the Arctic aerosol will be held at the University of Rhode Island.

The second year's activities, while basically the same as the first year's, will of course be tailored to the results of the first year. We will try to arrange for one month's use of the NCAR Electra for a comprehensive airborne study of various regions within the Arctic, probably during spring 1980. Details of this program such as location of sampling, time of year, elevations, etc., will depend on developments during FY 79. A spring campaign with the Electra would replace a ground-based Alaskan and Greenland spring campaign.

It should be noted that other sponsored research is now beginning to supplement our ONR work. Since 1 April 1978 Drs. Shaw and Rahn have been funded by NSF for further work on Arctic haze, mostly optical in nature. Currently, Drs. Rahn and McCaffrey have a proposal before NSF to study aerosol-snow fractionation in the Arctic. As will be mentioned below, NOAA has recently offered us modest funding and increased observer time at their Barrow site to continue our work there. As time goes by, our base of operations is thus being broadened.

The following section gives details of our intentions for FY 79 and 80.

B. General plan of the work

1. First year

a. Ground stations (KAR, TJC, GES, RDB)

During FY 78 we operated 4 Arctic and Arctic-related ground stations, each of which sampled the aerosol continuously: Barrow, Fairbanks, New York City, and Rhode Island. In addition, we received continuous sets of filters from the Norwegian sites of Spitsbergen and Bear Island, and winter and summer filters from Danish sites in northern and southern Greenland (see Section I.M.3. for details of sampling). We are analyzing all the filters for a number of trace elements by neutron activation at the University of Rhode Island. Although the analyses are still incomplete, the data so far have been invaluable in further documenting the general picture of transport of midlatitude aerosol to the Arctic which we are developing. We plan to continue this work for some years more, for several reasons: (1) The first two years of the study have been anomalous winters climatically, at least in interior Alaska; (2) The first two years' data from Barrow seem to be showing that the general winter-summer contrast in aerosol has sizeable difference from one year to the next, which are presumably related to variability in the general circulation. A thorough picture of the Arctic aerosol will thus require several years' data; (3) Our stations are part of the developing Arctic Air-Sampling Network, which will only begin full operation in the fall of 1979.

During FY 79 we hope to establish samping stations in Iceland and Ireland, in addition to the joint Canadian-American site at Alert, NWT which will begin operation in summer of 1979. The Iceland site is still very tentative; the Ireland site seems firm, though, and will be a cooperative venture with

Dr. Edward Monahan of the Department of Oceanography of University College, Galway. We expect to be able to get a good site on the western coast of Ireland, at which sampling could begin in spring 1979.

Although the analysis of so many filters requires a great deal of time and money, we feel strongly that the atmospheric chemistry at these Arctic sites cannot be properly characterized without year-round sampling, an approach which few research groups use. We have found that continuous sampling for a year or more at a given site illuminates the main sources of its aerosol in a way that is not otherwise possible. We expect that during FY 79 our continued analysis of filters from the Arctic Network will pay huge dividends.

Our feelings about the utility of this type of long-term study have recently been supported by the NOAA GMCC (Geophysical Monitoring for Climatic Change) program, observers for which change our filters at their site in Barrow. Dr. Kirby Hanson, director of the GMCC program, has been kept informed about the progress of our studies there. Recently he offered to partially support our work by purchasing replacement sampling equipment, providing increased observer time, and funding continuing sulfate analysis. With their help we will also begin particulate hydrocarbon sampling and turbidity monitoring at Barrow this fall.

We are requesting funds from ONR to set up a radon monitor for use at our ground sites, particularly Barrow. This instrument will be a portable beta detector which can measure the short-lived daughters of ^{222}Rn, which will provide a much-needed index of continentality of the air masses at Barrow (the principal source of ^{222}Rn, a radioactive noble gas, is degassing from the continental crust). With this easily transportable system it should be possible to derive a figure for the number of days since a given air mass has passed over a mid-latitude continental region. Our system will be based on the one developed about three years ago by Dr. Willy Maenhaut, then of the University of Maryland, and used at the South Pole, where the ^{222}Rn concentrations are considerably lower than those expected for Barrow. Although it will be mainly used in Barrow, we also plan to use this system in the Canadian Arctic and in Greenland. We feel that these measurements will give us much useful information about rates of transport of aerosol from midlatitudes to the Arctic; and possibly also about aerosol residence times in the Arctic.

b. Winter Barrow study (GES)

During the past few months there has arisen a great discussion within our group concerning whether the "spring" maximum of Arctic haze might really be a winter-long maximum. The reasoning here is very simple: chemical analysis of the ground-level filters from Barrow has shown that most elements in the aerosol, including vanadium and sulfur (as sulfate) have a broad winter maximum rather than a spring maximum. Assuming that these constituents, particularly sulfate, are the "raw materials" for Arctic haze, one would expect the haze to be present whenever they and high humidities were both present, namely all winter. According to this view, the spring "maximum" of haze in the Arctic is an artifact of measurement with radiation instruments which use the disk of the sun, and can thus only gather data between March and October.

To test this idea we have worked out a number of approaches to the question of winter haze at Barrow. The first and simplest involves a series of flights at Barrow during December 1978, during which Arctic haze will be sought by eye, looking toward the twilight part of the sky. In addition, this region will be photographed in order for it to be objectively compared with twilight photographs that will be taken later in spring, when haze is present and quantified.

We are also developing an alternate method of sensing haze from an aircraft, by impacting the aerosols onto a Collodion-coated 3-mm-diameter transmission-electron-microscope grid. The time of exposure is very short, about 4 minutes, so a series of samples can be exposed at, say, twenty different altitudes during a two-hour flight. The collected aerosols are then coated in a vacuum evaporator and analyzed with the Geophysical Institute's transmission electron microscope to obtain the particle concentration, mass loading and, for certain selected samples, an estimate of the particle-size distribution function by counting and classifying the particles according to their equivalent diameters. This method was developed and extensively applied by Dr. Keith Bigg, Division of Cloud Physics, CSIRO, Australia. Dr. Bigg visited the Geophysical Institute in June, 1978 and spent one week demonstrating and actually trying out the method there. During this time we independently used the method, and so already have a certain experience with it. We believe that this direct sampling method will pay high scientific dividends by allowing us to probe Arctic Haze at various altitudes during the winter.

But the key approach to the question of winter haze at Barrow will involve use of a photometer which monitors the brightness of Polaris during the polar night. Two Polaris photometers already exist, having been developed and proven in actual use by Dr. Gerald Romick of the Geophysical Institute. They were constructed for the purpose of deriving atmospheric optical extinction as part of the Geophysical Institute's auroral and airglow studies. Because these instruments, which are installed and operating at Ft. Yukon and Poker Flat Optical Observatories in Alaska, receive heavy use during the winter, it will be impossible for us to borrow either of them even for short periods. Rather, we plan to have a third identical instrument built for us at the Geophysical Institute, at a fraction of the cost of the prototypes. Funds for this instrument are expected to come from the NSF Arctic haze grant of Drs. Shaw and Rahn.

We will being constructing the photometer in September or October 1978, and after initial testing at Ester Dome Observatory, the instrument will be taken to Barrow by Dr. Shaw in December 1978. If the instrument works successfully, it will be left at Barrow for continued operation by personnel at the NOAA GMCC observatory.

c. Spring 1979 Barrow and Greenland campaigns (KAR, TJC, GES, RDB)

Our present idea of Arctic haze is that it is basically a combination of sulfate and water. One of the implications of this is that conditions suitable for its formation should be found throughout the Arctic during winter, because sulfate is a widespread, general pollutant. Recently, however, we have heard a report that Arctic haze is quite limited in extent, i.e. is not a general phenomenon of the Arctic. To settle the question once and for all we have decided that it is time to begin a systematic survey of the occurrence and properties of Arctic haze. Is it found as well over land as over the pack ice? Is it, as some reports would suggest, limited to areas near the Alaskan coastline? Does it occur in patches or is it really homogeneous? If large variations can be found, can they be related to synoptic-scale features of the circulation? Is it primarily associated with layers of high relative humidity, as our spring 1978 results would suggest? Also, what about the hypothesized surface clear layer? Is it a general feature associated with Arctic haze? These and other features can, we feel, be appropriately addressed by a series of surveys using sun photometers in aircraft, beginning in spring 1979. We plan to carry this out in two parallel operations, with G. Shaw and R. Borys at Barrow and K. Rahn and T. Conway in Greenland. At Barrow we will use NARL as a base, unless the scope of its facilities has already been too far reduced, in which case commercial planes and hotels will be used. In Greenland we plan to divide our time between Thule Air Base and Station Nord. Many details of all these sites can only be worked out much later, but the general plan at all of them is the same: to use sun photometers in aircraft, either on our own flights or those of others, to take carefully planned vertical profiles and/or widely spaced measurements of horizontal homogeneity. Given enough flight time, we are confident that a sufficiently broad data base can be established to begin to answer the above questions.

In addition to these survey measurements, more concentrated studies will be performed as time and facilities permit. At Barrow, for example, we expect to conduct a series of optical, chemical, and physical measurements at ground level. In Greenland we may be able to secure some high-volume aerosol and/or radon samples.

d. Optical studies (GES)

Although the principal task of Dr. Shaw during FY 79 will be construction of the Polaris photometer and its deployment in Barrow, additional effort will be expended in continuing to develop the various techniques that were used in the spring 1978 campaign and are described in Section I.H. These will be applied to the Fairbanks aerosol during the entire year and to the Barrow aerosol during the spring campaign of 1979. The principal immediate goals of these optical studies are to derive the particle-size distribution of the haze through inversion of optical data and to derive an estimate of the absorption term in the complex index of refraction of the haze aerosol; the long-term goal is of course to understand the potential climatic effects of Arctic haze. This optical work is also supported by our NSF Arctic haze grant.

e. Aerosol modeling (GES)

Work has been underway for several months on modeling the transport and time evolution of an aerosol as it is carried into the Arctic. First results of these theoretical studies are reported in Section I.E.; they have already improved our understanding of the Arctic aerosol. We propose to continue these studies during FY 79.

f. Meteorological analysis (RDB)

During FY 79 we will use meteorological analysis to determine large-scale air-mass trajectories from midlatitudes to the Arctic. Two techniques will be used, isentropic trajectory analysis and satellite imagery. Isentropic trajectory analysis is by far the best air-mass tracking method. It uses well-known conservative meteorological parameters to produce a three-dimensional picture of air motion. Dr. Elmar Reiter of CSU has a great deal of experience and expertise in this area, and has existing computer programs to aid in construction of these trajectories. The basic procedure is to construct a map of a surface of constant potential temperature for the desired portion of the atmosphere, then plot the air-parcel trajectory on it while conserving potential vorticity. This approach has limitations: it cannot be used with a precipitating air mass or with one whose potential temperature is constant over a great depth in the troposphere. This former can occur at any location in the Northern Hemisphere; the latter occurs in well mixed, dry atmospheres such as those of dust storms. Nevertheless, isentropic trajectories can be of great value, and we will construct them for a variety of situations.

Because of the paucity of meteorological data available from the Arctic and the North Atlantic and North Pacific Oceans, we will investigate the use of satellite imagery as an alternate technique to follow the advection of air masses to the Arctic. The CSU Department of Atmospheric Science has just installed a ground station to receive and record digitized pictures from the two GOES (Geostationary Earth-Orbiting Satellites) satellites located over the equator. In addition, the system can digitize photographs or use the original magnetic tape storage of photos from the polar-orbiting series of NOAA satellites. With its interactive terminal and color-enhancement techniques, coupled with the ability to make movie loops, this system should prove useful in our work. The system is called ADVISAR (All Digital Video Imaging System for Atmospheric Research), and is available for our use. It is the only system of its kind at a university at the present time. It represents a unique opportunity, and we intend to carefully test its feasibility.

g. Cloud-active Arctic aerosol

(The following is a mini-proposal from Mr. Randolph D. Borys, a graduate student in the Department of Atmospheric Science at Colorado State University. Formerly associated with our program at the University of Rhode Island, Mr. Borys has chosen the important topic of cloud-active Arctic aerosol as the subject of his Ph.D. research, and our program is providing half his graduate support. Because Mr. Borys has recently passed his qualifying examinations and is ready to begin his research in earnest, we felt that now was the time to offer this first full explanation of what he wants to do and why.)

Introduction

In order for the atmospheric scientist to properly assess the impact of human activity on weather and climate, it is necessary to know the distribution and effects of man-made contaminants on a global scale. Near urban areas, for example, it is well known that the local circulation, energy exchange, moisture budget, physical and chemical properties of the aerosol, and distribution of precipitation can be altered. But on the global scale, comparable data are almost completely lacking.

Our studies of Arctic haze and the Arctic aerosol, as supported by this ONR Contract, have led to the conclusion that the large turbidities of the Arctic atmosphere during winter may be largely due to anthropogenic aerosols interacting with water vapor. As far as we know, these studies are some of the very first to emphasize the potentially great environmental effects of anthropogenic aerosols at such great distances from their sources, which are presumed to be the midlatitudes. The intensity, and persistence, and probable widespread distribution of this haze has caused us to consider seriously whether there might be some kind of climatic effect from it.

It is important to note that the climatic effects of Arctic aerosol are due almost exclusively to the fact that they take up large amounts of water vapor from the atmosphere and thereby increase their effective mass by a large factor, which we have estimated at roughly 20. From a climatic point of view, it is therefore important to investigate in more detail the nature of this interaction between Arctic aerosol and water vapor. This is what we propose to study at CSU over the next few years. We will determine the amount of cloud-active Arctic aerosol as a function of location and season, the source(s) of this aerosol (which may be quite different from the sources of the total aerosol), and the characteristics of the Arctic cloud-active aerosol. Finally, we will attempt to specifically estimate the anthropogenic component of the total cloud-active aerosol, and predict the changes in haze, clouds, and precipitation in the Arctic that would result from changes in this component. This will be done by assessing the impact of anthropogenic aerosol on the mass, size distribution, index of refraction, and shape of the total Arctic aerosol (these are the aerosol parameters of importance to the Arctic radiation budget). In this way, we hope to derive a feeling for the sensitivity of Arctic climate to increasing human activity, both inside and outside the Arctic.

The importance of cloud-active aerosols

1. Cloud-condensation nuclei

Cloud-active aerosols can be defined as those dry particles which, when present in an atmosphere with sufficient water vapor, will initiate condensation of the water and grow in size as a function of the ambient water-vapor saturation ratio (relative humidity). These are generally called cloud-condensation nuclei (CCN), and can begin to condense water and grow at saturation ratios less than 0.3 (30% RH) (Winkler, 1973). When the relative humidity is sufficiently high, these aerosols will grow to cloud droplet size (5-50 μm). These droplets then interact very strongly with solar radiation in the visible portion of the spectrum, where most of the radiant power from the sun is located. The reflectivities of the cloud droplets are high and their transmissivities are low. In the terrestrial wavelengths, clouds are essentially black bodies. Welch and Cox (unpublished data, 1977a) have shown by using models that radiative properties of clouds depend on the concentrations and sizes of cloud droplets, and that accurate modeling depends on correct values of these parameters. Their work indicates that cloud reflectivity is primarily determined by the small cloud droplets, in the range of

5-10 μm in radius. A significant increase in the concentration of cloud condensation nuclei would affect the size range of cloud droplets, because the cloud-condensation nuclei would compete for available water vapor as their separation distance decreased. This would cause a decrease in their growth rate and tend to produce a cloud-droplet size spectrum with a peak at smaller radii.

Work done in Japan by Yamamoto and Ohtake (1953 and 1955) has shown that the largest fraction of the cloud-droplet nuclei observed at mountain sampling sites are combustion products. Kuroiwa (1951 and 1956) has shown that less than 50% of the sea-fog droplets whose nuclei were determined were composed of sea salt. The remainder of the nuclei analyzed were non-hygroscopic combustion or soil particles. More recent work by Van Valin _et al_. (1975) suggested that combustion of crude oil produced large amounts of CCN due to the formation of particulates with a high surface solubility. Van Valin and Pueschel (1976) also showed that CCN concentrations inside a plume downwind of a coal-fired power plant were a factor of two above that outside the plume. An increase in CCN was correlated with a decrease in SO_2, which suggested that a gas-to-particle conversion process was the mechanism for CCN production. Van Valin _et al_. (1976) found that CCN in the Denver, Colorado area could be attributed to traffic-derived substances, and that light scattering was primarily due to the CCN. Radke _et al_. (1976), in a study done in Barrow, Alaska in March 1970, showed that the largest concentrations of CCN occurred when the wind was from the northeast. They suggested that the high concentrations might have been due to transport from the Prudhoe Bay area of Alaska, or to long-range transport from Canada and the northeastern United States. The studies cited above have shown that CCN are quite varied in source and composition, and that the activities of man can play a role in the atmospheric condensation processes that lead to haze and cloud formation. This strongly suggests that a more detailed study of Arctic CCN is needed, in order to determine their source(s) and assess the importance of long-range transport to the Arctic.

Some of the above-mentioned studies found correlations between CCN and light scattering. The Arctic haze which we are studying is most likely due to condensation occurring on aerorols which might later become cloud droplets if given the proper conditions for further growth. Indeed, a gradation of haze into clouds was observed this spring near Barrow, Alaska. It is obvious that if measurements of the nature of CCN specify their source, the source of Arctic haze will also be determined. Arctic haze is a collection of aerosol particles which have grown into cloud droplet embryos which are in the optical size range (approximately 0.1 to 1.0 μm). These aerosols are those that have interacted with the available water vapor first. They are also the aerosols that a CCN counter will activate and grow to a visible size for subsequent counting and collection. Therefore a study of CCN is a study of the haze aerosol as well.

2. Ice Nuclei

Cloud-active aerosols also include ice nuclei (IN), which are responsible for the conversion of supercooled liquid water clouds to ice clouds, and are generally held to be responsible for the initiation of cold rain and snow. From a climatological point of view the Arctic is a desert. Being in the polar regions, IN play a significant role in the formation of precipitaion. A change in the IN concentration in such a region could have a significant effect on the amount of precipitation that falls. This would affect snow cover and consequently the surface albedo of the region. IN can affect clouds in two ways: (1) Initiating the freezing of a few droplets which would grow at the expense of neighboring droplets, and thus dissipate the cloud by acting as a seeding agent and precipitating the liquid cloud water;

(2) With an overabundance of IN, overseeding would occur, thus glaciating the cloud. The first would have an effect on cloud cover, the second would be important radiatively because of the change in the index of refraction of the cloud (water to ice). This would also form an ice cloud with a small mean radius of ice crystals. As noted above, Welch and Cox (1977, unpublished data) have shown from models that the concentration of small particles is important in determining the reflectivity and absorptivity of the cloud.

The composition and concentrations of natural background ice nuclei have been determined (Mason, 1971). These nuclei are generally soil or clay particles. Early work done in Japan at mountain sites by Kumai (1951) and Isono (1955) on snow crystal nuclei found a predominance of soil and clay particles at the center of each snow crystal, with combustion and hygroscopic particles also observed. Isono et al. (1959) attributed the source of these nuclei to the arid regions of north China or to volcanic eruptions in Japan. Later work (Isono et al., 1971) attributed the ice nuclei found at sites around the north rim of the Pacific Ocean, including Fairbanks, Alaska, to the long range transport of soil and clay material from the arid regions of the Asian continent. Hobbs et al. (1971) showed that ice nuclei "storms" observed at Fairbanks, Alaska; Mauna Loa, Hawaii; and Blue Glacier, Washington were related by the long-range transport of the ice nuclei from one location to the other. We have shown (Rahn et al., 1977) that these Asian soil aerosols can be advected well into the Arctic. It is quite apparent that natural ice-nuclei sources in mid-latitudes, combined with transport to the north, can possibly play a key role in the spatial and temporal variation of ice nuclei in the Arctic.

The effect of man-made aerosol on ice-nuclei concentrations has also been postulated (Schaefer, 1969) and shown (Weickmann, 1972) to have an effect on weather. Van Valin et al. (1975) showed that the combustion of crude oil led to an order-of-magnitude increase in IN concentrations. However, a similar study (Van Valin et al., 1976) failed to show an enhancement in IN concentrations in a coal-fired power-plant plume. It appears that different anthropogenic sources of aerosol behave very differently with regard to IN production. No work has been done on the effect of long-range transport of pollutants on IN concentration in remote regions. Radke et al. (1976) showed that highest IN concentrations occurred at Barrow, Alaska in March, when winds were out of the northern sector. This suggests a local Alaskan source.

Objectives

The proposed work is designed to obtain information on the climatic importance of cloud active aerosols in the Arctic by the following specific objectives:

1) Determine the concentration of CCN and IN at specific sites in the Arctic and suspected non-Arctic source regions.
2) Determine the elemental composition of these nuclei by electron microprobe analysis and relate the results to the transport paths of the nuclei to the Arctic, in order to delineate specific source regions.
3) Use the elemental composition of the bulk aerosol collected concurrently with the nuclei to aid in the identification of source regions.
4) By noting the morphology and size of the nuclei in conjunction with (2) and (3), determine what processes are important in the generation of the nuclei. Possible important sources include combustion, industrial processes, dust storms, natural fires, sea salt, gas-to-particle conversion, and production of aluminum oxide spheres.
5) Perform ancillary meteorological analyses to aid in the identification of source regions. Isentropic trajectory analyses will be performed when feasible, and isobaric trajectory analysis will be used when the available data coverage is too limited. Satellite imagery in the visible and infrared will also be used to track air-mass movements.

Plan of the work

1. Duration

This work is proposed for a two-year period. It will consist of concentrated field programs during winter and summer, each lasting about six weeks. The times chosen for these field programs will depend on our past experience with aerosol transport to the Arctic, and general knowledge of the seasonal variation of atmospheric transport processes.

2. Field sites

The solid line of Figure II.B.1.g.1. depicts the mean relative topography along 50°N for the normal maps of January given as departures from the mean value of the layer of the atmosphere between 100 to 1000 mb (Reiter, 1969). This shows the importance of a two-wave atmospheric planetary wave regime, primarily controlled by the cold Asian and North American troughs. The longitudinal location of these troughs is given by the valleys in the graph. The longitudinal regions of this plot, where the departure of relative topography is increasing, are regions of persistent transport to the north (30-90°W, 150-130°E). These correspond well to the major regions of cyclogenesis or eddy development in the Northern Hemisphere. Once cyclones or eddies have formed in these areas, they are advected to the north and east by the steering winds aloft. Therefore there are two major ways to transport air to the Arctic, mean transport on the persistent two-wave pattern, and transport via eddies on the mean. Peixoto (1960) and Starr and Wallace (1964) have shown that the eddy transport is even more important than transport via the mean in middle latitudes.

Figure II.B.1.g.2 shows a tentative model of the importance of mean meridional versus eddy flux of energy in the form of sensible heat plus potential energy in the Northern Hemisphere for summer and winter as shown by

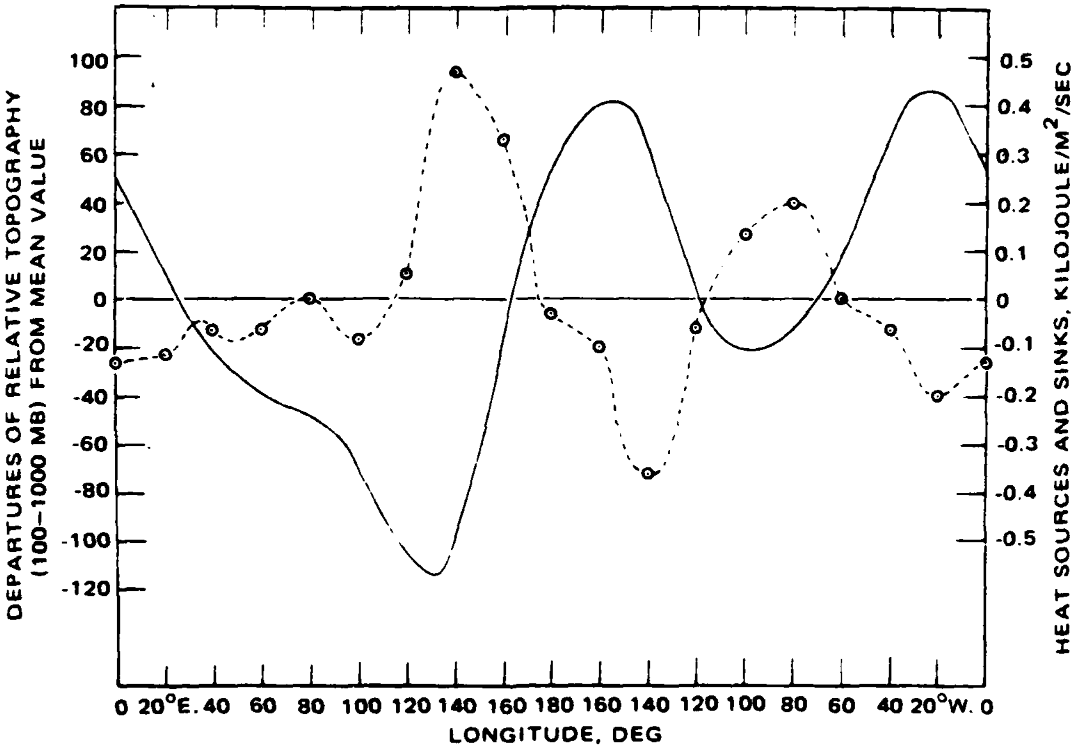
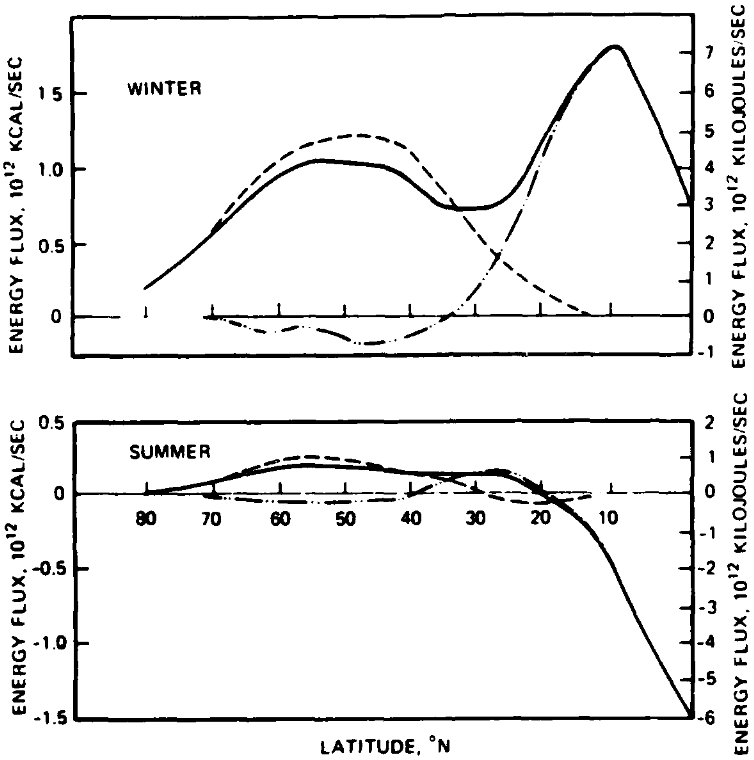


Figure II.B.1.g.1. Mean relative topography (solid line) along 50°N for the the normal maps of January, as departures from the mean value of the layer of the atmosphere between 100 and 1000 mb (after Reiter, 1969).



(a)

Figure II.B.1.g.2. Mean poleward energy flux for the northern hemisphere atmosphere (after Reiter, 1969). — = total flux, — ·· — = flux associated with mean meridional circulation, ------ = flux associated with zonal eddies.

Reiter (1969, pp 98-99). It is apparent from these curves that eddy transport dominates the mean, and is extremely important in the winter season. The eddy-energy transport is associated with cyclonic activity.

Petterssen (1958) summarized the eddy transport paths as follows: "On the Pacific side, we note a broad band of high cyclone activity extending from Southeast Asia to the Gulf of Alaska. Most of these cyclones form on the Pacific polar fronts... During the cold season, these storms acquire great intensity. Most of them travel northeastward and accumulate in the Gulf of Alaska, and this accounts for the high frequency in this region. On the Atlantic side, the conditions are similar to those on the Pacific Ocean. Storms develop frequently on the Atlantic polar front. The most favored region is the coast of Virginia and the general area to the east of the southern Appalachians. These move more or less along the Gulf Stream, develop to great intensity, and tend to stagnate in the vicinity of Iceland or over the waters between Greenland and Labrador. Many cyclones form or redevelop on the Atlantic arctic front and move eastward to the Barents Sea, as far east as Novaya Zemlya. Some of them continue along the entire coast of Siberia."

It is apparent that the most important gateway to the Arctic for mid-latitude aerosols is in the North Atlantic sector, and that the input to the Arctic may be dominated by a "pulsed" eddy mode on the mean. Therefore the best locations from which to investigate the effects of this transport during winter would be (1) in or downwind of major aerosol sources, (2) along the eddy transport path, (3) at the final or endpoint of the transport path to the north. During summer, field work performed at the same field sites would be important to evaluate the importance of the meridional transport in the winter, versus the lack of transport in the summer, on the nature of the cloud-active aerosol population at each location. The sites we have chosen are as follows:

a) The American Arctic

By American Arctic we specifically mean Barrow and Fairbanks, Alaska, where we already have aerosol sampling stations in operation, supported by local cooperation. These two sites are separated by the Brooks Range, which has a major effect of the distribution and type of aerosol found in Alaska. Barrow is dominated by true Arctic aerosol due to the prevailing northeast surface winds. It is located within the lower tropospheric arm of the direct-driven polar circulation cell. This places Barrow in the unique position of being near the "end of the line" for aerosol transport to the north in the Northern Hemisphere. This is a highly significant feature of the Barrow aerosol; Barrow is therefore an important location whenever studying the true aged Arctic aerosol. Figure II.B.1.g.3. depicts the mean meridional circulation streamlines (Van Mieghem and van Hamme, 1962). This demonstrates that transport from midlatitutdes to the north occurs in the lower troposphere before entering the polar circulation cell. The latter is the polar counterpart of the tropical Hadley cell. It is driven by the terrestrial radiative cooling that takes place in the polar regions, rather than the solar heating which drives the tropical Hadley cell.

Fairbanks (representing interior Alaska) is under the influence of transport to the north from regions to the south and west, which makes its aerosol quite different from the Barrow aerosol. We therefore believe that Fairbanks will be a good location from which to study the effects of aerosol transport from the North Pacific. This is especially true in the winter, when the local surface is snow-covered and much of the natural aerosol from interior Alaska (soil dust and biogenic material) is absent.

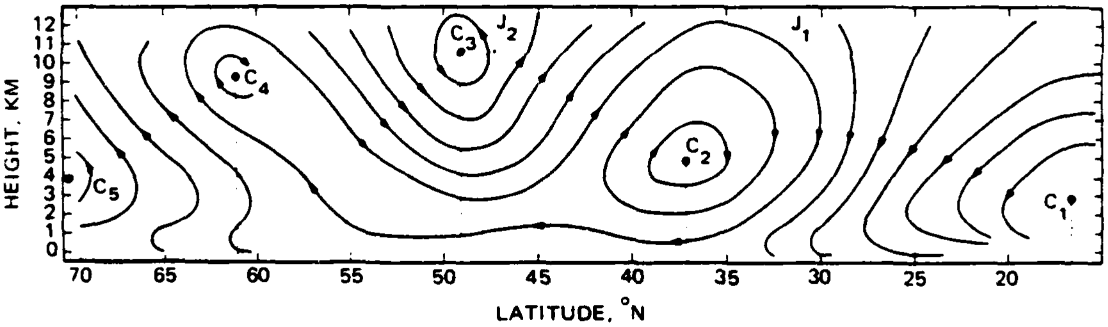


Figure II.B.1.g.3. Mean meridional circulation streamlines (after Van Mieghem and van Hamme, 1962).

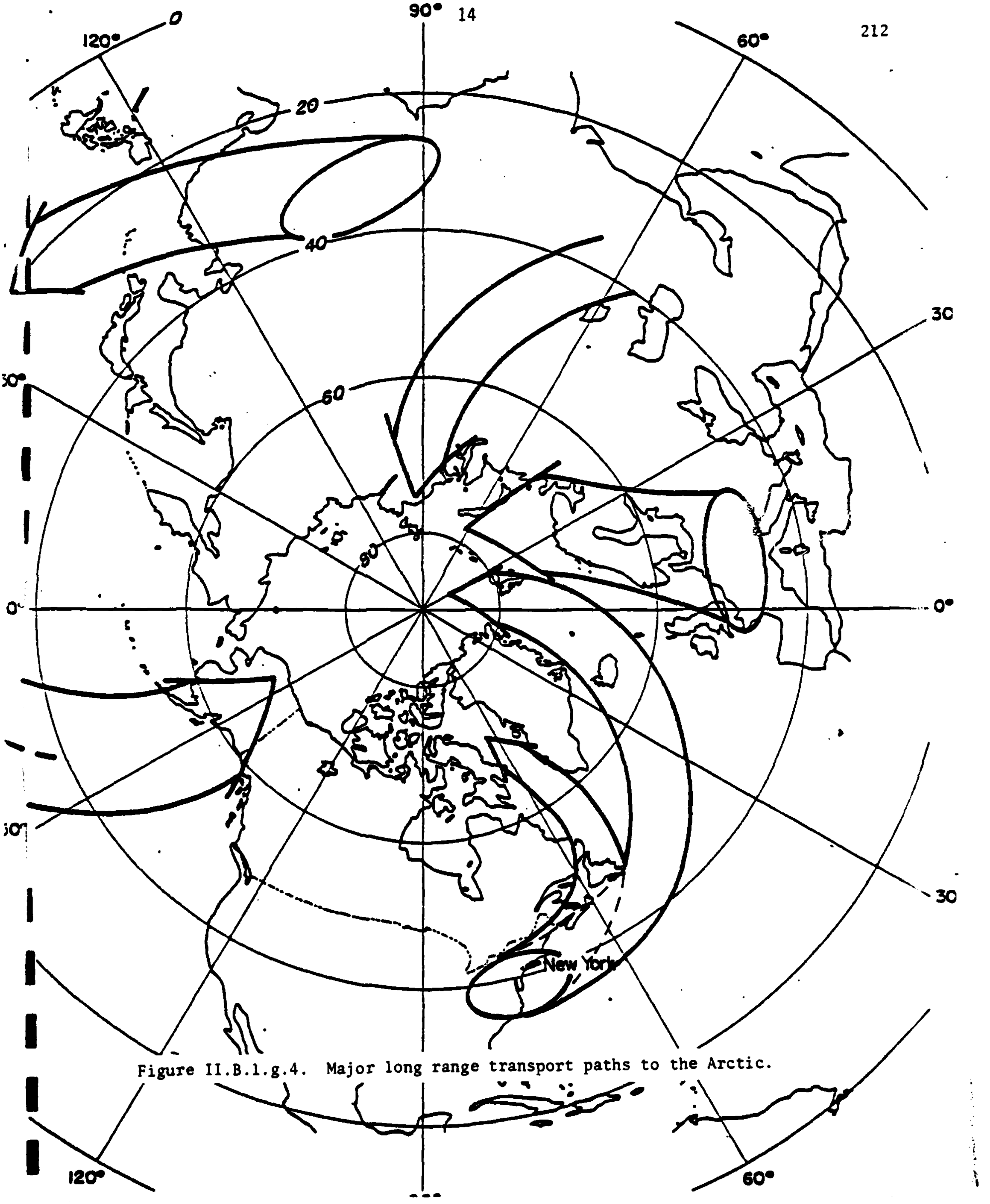


Figure II.B.1.g.4. Major long range transport paths to the Arctic.

b) The Canadian Arctic

Baffin Island is an important site because it is located midway between Barrow and the northeastern United States, along a favorable low-level transport path, as shown in Figure II.B.1.g.4. We feel this is a viable pathway to the North, and the shortest route of pollutants to the American Arctic. This pathway was also hypothesized by Radke et al. (1976) to explain the advection of CCN to Barrow, Alaska.

There is a provincial park with headquarters located in Pangnirtung, NWT, Canada on Baffin Island, just off Cumberland Sound. To date, no aerosol sampling has been done in this general region. We are initiating the procedures to make arrangements with the park personnel for a short visit.

c) The Eastern Arctic

Iceland is situated along the major transport path from North America to the Arctic (Figure II.B.1.g.4.). At this time there is no aerosol-sampling site there, but an Arctic-Network site is planned for the future (see Section I.M.3.). Our nucleus sampling does not require a support facility, and so can be conducted independent of the Arctic-Network site. Because Iceland is seldom affected by European aerosol, measurements there should represent aged North American aerosol.

Spitsbergen has many favorable aspects: (1) It has continuous aerosol sampling operated by Dr. B. Ottar of the Norwegian Institute for Air Research, who is currently sending portions of all samples to GSO-URI for trace-element analysis. (2) It is along transport paths from both North America and Europe. This will provide a unique location from which to determine the differences of the aerosol being advected from these two regions to the North. (3) At 78°N, it is well within the Arctic and will also be affected by polar air masses. Taken together, these three features of Spitsbergen will serve to provide a wealth of information from one location.

d) Source Area: Northeast United States

Based on results from our Arctic aerosol sampling, trajectory analysis, and general knowledge of ciruclation patterns descrived above, we feel that the Northeastern United States may well be one of the major sources of (anthropogenic) aerosol for the Arctic. For this reason, it is important to perform the same aerosol experiments in or near this source as will be done in the Arctic. Therefore, the Rhode Island GSO-URI site will be used to determine the nature of the cloud-active aerosol fresh from a strong source region.

3. Experiments to be performed at each site

At all locations, ground-based measurements of Aitken nuclei, CCN, and IN concentrations will be determined. A Nuclepore filter will be used for determination of particle-size distributions. Individual CCN and IN will be collected by using a Formvar replication technique (Schaefer, 1962; Parungo and Pueschel, 1973) for later analysis using a scanning electron microscope equipped with an electron microprobe and an energy-dispersive X-ray analyzer. When possible, replications will be made of falling snow crystals for comparison with the IN collected.

At Barrow, Alaska, an existing air sampling system will be installed on a Cessna 180 to determine the vertical profile of the cloud-active aerosol. Cloud droplets will be collected to compare their nuclei with those collected in the Mee thermal-diffusion chamber described below.

At all sampling sites except Iceland, a high-volume aerosol sample will be collected on acid-washed cellulose filters for 24-hour periods, as part of the Arctic Aerosol-Sampling Network. They will be analyzed by neutron activation analysis at GSO-URI for up to 35 trace-elements. These samples will be critical in the interpretation of the aerosol sources.

Instrumentation and methods

1. Meeda thermal diffusion chamber for IN analysis

Ice nuclei will be collected on Millipore filters, and will be analyzed by the Stevenson (1968) method using a commercial diffusion chamber produced by Meeda Scientific Instrumentation LTD, Israel. This instrument is available at Colorado State University's Cloud Simulation and Aerosol Laboratory. The chamber will be modified to allow the replication of the grown ice crystals for later SEM-EMP analysis on the nuclei. This technique has been used by M. Grosch and H.W. Georgii at the Institut für Meteorologie, Frankfurt, W. Germany. We are in contact with their group to become familiar with the technique.

2. Mee thermal diffusion chamber for CCN analysis

Cloud-condensation nuclei will be counted from photographs of the droplets developed in a Mee thermal diffusion Chamber Model 130. The counter will be modified to use an He-Ne laser light source to improve the photographic image and possibly permit droplet size distributions to be determined. The counter will be further modified to allow the collection and replication of the activated CCN for later analysis on the SEM-EMP. This instrument is available at CSU.

3. Gardner counter

Aitken nuclei concentrations will be determined using a portable Gardner counter.

4. Scanning electron microscope (SEM) size-distribution determination

Aerosol size distributions will be determined from photographs of the aerosol made on an SEM. The Aitken counts will be used to fill in the small size fraction not attainable with the SEM. This instrument is available at CSU.

5. Electron microprobe for individual particle analysis

The replicated IN and CCN samples will be analyzed using an electron microprobe for single-particle analysis. This technique has been used at the NOAA laboratories in Boulder, Colorado. Their experience and expertise with this method and their proximity to CSU will permit us to collaborate and will ensure our success. Only qualitative information will be gathered at the start. If time permits, quantitative analysis will be attempted. This instrument is available at CSU.

Field-sampling methods

All of the aerosol-collecting and counting equipment (Mee counter, Gardner counter, Millipore filter holders and pump) will be assembled in a portable unit requiring only battery power. All this equipment will operate on 24-V dc power, which will permit it to be used aboard aircraft, from an automobile, and from fixed ground sites. This will allow us to be flexible in selecting our sampling sites, in that we can easily avoid local contamination. The final trace-element analysis of individual aerosol particles will be done at CSU, with the only costs being for photographic film and developing.

Timing

The first year will be devoted to modification and testing of the field equipment and the field programs themselves. Analysis of samples will be begun, and investigations into the use of satellite data for air mass tracking will start. Isentropic trajectories for important past aerosol episodes in the Arctic will be constructed. The second year will be used to complete the analysis of the first year's samples, construct air mass trajectories for the interesting samples of this study, and to compile the results. Further field work will be undertaken as deemed necessary.

h. "Historical" studies

Now that the strong possibility that Arctic haze is significantly pollution-derived has been raised, we would like to try to test this idea by some sort of historical study of the haze. A number of proposals have been offered, all of which contain major problems. For example, the obvious approach of trace-element profiles through glacial cores from Greenland or northern Alaska, which is already being investigated by other groups, has to use samples from elevations of about 2000 meters or greater, where the ice does not melt significantly during the summer. But this is just about the upper limit of elevation of the heaviest Arctic haze, at least at Barrow, so that we are not certain that historical records deduced from Greenland would apply to the surface at Barrow or other Arctic sites. There do not seem to be any reliable near-surface glaciers in the Arctic which we could investigate.

Another possibility would be to examine the sediment record in Arctic lakes, such as those of northern Alaska or Canada. The problem with this approach, other than the obvious one that we have no guarantee as to just what these records would represent, is that most of the sediment would probably be derived from local terrestrial sources, and would therefore contain a great deal of crustal material, which would interfere with the smaller signal from the atmosphere that we were seeking. Further, during the winter when Arctic haze is present, the lakes are frozen, and direct entry from the atmosphere is thus blocked. For all these reasons we hesitate to begin a study of Arctic lake sediments.

An entirely different approach is to seek our photographic records of Arctic haze and/or recollections from persons who have flown over the Arctic as long ago as possible. The former weather officers of the Ptarmigan weather reconnaissance flights, which operated until the early 1960's, would seem to be an obvious group to start with. In cooperation with Dr. Paul F. Twitchell of the ONR Boston Branch Office, himself a former Ptarmigan weather officer, we have therefore come into contact with two other retired Ptarmigan officers and observers. Both are living in California and have expressed a willingness to be interviewed, even though they don't have any good slides. We are trying to locate more Ptarmigan personnel, and feel that this effort will pay reasonable dividends at low cost. We are therefore requesting a small amount of funding to pay for side trips to visit these or other persons, whenever a major trip of KAR brings him near one of them.

In the meantime, we will continue to consider various ways to obtain valid historical information about the intensity of Arctic haze. The most reasonable approach seems to be to investigate just how representative the aerosol over the Greenland Ice Cap is of the surface aerosol of the Arctic. Within the next two years we should have some information on this, provided by our spring field trips to Greenland for this project and by summer work in Greenland by the foreseen aerosol-snow fractionation project of Drs. Rahn and McCaffrey which is under consideration by NSF. (Incidentally, sulfate in recent snows from Station Milcent, Greenland, seems to be about 2.5 times more concentrated than it was in pre-1900 snows (Herron _et al._, 1977). If this figure is representative of the atmospheric change as well, then the majority of Arctic haze, which we feel is attributable to sulfate particles, would seem to be pollution-derived.)

i. Conference on the Arctic aerosol

As part of the plans for establishing the Arctic Air-Sampling Network, a conference on the Arctic aerosol was originally scheduled for April 1978 somewhere in Scandinavia. In January 1978, when it became apparent that the progress of most of the European groups studying the Arctic aerosol was considerably slower than previously anticipated, the date for this conference was postponed until September 1979 and the location was shifted to the University of Rhode Island, with K. Rahn as chairman and host. We are now beginning to plan actively for this conference. We expect that 50-100 persons will attend. The three-day conference will feature one or two invited talks, submitted presentations, informal presentations of very new data, and generous amounts of time for discussion. URI's Graduate School of Oceanography has offered to underwrite part of the costs of this conference; in addition, we will soon submit a small proposal to ONR to cover the rest of the costs. We hope that this conference will demonstrate to all who attend that the Arctic and its aerosol really are unique, and will also serve to establish Arctic air chemistry as a recognized discipline within the atmospheric sciences.

2. Second year

If the past history of our project is any guide, it can be safely said that the second year's work will reasonably resemble the first year's, because our general approach to the Arctic aerosol has proven successful, and we do not wish to tamper with it. We will therefore continue with our optical, chemical, physical, and meteorological approach during the second year, with brief winter, spring, and summer field experiments. On the other hand, experience has shown that each of our years' work has modified the next, and we have no reason to expect that the coming two years will be any different.

Therefore, rather than discussing in detail the work plan for the second year, we merely note here some of the ways in which it will differ from the first year.

The biggest potential difference in the second year's work will be a proposed spring 1980 campaign with the NCAR Electra aircraft. The availability of this aircraft is not assured - it is heavily scheduled far in advance. We will, though, attempt to get it for about a month in the spring. If successful, we envision flying it all over the Arctic. A major aircraft experiment would be particularly appropriate at that time, because we have recently become painfully aware both of how difficult it is to secure large aircraft for use in the Arctic, and of how much data on the upper-level aerosol really are needed to complement our copious ground-level data.

Dr. Shaw's research for the second year will likely be quite different from that of the first year, because it is expected that he will be able to get the Polaris photometer working properly by December 1978 or January 1979. After this, its use in Barrow should not be very time-consuming, and during the second year he will be able to turn his attention to other optical measurements of the Arctic aerosol, the exact nature of which has not yet been decided.

3. Specific timetable

November 1978	-	Move Ester Dome sampler to Poker Flat, AK. Set up Korean sampling system?
December 1978	-	Barrow experiment to look for winter haze with aircraft and Polaris photometer.
January 1979	-	Second technical meeting of the Arctic Network, URI.
March, April 1979	-	Field experiments in Barrow and Greenland. Install aerosol samplers in Iceland, Ireland?
June-August 1979	-	Field work in Barrow, NE USA, Canada, Iceland, Spitsbergen (RDB).
September 1979	-	Conference on the Arctic Aerosol, URI.
December 1979 or January 1980	-	Possible winter experiment at Barrow.

3. Specific timetable (cont.)

January, February 1980 - Field work at NE USA, Canada, Ireland, Spitsbergen (RDB).

March, April 1980 - Field work at Barrow and Greenland or NCAR Electra airborne sampling experiment.

June-August 1980 - Possible further field work in Barrow, NE USA, Canada, Ireland, or Spitsbergen (RDB).

C. Facilities available

University of Rhode Island

Two well-equipped chemistry laboratories, one in the Horn Building at the Graduate School of Oceanography and the other in the Rhode Island Nuclear Science Center (RINSC) adjacent to the School of Oceanography, will be used in this work. A new $30,000 Class 100 clean laboratory has just been constructed in the RINSC and is available for use. Also available for this project are two laminar-flow clean benches. A machine shop is located on the main campus.

All neutron activation analysis will be performed at the RINSC. The RINSC swimming-pool reactor operates at two megawatts and delivers a thermal neutron flux of approximately 4×10^{12} n $cm^{-2}sec^{-1}$ at the irradiation sites. Counting equipment available for this work includes several large Ge(Li) solid-state detectors and associated electronics, which may be used with Nuclear Data Model 2200 or Canberra Industries Model 8100 4096-channel analyzers or a Digital Equipment Corporation PHA-11 pulse-height analysis system. Data and spectrum reduction on these systems can either be done via magnetic-tape output with subsequent use of the IBM 370-65 computer on the main campus or directly on the PDP-11/40 computer which is part of the PHA-11 system.

Also located at the RINSC is a complete atomic absorption analysis laboratory, including three Perkin-Elmer instruments (Models 360, 503 and 603), HGA-2000 and HGA-2100 heated graphite atomizer attachments and other accessories.

For possible colorimetric analysis of sulfate, nitrate, etc., the RINSC has a Bausch and Lomb Spectronic 21 colorimeter which is freely available for our use. The Graduate School of Oceanography has a Stereoscan S4 scanning electron microscope (Cambridge Scientific Instruments, Lts.) which is available for general use. It features two CRT displays, a magnification range of 10-200,000 X and a resolution in the secondary election imaging mode of 150A at 30 kV. In addition, the GSO has a JEOL 50-JXA electron microprobe with 3-wavelength spectrometers and the KRISEL automation package, including a PDP-11/05 16K computer. This unit has 70-A resolution and a 1-μm beam.

University of Alaska

The Geophysical Institute is housed in the eight-story C.T. Elvey Building which was completed in 1970 on the West Ridge of the Fairbanks campus. Besides staff offices and laboratories, the building accomodates supporting services such as machine and carpentry work, electronics design and fabrication, photography, drafting, stenography, computing, data processing, the library, archives, conference facilities, etc. The Electronics Shop is experienced in designing, building, testing and repairing a wide range of scientific instruments. Its capability ranges from building small metering devices to design and fabrication of data acquisition systems using the latest in microprocessor control. The Electronics and Photography Stockrooms maintain a parts inventory of over 6,000 line items. These are a vital, local source of the latest electronic components for new designs, spare parts supplies, and bulk quantities of film, paper and chemicals for the institute's photo needs. The Machine and Carpentry Shop is probably unique in Alaska.

Well equipped with modern tools ranging from a precision jig borer to shapers, planers, milling machines, grinders, lathes and specialized facilities such as anodizing equipment, it includes also the welding and woodworking shops. The Photography Section offers a variety of technical and graphic-arts services including printing in color and black and white, routine processing of film from geophysical recorders, motion picture processing, reproduction of records, photo-fabrication, and slides for visual presentations. The Drafting Section produces illustrations for articles, reports, and slides as required by the scientific staff. The Electron Micriscope Laboratory is well equipped for biological and physical applications of electron microscopy. The JEM-6AS transmission electron microscope was acquired in 1964. A new addition to the laboratory is the JSM-35U scanning electron microscope, installed in the fall of 1977. Equipment such as a JEOL vacuum evaporator, a Zeiss compound research light microscope, and three Porter-Blum ultramicrotomes are available for use in specimen preparation.

Computer programming and data processing: The programming group is familiar with a variety of computers and a number of different programming languages and operating systems. The staff are available to write applications programs on the University's Honeywell 66/40 computer system or to provide consulting services for investigators. Time-share terminals to the computer are available throughout the building. A batch-entry station is available in the adjacent O"Neill Building. The Institute's data-processing system is built around a NOVA mini-computer which controls analog/digital conversion, plotting, two magnetic tape drives, and more specialized equipment. Personnel are available for key punching, data entry, scaling and other data-processing services. The Geophysical Institute Library offers a comprehensive coverage of solar-terrestrial physics, aeronomy, meteorology, climatology, glaciology oceanography, the solid-earth sciences, and environmental issues. The present collection includes more than 15,000 volumes, supplemented by reports and data compilations. The library subscribes to some 430 journals, magazines and newsletters from all over the world. The Geophysical Archives have been recently combined with the remote-sensing data library to provide shared facilities and a convenient broad data base. This combined facility is located adjacent to the library which provides easy access to scientific books, journals and reports as well. The geophysical archives contain a worldwide collection of auroral and magnetic records, together with a more selective sampling of records in the other geophysical disciplines, and the most complete collection of Alaskan remote-sensing data in the State. This includes Landsat and NOAA satellite imagery, low and hi-altitude aerial photography, side-looking airborne radar imagery and microform listings of current imagery acquisitions. Analysis equipment is also available, such as a roll-film viewer, microfilm reader, microfiche reader/printer, light tables, and stereoscopes.

Colorado State University

Relevant facilities at CSU are discussed in Section II.B.1.g.

D. Current support and pending applications

Dr. Kenneth A. Rahn - University of Rhode Island

Title	Agency	Duration	Amount	P.I. Time
Arctic Haze: Natural of Pollution? (This proposal N00014-76-C-0435)	ONR	1 Oct 1977- 30 Sept 1978 (renewal expected)	$88,262 (URI portion $74,742)	50%
Climatically Important Properties of Arctic Haze (with Dr. G.E. Shaw of the University of Alaska)	NSF/DPP	1 Apr 1978- 31 Mar 1979	$69,600 (URI portion $31,661)	50%

D. Current support and pending applications (cont.)

Title	Agency	Duration	Amount	P.I. Time
Pending Applications				
Methyl Iodide and the Atmospheric Iodine Cycle (with Dr. R.A. Duce and Mr. E.L. Butler of URI)	NSF	15 Oct 1978- 14 Oct 1981	$127,980	10%
Aerosol-snow Fractionation of Trace Elements (with Dr. R.J. McCaffrey)	NSF	1 Nov 1978- 31 Oct 1980	$154,536	15%
Dr. Glenn E. Shaw - University of Alaska				
DPP76-20629 Studies of the Atmospheric Radiation Field in Antarctica	NSF	7 Mar 1978 7 Mar 1979	$41,600	4 mo.
ATM77-04432 Studies of Scattered Sunlight in the Twilight Sky	NSF	15 Jul 1977 31 Dec 1978	$55,500	5 mo.
#55709 Arctic Haze: Natural or Pollution? (This proposal N00014-76-C-0435)	ONR	1 Oct 1977 30 Sept 1978 (renewal expected)	$18,767	2 mo.
#56729 Climatically Important Properties of Arctic Haze DPP77-27242	NSF	1 Apr 1978 30 Sept 1979	$37,939	4 mo.
Pending Applications				
Non-Local Sources of Arctic Haze	NSF	1 year	$61,021	
The Magnitude and Variability of Solar Spectral Irradiance	NSF	2 years	$185,711	
Submicron Particles in the Antarctic Atmosphere	NSF	1 year	$55,117	

E. Budget - Fiscal Year 1979

		URI	UA
(1)	Salaries		
	Co-principal investigator Dr. Kenneth A. Rahn Research Associate - 7 months	13,417	
	Mr. Thomas J. Conway Research Assistant - 12 months	14,000	
	Dr. Richard J. McCaffrey Research Associate - 1 month	1,600	
	Ms. Carla N. Pickering Secretary - 6 months	4,500	
	Co-principal investigator Dr. Glenn E. Shaw - 2 months @ 3382		6,764
	Technician - ½ month @ 2071		1,035
	Electron microscope technician - ½ month @ 2472		1,236
	Machinist - ½ month @ 2707		1,354
	Electronic technician - ½ month @ 2387		1,193
	SUBTOTAL		11,582
	10% Salary increment		1,158
	SUBTOTAL		12,740
	Reserve for annual leave 12%		1,529
	Holiday and sick leave 9.5%		1,210
	TOTAL SALARIES	33,517	15,479
(2)	Staff benefits: Hospitalization, social security, retirement 12% of total salaries		1,857
(3)	Permanent equipment		
	Centrifuge for sulfate analysis	600	
	Radon-analysis equipment	5,000	
	2 Rotron high-volume pumps @ 500	1,000	
	3 Sampling shelters (Iceland, Poker Flat, Ireland) @ 300	900	
	HP-67 calculator	450	
	Sun photometer	2,700	
	2 24-V DC vacuum pumps @ 225 (CSU)	450	
	30-A battery charger (CSU)	300	
	Impactor		1,300
	TOTAL PERMANENT EQUIPMENT	11,400	1,300

	URI	UA
(4) Expendable equipment and supplies		
Miscellaneous chemicals, labware, field supplies (URI)	2,000	
Miscellaneous chemicals, labware, field supplies (CSU)	750	
Filter holders, tubing, and supplies for 3 sampling shelters	1,900	
6 Magnehelic vacuum gauges (CSU)	350	
100-watt inverter (CSU)	75	
Filter holders (CSU)	200	
4 Batteries (CSU)	300	
Miscellaneous for modification of nucleus counting equipment (CSU)	1,000	
Aircraft-sampling supplies; miscellaneous for modification of aircraft-sampling equipment (CSU)	500	
Miscellaneous		500
TOTAL EXPENDABLE EQUIPMENT AND SUPPLIES	7,075	500
(5) Travel		
Domestic:		
Attend Hawaii ACS Meeting (1)	800	
RI - Barrow (2)	2,000	
Interview weather officers in California	600	
Barrow field expenses (winter 1978, spring and summer 1979)	11,600	
Field work in N.E. USA	500	
Colorado - Barrow (2) (CSU)	1,400	
Attend U.S. Meeting (1) (CSU)	250	
Colorado field tests (CSU)	150	
Fairbanks - Barrow (2)		326
Fairbanks - East coast, including 5 days subsistence @ $35/day		840
Fairbanks - Mauna Loa, including 5 days subsistence @ $35/day (for instrument calibration)		625
TOTAL DOMESTIC TRAVEL	17,300	1,791
Foreign:		
RI - Ireland, Iceland (set up 2 air-sampling systems)	2,000	
Thule AB, Greenland (30 man-days)	450	
Field work in Eastern Arctic	1,500	
Field work in Canada (CSU)	1,000	
TOTAL FOREIGN TRAVEL	4,950	-
TOTAL TRAVEL	22,250	1,791

		URI		UA
(6)	Publications	1,000		500
		100	(CSU)	
	TOTAL PUBLICATIONS	1,100		500
(7)	Other			
	Computer	1,000		
	Maintenance of sampling and analytical equipment	1,000		
	Freight	4,000		
	Telephone	1,000		
	SEM, EMP	500		
	Meteorological maps and microfilm	500		
	R. Borys, Colorado State University, nucleus counts	3,500		
	ADVISAR costs (CSU)	750		
	Maintenance of sampling and analytical equipment (CSU)	300		
	Freight (CSU)	750		
	SEM, EMP (CSU)	500		
	Satellite photos, tape, microfilm (CSU)	200		
	Postage and telephone			250
	Electricity for air-sampling sites			500
	SEM, 50 hr. @ $20/hr			1,000
	TOTAL OTHER	14,000		1,750
	TOTAL DIRECT COSTS	89,342		23,177
(8)	Indirect costs			
	Overhead @ 55% of total salaries	18,434		
	Overhead @ 57.9% of total salaries			8,962
	TOTAL COSTS	107,776		32,139
	GRAND TOTAL		$139,915	

Budget - Fiscal Year 1980

		URI	UA
(1)	Salaries		
	Co-principal investigator Dr. Kenneth A. Rahn Research Associate - 9 months	18,750	
	Mr. Thomas J. Conway Research Assistant - 12 months	15,400	
	Ms. Carla N. Pickering Secretary - 9 months	7,500	
	Co-principal investigator Dr. Glenn E. Shaw - 2 months @ 3382		6,764
	Technician - ½ month @ 2071		1,035
	Electron microscope technician - ½ month @ 2472		1,236
	Machinist - ½ month @ 2707		1,354
	Electronic technician - month @2387		1,193
	SUBTOTAL		11,582
	10% salary increment		1,158
	5% Salary increment		579
	SUBTOTAL		13,319
	Reserve for annual leave 12%		1,598
	Holiday and sick leave 9.5%		1,265
	TOTAL SALARIES	41,650	16,182
(2)	Staff benefits: Hospitalization, social security, retirement 12% of total salaries		1,942
(3)	Permanent equipment		
	1 Rotron high-volume pumps	500	
	4 Gast low-volume pump	1,200	
	1 Sampling shelter	300	
	EG&G Frost-point hygrometer	6,000	
	1 sun photometer		3,000
	TOTAL PERMANENT EQUIPMENT	8,000	3,000

Budget - Fiscal Year 1980 (Cont.)

	URI	UA
(4) Expendable equipment and supplies		
Miscellaneous chemicals, labware, field supplies (URI)	2,000	
Miscellaneous chemicals, labware, field supplies (CSU)	750	
Filter holders, tubing, and supplies for 1 sampling shelter	600	
Miscellaneous		1,000
TOTAL EXPENDABLE EQUIPMENT AND SUPPLIES	3,350	1,000
(5) Travel		
Domestic:		
Attend US Meeting (4)	2,000	
RI - Barrow (2)	2,000	
Barrow field expenses (winter 1979, spring & summer 1980)	12,000	
Field work in N.E. USA (CSU)	500	
Colorado - Barrow (2) (CSU)	1,400	
Attend U.S. Meeting (1) (CSU)	250	
Colorado field tests (CSU)	150	
Fairbanks - Barrow (2)		360
Fairbanks - East coast, including 5 days subsistence @ $35/day		900
Fairbanks - Mauna Loa, including 5 days subsistence @ $35/day		700
TOTAL DOMESTIC TRAVEL	18,300	1,960
Foreign:		
Attend GAF Annual Meeting	1,300	
Thule AB, Greenland (30 man-days)	450	
Field work in Eastern Arctic (CSU)	1,500	
Field work in Canada (CSU)	1,000	
TOTAL FOREIGN TRAVEL	4,250	-
TOTAL TRAVEL	22,550	1,960
(6) Publications	1,000 100 (CSU)	500
TOTAL PUBLICATIONS	1,100	500

Budget - Fiscal Year 1980 (Cont.)

	URI	UA
(7) Other		
Computer	1,000	
Maintenance of sampling and analytical equipment	1,000	
Freight	4,000	
Telephone	1,000	
SEM, EMP	500	
Meteorological maps and microfilm	500	
R. Borys, Colorado State University, nucleus counts	4,000	
ADVISAR costs (CSU)	750	
Maintenance of sampling and analytical equipment (CSU)	300	
Freight (CSU)	750	
SEM, EMP	500	
Satellite photos, tape, microfilm (CSU)	200	
Postage and telephone		250
Electricity for air-sampling sites		500
SEM, 50 hr. @ $20/hr		1,000
TOTAL OTHER	14,500	1,750
TOTAL DIRECT COSTS	91,150	26,334
(8) Indirect costs		
Overhead @ 55% of total salaries	22,908	
Overhead @ 57.9% of total salaries		9,369
TOTAL COSTS	114,058	35,703
GRAND TOTAL	$149,761	

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F. Comments on the budget

First Year

We are requesting a total of $139,915 from ONR for FY 79. Of this amount, $78,249, or about 56%, is salaries, fringe benefits, and overhead. Specific comments on the various sections of the budget follow.

(1) Salaries: We are requesting 7 months' salary for Co-Principal Investigator Dr. Kenneth A. Rahn of URI. This approximately half-time level of participation is formally the same as it has been in previous years, but is in reality essentially 100% on Arctic work because of supporting funding from an NSF Arctic haze grant which began 1 April 1978. This full-time participation on a single project is one of the main reasons that our work has been able to advance so much in the last few months.

We are also requesting 12 months' salary for Mr. Thomas J. Conway, our technical assistant on this project.

One month of salary is requested for Dr. Richard J. McCaffrey, who is presently working full-time on this project analyzing all our back samples from Barrow and Fairbanks for sulfate, using the ^{133}Ba tracer technique he has recently developed. This work has been enormously successful, and he will continue at it until (hopefully) he can be supported full-time starting 1 November 1978 on an NSF-sponsored aerosol-snow fractionation project, for which a proposal with Dr. Rahn is pending.

We are requesting 6 months' secretarial support, a level which is sharply increased from last year's 2 months. In fact, the success and expansion of our project has been such that it now consumes more than 50% of our secretary, Ms. Carla Pickering's time, with no letup in sight.

University of Alaska

We are requesting two months' salary for Co-Principal Investigator Dr. Glenn E. Shaw. In truth, Dr. Shaw is likely to spend more than two months on this work, especially now that he is drawing 4 months' support from the NSF Arctic haze grant. We are requesting ½ month of technician time for routine assistance in various matters, ½ month support for an electron microscope technician to assist with the analyses of Arctic haze aerosol samples taken directly on electron microscope grids according to the Keith Bigg technique described in Section II.B.1.b., and ½ month each of machinist and electronic technician time for construction of the Polaris photometer (also described in Section II.B.1.b.) and minor modifications of existing optical instruments. It should be noted that this construction time represents the only cost to ONR for obtaining the Polaris photometer - the majority of the funds will come from our NSF Arctic haze grant.

(3) Permanent equipment: We are requesting quite a bit of permanent equipment this first year. The largest single item is a radon-analysis setup for $5,000. We judge this piece of equipment to be a key one in our future work, because, as described in Section II.B.1.b., radon provides an index of continentality in an air mass. Because we have used the chemistry of the winter Arctic aerosol to deduce that it is primarily derived from polluted continents and is transported more rapidly during winter, we predict that radon concentrations should be higher at Barrow in winter than in summer. Confirmation of this idea by actual measurement would be a big boost to our understanding of the Arctic aerosol and its sources. This setup itself should be easily portable, and we plan to use it wherever we sample in the North.

We are requesting a centrifuge for our sulfate procedure. The centrifuge which we are presently using is borrowed from another group. Because this sulfate analysis will continue at the rate of several hundred samples per year (by a student assistant funded by NOAA), and because the sulfate data has proven so valuable to our work, we feel justified in requesting our own centrifuge.

We are requesting funds for two complete aerosol-sampling setups for Iceland and Ireland (stations in the Arctic Air-Sampling Network), and for one of our new-style shelters to be placed at Poker Flat, north of Fairbanks, when we move the Ester Dome sampling station this fall.

We wish to purchase an HP-67 electronic calculator, primarily for Dr. Rahn's use, to replace his personal aging HP-55. The HP-97 which we bought previously with ONR funds is receiving heavy use by T. Conway, and is essentially unavailable to K. Rahn. The HP-67 is the hand held version of the HP-97. Both calculators use identical magnetic cards for recording programs; all programs for both calculators are identical and the cards are interchangeable. With the great amount of calculation that we do, we feel that a second calculator is now necessary.

We are requesting $2,700 to purchase a sun photometer from Dr. Shaw for exclusive use by the URI group. For the last year we have been using a $100 Volz three-wavelength sun photometer for optical measurements at URI, first results of which appear in Section I.N.2. This instrument is very simple, however, and has severe limitations in sensitivity, drift, and calibration. We feel the need for a higher-quality instrument, especially because our field work of spring 1979 will for the first time have simultaneous operations in Alaska and Greenland, each of which will be strongly based on sun photometry. Dr. Shaw is making one of two new Mark V 10-wavelength sun photometers, a design of his that is perhaps the most accurate, sensitive, and reliable sun photometer in the world today, available to us at the cost for which they are being manufactured at the Geophysical Institute. With one of these photometers, we at URI can be assured of the greatest flexibility and accuracy in our chemical-optical Arctic field work.

We are requesting three items of permanent equipment for Mr. Borys at CSU, two 24-V DC vacuum pumps and a 30-A battery charger. These will be part of the field-sampling package he will be assembling for collection of cloud-active aerosol particles (see Section II.B.1.g.). This unit will be his basic sampling gear for all the field trips involved with his Ph.D. thesis research.

Lastly, we are requesting $1,300 for Dr. Shaw to construct a Keith Bigg-style impactor for electron microscope studies of Arctic haze particles. This will be a very small unit, which can be used either at the surface or from a small airplane. One of its potential uses, for studies of winter Arctic haze aloft, has been discussed in Section II.B.1.b. This unit would be constructed at the Geophysical Institute.

(5) Travel: We are requesting approximately $20,000 of travel funds for FY 79, approximately three-quarters of which is for field work in Barrow, Greenland, Eastern Canada, and the northeastern United States and Mauna Loa. Inasmuch as the majority of these funds are for Barrow expenses that previously were nonreimbursible, we feel that the amount is reasonable. The one conference specifically mentioned (American Chemical Society, Hawaii, April 1979) is having three sessions that are directly relevant to our Arctic work; transformation of gaseous sulfur to particulate forms (discussed here in Section I.N.4.), long-range transport of aerosol,

and deposition from the atmosphere (our problem of aerosol-snow fractionation). We have submitted two abstracts for consideration, but have not yet yet heard whether either has been accepted.

For foreign travel, the majority of the funds requested are for field work, in Greenland, the Eastern Arctic, and Canada. If anything, the amounts requested here are too small. In addition, we are requesting $2,000 for a trip to Iceland and Ireland to set up two air-sampling systems for the Arctic Air-Sampling Network. We hope that these sites can become operational in spring 1979.

We also anticipate another trip to Korea during FY 79. Funds for this will, however, be taken from FY 78 travel funds which remain.

(7) Other: We are requesting $3,500 as half graduate stipend for Mr. Randoph D. Borys at Colorado State University, to support his work on cloud-active nuclei in the Arctic atmosphere. The results of this study should be of great value to this project, and will constitute his Ph.D. thesis there. The other CSU costs identified here, such as the ADVISAR system, are explained in Section II.B.1.g, and are associated with his thesis work.

Second Year

We are requesting a total of $149,761 from ONR for FY 80. Of this amount, $92,051, or about 61%, is salaries, fringe benefits, and overhead. Specific comments on the various sections of the budget follow.

(1) Salaries: We are requesting 9 months' salary for Co-Principal Investigator Dr. Kenneth A. Rahn of URI. This represents an effective increase of 3 months over his 50% rate that has held since the beginning of this project. The basic reason for this increase is the success of our ONR work, which is now demanding more and more of Dr. Rahn's time. NSF

support for Dr. Rahn seems guaranteed for 3 months yearly for at least the next 2 years, we have therefore decided to request the remainder from ONR. There is also the chance of obtaining additional support for Dr. Rahn from a renewal of the NSF Arctic haze grant; if this is successful, the freed-up portion of his salary money will probably be used to add another technician to our URI staff. An extra body to assist in analysis of the large number of samples that we are obtaining from the Arctic Air-Sampling Network is more and more needed.

We are also requesting 12 months' salary for Mr. Thomas J. Conway, our technical assistant on this project.

We are also increasing our request for secretarial support from 6 months in FY 79 to 9 months in FY 80. This is an accurate reflection of the demands of our work on the time of our secretary, Ms. Carla N. Pickering.

University of Alaska

We have basically the same salary request for FY 80 that we had for FY 79, namely two months for Co-Principal Investigator Dr. Glenn E. Shaw and ½ month each for a general technician, an electron microscope technician, a machinist, and an electronic technician. While it is not possible to be as specific about the exact tasks of these technicians as it was for the FY 79 budget, our experience has shown that there will be an abundance of jobs for them generated by our project, particularly for the technicians who modify the various optical instruments of Dr. Shaw. We therefore consider these requests minimal.

(3) Permanent equipment: Our requests for permanent equipment are reduced from those in FY 79, primarily because the CSU nucleus-counting requirements will all have been taken care of in the first year. We are requesting one more Arctic-style high-volume air-sampling setup to give us

additional flexibility in our field operations. In addition, we are requesting 4 Gast low-volume vacuum pumps, of the type that we will use for our SO_2 sampling, because our inventory of these is so low. The largest item of equipment is an EG & G frost-point hygrometer, designed to be installed on various aircraft and used in conjunction with our sun-photometer measurements of vertical profiles of Arctic haze. A special hygrometer is needed for measurement of dewpoint in the winter Arctic atmosphere, where the water content is so low. This hygrometer will give us the most accurate measurements of dewpoint that are possible today, which toegether with the basic temperature readings from the aircraft will allow us to calculate vertical profiles of relative humidity. Examination of the relative-humidity dependence of the haze concentrations should give us further insights into the extent to which relative humidity controls the haze, the mechanism proposed in Section I.N.2. At present we have to rely upon radiosondes for our humidity information. Radiosonde density in the Arctic is very low, however, and humidity data often are available only for site which are hundreds of kilometers from where our aircraft data are taken.

For the University of Alaska we are requesting $3,000 for another sun photometer. At present we envision that this instrument could be very profitably used in conjunction with the Arctic Network, either by being based at one particular station or by roving between a series of sites. We feel that these measurements of turbidity, which apparently will not be conducted by other participating countries in the Arctic Network, will be valuable for us in eventually assessing the possible climatic effect of Arctic haze.

(5) Travel: We are requesting a somewhat reduced travel budget relative to FY 79. As in FY 79, most of both the foreign and domestic sub-budgets will go to field expenses for Barrow, Greenland, Canada, the

northeastern United States, Iceland, and Spitsbergen. As mentioned in the body of the proposal, during FY 80 we will try to obtain the NCAR Electra for a month-long field season in the Arctic. This, however, would not reduce our field expenses significantly, because meals and lodging would still have to be provided at the various bases of operation. In place of the Hawaii meeting we have substituted a series of unnamed US meetings, because we anticipate that by this time our results from the Arctic will be much more recognized and appreciated than they are now (we will also have more to say).

We are listing a single conference under foreign travel, the German GAF (Gemeinschaft für Aerosolforschung) annual meeting. Dr. Rahn is a member of this society, which is growing rapidly and whose annual meeting is beginning to attract great interest. Attendance at this meeting is very useful to Dr. Rahn, for it brings him in contact with European aerosol specialists that he otherwise would not meet. This meeting also provides an occasion to visit the Max-Planck-Institut für Chemie in Mainz, West Germany, the laboratory of Prof. C. Junge and the foremost institute of atmospheric chemistry. These visits are always invaluable. MPI and URI have a very close working relationship: Dr. Lothar Schütz of MPI visited URI for nine months during 1977, and Dr. Rahn spent 8 months at MPI in 1975 and 1976. MPI and URI will continue to cooperate both on desert-aerosol studies and on Arctic studies.

(7) Other: This sub-budget is nearly the same for FY 80 as it was for FY 79. The item most worthy of comment is the $4,000 for a half graduate stipend for Mr. Randolph D. Borys at Colorado State University, to support his continuing work on cloud-active nuclei in the Arctic atmosphere.

Co-Principal Investigator

NAME: Kenneth A. Rahn

EDUCATION: B.S. Massachusetts Institute of Technology, 1962
(Chemistry)

Ph.D. University of Michigan, 1971
(Meteorology)

PROFESSIONAL EXPERIENCE:

1976 - Present	Research Associate, Graduate School of Oceanography University of Rhode Island
1975 - 1976	Invited Visiting Scientist Max-Planck-Institut für Chemie, Mainz, West Germany
1973 - 1975	Research Associate, Graduate School of Oceanography University of Rhode Island
1971 - 1973	Research Associate, Institute for Nuclear Sciences University of Ghent, Belgium
1968 - 1971	Graduate Assistant, University of Michigan Ann Arbor, Michigan
1970 - summer	Lawrence Radiation Laboratory, Livermore, California
1963 - 1968	Science and Mathematics teacher Classical High School and Barrington College Providence, Rhode Island

PROFESSIONAL SOCIETY MEMBERSHIPS: American Chemical Society
American Association for the Advancement of Science
American Meteorological Society
Gesellschaft für Aerosolforschung

RECENT PUBLICATIONS:

Dams, R., J.A. Robbins, K.A. Rahn, and J.W. Winchester, "Non destructive neutron activation analysis of air pollution particulates", *Anal. Chem.*, *42*, 861 (1970).

Harrison, P.R., K.A. Rann, R. Dams, J.A. Robbins, J.W. Winchester, S.S. Brar, and D.M. Nelson, "Areawide trace metal concentrations in Northwest Indiana as determined by multielement neutron activation analysis: a one-day study", *J. Air Poll. Cont. Assoc.*, *21*, 563 (1971).

Rahn, K.A., R. Dams, J.A. Robbins, and J.W. Winchester, "Diurnal variations of aerosol trace element concentrations as determined by nondestructive neutron activation analysis", *Atm. Env.*, *5*, 413 (1971).

Dams, R., K.A. Rahn, G.D. Nifong, J.A. Robbins, and J.W. Winchester, "Nondestructive multielement analysis of air pollution particulates", Isotopes and Radiation Technology, 9, 54 (1971).

Rahn, K.A., J.J. Wesolowski, W. John, and H.R. Ralston, "Diurnal variations of aerosol trace element concentrations in Livermore, California", J. Air Poll. Cont. Assoc., 21, 406 (1971).

Dams, R., J.A. Robbins, K.A. Rahn, and J.W. Winchester, "Quantitative relationships among trace elements over industrialized Northwest Indiana", Nuclear Techniques in Environmental Pollution, International Atomic Energy Agency, Vienna (1971).

Dams, R., K.A. Rahn, and J.W. Winchester, "Evaluation of filter materials and impaction surfaces for nondestructive neutron activation analysis of aerosols", Env. Sci. Technol., 6, 441 (1972).

John, W., R. Kaifer, K. Rahn, and J.J. Wesolowski, "Trace element concentrations in aerosols from the San Francisco Bay area", Atm. Env., 7, 107 (1973).

Rahn, K., M. Demuynck, R. Dams, and J. DeGraeve, "The chemical composition of the aerosol over Belgium", Proceedings of the Third International Clean Air Congress, Düsseldorf, Germany, C81-C84, VDI-Verlag GmbH, Düsseldorf, West Germany (1973).

Heindryckx, R., M. Demuynck, R. Dams, M. Janssens, and K.A. Rahn, "Mercury and cadmium in Belgian aerosols," Colloquium on the Problems of the Contamination of Man and His Environment by Mercury and Cadmium, Luxembourg, July 1973, Sponsored by the Commission of the European Communities, Directorate Health Protection.

Rahn, K.A., G. Beke, and G. Windels, "An automatic filter changer for collection of short-period high-volume aerosol samples", Atm. Environ., 8, 635 (1974).

Rahn, K.A., R.D. Borys, and R.A. Duce, "The University of Rhode Island's air sampling program in the Northwest Territories", Report of Polar Meteorology Workshop, Reno, Nevada, 1975. Desert Research Institute Laboratory of Atmospheric Physics, Technical Report, Series P (Physical Sciences) No. 18, pp. 85-87, (1975).

Harrison, P.R., K.A. Rahn, R. Dams, J.A. Robbins, and J.W. Winchester, "Areawide trace metal distributions in northwest Indiana aerosols", in Trace Contaminants in the Environment, American Institute of Chemical Engineers Symposium Series, No. 149, pp. 19-25, André F. LeRoy, Ed., 1975.

Rahn, K.A., "Chemical composition of the atmospheric aerosol: a compilation I", Extern, 4, 286-313 (1975).

Rahn, K.A., "Chemical composition of the atmospheric aerosol: a compilation II", Extern, 4, 639-667 (1975).

Rahn, K.A. and P.R. Harrison, "The chemical composition of Chicago street dust", in Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants (1974), Symposium Proceedings, CONF-740921, NTIS, U.S. Dept. of Commerce, Springfield, VA 22161, pp. 557-570 (January, 1976).

Demuynck, M., K.A. Rahn, M. Janssens, and R. Dams, "Chemical analysis of airborne particulate matter during a period of unusually high pollution", Atmos. Env., 10, 21-26 (1976).

Rahn, K.A., R.D. Borys, and R.A. Duce, "Tropospheric halogen gases: inorganic and organic components", Science, 192, 549-550 (1976).

Rahn, K.A. "Silicon and aluminum in atmospheric aerosols: crust-air fractionation?", Atmos. Env., 10, 597-601 (1976).

Rahn, K.A., "Systematic chemical differences between the atmospheric aerosol and its deposition", Jahreskongress 1975 der Gesellschaft für Aerosolforschung e.V., 15-17 October 1975, Bad Soden (Tr., West Germany), 53-56 (1976).

Rahn, K.A., "The chemical composition of the atmospheric aerosol", University of Rhode Island Technical Report, 1 July 1976, 265 pp.

Rahn, K.A., R.D. Borys and R.A. Duce, "Determination of inorganic and organic components of gaseous chlorine, bromine, and iodine in the atmosphere", Special Environmental Report No. 10. Air pollution measurement techniques. World Meteorological Organization Report No. 460, Geneva, Switzerland, pp. 172-178 (1977).

Rahn, K.A., L. Schütz and R. Jaenicke, "The crustal component of background aerosols: its importance in interpreting heavy metal data", Special Environmental Report No. 10. Air pollution measurement techniques. World Meteorological Organization Report No. 460, Geneva, Switzerland, pp.150-156 (1977).

Rahn, K.A., R.D. Borys and G.E. Shaw, "The Asian source of Arctic haze bands", Nature, 268, 713-715 (1977).

Rahn, K.A., R.D. Borys and G.E. Shaw, "Asian desert dust over Alaska: Anatomy of an Arctic haze episode," Proceedings of the AAAS Symposium "Desert Dust: Origin, Characteristics, and Effect on Man", Denver, 22-23 February 1977, University of Arizona Press (Submitted).

Rahn, K.A., R.D. Borys, G.E. Shaw, L. Schütz and R. Jaenicke, "Long-range impact of desert aerosol on atmospheric chemistry: two examples", Proceedings of the Saharan Dust Workshop, Gothenburg, Sweden, 25-28 April, 1977. Sponsored by the Ecological Research Committee (Secretariat for International Ecology, Sweden) of the Swedish National Research Council, Sveavägen 166, 15 tr, S-11346 Stockholm, Sweden (In press).

Rahn, K.A., R.D. Borys and G.E. Shaw, "Particulate air pollution in the Arctic: Large-scale occurrence and meteorological controls", *Proceedings of the 9th International Conference on Atmospheric Aerosols, Condensation and Ice Nuclei*, Galway, Ireland, 21-27 September 1977 (In press).

Larssen, S. and K.A. Rahn, "Elemental concentrations of total suspended particulate matter in background areas in Scandinavia as a function of Northern Latitude." Discussion Paper No. R.3/COM,5, presented at Seminar on Fine Particles, Economic Commission for Europe, Villach, Austria, 17-22 October 1977. To appear in *Proceedings*.

Harrison, P.R. and K.A. Rahn, "Atmospheric particulate pollutants," In: *Review of Research on Modern Problems in Geochemistry*, UNESCO Report SC/GEO/544/3 (In press).

Walsh, P.R., K.A. Rahn and R.A. Duce, "Erroneous mass-size functions resulting from particle bounce-off in a high-volume cascade impactor", *Atmos. Env.* (In press).

Rahn, K.A., R.D. Borys, E.L. Butler and R.A. Duce, "Gaseous and particulate halogens in the New York City atmosphere", New York Academy of Sciences Monograph (Submitted).

Bernstein, D.M. and K.A. Rahn, "New York summer aerosol study: trace element concentration as a function of particle size", New York Academy of Sciences Monograph (Submitted).

Lioy, P.J., G.T. Wolff, K.A. Rahn, T.J. Kneip, D.M. Bernstein and M.T. Kleinman, "Characterization of aerosols upwind of New York City. I. Aerosol composition." New York Academy of Sciences Monograph (Submitted).

Rahn, K.A., "The Arctic Air-Sampling Network", *Arctic Bulletin* (In press).

Graham, W., L. Schütz and K.A. Rahn, "The transport of phosphorus to the North Atlantic by the Saharan dust plume", *J. Geophys. Res.* (To be submitted).

Leaderer, B.P. et al., "Summary of the New York Summer Aerosol Study (NYSAS)", *J. Air Poll. Control Assoc.* *28*, 321-327 (1978)

Rahn, K.A. and R.J. McCaffrey, "Low 'natural' enrichment of elements in Arctic snow: Derived from fractionated pollution aerosol?" *Nature* (Submitted).

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PH.D. DISSERTATION:

An Experimental Study of Atmospheric Turbidity Using Radiometric Techniques, May, 1971, The University of Arizona.

PUBLICATIONS:

Published Articles

Shaw, G. E., Cosmic count increase associated with thunderstorms, J. Geophys. Res., 72, 4623, 1967.

Shaw, G. E., Astrophotography with a short-focus lens, Sky and Telescope, 33, No. 6, 394-395, June 1967.

Shaw, G. E., Using a surplus aero-ektar, The Review of Popular Astronomy, p. 24, June 1967.

Shaw, G. E., Lightning current measurements collected at Mount Lemmon, Arizona, J. Geophys. Res., 75, No. 12, 2159-2164, April 1970.

Shaw, G. E. and G. Wendler, Atmospheric turbidity measurements at McCall Glacier in northern Alaska, Proceedings of the Atmospheric Radiation Conference, Fort Collins, Colorado, August 7-9, 1972.

Shaw, G. E., J. A. Reagan and B. M. Herman, Investigations of atmospheric extinction using direct solar radiation measurements made with a multiple wavelength radiometer, J. of Applied Meteorology, 12, 374, 1973.

Shaw, G. E., Observations and theoretical reconstruction of the green flash, Pure and Applied Geophysics, 102, 223, 1973.

Shaw, G. E. and K. A. Neiland, Electrocution of a caribou herd caused by lightning in central Alaska. The Journal of Wildlife Disease, 9, 311, 1973.

Shaw, G. E., R. L. Peck and G. R. Allen, A filter-wheel solar radiometer for atmospheric studies, Rev. Sci. Instrum., 44, 12, December, 1973.

Shaw, G. E., The vertical distribution of atmospheric aerosols at Barrow, Alaska, Tellus, 27(1), 39-50, 1975.

Weller, G., S. A. Bowling, B. Holmgren, K. Jayaweera, T. Ohtake and G. Shaw, The radiation matrix in the Arctic, Proceedings of Climate of the Arctic, 24th Alaska Science Conference, AAAS, Geophysical Institute Publication, 1975.

Shaw, G. E., Sky brightness and polarization during the 1973 African Eclipse, Applied Optics, 14, 386-394, February 1975.

PUBLISHED ARTICLES (Cont'd):

Shaw, G. E., An intercomparison of equatorial and polar multi-wavelength atmospheric optical depths and sky radiance, *Proceedings of the International Tropical Meteorological Meeting*, Nairobi, Kenya, 1974.

Russell, P. B. and G. E. Shaw, Comments on "The Precision and Accuracy of Volz sunphotometry", *J. Appl. Meteorology*, *14*, 1206-1209, September 1975.

Shaw, G. E. and C. S. Deehr, A photoelectric coronameter for atmospheric turbidity studies, *J. Appl. Meteorology*, *14*(6), 1203-1205, September 1975.

Shaw, G. E. and R. D. Hunsucker, A study of possible correlation between fairweather electric field and auroral activity. Conference Proceedings of the Fifth International Conference on Atmospheric Electricity, Garmisch Partenkirchen, W. Germany, September 2-7, 1974.

Holmgren, B., G. E. Shaw and G. Weller, Turbidity in the arctic atmosphere, AIDJEX Bulletin, No. 27, 135-148, November 1974.

Shaw, G. E., The polar aerosol-climatic implications, Workshop on Polar Meteorology, Reno, Nevada, 1975. Published by Desert Research Institute, Laboratory of Atmospheric Sciences, Technical Report 18, 94-98, 1976.

Shaw, G. E., The central antarctic aerosol-climatic implications, *Antarctic Journal of the United States*, *X*(4), July 1975.

Shaw, G. E., Observations of two stratospheric dust events, *J. Applied Meteorology*, *14*(8), 1614-1620, December 1975.

Shaw, G. E., Error analysis of multi-wavelength sunphotometry, *Pure and Applied Geophysics*, *114*, 1, 14, February 1976.

Shaw, G. E., Solar spectral irradiance: the role of earth-based measurements, in *Proceedings of the Solar Constant Workshop*, Calif. Inst. of Tech., Big Bear Solar Observatory Publication, 210-231, May 1975.

Shaw, G. E., Possible climatic consequences of the aerosol layer over the central Antarctic ice sheet, submitted to *J. Applied Meteorology*, October 1975.

PUBLISHED ARTICLES (Cont'd)

Shaw, G. E., Properties of the background aerosols and their effects on climate, Science, Vol. 192, pp. 1334-1336, June, 1976.

Shaw, G. E., Size distribution of background aerosols determined from multispectral measurements of atmospheric transparency, Antarctic Journal of the United States, X(5), September 1975.

Meinel, A. B., M. P. Meinel and G. E. Shaw, Trajectory of the Mt. St. Augustine 1976 Eruption ash cloud, Science, Vol. 193, July 30, 1976, pp 420-422.

Shaw, G. E., Nitrogen dioxide-optical absorption in the visible, J. Geophys. Res., 81, 33, pp. 5791-572, Nov. 1976.

Kienle, J. and G. E. Shaw, Augustine Volcano eruption: Observation during the initial explosive phase, submitted for publication in J. of Volcanology and Geothermal Res., Nov. 1977.

Shaw, G. E., A theoretical model of sky radiance during a total solar eclipse, Applied Optics, January 1978.

Rahn, K. A, R. D. Borys and G. E. Shaw, The Asian source of arctic haze bands, Nature, Vol. 268, p. 713, August 25, 1977.

Rahn, K. A. R. D. Borys, and G. E. Shaw, Arctic-wide aerosol pollution, submitted to Science, August 1977.

Papers Presented at Scientific Conferences

Shaw, G. E. and G. Weller, Airborne optical measurements of atmospheric aerosols near Barrow, Alaska. Presented at Annual Meeting, Pacific Northwest Regional Section, American Geophysical Union, Vancouver, B.C., Canada, October 16-19, 1972.

Shaw, G. E., Background aerosol size distribution at Mount Montezuma, Chile. Presented at Annual Meeting, Pacific Northwest Regional Section, American Geophysical Union, Missoula, Montana, October 18-19, 1973.

Shaw, G. E. and C. S. Deehr, Measurements of absolute sky brightness near the sun and their relation to atmospheric aerosols. Presented at the Annual Fall meeting, American Geophysical Union, San Francisco, California, December 10-14, 1973.

Shaw, G. E., Solar spectral irradiance, the role of earth-based measurements, presented at the Cal-Tech Solar Constant Workshop at Big Bear Solar Observatory, May 19-21, 1975.

Shaw, G. E., Climatic influence of the aerosol above the central Antarctic ice sheet, presented at IUGG Assembly, Grenoble, France, August, 1975.

PAPERS (Cont'd)

Shaw, G. E., Solar radiation research being carried out at the Mauna Loa Observatory, Presented at the conference on Global Monitoring for Climatic Change sponsored by the U. S. National Oceanic and Atmospheric Adminsitration, Boulder, Colorado, February, 1976.

Shaw, G. E., Derivation of solar spectral irradiance from ground-based stations. Presented at International Conference on Aerosols and Atmospheric Radiation, Garmisch Partenkirchen, W. Germany, August 1976.

Shaw, G. E., Physical and Climatic Properties of the Global aerosol. Presented at International Conference on aerosols and atmospheric radiation. Garmisch Partenkirchen, W. Germany, August 1976.

Rahn, K. A., R. D. Borys, G. E. Shaw, L. Schutz, R. Jaenicke, Long range impact of desert aerosol on atmospheric chemistry: two examples, Workshop on Saharan Dust Transport, Gothenburg, Sweden, April, 1977.

Shaw, G. E., Optical studies of Arctic haze, Workshop on Source and significance of natural and man-mand aerosols in the Arctic, Lillestrøm, Norway, April, 1977.

Rahn, K, R. D. Borys, and G. E. Shaw, Particulate Air Pollution in the Arctic-Large Scale Occurrence and Meterological Controls, Conference on Cloud Physics, Galway, Ireland, September, 1977.

Reports

Weller, G., S. Bowling, K. Jayaweera, T. Ohtake, S. Parker, G. Shaw and G. Wendler, Studies of the solar and terrestrial radiation fluxes over Arctic pack ice, ONR Contract N00014-71-A-0364-001.

Shaw, G. and C. S. Deehr, Relations between circumsolar sky radiation and atmospheric aerosols. Environmental Protection Agency Scientific Report, Research Triangle Park, North Carolina, EPA Report 650/4-75-012, 101 pp., June 1974.

Shaw, G. E., Radiative properties of atmospheric aerosols at Mauna Loa Observatory, Geophysical Institute, University of Alaska Report UAG R-238, 55 pp., June 1975.

Viezee, W., W. F. Dabberdt and G. E. Shaw, Lidar studies of the urban atmosphere in Fairbanks, Alaska, Alaska, SRI Project Report 3061, 45 pp., June 1975.

Shaw, G. E., Non-resonant scattered sunlight at twilight in Alaska, Geophysical Institute, University of Alaska Report UAG R-244, 51 pp., February 1976.

Reports (Cont'd)

Shaw, G. E. A rocket Investigation of mid-latitude mesospheric haze. Final report for National Science Foundation grant no. ATM73-00661

Shaw, G. E., Multi-wavelength turbidity at the Mauna Loa Observatory, Final Report, NOAA contract 036-032-35154, October, 1977.

Rahn, K. A., R. D. Borys, and G. E. Shaw, Asian desert dust over Alaska: Anatomy of an Arctic Haze Episode, Report for ONR project N00014-76-C-04J5, 69 pp.

Patents

G. E. Shaw, C. Deehr, Patent No. 3,979,596, Coronametric Instrument for aerosol measurement, September 7, 1976.

November 1977

III. References

Herron M.M., Langway C.C. Jr., Weiss H.V. and Cragin J.H. (1977) Atmospheric trace metals and sulfate in the Greenland Ice Sheet. Geochim. Cosmochim. Acta 41, 915-920.

Hobbs P.V., Bluhm G. and Ohtake T. (1971) Transport of ice nuclei over the North Pacific Ocean. Tellus 23, 28-39.

Isono K. (1955) On ice-crystal nuclei and other substances found in snow crystals. J. Meteor. 12, 456-462.

Isono K., Komabayasi M. and Ono A. (1959) The nature and the origin of ice nuclei in the atmosphere. J. Meteor. Soc. Japan 37, 211-233.

Isono K., Komabayasi M., Takeda T., Tanaka T., Iwai K. and Fujiwara M. (1971) Concentration and nature of ice nuclei in the rim of the North Pacific Ocean. Tellus 23, 40-59.

Kumai M. (1951) Electron-microscope study of snow-crystal nuclei. J. Meteor. 8, 151-156.

Kuroiwa D. (1951) Electron microscope study of fog nuclei. J. Meteor. 8, 157-160.

Kuroiwa D. (1956) Composition of sea-fog nuclei as identified by electron microscope. J. Meteor. 13, 408-410.

Mason B. (1966) Principles of Geochemistry, 3rd ed., Wiley and Sons, Inc. New York.

Mason B.J. (1971) The Physics of Clouds. Clarendon Press, Oxford, 671 pp.

Misaki M., Ikegami M. and Kamazoawa (1975) Deformation of the Size Distribution of Aerosol Particles Dispersing from Land to Ocean. J. Met. Soc. Japan 53, No. 2, 111-120.

Peixoto J.P. (1960) Hemispheric temperature conditions during the year 1950. Scientific Report No. 4, MIT.

Penkett S.A. et al. (1977) AERE Harwell Report R8723, Environmental and Medical Sciences Division, AERE Harwell, England.

Petterssen S. (1958) Introduction to Meteorology, McGraw-Hill Book Co., 327 pp.

Radke L., Hobbs P.V. and J.E. Pinnons (1976) Observations of cloud condensation nuclei, sodium containing particles, ice nuclei and the light scattering coefficient near Barrow, Alaska. J. Appl. Meteor. 15, 982-995.

Rahn K.A. (1976) Silicon and aluminum in atmospheric aerosols: Crust-air fractionation? Atmos. Environ. 10, 597-601.

P. 252 Blank

Rahn K.A. (1976a) The chemical composition of the atmospheric aerosol. University of Rhode Island Technical Report, 265 pp.

Rahn K.A., Schütz L. and Jaenicke R. (1976) Elemental composition of Sahara aerosol and Sahara soil. Presented at the Second Conference on Ocean-Atmosphere Interactions, Seattle, Washington, April 1976.

Rahn K.A., Borys R.D. and Shaw G.E. (1977) The Asian source of Arctic haze bands. Nature 268, 713-715.

Reiter E.R. (1969) Atmospheric Transport Processes Part I: Energy Transfers and Transformations. NTIS, TID-24868.

Schaefer V.J. (1962) The vapor method for making replicas of liquid and solid aerosols. J. Appl. Meteor. 1, 413-418.

Schaefer V.J. (1969): The inadvertent modification of the atmosphere by air pollution. Bull. Amer. Meteor. Soc. 50, 199-206.

Schütz L. and Jaenicke R. (1974) Particle number and mass distributions above 10^{-4}cm radius in sand and aerosol of the Sahara desert. J. Appl. Meteor. 13, 863-870.

Shaw G.E. and Deehr C.S. (1975) A photoelectric coronameter for atmospheric turbidity studies. J. Appl. Meteor. 14, 1203-1205.

Starr V.P. and Wallace J.M. (1964) Mechanics of eddy processes in the tropical troposphere. Pure Appl. Geophys. 58, 138-144.

Stevenson C.M. (1968) An improved Millipore filter technique for measuring the concentrations of freezing nuclei in the atmosphere. Quart. J. Roy. Meteor. Soc. 94, 35-43.

Twomey S. (1965) The application of numerical filtering to the solution of integral equations encountered in indirect sensing measurements. J. Franklin Institute 279, 2.

Twomey S. (1977a) Introduction to the Mathematics of Inversion in Remote Sensing and Indirect Measurements. Elsevier Scientific Publishing Co., N.Y., 237 pp.

Twomey S. (1977b) Atmospheric Aerosols. Elsevier Scientific Publishing Co., Amsterdam, 301 pp.

Van Mieghen J. and van Hamme J. (1962) Sur la production, la redistribution et la dissipation de l'energie cinêtique dans la circulation meridienne snogenne. Beitr. Phys. Atmos. 35, 213-233.

Van Valin C.C. and Pueschel R.F. (1976) Cloud nuclei formation in the plume of a coal fired powerplant. T. Amer. Geophys. Union 57, 925.

Van Valin C.C., Pueschel R.F. and Parungo F.P. (1975) Formation of cloud and ice nuclei by the combustion of crude oil. J. Appl. Meteor. 14, 1200-1203.

Van Valin C.C., Pueschel R.F., Parungo F.P. and Proulx R.A. (1976) Cloud and ice nuclei from human activities. Atmos. Environ. 10, 27-31.

Weickman H. (1972) Man-made weather patterns in the Great Lakes Basin. Weatherwise 25, 260-267.

Welch R. and Cox S. (1977) Absorption of solar radiation in clouds Part II: The effect of cloud bimodal drop size distributions upon the radiation field. Atmospheric Science Paper, Colorado State University.

Welch R. and Cox S. (1977a) Absorption of solar radiation in clouds Part III: Ice clouds. Atmospheric Science Paper, Colorado State University.

Weiss H.V., Herron M.M. and Langway C.C. Jr. (1978) Natural enrichments of elements in snow. Nature 274, 352-353.

Winkler P. (1973) The growth of atmospheric aerosol particles as a function of relative humidity - II. An improved concept of mixed nuclei. J. Aero Sci. 4, 373-387.

Yamamoto G. and Ohtake T. (1953) Electron microscope study of cloud and fog nuclei. Sci. Rep. Tohoku Univ., Ser. 5, Geophys., 141-159.

Yamamoto G. and Ohtake T. (1955) Electron microscope study of cloud and fog nuclei, II. Sci. Rep. Tohoku Univ., Ser. 7, Geophys., 10-16.