10.3 MEASUREMENTS OF NATURAL ICE NUCLEI COMPOSITION

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1. INTRODUCTION

The nature of ice initiation in clouds remains as an outstanding question in cloud physics. Understanding ice formation processes is important for developing physically based numerical models of precipitation and for predicting changes in precipitation and cloud radiative properties that might ensue due to anthropogenic influences on the atmosphere. There is a great need to identify the role of certain aerosol particles as indirect forcing agents on the cloud/climate system. Most research in this area has focused on aerosol effects on warm clouds. The Intergovernmental Panel on Climate Change (IPCC 2001) notes that effects of aerosols on ice-phase cloud processes are poorly understood, including the role of aerosols in altering precipitation formation processes and the radiative properties of cold clouds, particularly cirrus clouds.

Progress has been made in measuring the number concentrations, spatial and temporal variability, and activation conditions of aerosols that serve as heterogeneous ice nuclei in the atmosphere (see, e.g., Rogers et al. 2001 and references therein). Some experiments have directly related heterogeneous ice nuclei measurements to ice formation in clouds (Rogers and DeMott, 2002). Progress has also been made in laboratory studies to understand the homogeneous nucleation process that occurs on soluble aerosol particles in cirrus cloud conditions (see, e.g., DeMott, 2002 and references therein). Progress in identifying the chemical nature of particles that act as primary ice nuclei (IN) or alter the homogeneous freezing process has heretofore depended on tedious electron microscopy (EM) analyses of ice crystal residuals, collected from clouds by counterflow virtual impaction (e.g., Heintzenberg et al., 1996) or from ice nuclei processing chambers by direct impaction (Chen et al. 1998). While EM methods give excellent information on particle morphology and elemental speciation, the selection of particles for analysis can introduce subjective biases, statistics may be poor, the collection and storage process may modify particle characteristics, and detection of volatile species is not possible. A substrate-less method that indicates volatile and nonvolatile chemical composition could give better inferences to regional and global sources of aerosols that influence ice initiation processes.

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This paper presents preliminary results from measurements made with a new system for real-time measurement of the chemical composition of ice nucleating aerosol particles. This system utilized a continuous flow diffusion chamber (CFDC) to activate natural aerosols as ice nuclei, a counterflow virtual impactor to separate nucleated crystals from other aerosols in a flow system and a single particle mass spectrometer to measure the ionic composition of ice crystal residuals from the CFDC. The focus of the first measurements with this system was the role of different natural aerosols in forming cirrus clouds. Therefore aerosols were processed as ice nuclei at temperatures between –30 and –65^{o}C. Measurements were made in free tropospheric air sampled at a high altitude laboratory in November 2001 as a prelude to future aircraft deployment. Ancillary measurements were made of aerosol size distributions and meteorological parameters.

The results of this study have implications with regard to the long-range sources of natural IN, their relation to aerosol concentrations and properties, the contributions of anthropogenic sources to IN populations, and the interplay of heterogeneous and homogeneous ice nucleation as mechanisms for cirrus cloud formation.

2. METHODS

The key instruments interfaced in this study were the Colorado State University CFDC and the NOAA Particle Analysis by Laser Mass Spectrometry (PALMS) instrument. This instrument system is the subject of a separate paper (Cziczo et al. 2002) and so will be described only in modest detail here.

The CFDC IN processing device used in this study is essentially the same as described by Rogers et al. (2001), but with alterations to refrigeration systems to achieve aerosol processing temperatures as low as -65°C. In this diffusion chamber, airflow is directed vertically between two concentric ice-coated cylinders held at different temperatures, creating an ice-supersaturated zone in the annular region. The sample air containing aerosol particles, representing 10% of the total flow, is focused between two particle-free flows in order to define processing conditions. A one-way flow of compressed nitrogen provided sheath flow for this study since recirculation of air from PALMS was not feasible. Figure 1 shows the conditions at the aerosol lamina for various controlled wall temperatures in the operating regime used for most of this study. Residence time is sufficient to grow activated ice particles to sizes greater

than a few microns so that they may be optically detected as distinct from background aerosol particles. Further details on this instrument may be found at http://lamar.colostate.edu/~pdemott/cfdc/cfdc.html.

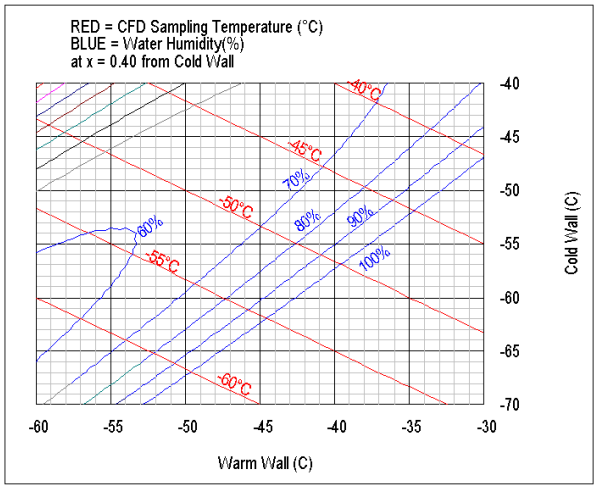

Figure 1. Continuous flow diffusion chamber aerosol processing conditions as a function of warm and cold cylinder temperatures in the processing regime used for most of this study. Figure courtesy of David Rogers (National Center for Atmospheric Research).

The NOAA PALMS instrument is described in detail by Thomson et al. (2000). This instrument has been used previously for a variety of studies of tropospheric and stratospheric aerosols. A web-based description and list of publications may be found at http://www.al.noaa.gov/PALMS. Aerosol particles are drawn by vacuum into PALMS. A fraction of these particles are detected by a YAG laser (λ = 532 nm), the scattered light from which triggers an excimer laser (λ = 193 nm) that ablates and ionizes individual particles. A complete positive or negative mass spectrum is obtained on particles above about 0.2 μm in diameter using a time-of-flight mass spectrometer. The primary motivation for using PALMS in this study were the ability to resolve both refractory and volatile components of aerosols and to do so in real-time. An aerodynamic focusing lens was adapted to the inlet of the PALMS instrument for this study in order to improve the fraction of particles detected (see Cziczo et al. 2002), an important factor when measuring IN populations.

The final key element of the measurement system in this study was a laboratory counterflow virtual impactor (LCVI) for removing nucleated ice crystals from the particulate flow exiting the CFDC. The operational principle of the LCVI was to counter the incoming flow with a warm, dry gas flow so that only particles of sufficient inertia were transmitted. The rate of counterflow determined the size of particles retained and actually enriched their number concentrations. The water in the retained ice crystals evaporated during transit to PALMS. This first application of CVI methods to in-line sampling is discussed in Cziczo et al. (2002).

Aerosol sampling using the experimental system was done during the INSPECT (Ice Nuclei Spectroscopy) program, conducted at Storm Peak Laboratory (SPL), located on Mt. Werner, elevation 3200 m MSL, in western Colorado. Borys and Wetzel (1997) describe this site and its use as a research facility (see, also, http://www.dri.edu/projects/spl). The key motivation for using this site was knowledge that it could reside within the free tropospheric air for extended periods of time. Ancillary aerosol concentration and size distribution measurements were also available from fine and ultrafine condensation particle counters, a scanning mobility particle sizing (SMPS) system and an aerodynamic particle sizer (APS).

The INSPECT experimental system is depicted in schematic form in Figure 2. A cyclone impactor sampling from an intake located about 10 m above ground level removed larger aerosols. This was a necessary step in order to reliably differentiate ice crystals from background aerosols using the CFDC optical particle detector. The lower “cut size” of the inlet impactor was set so that an optical particle counter detected no particles larger than 1 μm downstream. While a larger inlet cut size is typically used with the CFDC, slow ice crystal growth rates at the lower temperatures and flow conditions selected for use in INSPECT necessitated sampling smaller ice particles. While the inlet impactor limited the range of natural IN sizes that could be assessed, the mode size of IN apparent from earlier studies (Chen et al. 1998) was retained. A critical orifice (CO) was used upstream of the CFDC in order to lower pressure in the system to 500 mb, deemed optimal for LCVI operation. A nafion dryer fed by N_2 was used following the CO to lower water vapor pressure in the sample air so that spurious supersaturations did not occur during the initial cooling within the CFDC. Only ice crystals were noted at sizes above 1.5 μm for any CFDC processing conditions. Therefore, this size was selected as the size above which the LCVI would transmit particles to the PALMS instrument. The experimental methodology was validated in laboratory studies, using IN and non-IN particles, prior to deployment at SPL (Cziczo et al. 2002). Particle losses and transmission efficiencies were also determined. It was found possible to obtain one particle mass spectrum per 5 minutes when IN concentrations were 0.01 cm^{-3}. The LCVI/PALMS section was detached from the CFDC during selective sampling periods to collect direct impactor samples that are being analyzed by Transmission Electron Microscopy (TEM), the technique previously employed for analyzing ice crystal residuals from the CFDC (Chen et al. 1998).

In daily operations, PALMS would first sample aerosols directly from ambient air, with and without the cyclone impactor, prior to connection to the CFDC. The CFDC included a filtered-bypass for monitoring baseline ice particle production that might indicate non-aerosol induced frost particle formation in the instrument. It was possible to operate the CFDC for periods up to 3 hours before ice surfaces required refinishing.

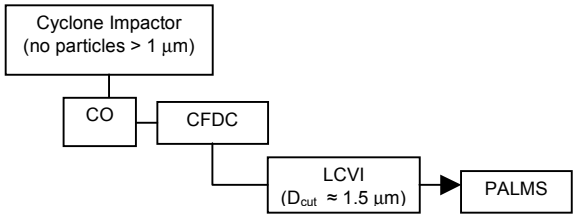

Figure 2. Schematic representation of the sampling procedure for INSPECT. Acronyms are described in the text.

3. RESULTS

3.1 Meteorology and Aerosols

The INSPECT sampling period, November 1 to November 19, 2002, was dominated by weak atmospheric flow conditions at the SPL site. Very few precipitating systems transited the area and, consequently, fewer than usual air mass changes occurred. Five-day (backward) air mass trajectories from the NOAA HYSPLIT model suggested that only three different source regions of particulate matter were represented. Air from the mid- and upper troposphere over East Asia and the Northwest Pacific Ocean was projected to have reached SPL during six project days (11/1-11/5, 11/19), most of these during the early part of the sampling period. This type of air mass was highly desirable due to the remote tropospheric origin and the potential contribution of dust aerosols from Asian desert regions, known to be a likely source of heterogeneous ice nuclei (e.g., Isono et al. 1959). During the remainder of the project, two similar air mass source regions were represented, differing only in the amount of time air was projected to have resided over continental areas. In half of these remaining days, trajectories suggest that air resided for extended periods under high pressure conditions over the Southwestern United States. During the other half, the 5-day back trajectories suggested mid-tropospheric origins in the Pacific Ocean off of Baja and Southern California. Precipitation events occurred on 11/8 and 11/18/01.

A time series of some aerosol data is shown in Figure 3. This indicates occasional diurnal cycles of aerosol concentrations (possibly valley air during the day and sinking mid-tropospheric air at night), some periods of lowered fine mode and accumulation mode aerosols, but also extended periods of similar aerosol distribution conditions. Two sampling periods of distinctly different accumulation mode distributions are noted by two arrows in the figure. These periods are examined next.

3.2 IN Concentrations and Nucleation Mechanisms

A comprehensive analysis of the IN data from the field study is not yet complete. For this paper, some characteristic results are presented, from which preliminary conclusions are drawn. A typical experimental time series of IN concentration, processing temperature and processing water vapor supersaturation (RH_w-100) is shown in Figure 4 based on data from November 9, 2001. Temporal variability in IN concentrations is evident, but peak concentrations (average concentrations as well) are seen to be sensitive to both temperature and water vapor supersaturation. The particularly strong feature in Figure 4 that occurs as relative humidity approaches 100% with respect to water reflects the transition from heterogeneous nucleation on a small fraction of the ambient aerosols to homogeneous freezing nucleation of a much larger fraction of liquid haze particles. These represent the first measurements of this phenomenon on a natural population of aerosols. IN concentrations ranged from ~0.001 cm^{-3} to 0.100 cm^{-3} in the heterogeneous regime, while nucleated concentrations in the homogeneous freezing regime were as high as 1000 cm^{-3}. The transition condition depended on temperature and daily aerosol characteristics. Some examples follow.

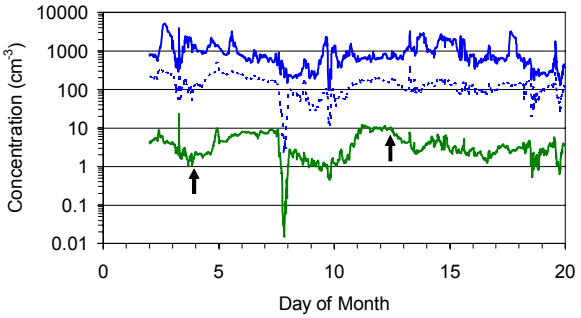

Figure 3. Selected aerosol data during the project period in November 2001. The blue lines are data from the SMPS system. The solid line is for the size range 12 to 350 nm, while the dashed line is for particles from 100 to 350 nm. The solid green line is for data from the APS instrument (542 to 20000 nm). Arrows indicate the two sampling periods highlighted in Figures 5 and 6.

CFDC data from two days representing different aerosol distributions and different apparent air mass sources are contrasted in Figures 5 and 6. Trajectory analyses place the sampling period early on the 4th of November within the category of Asian/North Pacific air masses, while the data on the 12th of November come from a period of transitions from the category of rather stagnant Southwest U.S. air masses to those originating off the coast of the Baja peninsula. Concentrations of particles with diameters larger than 0.1 μm on the 12th were higher by a few to 10 times those from the 4th of November. The plots shown in Figures 5 and 6 summarize IN concentrations as a function of water vapor supersaturation. There was only modest overlap of processing temperatures and relative humidities on

the two days. Nevertheless, IN concentrations appeared to reflect differences in accumulation mode particle concentrations for these similar processing conditions. At around -50°C, with water supersaturations in the –8 to –10% range (RH ≈ 90%), IN concentrations were about a factor of 3 higher on the 12th.

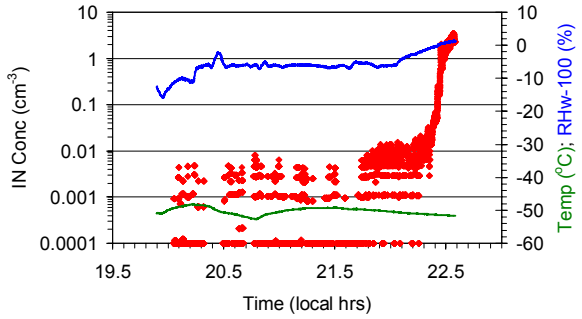

Figure 4. CFDC ice nuclei (IN) concentration (red data points; 30 s running mean values) as a function of processing temperature and relative humidity on November 9. Gaps in IN data are filtered data for determination of baseline. Data points plotted at 0.0001 cm^{-3} are zeroes.

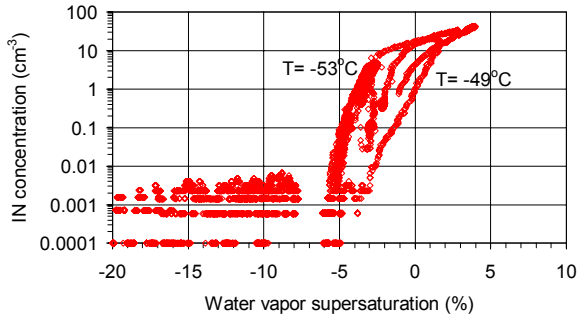

Figure 5. CFDC ice nuclei concentration from early on November 4, 2001, plotted as a function of water vapor supersaturation. Sampling temperatures between -45 and -53°C are represented. Temperature labels indicate the CFDC operating temperature when a temporal transition to homogeneous freezing nucleation occurred.

Transition conditions from heterogeneous ice nucleation processes to homogeneous freezing are indicated in Figures 5 and 6 by the sharp increases in apparent IN concentration at high RH. It is expected that homogeneous freezing of the dominant soluble aerosol populations should occur in this subsaturated regime when the temperature is below -40°C because the solute effect on lowering the homogeneous freezing point can be overcome within dilute haze particles (DeMott 2002). Likewise, it is also expected that the transition to homogeneous freezing will occur for more concentrated haze particles and therefore at lower relative humidity (greater subsaturation) as temperature decreases. The transition conditions shown in Figures 5 and 6 are wholly consistent with the homogeneous freezing conditions of sulfate aerosols measured in various laboratories (DeMott 2002).

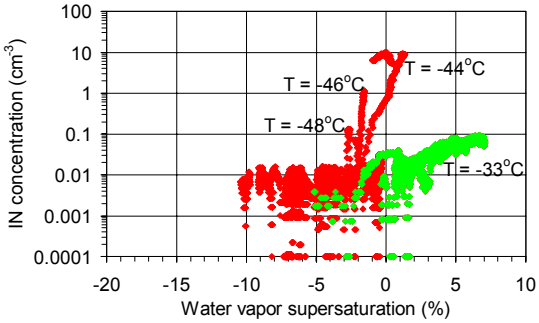

Figure 6. CFDC ice nuclei concentration from sampling periods on November 12, 2001, plotted as a function of water vapor supersaturation. Sampling temperatures between -33 and -50°C are represented. The data from around -33°C are highlighted as green data points. Temperature labels for the colder temperature data indicate the temperature when a transition to homogeneous freezing nucleation was inferred.

Figure 6 also contrasts results obtained at warmer versus colder cirrus temperatures on the same day. IN concentrations are lower under water subsaturated conditions at -33°C than at much colder temperatures, as might be expected for heterogeneous freezing or deposition nucleation processes. Additionally, no homogeneous freezing transition occurred at this temperature, since water cannot homogeneously freeze there. Instead, IN concentrations increased in relation to supersaturation up to a point then reached a plateau. This behavior is exactly as noted previously when sampling upper tropospheric aerosols in this warmer temperature regime (DeMott et al. 1998). The plateau in concentrations was previously interpreted as indicating the RH condition necessary to completely immerse most aerosol particles within dilute liquid droplets, such that the maximum population of freezing nuclei is achieved.

3.3 Aerosol and IN Composition

The composition of total aerosols during the INSPECT program, as measured by PALMS, was dominated (85-90%) by sulfate particles, neutralized to some extent by ammonium ion, and with organic components present. This result mimics those found previously in upper tropospheric conditions (Murphy et al. 1998). A very different chemical speciation was noted for heterogeneous ice nuclei processed at cirrus temperatures, in good agreement with previous CFDC/impactor/TEM studies at warmer temperatures (Chen et al. 1998). Table 1 provides a very general summary of the IN compositions during INSPECT and Figures 7 and 8 give some specific examples of positive ion mass spectra.

Table 1. Generalized Summary of IN compositions

Aerosol type	% of particles
Relatively pure mineral dust or industrial fly ash	45
Sulfates with refractory inclusions	30
Anthropogenic particulate matter	15
Other	10

The most dominant category of particles detected as IN included ionic components that are representative of relatively pure mineral dusts. An example of one such particle is shown in Figure 7. These could always be present in variable concentrations due to global transport from arid regions. A caveat must be stated, nevertheless, that similar components are found in industrial fly ash particles. The difference should be detectable by the particle morphologies and the presence of exotic metal species. In particular, fly ash particles are often spherical and contain rare metals. Preliminary analyses of some of the TEM samples indicate that the occurrences of spherical IN were rare. For this reason, particles like that shown in Figure 7 are probably of mineral dust origin.

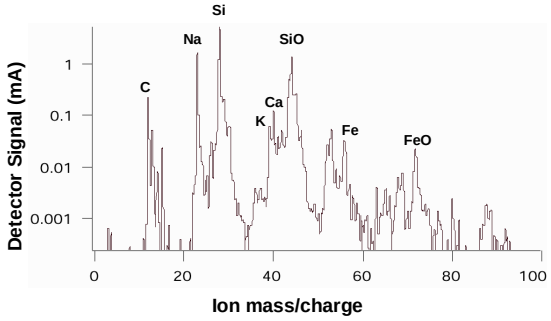

Figure 7. PALMS positive mass spectrum of ice nucleus particle with a likely source from mineral dust. The lack of volatile components is surprising, suggesting either "fresh" production or little contact with lower tropospheric pollution.

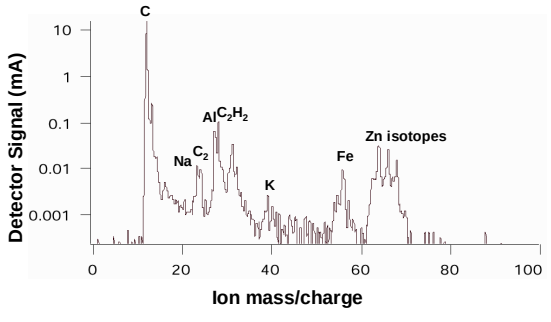

Figure 8. PALMS positive mass spectrum of ice nucleus of likely anthropogenic origin.

The second category of IN were sulfate particles that included refractory components. These particles were most frequently sampled in the relative humidity regime during transition from heterogeneous nucleation to the homogeneous freezing process. These particles usually included carbon and silicon. Sometimes these particles included potassium, suggesting a possible source from biomass burning. Therefore, it is difficult to know what percentage of these IN are naturally produced or are the product of human activities. Some sulfate-coated mineral dusts are also in this category.

The final category of IN that was clearly defined indicated an anthropogenic source. An example is given in Figure 8. The reason to suspect an anthropogenic source is the combination of metals and organics without crustal-derived silicon that is rarely seen in nature.

The "other" category in Table 1 includes particles that had unusual compositions that were rarely repeated. Many particles were also sampled by PALMS during processing conditions that led to homogeneous freezing. In this case, particle compositions included all of the various IN categories, but were dominated by sulfate/organic compositions present in the total aerosol.

4. CONCLUSIONS

This study presents the first real-time measurements of the composition of free tropospheric ice nuclei using a unique method. While the focus was on conditions relevant to cirrus cloud formation, the techniques used are applicable throughout the regime of supercooled clouds. The focus on cirrus cloud formation also permitted investigation of the conditions required for IN activation versus onset conditions for homogeneous freezing nucleation of haze particles. The conditions noted for activation of homogeneous freezing were usually in agreement with those expected for the background sulfate compositions based on previous laboratory studies. While further analyses will consider the entire INSPECT data set, preliminary results indicate rather modest concentrations (0.001 to 0.03 cm^{-3}) of IN present under activation conditions that are more favorable for cloud formation than those needed to activate homogeneous freezing. Although the presence of any numbers of IN will affect cirrus formation, observed IN concentrations of a few to a few tens per liter of air could be expected to place an effective control on cirrus properties only for modest updraft forcing conditions (see, e.g., DeMott et al. 1997). Stronger forcing conditions would lead to homogeneous freezing and higher overall ice crystal concentrations.

The compositions of free tropospheric IN active at cirrus temperatures are dominated by components that are present in mineral dusts. The effect of such particles on cold clouds during large-scale dust events has already been inferred (Sassen, 2002). The present results suggest a direct link between such particles and ice nucleation and support the possibility that dust source regions could control the global distribution of IN.

Nevertheless, fly ash contains similar elemental components, so it will be important to distinguish the morphology and behavior of the natural versus industrial particulates having such compositions. Already, the data indicate a significant anthropogenic contribution to IN populations that could be susceptible to future change. The data set provides general guidance for focusing laboratory investigations to validate the importance of different particulate types as atmospheric IN and help resolve issues of natural versus industrial sources.

Further analyses are underway to elucidate the temperature, relative humidity and air mass source dependencies of IN concentrations and compositions. Ultimately, it will be important to make similar measurements in-situ in the upper troposphere. Even the high altitude site selected for the INSPECT program was not immune to local and regional pollution sources. Alternately, it is also possible that aerosols in the upper troposphere have been processed in a manner that leads to greater IN activity. In a program focused around cirrus clouds, the IN and homogeneous freezing measurements could be directly related to cloud formation properties (required ambient RH and updraft) and resulting cloud microphysical properties. An aircraft-based measurement campaign could also investigate different regions nearer and farther from suspected IN sources.

5. ACKNOWLEDGMENTS

This work was supported by the National Science Foundation's Atmospheric Chemistry and Physical Meteorology Programs under Grant Numbers ATM-9714177, ATM-0071321 and ATM-124927 and the National Aeronautics and Space Administration under contract number NAG5-9308. Any opinions, findings and conclusions are those of the authors and do not necessarily reflect the views of NSF and NASA. A.J. Prenni acknowledges support of a postdoctoral fellowship from the NOAA Climate and Global Change Program, administered by UCAR. R.J. Lee Incorporated is acknowledged for their ongoing electron microscope analyses of filter samples. Joyce Harris of the NOAA-Climate Modeling and Diagnostics Laboratory is acknowledged for supplying the HYSPLIT model results.

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