

Contract Report 568

**DETERMINING THE CHEMICAL COMPOSITION
OF CLOUD CONDENSATION NUCLEI**

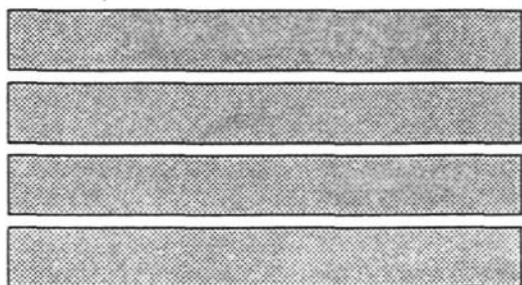
**Fourth Progress Report
Grant Number DE-FO2-90ER61017**

by Allen L. Williams, Michael E. Caughey, and Kent E. McClure
Offices of Precipitation Quality and Atmospheric Chemistry

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Sponsored by the
U.S. Department of Energy
Office of Health and Environmental Research
Washington, D.C.

February 1994



Illinois State Water Survey
Atmospheric Sciences Division
Champaign, Illinois

A Division of the Illinois Department of Energy and Natural Resources

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I. Abstract

The purpose of the present effort is to develop the capability to measure the chemical composition of cloud condensation nuclei (CCN). The sampling strategy is to expose ambient air to different saturated and supersaturated conditions inside cloud chambers, and form droplets on the CCN particulate. The droplets are then separated from the ambient aerosol by inertial impaction, and collected on filters for chemical analysis. Two versions of the apparatus have been constructed, one a stationary version at the University of Missouri-Rolla, and a mobile version at the Illinois State Water Survey. Both versions are presently operational.

Results from extended sampling at Rolla are presented. The CCN composition consists mainly of ammonium sulfate, organic carbon, and elemental carbon. It appears that the percent of $(\text{NH}_4)_2\text{SO}_4$ decreases with particle size. Limited data using a micro-orifice impactor to further segregate the CCN particles show that below $0.08 \mu\text{m}$ particle diameter there is insufficient $(\text{NH}_4)_2\text{SO}_4$ to account for the observed CCN properties. This implies that the organic material is an active CCN constituent.

Limited analysis from samples collected at Champaign, IL confirm the basic CCN composition of $(\text{NH}_4)_2\text{SO}_4$, organic carbon, and elemental carbon, although there was appreciable nitrate in the Champaign samples. Methane sulfonic acid (MSA) has been detected in samples from both locations, and is present in the Rolla samples to the extent of 2% of the sulfate mass. This is the first actual measurement of MSA in CCN particles to our knowledge.

II. Introduction

It is widely recognized that clouds and aerosols affect the global radiation balance, and would do so in the absence of anthropogenic activities. For warm clouds and aerosols the net effect is to scatter or reflect sunlight back to space and produce a cooling influence. Along with the increase in carbon dioxide and other greenhouse gases from anthropogenic activities, there has been an increase in emissions of aerosols and the gases from which aerosols form. The extent to which the anthropogenic aerosol emissions exert a climate cooling effect that offsets the greenhouse warming is an important issue, (Schwartz, 1988; Wigley, 1989) and presents a potential dilemma regarding the regulation of industrial emissions.

Anthropogenic aerosols exert a "direct effect" (Charlson et al., 1992) on the incoming solar radiation, which is taken to include the influence of haze droplets that are formed by hygroscopic aerosols in response to humid conditions. The "indirect effect" results from the formation of cloud droplets on anthropogenic aerosols. Essential parameters in an appraisal of the significance of the direct effect include the degree of response of the aerosol to humidity, and the refractive index of the aerosol and solution droplets (Charlson et al., 1992; Kiehl et al., 1993). The significance of the indirect effect depends on the extent the level of cloud condensation nuclei (CCN) is increased by anthropogenic activities (Twomey et al., 1984; Charlson et al., 1987; Wigley, 1989).

Measurements of the composition of haze nuclei over a wide geographical domain are essential for refinements of the radiation forcing by the direct effect. Determination of the CCN composition is important for the apportionment of CCN sources between natural and anthropogenic constituents, since the indirect effect is based on a postulated global increase in CCN due to anthropogenic emissions. Results are reported here of measurements of the CCN and haze nuclei compositions at Rolla, MO and at Champaign, IL.

Our measurements of CCN composition have shown ammonium (NH_4^+), sulfate (SO_4^{2-}), organic carbon (OC), and elemental carbon (EC) to be the major CCN components. The presence of organic compounds and elemental carbon in the CCN material is an important result of the present research, and determining the role of the carbon containing materials has become a major focus. Resolving the OC mass into its constituent molecular compounds is necessary for identifying the sources and CCN related properties of the OC material. Classification of the sources of organic material into categories of continental or maritime and anthropogenic or natural are basic questions. The extent that surfactant properties and water solubility characteristics of the OC materials influence CCN properties are critical to understanding their significance. The role of EC in CCN formation is an important question. EC is not water soluble, but may serve as a site on which water active CCN material collects.

Whether the OC is necessarily associated with the EC for CCN formation is an important issue. Atmospheric EC is primarily of continental origin, and can originate from either anthropogenic or natural combustion. If the OC has to be associated with EC surfaces to form CCN, then the potential effect on global warming may be limited. The lack of maritime EC sources would diminish its effectiveness over the oceans. Over the continents, where the CCN concentrations are high, the associated increase in CCN would not produce a big effect on cloud cover. The question of increased continental haze due to the EC/OC CCN source could be of some importance.

On the other hand, if the OC material is also found to be an active CCN material and capable of CCN formation in the absence of EC, the consequences could be very important from a global heat balance perspective. The key would then be to determine the sources of the active OC materials. Oceans are major sources of organic material. The identification of strong maritime OC sources of CCN material would be important from the standpoint of global warming issues. Sulfate CCN, produced from the breakdown products of dimethyl sulfide (DMS) emitted from the oceans, is considered to be the major maritime CCN source, and the identification of significant alternative CCN sources would be important.

If the OC is found to result from anthropogenic CCN sources, and to be principally of continental origin, then its range of atmospheric transport is important. Although anthropogenic sulfur dioxide sources are much larger

than natural sources, most of the sulfur leaving the continents is removed quickly enough that over the oceans the CCN from DMS emissions are thought to dominate CCN from anthropogenic SO_2 production. This is a delicate balance, for if the anthropogenic SO_2 were transported over greater distances before producing CCN, the anthropogenic CCN sources would dominate the maritime CCN production. The identification of an organic material of anthropogenic origin that is capable of producing CCN on the remote seas would be very important.

The results reported here are from CCN measurements made on the campus of the University of Missouri, Rolla using the laboratory version of the CCN collection system developed in this project. Some initial results are becoming available from the portable version of the apparatus that was built at the Illinois State Water Survey in Champaign, Illinois, and which will be operated at a variety of locations, including maritime sites. The data presented quantify the different constituents based on the amounts of ammonia, sulfate, organic carbon, and elemental carbon. Results will be presented describing the experimental determination of the different CCN size classes measured. A discussion of preliminary results of the detailed molecular analysis of the organic CCN material is included. Other preliminary measurements are presented showing that there is insufficient sulfate in the smallest CCN to account for their droplet activation properties. A copy of the preprint for a paper presented at the American Meteorological Society Conference on Atmospheric Chemistry in Nashville, Tennessee, January 23-28, 1994 is included in the appendix.

III. CCN Sampling System

Figure 1 is an overall schematic of the collection system. A more detailed description of the system design and operation is presented in previous reports (Williams et al., 1992a, 1992b, 1992c). The system consists of two continuous flow cloud chambers for growing water drops on the CCN, three virtual impactors for inertially separating the small and large particles, and three filters for collecting particles for subsequent chemical analysis. The air sample flow into the system is 1333 lpm, and the air first passes through the tubes of a stainless steel shell-and-tube heat exchanger to bring the wet bulb temperature of the incoming air to 25° C. The sample then enters impactor 1, which operates at a cutpoint of 0.5 μm. Particles larger than the cutpoint are discarded, while the particles smaller than the cutpoint flow into the haze

chamber. The haze chamber consists of a box containing 9 vertical aluminum plates 4 feet high by 12 feet long. The plates are spaced 1 cm apart. The sample air flows horizontally in the 1 cm spaces between the plates. The plates are covered with cotton cloth to serve as a wicking material, and are supplied with sufficient water at the top edge to keep their entire surface wet on both sides. The temperature of the plates is set by adiabatic heat exchange with the sample air, is nearly isothermal, and is equal to the wet bulb temperature of the incoming air.

The air reaches 100% relative humidity as it passes through the haze chamber. The hygroscopic particles in the air stream grow to become haze droplets. Particles with a critical supersaturation below 0.16% are able to grow to above 0.5 μm while in the haze chamber. Upon exiting the haze chamber the flow passes through impactor 2, which also has a

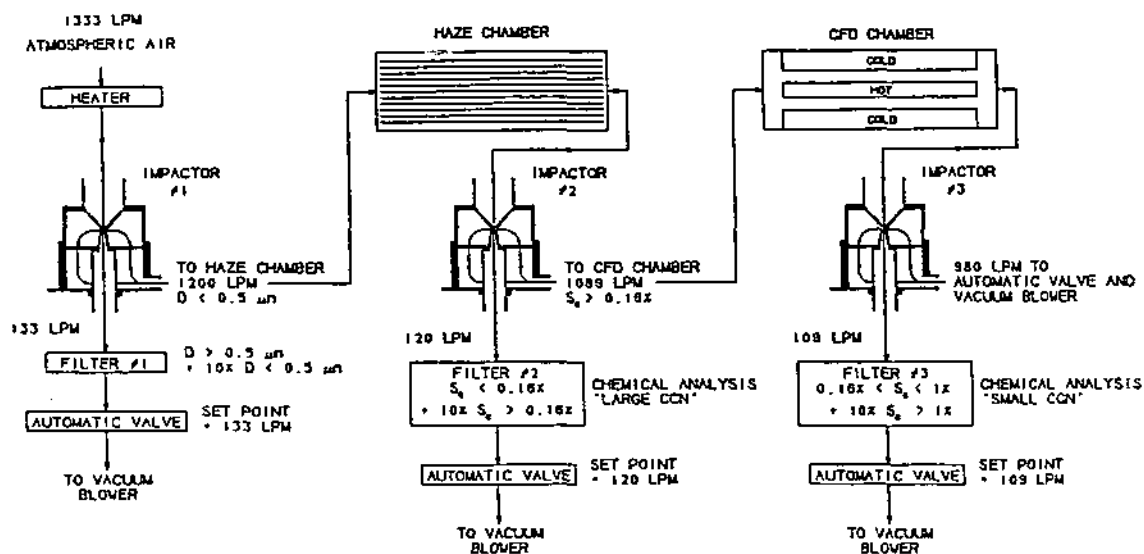


Figure 1. Schematic of the CCN collection system.

cutpoint of 0.5 μm . Droplets larger than the cutpoint are removed from the air stream and are collected on a filter as the "large CCN" sample. The fine flow, containing particles smaller than the cutpoint, pass into the continuous flow diffusion chamber (CFD).

The CFD consists of three vertical plates 4 ft high by 12 ft long. The plates are again spaced 1 cm apart, with the air flowing horizontally in the 1 cm space between the plates. The inner plate is heated to 25° C by internal electric heaters. The outer plates are cooled to 20° C by water jackets. Both sides of the inner plates are covered with cotton cloth and water is supplied at the top edge in sufficient quantity to keep both hot plate surfaces uniformly wet. The two cold plate surfaces are kept wet by the condensation taking place on them. The inlet air is at 25° C and at 100% relative humidity.

A supersaturation slightly above 1% is produced midway between the plates. This supersaturation is chosen because the accepted definition of CCN is that they are particles with critical supersaturation, S_C , below 1%. Not all the air passing through the CFD experiences 1% supersaturation, because there is a spatial variation of supersaturation between the plates. This variation is approximately parabolic, with zero supersaturation at the plates, and a maximum supersaturation approximately half way between the hot plate and cold plates. Fortunately, the velocity profile is also parabolic, so that where the supersaturation is low, the velocity is also low. This helps make final drop size less dependent upon transverse position between the hot and cold plates.

Calculations show that only particles with S_C below about 1% will grow large enough to be above the 1 μm cutpoint of impactor 3, which is located at the exit of the CFD. The resulting droplets larger than 1 μm are separated from the main flow by impactor 3 and collected on a filter as the "small CCN" sample.

The CCN sampling procedure is to collect the particles on 47 mm quartz filters. The filter holders are located at the coarse flow of impactors 2 and 3. Another sample is collected at the inlet of the system in front of the preheater. Since there is some loading on backup quartz filters when two filters are placed in series, a front and backup filter are collected at each of the sampling points. In addition to the two quartz filters, C-18 Empore filters are employed as the second backup filter at each of the three sampling points. The Empore filter material is very efficient at collecting organic vapors, and their analysis is useful for identifying organic vapors that may transit the quartz filters.

A sampling time of approximately 24 hours for the Rolla samples is needed to obtain loadings ranging from 200 μg to 500 μg . Experience has shown that the relative composition of each constituent composing the sample tends to be constant for sampling times ranging up to a week. For detailed organic chemical analysis, larger mass loadings are essential, requiring sample periods of several days.

IV. CCN Composition

a. Compounds

Ammonium, sulfate, organic carbon, and inorganic carbon dominate the CCN composition of the Rolla samples. This appears consistent with the few samples that have been analyzed from experiments at Champaign, except that significant nitrate levels have been detected in the Champaign samples. The Rolla samples show no appreciable amounts of earth crustal materials.

A major finding of this effort is that there is a significant organic component to the CCN. Table I shows the mass of the different compounds identified divided by the gravimetrically determined loading on the filters. As shown in Table I the small CCN samples have a proportionately higher fraction of organic material than the large CCN samples. If sulfate and ammonium are present as $(\text{NH}_4)_2\text{SO}_4$

	Large CCN	Small CCN
NH_4^+	11 + 2	5 + 1
$\text{SO}_4^{=}$	32 ± 4	16 + 3
Organic Carbon	13 + 2	20 + 2
Elemental Carbon	3 + 1	5 + 2

Table I. Percent mass of measured different components compared to gravimetric mass for large and small CCN samples. The sample size is 13 determinations for each the large and small CCN.

their ratio would be .375, which is fairly close to the corresponding ratios from Table I for both the large and small CCN values. Accordingly, the percent of ammonium sulfate is approximately the sum of the NH_4^+ and $\text{SO}_4^{=}$ entries in the table. The organic carbon mass listed differs from the total mass associated with the organic carbon compounds. If the listed compounds are to account for the entire filter loadings, the carbon compound mass would be about 4 times the carbon compound mass.

Another approach, which gives slightly different values, can also be used to determine the composition of different compounds in the CCN samples. Since the sampling period for the data being considered was not constant, but ranged from a few hours to several days, the total mass on the filters correlates with the individual compounds measured. This is an important diagnostic tool, since a linear relation between the organic material collected, for example, and the total mass would not be maintained over different sampling times if significant volatilization of the material from the filter were occurring. Each of the measurements are blank corrected, so a plot of each compound mass to the total mass should pass through the origin. The regression of the constituent compounds with the total mass yields an estimate of the fraction of total mass represented by each component. With this approach the ammonium and sulfate again are present in the approximate ratio equivalent to ammonium sulfate. The regression approach yields ammonium sulfate values higher by about 10% and a carbon compound to organic carbon mass ratio of about 2.5 is needed to account for the total mass on the filter.

In an attempt to simplify the interpretation of the chemical measurements, factor analysis techniques are employed. The present analysis actually uses principal component analysis (PCA) as distinct from factor analysis. All the measurements from the large and small CCN samples are combined into a single 26 sample data set consisting of ammonium, sulfate, organic carbon, and elemental carbon mass measurements. The mass of each component measured on the filters is divided by the volume of air sampled to yield the aerosol particulate concentrations as the variables for analysis. The PCA technique then assigns to the first factor the linear combination of variables that explains the maximum variance of the data set. The second factor is that linear combination of variables that explains the maximum amount of remaining variance, and is independent of the first factor.

In the present analysis only 2 factors are retained. Table II shows the communality or fraction of variance of each variable explained by the two factors. The eigenvalues of the retained factors were 2.4 and 1.4, while that of the first discarded factor was 0.3. This is consistent with the commonly applied criterion that factors with eigenvalues smaller than unity be discarded.

Following factor extraction the solution was subjected to a varimax orthogonal rotation, which is a helpful procedure for factor interpretation. As is common practice each of the variables was standardized prior to the analysis by subtracting the mean and dividing by the standard deviation, so all variables had a

mean of zero and a standard deviation of unity. The resulting factor scores, which represent the weight assigned to the factors to account for each observation, are also normalized. A procedure introduced by Thurston and Spengler (1985) was used to rescale the factor scores to the original data. This procedure involves regressing the factor scores with the total mass concentration. The factor scores were regressed with the mass concentration determined from the sum of the component masses rather than the gravimetric mass concentration. Thus the PCA results are normalized to a different total mass than the results shown in Table I.

Compound	Communality
NH₄⁺	.99080
SO₄⁼	.99039
Organic Carbon	.87380
Elemental Carbon	.86899

Table II. Communality or amount of variance of each factor explained by the two-factor model under consideration.

The CCN composition, resulting from the PCA model, is composed of two independent factors. The average concentration of each the components comprising the factors is given in Table III. Table IV gives the corresponding concentrations when only the large CCN are considered, while Table V is a similar

treatment of the small CCN portion of the total sample. The Table III entries are therefore averages of the corresponding entries in Tables IV and V.

The fact that both the large and small CCN data are explained by a simple model involving two factors is a major simplification for interpreting the measurements. The essential features of the factor analysis results are that factor 1 consists mainly of ammonium and sulfate while factor 2 consists of organic and elemental carbon. From Table III about 80% of the ammonium and sulfate are in factor 1 and about 90% of the OC and essentially all of the EC are in factor 2. The ratio of the ammonium to the sulfate mass is .33 in factor 1 and .36 in factor 2, while the ratio is .375 for ammonium sulfate. While both factors show a slight excess of sulfate, for the present discussion the ammonium and sulfate will be considered present as ammonium sulfate.

factor can represent an internally mixed aerosol or an externally mixed aerosol.

In the present situation, the first factor essentially consists of ammonium sulfate, while the second factor is a mixture containing organic carbon, ammonium sulfate, and elemental carbon. No conclusion can be drawn as to whether the aerosol represented by the different factors are internally or externally mixed. The organic carbon and ammonium sulfate identified in factor 2, for example, need not necessarily be internally mixed in the same particles.

	Factor 1	Factor 2
NH₄⁺	18	17
SO₄⁼	57	48
Organic Carbon	4	115
Elemental Carbon	<1	37

Table V. Small CCN mass concentration (ng/m³) of the different compounds in each factor. The average mass is 80 ± 20 ng/m³ in factor 1 and 216 ± 20 ng/m³ in factor 2.

It is indeed a significant simplification that the data for both the large and small CCN samples combined can be fitted to such a simple model. Apparently, the CCN formation can be explained by identifying the conditions leading to the formation of the two distinct aerosol chemistries identified by the factors. It seems likely that a portion of the observed correlations underlying the factor assignments is influenced by

atmospheric processes rather than merely being emitted by the same source. Atmospheric sulfur dioxide, for example, becomes particulate only after being converted to sulfate. The sulfate formation rather than the sulfur dioxide emission would produce the correlations leading to factor assignment.

Comparing Tables IV and V, it is interesting that the absolute amount of material in factor 2 only slightly decreases in going from the large to the small CCN, while the factor 1 material decreases by sevenfold. In both factor 1 and factor 2 the relative amounts of ammonium and sulfate are in the approximate proportion of ammonium sulfate. The presence of ammonium salts of organic compounds or other factors that would alter the relative ammonium and sulfate amounts might be indicated by a more complete analysis in which the organic carbon is replaced by its constituent compounds. However, there is apparently a significant amount of ammonium sulfate in both factors. Since the organic carbon material must be associated with organic compounds, the mass of organic material is considerably larger, perhaps by as much as a factor of 3 to 4, than organic carbon masses listed in the tables. Thus, although there is ammonium sulfate present in the second factor, the total mass of this factor is dominated by organic material.

The ammonium sulfate associated with the first factor must have a different source or undergo different atmospheric processes to be separated in the model from the ammonium sulfate of the second factor. Also, the ammonium sulfate of the second factor either has a common origin with the organic material, or they

must share some common process that causes the correlation underlying their common factor. The elemental carbon must result from combustion processes, and be initially present as particulate carbon.

b. Size Distribution of Large and Small CCN

The criteria for selecting the large and small CCN size classes is based upon the growth of the ambient aerosol under saturated conditions. In order to estimate the size of the particles composing the large and small CCN samples, assumptions about the CCN composition must be made. Measurements of the dry size of the large and small CCN aerosol are reported here.

The haze chamber operates at 100% relative humidity. The virtual impactors before and after the haze chamber have identical cutpoints of 0.5 μm . Only particles smaller than 0.5 μm enter the haze chamber, and those that grow to droplet size greater than 0.5 μm while inside the haze chamber are collected in the large CCN sample. Using classical Kohler theory the droplet sizes selected in the haze chamber can be related to the critical supersaturation (S_c) of the CCN particles, with the conclusion that the large CCN sample pertains to particles with $S_c < 0.16\%$. The remaining aerosol transits the CFD, where those CCN active below 1% supersaturation are activated. These are removed in impactor 3 following the CFD, and represent the small CCN sample. The CFD selection criteria is to remove into the small CCN sample those CCN active at $S_c < 1\%$ that pass impactor 2 with $S_c > 0.16\%$.

The size distributions at filters 2 and 3 were measured using instruments that operate in steady flow. In order to assure that the particles would be at their dry diameter (D), a flow of dry air was added to the sample air stream. An optical particle counter (OPC) and a differential mobility analyzer (DMA) were used together to cover the size range $0.2 \mu\text{m} < D < 2.0 \mu\text{m}$ with the OPC covering the size range above 0.5 μm . The particle concentration leaving the EAC was measured with a condensation nucleus (CN) counter (TSI model 3022a alcohol counter).

The mathematical model of the CCN collection system, described in previous progress reports, has been progressively improved as data on various components become available to see how system performance is influenced. The model calculates the mass median diameter of the large and small CCN samples collected at filters 2 and 3.

Figure 2 shows the results for the large CCN, with the solid line denoting the

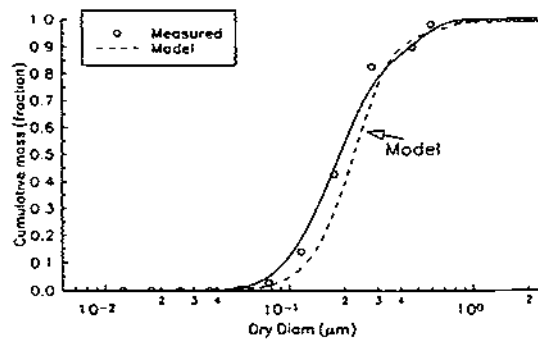


Figure 2. Cumulative mass distribution (fraction) vs. particle dry diameter (μm) for large CCN samples. Mass median diameter is 0.19 μm .

measured results and the dotted line the model results. The ordinate shows the mass fraction of particles smaller than the diameter shown on the abscissa. The diameter corresponding to a mass fraction of 0.5 is the mass median diameter, which is $0.19 \mu\text{m}$ for the measured size distribution. The measured distribution shows that 80% of the mass is due to particles in the range $0.1 \mu\text{m} < D < 0.5 \mu\text{m}$. As can be seen, the model results agree quite well with the measured distribution.

Figure 3 shows similar results for the small CCN sample collected at impactor 3. There is again fairly good agreement between the measurements and the model. The measured mass median diameter is $0.137 \mu\text{m}$, and 80% of the mass is due to particles in the diameter range $0.09 \mu\text{m} < D < 0.25 \mu\text{m}$.

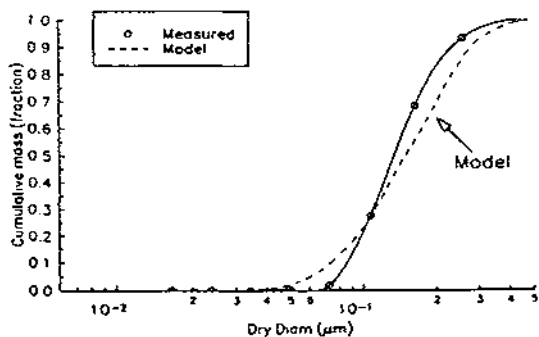


Figure 3. Cumulative mass distribution (fraction) vs. particle dry diameter (μm) for small CCN samples. Mass median diameter is $0.137 \mu\text{m}$.

c. Molecular analysis

Detailed chemical analyses are needed to determine the properties and deduce the sources of individual components in the complex mixture of analytes collected on the impactor filters. To date we have employed three instrumental methods: ion chromatography (IC), gas chromatography/ mass spectrometry (GC/MS) and reverse-phase high performance liquid chromatography/ mass spectrometry (RP-HPLC/MS).

IC separates water-soluble ionic species on an ion-exchange column (Dionex AS4), and detects them by monitoring changes in the eluate conductivity during the run. Identification and quantitation of specific ions rely on comparing peak retention times and magnitudes with those of reference standards run separately using the same chromatographic conditions. In addition to sulfate and other inorganic ions normally found in CCN samples, there are also a number of unknown peaks (perhaps organic acid anions). Unknown ionic species can be separated by an IC column, but they cannot be precisely identified or quantitated using a conductivity detector. Mass spectrometry is usually the most specific means of identifying unknown organic components, once they have been separated chromatographically. Neither GC nor HPLC can be used effectively to separate all classes of organic analytes, but the techniques complement each other well.

In general, GC is applicable to comparatively non-polar organic compounds that can be volatilized (without decomposing) at temperatures

less than 300 C. Compounds with polar functional groups can often be successfully analyzed by GC if they are chemically derivatized first. For example, methyl esterification of carboxylic acids decreases their boiling points, and improves their resolution on the chromatographic phases commonly used with mass spectrometers. Unfortunately, most GC derivatization reagents are incompatible with aqueous solvents, requiring an initial evaporation or extraction step that can cause analyte losses. After derivatization, one or more clean-up steps may be required to remove excess reagents that would otherwise interfere with the analysis. Successful choices of the derivatization and the clean-up method depend upon correctly anticipating the composition of the analyte mixture.

HPLC has the advantage that it is applicable even to analytes that have polar functional groups without sample derivatization. Unfortunately, chromatographic resolution is somewhat poorer with HPLC than with GC, especially when interfaced to a mass spectrometer. HPLC/MS interfaces sharply limit the possible choices of eluants. RP-HPLC was the first method tested because it could be performed using available equipment and required the least trial-and-error optimization. HPLC/MS sensitivity is much less predictable than GC/MS, because it depends on several interrelated operational variables. Some analytes elute from the RP-HPLC column (as indicated by an in-line UV absorbance detector) and yet do not produce usable mass spectra.

Mass spectra generated by GC/MS or HPLC/MS may be interpreted by comparison with library reference spectra, or by deducing the molecular structures from general principles of mass spectral interpretation. When mixtures are complex and analyte concentrations are low (due to inherent sample collection limitations) it is not always possible to determine the carbon numbers or isomeric configurations exactly. For example, while it can be apparent that a particular chromatographic peak is an iso-fatty acid ester, the mass spectrum alone may not unambiguously determine the molecular weight or branching pattern.

Before the organic CCN components can be separated chromatographically, they must be extracted into solution from the quartz filters. Because of the complex assemblage of analytes present in the CCN material, we find it advantageous to elute the filters sequentially using a series of increasingly polar solvents. An initial rinse with pentane primarily removes phthalate esters and siloxanes part of which we believe are contaminants not related to CCN activity. A second extraction with methyl-t-butyl ether extracts organics of low to intermediate polarity which can be analyzed by GC/MS. A third extraction with n-propanol dissolves a major fraction of the more polar organics without dissolving appreciable quantities of ammonium sulfate. The propanol fraction can be analyzed directly by RP-HPLC/MS or, after evaporation, derivatization and clean-up, by GC/MS. The final water extract, containing both organic and inorganic polar analytes, is analyzed both by IC and by RP-HPLC/MS.

Classes of organic compounds repeatedly identified in CCN filter extracts include: phthalate esters, adipic acid esters, polysiloxanes, monocarboxylic acid esters, dicarboxylic acid esters, alkyl sulfonic acids and other oxygenated organics, including aldehydes, ketones and alcohols. It is currently assumed that the phthalate esters, adipic acid esters and polysiloxanes are non-CCN related contaminants. The various organic acids were most likely present in the aerosol as ammonium salts prior to extraction and derivatization. Such carboxylate and sulfonate salts are probable candidates as active hygroscopic nuclei. The specific monocarboxylic acids identified so far are primarily even-numbered and range in size from eight to thirty carbons. The presence of C-9 acids suggests the cleavage of oleic acid (C-18 monounsaturated) by atmospheric photooxidation (Stephanou and Stratigakis, 1993). The methyl esters of shorter chainlength oleic cleavage products may be too volatile to recover quantitatively. Consequently in the future we intend to use the less volatile butyl esters as employed by Kawamura and Ikushima (1993) to analyze specifically for smaller oxocarboxylic acid fragments.

Perhaps the most unexpected discovery to date is the identification by RP-HPLC/MS and by IC of methane sulfonic acid (MSA) in the water-extractable fraction of samples collected both at Rolla and at Champaign. Quantitation of MSA by IC in a limited number of samples indicates that mass of MSA is approximately 2% of the mass of sulfate in both the large and the small CCN.

d. Percent Solubility

An important question central to the objectives of this research is whether the organic material composing the CCN is capable of droplet activation, or if there is always enough inorganic soluble material present to determine the CCN properties. This is a key question that, if answered in favor of organics being active, would have a significant impact on the interpretation of CCN formation, and would have broad implications for the assessment of the effects of clouds on global warming.

The accepted notion is that inorganic material, particularly $(\text{NH}_4)_2\text{SO}_4$, is responsible for the CCN behavior. Cities (Fitzgerald and Spyers-Duran, 1973), cane fires (Warner and Twomey, 1967), and diesel exhaust (Hudson, 1991) are among documented sources of CCN. It is clear that organic material is produced in these emissions, but it is assumed, usually implicitly, that an inorganic component is the active CCN ingredient. From our measurements it is clear that the CCN themselves contain organic material from samples taken at Rolla and at Champaign. Novakov and Penner (1993) reach similar conclusions from their analysis of samples taken at El Yunque peak in Puerto Rico. Zhang et al., (1993) concluded that carbon is a major constituent of the hygroscopic particulate at both Los Angeles and the Grand Canyon. However, none of these studies are able to determine whether the organic carbon, itself, is capable of droplet activation.

There are, basically, two recognized ways in which the organics could directly affect droplet activation. The surfactant properties could be important. A surfactant coating on a soluble material is found to slow down droplet growth and evaporation, but it is questionable if this is of atmospheric significance for droplet activation (Rood and Currie (1989): Surfactant coated haze particles may just take a few seconds longer to reach their equilibrium size. Another potential effect is to lower the surface tension, and essentially decrease the critical supersaturation of a given sized droplet (Corradina and Tonna, 1979). Andrews and Larson (1993) found hygroscopic behavior of a surfactant coated carbon particle, while neither the carbon particle or the surfactant by themselves were hygroscopic. The mechanism here is not at all clear, since the dimension of the water layer that forms on the surfactant coated carbon surface appears to be much larger than the range of influence of the surfactant material. The surfactant effects are not fully understood.

If the organic material were sufficiently water soluble, it would promote droplet activation. Water extracts from the filters used in the present analysis contain essentially all the organic carbon collected on the filter. The total carbon left on a filter, after extraction, is only slightly greater than the elemental carbon determined by separate analysis. This is a direct measurement indicating that the CCN organic material is water soluble. However, it is the degree of solubility that is important. Calculations from Raoult's law and the Kelvin equation show that the organic must dissolve on the order of 10 mg per gm of water. The solubility measurements made here were

for 0.1 mg of OC per gm of water. In the course of sample analysis, water extracts have been concentrated by on the order of a factor of 100, eg. from 10 ml to 100 μ l, without noticeable precipitation of the organic material. It appears, qualitatively, that the organic material is soluble enough to account for the observed CCN properties.

Another approach to determining whether the inorganic material controls the activation properties is to measure the amount of inorganic material, and compare it to the theoretical minimum required to account for the observed CCN behavior. Some preliminary results are available that address this point. A micro-orifice impactor (MOI) was placed in the sample flow at impactor 3 to further segregate the small CCN material. Dry, particle-free air was mixed with the sample to dry the droplets before reaching the MOI. Either stage 7 or 8 and a quartz backup filter were placed in the impactor. The idea is to collect that material smaller than the cutoff diameter of the impactor stage onto the backup filter for analysis. Although stage 8, according to the manufacture specifications, has a cutoff diameter of 0.056 μ m, it was determined experimentally, using a mobility analyzer and a CN counter, that the mass median diameter is 0.08 μ m. The manufacture specification for stage 7 is 0.093 μ m, which has not been experimentally checked.

The percent sulfate as a function of particle size is shown in Table VI. The trend is clearly that the percent of sulfate decreases with decreasing particle size. A model that examines the critical supersaturation, S_c , for internally mixed

Mass median diameter (μm)	Percent sulfate by mass in CCN
0.19	37 ± 6
0.14	16 ± 3
0.09	12 ± 1
0.08	33 ± 0.1

Table VI. Percent sulfate by mass for different CCN sizes.

soluble-insoluble particles of diameter X_0 , that contain a fraction by volume, ϵ_v , of soluble material has been presented by Fitzgerald et al. (1982). Alofs et al. (1989) extended the arguments to find the expression

$$S_c \epsilon_v^{1/2} X_0^{3/2} = .0048 \quad (1)$$

which applies to $(\text{NH}_4)_2\text{SO}_4$. Using a value of $S_c = 0.64$, which was the operating condition for the MOI data, and using the densities of 1.38 gm/cm^3 for $(\text{NH}_4)_2\text{SO}_4$ and 1 gm/cm^3 for the total particle mass to convert between volume fraction and mass fraction, the minimum amount of sulfate that can account for the observed droplet activation can be found. The calculation yields, for the stage 8 experiment with $X_0 = 0.08 \mu\text{m}$, that the sulfate amount must be larger than 11.3 % to activate at the 0.64% operating supersaturation, while the entry in the last row of Table VI shows that only 3.3% sulfate is measured in the corresponding CCN samples. This result indicates that the smallest CCN do not contain enough $(\text{NH}_4)_2\text{SO}_4$ to account for their activation properties. Although carbon results are not yet available for the MOI samples, the filter deposits have the same dark appearance as the large and small CCN samples, which implies there is

elemental carbon present. More data need to be analyzed to clearly determine the percent sulfate in the small CCN at these different sizes. This finding must be regarded as a significant result for it implies that the organic material is responsible for the properties of the CCN.

V. Discussion

Perhaps the most convincing evidence that $(\text{NH}_4)_2\text{SO}_4$ is the active CCN component are from volatility experiments in which an aerosol sample is heated prior to entering a supersaturated cloud chamber (Twomey, 1971). It was found that ambient aerosols lose their distinctive CCN behavior at about the volatilization temperature of $(\text{NH}_4)_2\text{SO}_4$. Further, an artificially generated $(\text{NH}_4)_2\text{SO}_4$ aerosol behaves in much the same way. On the other hand, the hygroscopic properties of NaCl remain unchanged to much higher temperatures, consistent with its higher volatilization temperature. This experimental technique was very important for ruling out NaCl as a dominant CCN material, even over the ocean (Dingle et al., 1970). Much subsequent work has been focused on the pathways for sulfate particulate formation (eg. Fitzgerald, 1991). The gas to particle transformation of atmospheric SO_2 to a sulfate aerosol is considered the primary pathway for CCN formation. The notion that $\text{SO}_4=$ is the primary CCN constituent is the basis for projections of the effects of aerosols and CCN on the global heat balance. In contrast, the measurements reported here indicate that there is not enough sulfate on the smaller CCN particles to account for their nucleation properties. It appears that

organic materials, instead, are the active CCN component at least for the CCN particles smaller than 0.08 μm in diameter. It is significant that the measurements were made in the Midwest where the anthropogenic sulfate levels are known to be high.

The factor analysis results presented above suggest that two independent aerosol types compose the CCN. Factor 1 is primarily $(\text{NH}_4)_2\text{SO}_4$ and dominates the large CCN samples, which form haze droplets at a supersaturation below 0.16%. The activation of the large CCN in the sampling system is through exposure to 100% relative humidity. We identify the factor 1 material as haze nuclei (HN). We identify factor 2, which is composed mainly of carbon material, as small CCN. The HN, as defined here, do not include particles larger than 0.5 μm , which are certainly among the observed haze nuclei in the atmosphere. It therefore does not include the SO_4 -particulate that have been identified (John et al., 1990) as growing through sulfate formation on liquid particles that have deliquesced above $\sim 70\%$ relative humidity. These sulfate aerosols are larger, having diameters $\sim 0.6 \mu\text{m}$, and would also be a constituent of the atmospheric haze nuclei. The factor 2 small CCN composition has some $(\text{NH}_4)_2\text{SO}_4$.

Another experimental technique that distinguishes two hygroscopic aerosol types, that have similar characteristics to the HN and small CCN identified here, uses a tandem differential mobility analyzer (TDMA) arrangement (Covert et al., 1991, Svenningsson et al., 1992). With this procedure particles of a given size from an ambient aerosol distribution,

when subjected to humid conditions, reveal two distinctly different hygroscopic properties, which have been termed the "more" and "less" hygroscopic particles (Zhang et al. 1993). These particle types are considered to be externally mixed, since particles of a given size having different hygroscopic properties must have different composition. The more hygroscopic particles are typically more abundant. From supplemental impactor and microscopic analysis, Zhang et al. (1993) determined that, although particulate carbon is associated with both particle types, more is contained in the less hygroscopic fraction. The less hygroscopic particles measured at Los Angeles were less hygroscopic than the same fraction measured at the Grand Canyon. Their interpretation of this is that the Grand Canyon aerosol had more time to age, and acquire additional hygroscopic material.

The TDMA experiments have several aspects that are similar to the present CCN experiments. The large and small CCN are similar in size, with mass median diameters of 0.137 μm and 0.19

respectively, with considerable overlap in the distributions. To a first approximation they can be considered to be the same size. The HN and small CCN resulting from the factor analysis seem to correspond to the less hygroscopic and more hygroscopic particulate of the TDMA experiments, respectively. Although the factor analysis suggests that the two particle types are externally mixed, this point is firmly established by the TDMA approach. The composition of the particle types is more clearly seen through the CCN measurements.

The determination that there is insufficient $(\text{NH}_4)_2\text{SO}_4$ present on CCN below $0.08 \mu\text{m}$ diameter to control the droplet activation properties lends support to the interpretation that there exists a hygroscopic carbon based aerosol type. The results here suggest that the percent of $(\text{NH}_4)_2\text{SO}_4$, and other inorganic material, composing the CCN decreases with decreasing dry particle size. As an aerosol ages in the atmosphere, it increases in size, so the smaller organic CCN may be freshly formed particles. The experiments of Hudson (1991) suggest that anthropogenic CCN emitted from coastal cities and towns have their CCN properties as a result of their formation rather than acquiring them by atmospheric aging. Hudson et al. (1991) found similar result from forest fires in that most of the particulate was classified as CCN, and the influence of atmospheric changes during the short atmospheric transport were deemed minimal. The fact that the CCN measured in the present study contain elemental carbon suggest they result from a combustion process. The organic analysis generally supports this hypothesis in that most of the compounds present could have resulted from combustion processes. The even carbon number preponderance in the carboxylic acids suggest the source is fresh biological material as opposed to fossil fuel emission.

On the other hand, an argument for the CCN being influenced by atmospheric process can be supported by the presence of MSA in the samples, and the high ratio of organic carbon to elemental carbon. The MSA is probably a result of continental DMS emission. For the MSA

to be associated with the CCN it must have attached to the CCN particles after being formed through DMS degradation. This suggests that the CCN are aged. Also the ratio of organic carbon to total carbon in the samples is higher than ambient aerosol measurements. Gray and Cass (1986) found a ratio of 2.4 for their Los Angeles data compared to a value of 5 for the present data. This is consistent with the particulate acquiring organic material as it ages.

Establishing the presence of organic material in the CCN is an important step in identifying the CCN sources. The preliminary results showing that the organic material is itself an efficient CCN material is a key development. If the organic material does not require the presence of $(\text{NH}_4)_2\text{SO}_4$, or another inorganic material, to form CCN, then the organic emission and atmospheric interactions should be considered independently of the inorganic material. An important question is whether the elemental carbon is necessary for the organic CCN formation. If not, then maritime organic emissions forming CCN could be an important process. CCN composition measurements of maritime samples are needed to establish this point. Also, continental CCN measurements at a remote site not dominated by elemental carbon particulate could aid in determining whether an organic continental CCN occurs which is not associated with elemental carbon.

VI. Conclusions

The CCN composition data collected at Rolla, Mo show that organic materials and $(\text{NH}_4)_2\text{SO}_4$ are the major CCN

components. A statistical analysis of the data suggest that the carbon compounds and the $(\text{NH}_4)_2\text{SO}_4$ are to a degree independent, and are present as separate particle types. The percent of $(\text{NH}_4)_2\text{SO}_4$ decreases with particle size, and at sizes below $0.08 \mu\text{m}$, has decreased to the point that there is not enough to explain the observed droplet activation properties of the CCN. This implies that the organic material is an active CCN component.

The presence of elemental carbon in the CCN material implies that combustion processes are to some extent involved in the CCN formation for both the Rolla and Champaign samples. Whether the organic material, which is several times more abundant than the elemental carbon, forms on the elemental carbon as a result of the combustion process, or whether a significant portion is from different sources, remains an open issue.

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VIII. Appendix

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Measurements of the Chemical Composition of Cloud Condensation Nuclei

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1. INTRODUCTION

It is widely recognized that clouds and aerosols effect the global radiation balance, and would do so in the absence of anthropogenic activities. For warm clouds and aerosols the net effect is to scatter or reflect sunlight back to space and produce a cooling influence. Along with the increase in carbon dioxide and other greenhouse gases from anthropogenic activities, there has been an increase in emissions of aerosols and the gases from which aerosols form. The extent that the anthropogenic aerosol emissions exert a climate cooling effect that offsets the greenhouse warming is an important issue, (Schwartz, 1988; Wigley, 1989) and presents a potential dilemma regarding the regulation of industrial emissions.

Anthropogenic aerosols exert a "direct effect" (Charlson, 1992) on the incoming solar radiation, which is taken to include the influence of haze droplets that are formed by hygroscopic aerosols in response to humid conditions. The "indirect effect" results from the formation of cloud droplets on anthropogenic aerosols. Essential parameters in an appraisal of the significance of the direct effect include the degree of response of the aerosol to humidity, and the refractive index of the

aerosol and solution droplets (Charlson et al., 1992; Kiehl et al. 1993). The significance of the indirect effect depends on the extent that the level of cloud condensation nuclei (CCN) is increased by anthropogenic activities (Twomey et al., 1984; Charlson et al. 1987; Wigley, 1989).

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Measurements of the composition of haze nuclei over a wide geographical domain are essential for refinements of the radiation forcing by the direct effect. Determination of the CCN composition is important for the apportionment of CCN sources between natural and anthropogenic constituents, since the indirect effect is based on a postulated global increase in CCN due to anthropogenic emissions. Results are reported here of measurements of the CCN and haze nuclei compositions at a single Midwest location.

2. EXPERIMENT DESIGN

The present experimental arrangement is an extension of the method used by Harrison (1985), in which the active nuclei are identified by subjecting an ambient air stream to

supersaturated conditions. The activated droplets quickly reach micrometer sizes by diffusional growth. They are then removed from the ambient aerosol by inertial impaction, and subsequently collected on a filter. The present system (Williams et al., 1992) consists of a two-stage humidification process. In the first stage the aerosol passes through a virtual impactor to remove particles larger than $0.5\mu\text{m}$, through a haze chamber operated at 100% relative humidity, and then through a second impactor identical to the first. Only hygroscopic particles smaller than about $0.5\mu\text{m}$ diameter, and larger than about $0.1\mu\text{m}$ would be isolated by the second impactor. This sample is denoted as haze nuclei (HN), although such particles also would be good CCN.

The aerosol that escape the second impactor are passed into a continuous flow diffusion cloud chamber, maintained at a supersaturation of 1%, where, they grow and are removed by a third virtual impactor with a cutoff of $1\mu\text{m}$ diameter. This sample is denoted the small CCN sample. In addition to their importance regarding the direct effect, it is essential to remove the HN from the small CCN sample, since the massive HN, although smaller in number, would dominate the chemistry of the more numerous small CCN. The samples are collected on filter pairs placed in the air stream of the coarse flow of the second and third impactors. Each filter pair is in a series flow arrangement so a "front" and "backup" filter is collected at each impactor for a single experimental run.

The inlet flow to the system is 1333 lpm. The impactors are all of a linear slit design with a slit length of

30.48 cm (12 in). The plate dimensions of the haze and cloud chambers are 3.66 m (12 ft) by 1.22 m (4 ft) and the sample flows horizontally along the 3.66 m dimension. There are 11 aluminum plates in the haze chamber, each covered with cotton cloth and spaced 1 cm apart, through which the sample flows in a parallel flow arrangement. During operation the plates are continually wetted from above with deionized water, and an isothermal plate temperature is maintained at the wet bulb temperature (Sparrow and Chen, 1969) of the incoming air by adiabatic cooling of the wetted plates in the sample air stream. The wet bulb temperature of the incoming air is maintained at 25°C by a heat exchanger through which the incoming air passes.

The cloud chamber consists of three vertical plates spaced 1 cm apart. The inner plate is heated to 25°C by internal electric heaters. The outer plates are cooled to 20°C by water jackets. Both sides of the inner plates are covered with cotton cloth, and water is supplied at the top edge in sufficient amount to keep both hot plate surfaces uniformly wet.

The performance of the second virtual impactor during its operation after the haze chamber is found to be slightly degraded over its operation with dry test aerosols. It is found that about 10% by number of the HN will pass into the diffusion cloud chamber. These particles will become part of the small CCN sample, and calculations indicate that under the present operation the small CCN sample should consist of about equal amounts of HN and small CCN.

This figure will be used below to interpret the small CCN composition.

Although a few samples have been collected on Teflon and on Nuclepore filters, the samples discussed here were collected on 47mm Whatman quartz filters. The quartz filters are pre-fired to remove organic material, and equilibrated to 50 % humidity before weighing in a microbalance. After exposure the filters are again equilibrated to 50% humidity before weighing. The samples are then stored in a freezer until analysis. The loaded filters are cut into pieces which are separately analyzed by ion chromatography (IC) and by total carbon analysis to obtain the organic carbon and the elemental carbon components. The water extracts for IC were obtained by sandwiching the quartz filter piece between Nuclepore filters in a filter holder, and repeatedly flushing and sonicating the filter holder to extract the water soluble fraction, but leave behind the water insoluble particulate. In addition to IC analysis the water extracted sample was analyzed for total carbon to obtain the water soluble carbon amount.

3. EXPERIMENTAL RESULTS

A few Teflon filters were loaded and analyzed by x-ray fluorescence. Except for S and only a trace of K, Si, and Fe all other elements detected by this technique (essentially common elements heavier than and including AL) were below detection limits. These results are supported by analysis using inductively coupled plasma on water extracts of some 20.32 cm (8 in) by 27.94 cm (11 in) quartz and fiberglass filters that were heavily loaded.

Ion chromatography on numerous filters shows insignificant amounts of CL, NO₃, PO₄, Na, and K. NH₄ and SO₄ are consistently found of the front filters and in relative amounts corresponding to (NH₄)₂SO₄. In addition elemental carbon is found on the front filters, which is consistent with the dark appearance of the front filter deposits. Considerable organic carbon is found on both the front and backup filters, and this can be further partitioned into a water soluble and water insoluble portions.

The detailed results reported here consist of 9 sets of both front and back filters for impactor 2 and 3. The sample durations in hours were 2.75 and 3.25, three samples at 3.5, and samples at 16, 21, 114, and 124. The impactor #2 loadings averaged about 5 times the loading of impactor #3. Impactor #2 backup filter loadings were a few percent of the corresponding front filter, and the impactor #3 backup filters were of order 10% of the front filter loadings for the longer sample times. About half of the front filter organic carbon was water soluble, compared to about a fourth of the organic carbon on the backup filters.

The backup filter loadings consist essentially of organic carbon with only trace amounts detected of the other constituents. Since (NH₄)₂SO₄ is not present, but is amply present on the corresponding front filters there is apparently little contamination of the backup filters by water passing through to the backup filter. The absence of elemental carbon on the backup filters indicates that little particulate is passing through to the backup filter. It is concluded that the organic material on

the backup filters is of vapor origin. It could be a positive artifact (Fitz,1990) due to semi-volatile organic material that enters the system as a vapor, transits the cloud chambers, and collects on the quartz filters. In this case the material would have had to saturate the front filter in order to break through to the back filter. A positive artifact correction would be made by subtracting the carbon amount on the backup filter from the front filter. An argument against a positive artifact in the present application is that the cloud chambers, which operate by establishing a diffusive equilibrium for water vapor, should effectively remove water soluble organic vapors, yet about half of the backup filter carbon material is water soluble. The source of the carbon on the backup filter could be a negative artifact (Zang et. al., 1987) due to evaporation from the front filter during sampling. In this case the front filter carbon mass loading would be corrected by adding to it the backup filter mass loading. The artifact question has not yet been satisfactorily resolved, although it seems fairly certain that the carbon material is not a contaminate of the sampling system.

Table I shows the percent by mass of $(\text{NH}_4)_2\text{SO}_4$, organic carbon, and elemental carbon measured on the front filters. The values are obtained by a linear regression of the measured mass of the corresponding quantity to the total mass on the filter, which all showed strong correlations. In order to estimate the HN and small CCN compositions the data must be adjusted to

account for the mass of the compound associated with the organic carbon, the transfer of some of the material from

impactor #2 to impactor #3 that under more ideal system operation would not have occurred, and the organic carbon artifact.

	Impactor #2	Impactor #3
$\%(\text{NH}_4)_2\text{SO}$	63.3 \pm 1.7	39.6 \pm 1.1
$^4\%$ Organic Carbon	16.1 \pm 0.6	23.1 \pm 2.0
$\%$ Elemental Carbon	4.0 \pm 0.7	11.8 \pm 1.3

Table I. Measured percent compositions of the samples collected at the front filter of impactors #2 and #3 respectively.

A common approximation for atmospheric aerosols to obtain approximate carbon compound mass from measured carbon values is to multiply by 1.41 (Jaenike, 1978). With such a correction it is found that the gravimetric determination of the mass on the filters is systematically lower than the mass determined from each of the analysis techniques by from 10 to 20 percent. It is not likely that common atmospheric aerosol constituents at such levels would have been missed in the analysis. Filter blanks were obtained by subjecting the filter to the rigors of handling, insertion into the sampling system, and operating for a few seconds. The blanks were used to obtain blank corrections for each analysis technique as well as for the balance. Loaded and blank filters have been subjected to low humidity between weighings to check for water being retained on the filters. If the conversion factor from organic carbon mass to organic carbon compound mass is taken as 2, mass conservation among the different measurements is realized on

both front filter sets. This can be seen from Table I in which the columns nearly add to 100 % if the organic carbon value is doubled. The factor of 2 conversion is used in the subsequent calculations.

Since the artifact question is not settled, two scenarios for artifact correction will be considered which should represent the possible extremes. In model 1 the backup filter carbon will be subtracted from the front filter. In model 2 the backup organic carbon loading will be added to the front filter.

It remains to adjust the loadings on impactor #3 to account for material that would have been collected at impactor #2 under better impactor operation. Using the estimate that impactor #3 mass is a 50% mixture of HN, with the composition of the material found at impactor #2, and small CCN, the small CCN composition can be inferred. The results are shown in Table II for both artifact correction scenarios. For each of the artifact models the constituent compositions are given for haze nuclei, which here are taken to correspond to hygroscopic particles with dry diameters between 0.1 μ m and 0.5 μ m, and small CCN which correspond to dry particle sizes below 0.1 μ m.

Model 2	Model 1			
	HN	Small CCN	HN	Small CCN
(NH ₄) ₂ SO ₄	66.4	25.6	60.4	8.0

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Organic Carbon	29.1	42.5	35.1	73.9
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Elemental Carbon	4.1	22.7	3.8	16.8
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Table II. Haze and small CCN compositions (% mass) for different artifact correction scenarios. Both models assume a factor of 2 increase of carbon compound mass over the measured carbon values and a correction to account for observed impactor #2 performance.

4. CONCLUSIONS

The different models presented in Table II represent the range of small CCN and haze compositions inferred from data collected at Rolla, MO. The HN compositions differ only slightly for the two models and the HN mass is seen to be dominated by (NH₄)₂SO₄. The observed correspondence between ammonium and sulfate ions is very strong, leaving little chance that there is significant sulfuric acid or other sulfate compounds present. The amount of elemental carbon in the HN is quite small, and does not appear large enough to drastically alter the adsorption properties of the haze droplets. The organic material in the HN could have an effect on the radiation properties of the haze droplets by increasing the refractive index to which the haze scattering properties are sensitive (Kiehl et. al., 1993). A more definitive evaluation of this possibility can be made once the chemical identification of the HN organic material is resolved, and a realistic estimate of the refractive index of the haze droplets is made.

The small CCN composition changes considerably depending on the artifact correction scheme used. It, nevertheless, appears that the small CCN are dominated by organic material, and elemental carbon over $(\text{NH}_4)_2\text{SO}_4$. The present findings are in agreement with Fitzgerald et al., (1982) and Alofs et al. (1989) in that the small CCN are seen to contain appreciable insoluble material. The presence of organic material composing CCN is in accordance with the measurements of Bigg (1986). The question of the anthropogenic origin of the organic carbon may eventually be resolved by chemical identification of the compounds. However, the large elemental carbon content points to anthropogenic CCN influences. Elemental carbon (soot) in the atmosphere is usually regarded as a product of incomplete combustion. The soot is not itself water soluble, but it is a possible site for the adsorption of organic material as well as a possible surface for the oxidation of sulfur dioxide to form sulfate aerosol. It could be that the soot particles are the site of chemical reactions that accomplish the formation of a water soluble organic material.

If small CCN are predominately composed of ammonium sulfate as is normally assumed, it seems likely that the Midwest location at which the samples were taken would show more ammonium sulfate in their composition. It is not that there is a lack of ammonium sulfate in the atmosphere, since the more massive HN taken from the same air samples are dominated by ammonium sulfate. This finding is contrast to the usual notion that CCN are composed of ammonium sulfate.

In conclusion the composition of the haze nuclei sampled at a Midwest location show their composition to be dominated by ammonium sulfate. The findings are consistent with assumptions of HN composition on which recent modeling efforts are based (Charlson et al., 1992; Keihl et al., 1993). The presence of about 30% organic material in the haze solution droplets could, however, increase the haze particle refractive index, an effect that would increase the associated negative forcing.

The small CCN contain much less ammonium sulfate than is expected . They do contain significant elemental carbon which is quite probably of anthropogenic origin. Although large amounts of organic material is found in the small CCN, much of which is water soluble, its origin is presently unknown.

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