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DETERMINING THE CHEMICAL COMPOSITION OF CLOUD CONDENSATION NUCLEI

Third Progress Report
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by

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I. Abstract

This third progress report describes the status of our efforts to develop the instrumentation to collect cloud condensation nuclei (CCN) in amounts sufficient for chemical analysis. During the fall of 1992 we started collecting filter samples of CCN with the laboratory version of the apparatus at Rolla -MO. The mobile version of the apparatus is in the latter stages of construction.

The CCN material contains significant amounts of soluble organic material as well as ammonium sulfate. There does not appear to be significant amounts of earth crustal material. Analysis of the CCN filters yield approximately 38% ammonium sulfate, 38% water soluble organic material, and 24% water non-soluble material composed mostly of organic compounds. Sampling artifacts, which are a common occurrence when sampling organic aerosols, are a problem in the present configuration of the system. Sampling artifacts, as they pertain to our sampling system, are discussed. Limits on amount of soluble organic components of the CCN sample, after accounting for artifact corrections in different ways, are found to range from 0 to 60%. The higher amount appears most reasonable, and is based on the hypothesis that the cloud chambers remove most of the soluble organic vapor from the air preventing it from collecting on the filters. It is essential to establish a sampling procedure that minimizes sampling artifacts in order obtain meaningful results with the mobile unit as it is taken to various geographic locations. A review of the question of sampling artifacts is presented.

This report includes a fairly rigorous discussion of the operation of the CCN sampling system. A statistical model of the operation of the system is presented to show the ability of the system to collect CCN in the two different size ranges for which we plan to determine the chemical composition. A question is raised by the model results about the operation of one of the virtual impactors. It appears to pass a small percent of particles larger than its cut-point that has the potential of contaminating the smallest CCN sample with larger CCN material. Further tests are necessary, but it may be necessary to redesign that impactor.

The appendices of the report show pictures of both the laboratory version and the mobile version of the CCN sampling system. The major hardware has been completed, and the mobile version will be in operation within a few weeks.

II. Introduction

Cloud condensation nuclei (CCN) are atmospheric particulates that produce freely growing water droplets when exposed to supersaturated conditions found in clouds. Twomey's early calculations (1977a) linked possible global changes between CCN and planetary albedo. Subsequent investigations (Wigley, 1989; Twomey et al., 1984; Charlson et al., 1987) indicate that a doubling of CCN concentrations could produce a cooling effect that would approximately offset the effect of doubled carbon dioxide (CO_2) concentration. One would expect a global increase in CCN if there is a direct link with sulfur dioxide (SO_2) emissions (Balling and Idso, 1991). Kaufman and Fraser (1991) attempt to quantify such a link, and conclude that the burning of fossil fuel produces more SO_2 cooling than CO_2 warming. Another possible source of sulfates that is suspected to produce CCN is dimethylsulphide from phytoplankton in the oceans (Charlson et al, 1987; Meszaros, 1988; Schwartz, 1988)

Measurements of CCN sizes indicate that most are about 0.02 to 0.04 micrometers (μm) in diameter (Twomey and Severynse, 1964; Twomey, 1972, Twomey, 1977b; Fitzgerald et al., 1982). This small size puts them on the large end of the nucleation mode, which suggests that CCN grow mainly by condensation (rather than coagulation) after being formed by homogenous nucleation. Since CCN concentrations are typically only a few hundred per cm^3 , their resulting mass concentration in the atmosphere is in the range 10 - 100 nanograms per cubic meter (ng/m^3). At such low levels direct measurement of CCN chemical composition is difficult. Indirect evidence points to sulfates as the main constituent of CCN. (Meszaros, 1968; Twomey, 1971; Junge, 1972; Charlson

et al., 1974; Whitby, 1978; Georgii, 1978; Ono and Ohtani, 1980; Cobourn and Husar, 1982).

Rosinski et al. (1984) report direct measurements of CCN chemistry in which sulfates and nitrates are indicated as the negative ions, and NH_4 , Na, K and H as the positive ions. In most cases, sulfates predominated as the major negative ion, and the major positive ions varied. Perhaps abundant sulfur is always available and the elements in the positive ions are the rate-limiting constituents. This would explain why the major positive ion changes from one sample to the next. Direct measurements of CCN chemical composition by Harrison (1985b) indicate that submicron CCN and non-CCN particles contain quite similar amounts of sulfates, nitrates, and soot. This result is difficult to explain, however, in view of the Kohler type equations that describe equilibrium behavior of hygroscopic particles (Pruppacher and Klett, 1978).

These questions suggest the need for more measurements of the chemical composition of CCN. The samples should be taken so that the more numerous, smaller CCN are collected. A large sample is desirable to enable measuring not only the major constituents, but also species found in smaller quantities. One possibility for collecting samples is to refine Harrison's technique (1985a, b) of using a continuous flow diffusion (CFD) cloud chamber to grow micron-sized water droplets on the CCN. These water droplets were then passed into a virtual impactor to inertially remove the water droplets from the rest of the atmospheric aerosol. Either a micro-orifice or low pressure impactor could be placed downstream of a Harrison-type apparatus, in order to collect only CCN smaller than, say, $0.1 \mu\text{m}$ diameter (Harrison collected all CCN up to micron size). These

types of impactors have very small flow rates, however, and high flow rates are preferred because it would, otherwise, take many days to collect enough CCN material for chemical analysis.

A second possibility is to put two Harrison-type devices together in series, which would allow collecting only the CCN having critical supersaturations (S_c) above a particular value. This achieves the goal of only collecting the smaller CCN, assuming an inverse relationship between S_c and CCN size. One would prefer not to rely totally on this assumption, because there are probably times when it isn't valid for atmospheric aerosol, although it is usually true (Fitzgerald et al, 1982; Alofs et al, 1989), and the large flow rate achievable with such a collection system led us to adopt it.

Although all aspects of the system design are not yet fully implemented, the CCN compositions of samples collected at Rolla, MO during the fall of '92 reveal the surprising results that a significant portion of the active CCN material appears to be organic. There is little work reported on the possibility of CCN being composed of organic materials. The question was briefly addressed in a review by Hegg and Hobbs (1992) as an area deserving more attention. Bigg (1986) studied the question by using diffusion cloud chambers with the condensing vapors of ethanol in one case, and cyclohexane in another. Laboratory tests with this instrument showed that ammonium sulfate droplets do not appreciably activate using cyclohexane vapors at low supersaturations, indicating that ambient sampling with this arrangement can detect CCN exclusive of ammonium sulfate. Ambient sampling revealed that the majority of atmospheric aerosol particles have an appreciable component, presumably hydrocarbons, that causes them to respond

to cyclohexane vapors. Maritime samples, taken off the Tasmanian coast, generally contained far greater cyclohexane-CCN than contaminated air crossing Tasmania. These measurements suggest that marine air contains higher concentrations of organic CCN than continental air. Blanchard (1964; 1968) postulated the sea surface to contain an organic film that injects an organic CCN aerosol into the air by wave action, and bursting bubbles. Hudson (1991) reported that diesel exhaust is a good source of CCN material, and although the CCN active ingredient has not been identified, organics could well be responsible. It has long been known (Twomey, 1971) that cities are a prolific source of CCN, which could also be indicative of an organic CCN component.

Even an understanding of the broader area of organic material in the troposphere is "... primitive at best" as observed by Duce et al., 1983. The preponderance of organic material in the vapor phase over that in particulate matter is estimated to be a factor of from 5 to 100 (Duce, 1978; Jaenicke, 1978; Hahn, 1980). Not the least of the difficulties in classifying particulate organic matter (POM) is the existence of many different compounds. Ketseridis and Eichman (1978) identified nearly 500 organic compounds in samples collected off the relatively unpolluted west coast of Ireland. The total POM concentration was nearly $10 \mu\text{g}/\text{m}^3$, and the ether extractable organic material (EEOM) was about $1 \mu\text{g}/\text{m}^3$. Chemical separation of the EEOM yielded ~64% neutral compounds, ~27% acids and phenols, and ~8% basic materials. Gas chromatographic (GC) analysis of just the EEOM by Ketseridis et al., 1976 yielded over 100 individual chromatographic peaks. However, a relatively stable distribution of the POM composition was found with respect to the main groups of EEOM: the fraction of neutral organic compounds

(N), the aliphatic fraction of N, the aromatic fraction of N, the fraction of organic acids, and the fraction of organic bases. Since their samples were collected over a wide range of geographic locations, including marine locations, with an emphasis on clean background samples, the data was interpreted to suggest that either a common origin of POM or atmospheric formative processes were responsible. Of the over 100 organic compounds found in the gas phase by Cautreels and Cauwenberghe (1978), about 50 were found to be associated with both aerosol and gas samples. An important aspect of this work was the particulate sample preparation of derivatization by adding an excess of diazomethane solution in ether, following soxlet extraction by benzene and methanol. Consequently, carboxylic compounds were converted into methylesters, and phenolic compounds into methylethers, to increase volatility prior to separation by GC. POM is necessarily less volatile than the corresponding gaseous organic material, which is an impediment to separation by GC.

The effect of surface active films has received considerable attention (eg., Storozhilova, 1971; Silaev et al., 1971; Rubel and Gentry, 1985; Rood et al. 1991; Hameri et al. 1992; Podzimek, 1975) with regard to their influence on droplet growth. In a review of this subject Gill and Graedel (1983) identified over 80 surface active organic compounds commonly found in the atmosphere. Garret (1968) presented evidence that surfactants increase the concentration of CCN. MacIntyre (1972, 1974) and Blanchard (1964, 1968) identified a mechanism for the formation of particles containing organic material from the sea surface. According to this hypothesis, droplets coated with surface active organic material, present in ocean, are ejected into the atmosphere by the action of breaking waves. Husar and Shu

(1975) found evidence of surfactant films in aerosol samples collected in Pasadena, California. It must be emphasized, however, that surface active films are generally regarded as agents that retard droplet growth. The increase in CCN seen by Garrett (1968) was thought to be due to the surfactant causing smaller and more numerous particles to form from bursting bubbles in the sea water, and not due to the effect of the surfactant on the CCN so formed.

The presence of significant organic material in CCN also presents problems associated with sample collection. Semi-volatile organic material can attach to aerosol filters directly from the gas phase producing a positive artifact (Cadle et al, 1983). Precautions to avoid such positive artifacts include placing a denuder upstream of the filter (Fitz, 1990). Negative filter artifacts are caused by evaporation of the material (Appel et al., 1983; Van Vaeck et al., 1978; Van Vaeck et al., 1984; Zang and McMurry, 1987), and is exacerbated by the presence of a pressure drop across the filter. This becomes especially important for a loaded filter, where the pressure drop may have increased, and there is more material available for evaporation. Since the evaporation is a function of the vapor pressure of the specific material, each compound may have a different negative artifact, which could become very complicated for atmospheric organic material containing hundreds of different compounds.

Details of our CCN sampling system are presented, and its operation is analyzed using a computer model to establish the feasibility of collecting CCN samples in different size ranges of CCN dry particle size. Data is presented for the system, as it is presently being operated, in which CCN below about 0.5 μm dry diameter are collected. Chemical analysis of the CCN composition by various

techniques is presented. Despite questions of sampling artifacts, the case is made that CCN collected at Rolla Missouri indeed have significant organic material in addition to ammonium sulfate. A mobile version of the apparatus to investigate the geographical variation of CCN composition is being constructed.

III. Description of the CCN Collection System

Figure 1 presents an overall schematic of the collection system. The figure shows two steady flow cloud chambers for growing water droplets 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. Heated water flows through the shell, in order to heat the moisture laden atmospheric air, so that it emerges from the

heater with a wet bulb temperature of 25° C. In impactor #1 particles larger than 0.5 μm are removed, and the remaining smaller particles flow into the haze chamber, which 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 for water, 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 allowed to float, that is, the plates are adiabatic, and exchange heat only with the sample air, to a good approximation. An application of the analysis of Sparrow and Chen (1969) indicates that the adiabatic plates will be nearly isothermal, and, at steady state, will have a temperature equal to the wet bulb temperature of the incoming air. (Recall that the heater upstream of impactor #1 has raised the wet bulb temperature to 25° C.)

Figure 1. Schematic of the CCN collection system.

A brief explanation of why the haze chamber reaches 25° C is that evaporative cooling causes the plates to be colder than the air. In the steady-state there is an energy balance at the plate surfaces between heat conduction from the air and water evaporation. The result is that the plates are nearly isothermal at the wet bulb temperature of the incoming air-water vapor mixture. This provides for simple construction of the haze chamber.

Next the air passes into a virtual impactor called impactor #1. There are two air flows leaving. One is called the "fine flow", and contains only particles smaller than the "cut point" (0.5 μm diameter). The other contains particles larger than the cut-point, and is called the "coarse flow". The coarse flow contains small particles in the same concentration as at the input to the impactor. This is undesirable, and so could be termed a "leak". The transmission efficiency of the small particles into the coarse flow equals the coarse flow rate expressed as a percentage of the total flow.

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. The analytic solution of Brown (1960) is used to compute the temperature and vapor pressure fields between the plates. This analysis assumes the plates are isothermal, but is in other respects rigorous. The growth of the hygroscopic particles is modelled using condensational growth theory (Carstens, 1979; Hagen, 1979). The equilibrium size (x_0) of a hygroscopic particle at 100% relative humidity depends only on the S_C of the particle (Laktionov, 1972). The Laktionov relation is $x_0 = 0.08 / S_C$, with x_0 in μm and S_C in percent. The exact chemical composition does not effect this relation.

The solid line of Fig. 2 shows the calculated size of haze droplets leaving the haze chamber for particles that pass midway between the plates, and thus have a minimum residence time in the chamber. (The velocity profile between the plates is parabolic.) Particles which flow through the haze chamber closer to the plates have more time to reach their equilibrium size, and hence reach sizes as large or larger than the solid line in Fig. 2. The dotted line marked equilibrium is the Laktionov relationship. Fig. 2 shows that particles reach their equilibrium size if they are smaller than 1 μm diameter. This size is well above the cut-point of impactor #2 (0.5 μm). The S_C corresponding to 0.5 μm equilibrium size is 0.16%. Thus for hygroscopic particles, only particles with S_C larger than 0.16% will pass through the fine flow of impactor #2 and reach the CFD. The measurements of Alofs et al. (1989) indicate that atmospheric particles with this S_C have a median dry diameter of 0.13 μm . Thus, approximately, only hygroscopic particles

Figure 2. Performance of the haze chamber. The solid line represents the minimum final droplet diameter leaving the haze chamber. The dotted line represents the equilibrium droplet diameter at 100% relative humidity.

smaller than $0.13\ \mu\text{m}$ dry diameter, and non-hygroscopic particles smaller than $0.5\ \mu\text{m}$ dry diameter are passed into the 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. In order to keep the hot plate isothermal, it was necessary to assure that the inlet air is at 25°C and at 100% relative humidity. Otherwise the upstream edge of the hot plate would require greater heat flux than could be supplied by the electric heater. This is the main reason there is a heater upstream of impactor #1.

Figure 3. Performance of the CFD chamber. The three lines indicate final diameter of droplets leaving the chamber.

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 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.

Figure 3 shows the calculated performance of the CFD. The horizontal axis is S_c , the vertical axis is transverse position between the plates, measured in cm from the cold plate. The lines indicate the final diameter of droplets as they exit the CFD. For a cut-point of $1\ \mu\text{m}$ for impactor #3, it can be seen that only particles with S_c below about 1% will grow large enough to be above the cut-point. The analytical solution of Hatton and Turton (1962) was used to compute the temperature and vapor pressure profiles in the CFD. This solution is quite rigorous and accounts for the parabolic velocity profile. The growth of particles in the CFD was modeled, as in the haze chamber, using theory outlined by Carstens (1979) or by Hagen (1979).

The virtual impactors are of rectangular design, with narrow slits 12 inches long. This geometry allows a smooth transition of flow from the cloud chambers to the impactors. Fig. 4 shows anticipated performance of the impactors. This performance is similar to the performance theoretically determined by the computational fluid dynamics studies of

Marple and Chien (1980). The vertical axis of Fig. 4 shows transmission efficiencies of particles into the coarse flow and the fine flow, by the curves labeled coarse and fine, respectively. The horizontal axis of Fig. 4 is the square root of the Stokes number, which is proportional to particle diameter. It can be seen from Fig. 4 that the major change in efficiencies occur over about a factor of two range in diameter. The coarse efficiency for small particles is shown as 10% in Fig. 4, corresponding to a coarse flow equal to 10% of the total flow. For a 1% coarse flow, (also called a 1% leak), the coarse efficiency would be 1% for small particles.

IV. Numerical Model Description

a. Overview

The purpose of the numerical simulation is to predict the behavior of the CCN collection. The result will depend on a number of factors such as the aerosol size distribution, the hygroscopic/hydrophobic nature of the particles, the position relative to the plates that a particle passes through the chambers, and its flow path through the impactors. A statistical approach is adapted to account for the different results that would occur for identical particles that transit the system along different paths. The variation of aerosol properties is investigated by applying the model to a variety of assumed aerosol size distributions and chemical compositions.

Let $P(x) dx$ denote the probability of finding a particle with diameter between x and $x+dx$. This probability distribution is just the differential size distribution divided by the total aerosol population. The particle diameters are allowed to range between a minimum value, $x_{\min}$, and a maximum value, $x_{\max}$. Often these are chosen to be $x_{\min} = 0.006 \mu\text{m}$ and $x_{\max} = 19 \mu\text{m}$. This range picks up 99%

Figure 4. Performance of virtual impactors for coarse flow equal to 10% of the total flow. Lines represent efficiencies of transmission into fine of coarse flow, respectively.

of the mass from the Whitby (1978) "grand average continental" coarse mode aerosol.

For the current modeling studies, we assume that at any size, 10% of the particles are hydrophobic, the other 90% are hygroscopic, and composed of an internal mixture of ammonium sulfate and silica. The hydrophobic particles, assumed to be carbon, do not change size in the two cloud chambers. The volume fraction of ammonium sulfate, ϵ , for the hygroscopic particles is assumed either fixed at $0.5 \mu\text{m}$ diameter, or to vary linearly with particle surface area of particles ranging from 0.5 to $0.2 \mu\text{m}$ diameter. Measurements indicate that CCN have hygroscopic behavior like internally mixed particles composed of 50% ammonium sulfate and 50% insoluble material (Fitzgerald et al., 1982; Alofs et al., 1989). This chemistry assumption is made only for the current simulation studies. It does not constrain, in any way, the ultimate chemical analysis to be performed on the sampled atmospheric aerosols.

Our method is to follow the trajectories of

a large number of particles through the system to determine where they finally land. For a given particle, the first step in its treatment is to randomly pick its size. A linear mesh of particle sizes is generated with x_j from $x_{\min}$ to $x_{\max}$, a range covering almost four decades. Because the range is so large, the points in the particle size mesh are taken equally spaced in $\ln x$ space, i.e.,

$$x_j = x_{\min} e^{(\ln x_{\max} - \ln x_{\min}) (j-1)/(JX-1)} \quad (1)$$

where JX denotes the total number of particle diameter values. In order to randomly choose x_j , we employ the general Monte Carlo technique called the inversion method (Gillespie, 1976; Hammersley and Handscomb, 1964). A random number, Ψ , between 0 and 1, is generated for size selection. The size chosen corresponds to the j -value which minimizes $|FF(j)-\Psi|$, where $FF(j)$ denotes the probability distribution function:

$$FF(x) = \int_0^x P(x') dx' \quad (2)$$

b. Particle Trajectory

The size distribution and chemical characteristics, that determine whether a particle will activate a droplet and the extent it undergoes diffusional growth, are input parameters for the calculation. The task is to follow each particle's trajectory through the various devices comprising the CCN sampling system and determine where it lands in the system.

c. Impactor #1

The particle's Stokes number is calculated based on its dry size, and the dimensions and flow of the impactor. The impactor's fine efficiency, e_s , is calculated using an equation for the "fine" curve in Fig. 4. When a large number of particles having this Stokes number pass through the impactor, a fraction

of them are passed into the fine flow. To simulate this numerically we associate a length, e_s , of the unit interval with the fine flow. The portion from zero to e_s is chosen. A random number, Ψ , is generated for the impactor #1 transit. If $\Psi \leq e_s$, then the particle is passed through the impactor via the fine flow, and it continues on to the next subsystem (haze chamber). If $\Psi > e_s$, then the particle is lost in the impactor, and the simulation starts over with a new particle.

d. Haze Chamber

For particles making it to the fine flow of impactor #1, the next device in the system is the haze chamber. The Monte Carlo inversion method is again used here to select the particle's transverse position. A discrete probability density function is defined proportional to the air flow velocity at the different positions, h , between the chamber plates. This function is combined with a new random number to select h . The performance of the haze chamber is specified by a table, which gives the final haze droplet size for a variety of h and S_C values. The methods used to compute this table were discussed earlier in reference to Fig. 2. During the Monte Carlo runs, the table is used to determine the drop size at the exit of the haze chamber.

e. Impactor #2

The particle's Stokes number is calculated based on its size upon leaving the haze chamber. Equations for the curves in Fig. 4 then are used to compute the efficiency, e_s , and the transmission efficiency in the coarse flow, e_L . For a large number of particles, the fraction e_s would go to the fine stream, and a fraction e_L would go to the coarse stream. To numerically simulate this, we associate a fraction e_L (zero to e_L) of the unit interval with the coarse flow, and a portion e_s (from e_L to e_L+e_s) with the fine flow. The portion

of the unit interval (from $e_L + e_s$ to unity) is associated with particles which are lost in the impactor. A random number, Ψ , is generated for the impactor #2 transit. If $\Psi \leq e_L$, then the particle is collected on filter #2. If $e_L < \Psi \leq e_L + e_s$, then the particle is passed via the fine flow into the CFD chamber. If $\Psi > e_L + e_s$, then the particle is lost in the impactor.

f. CFD Chamber

The trajectory through the CFD chamber is accounted for by using the same techniques as are used for the haze chamber. A table is calculated to specify final drop size leaving the CFD, as a function of S_C and h (See the discussion of Fig. 3 for how these calculations are done). The method for choosing h is the same as for the haze chamber.

g. Impactor #3

The Stokes number is computed based on the size of the drop at the exit of the CFD, and the flow and dimensions of impactor #3. The impactor efficiencies, e_s and e_L , are calculated using equations for curves similar to those in Fig. 4. If the coarse flow is taken to be 1% of the fine flow, the coarse curve in Fig. 4 would be at 1% for a small Stokes number. A random number, Ψ , is generated for the impactor #3 transit. If $\Psi \leq e_L$, then the particle passes into the coarse flow, and is deposited on filter #3.

Table I. Parameters of the Grand average continental aerosol size distribution (Whitby, 1978).

Mode	Concentration	X_n	σ
Nucleation	7.7×10^4	0.013	1.70
Coarse	4.2	0.970	2.15
Accumulation	1.3×10^4	0.069	2.03

h. Model Results

The results for a Monte Carlo simulation of a grand average continental aerosol (Whitby, 1978) are shown in Fig. 5. This trimodal aerosol size distribution is represented by the sum of three log-normal distributions, with modal concentrations, geometric mean diameters, and geometric standard deviations shown in Table I. It represents an unweighted average of an urban and background continental aerosol. It is closer to an urban aerosol, however, which has a much higher concentration, and will thus dominate the average.

Figure 5 shows some results for the hygroscopic portion of the aerosol of Table I. Here, ϵ is fixed at 0.5, with a 1% leak in impactor #3, and with a $0.5 \mu\text{m}$ cut-point for impactor #3. The horizontal axis is S_C of the hygroscopic particles, and the vertical axis is differential mass of ammonium sulfate in the differential increment of $\ln(S_C)$. The top

Figure 5. Performance of the collection system for hygroscopic particles. The curves represent mass of $(\text{NH}_4)_2\text{SO}_4$ deposited on filter #3, filter #2, and the amount in the ambient aerosol.

Table II. Parameters of the Marine aerosol size distribution (Whitby, 1978).

Mode	Concentration	$\bar{X}_0$	σ
Nucleation	0.34×10^3	0.010	1.60
Accumulation	0.06×10^3	0.071	2.00
Coarse	3.1	0.620	2.70

curve represents mass in the atmospheric aerosol, the bottom curve represents mass deposited on filter #3, and the middle curve represents mass deposited on filter #2. It can be seen that the mass on filter #3 is largely due to particles in the S_C range from 0.16% to 1%, which confirms that the system performs as it was designed to for hygroscopic particles.

Figure 6 shows the performance of the system for nonhygroscopic particles. In this simulation a marine aerosol is assumed (Table II, taken from Whitby, 1978) with fixed ϵ , and with impactor #3 having a 1% leak and a $1.0 \mu\text{m}$ cut-point. The horizontal axis represents dry diameter, x , and the vertical axis represents differential mass in the differential increment of $\ln(x)$. The top curve represents the total mass (ammonium sulfate, silica, and carbon) of the atmospheric air. The middle curve represents the mass of ammonium sulfate on filter #3, and the bottom curve represents the mass of carbon on filter #3. The carbon particles are meant to model the behavior of hydrophobic particles that would not be CCN for sizes below $0.5 \mu\text{m}$. Thus the carbon that lands on filter #3 is undesirable. The bottom curve (carbon) is uniformly about three decades below the top curve. Two of these decades are due to the 1% leak of impactor #3; the other decade is due to the assumption that for 10 particles at any particle size, one will be carbon and 9 will be hygroscopic. If the leak of impactor

#3 was assumed to be 10%, the bottom curve of Fig. 6 would move up one decade everywhere. If the cut-point of impactor #3 was changed to $0.5 \mu\text{m}$, the bottom curve would move up in the vicinity of $0.5 \mu\text{m}$, but would remain the same for diameters far away from $0.5 \mu\text{m}$.

Table III lists the parameters of the Whitby (1978) clean continental aerosol size distribution.

The results of numerical simulations for the three different aerosols are given in Table IV. The notation for row 1 is as follows: "G.A. Cont" denotes the grand average continental aerosol, "Marine" denotes the marine aerosol, and "C. Cont" denotes a clean continental aerosol (Whitby, 1978). The notation for row 2 is that "F" denotes fixed ϵ ; "V" denotes variable ϵ . For row 3, "Leak (3,%)"

Table III. Parameters of the Marine aerosol size distribution (Whitby, 1978).

Mode	Concentration	$\bar{X}_0$	σ
Nucleation	1.00×10^3	0.016	1.60
Accumulation	0.80×10^3	0.067	2.10
Coarse	0.72	0.930	2.20

Figure 6. Performance of the collection system for hydrophobic aerosol. The curves represent mass of hydrophobic aerosol (assumed carbon) deposited on filter #2, mass of $(\text{NH}_4)_2\text{SO}_4$ deposited on filter #3, and mass of all species in the ambient aerosol.

denotes percent coarse flow assumed for impactor #3. For row 4, "Cut(3,μm)" specifies the cutoff chosen for impactor #3. Rows 5, 6, and 7 show micrograms of a specific material deposited on filter #2 per cubic meter of air flowing into the collection system. Rows 8, 9, and 10 show the same for filter #3.

Column 5 of Table IV shows how increasing the cut size of impactor #3 to 1.0 μm decreased the carbon on filter #3 by a factor of about 10, in comparison to columns 1-4. The explanation for the improved performance is as follows: Fig. 4 shows that the resolution of the impactors equals a factor of two on diameter. Thus impactor #3 requires a cut-point twice as large as that for impactor #2. Otherwise, the product of e_s for impactor #2 and e_L for impactor #3 will have large values near the two cut-points, which would allow

0.5 μm hydrophobic particles to pass through to filter #3.

Comparing the same columns, this time using the last two rows, shows that the amounts of silica and ammonium sulfate collected decrease only slightly when the cut-point of impactor #3 is increased to 1.0 μm. The reason for the decrease is evident after studying Fig. 3. The important conclusion is that a 1.0 μm cut-point is better than 0.5 μm for impactor #3.

By comparing columns 5-12 in Table IV, it can be seen that with a 1 μm cut-point for impactor #3, the amount of carbon on filter #3 is proportional to the percent coarse flow ("leak rate") of impactor #3. It is difficult to achieve a 1% coarse flow without attendant large particle losses in the impactor. However, it is important to do so for impactor #3

Table IV. Numerical simulation results for Grand Average Continental, Marine, and Clean Continental aerosol distributions for various assumed aerosol compositions and sampling conditions.

R o w ↓	Column →	1	2	3	4	5	6	7	8	9	10	11	12
1	Aerosol	G. A. Cont. F	G. A. Cont. F	G. A. Cont. V	G. A. Cont. V	G. A. Cont. F	G. A. Cont. F	G. A. Cont. V	G. A. Cont. V	Marine F	Marine V	C. Cont F	C. Cont V
2	ϵ	F	F	V	V	F	F	V	V	F	V	F	V
3	Leak (3,%)	1	10	1	10	1	10	1	10	1	1	1	1
4	Cut (3,μm)	0.5	0.5	0.5	0.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
5	Carbon (2)	0.457	0.457	0.458	0.458	0.445	0.445	0.447	0.447	0.003	0.003	0.029	0.028
6	Silica (2)	8.198	8.198	8.149	8.149	8.266	8.266	8.206	8.206	0.049	0.049	0.500	0.498
7	Am. Sulf.(2)	6.622	6.622	5.249	5.249	6.677	6.677	5.285	5.285	0.040	0.033	0.404	0.328
8	Carbon (3)	0.126	0.242	0.131	0.251	0.016	0.144	0.143	0.145	0.000	0.000	0.001	0.001
9	Silica (3)	1.279	1.314	2.587	2.752	1.200	1.241	2.415	2.591	0.006	0.012	0.064	0.133
10	Am. Sulf.(3)	1.033	1.062	0.450	0.459	0.969	1.002	0.426	0.437	0.005	0.002	0.051	0.024

to avoid transmitting hydrophobic particles to filter #3.

The effect of variable ϵ can be seen by comparing columns 5 and 7, 9 and 10, and 11 and 12. Variable ϵ causes the silica on filter #3 to increase by about a factor of 2, and the ammonium sulfate to decrease by about a factor of 2. Variable ϵ should not influence the amount of carbon on filter #3. The slight changes seen in some of the cases are due to poor resolution of the Monte Carlo technique due to insufficient numbers of carbon particles for good statistics.

The last column of Table V gives the sampling time to collect one microgram of CCN material (ammonium sulfate plus silica) on filter #3. These numbers are derived from Table IV. The marine aerosol yields the longest sampling time of 5.6 hours. Also shown in Table V are the CCN concentrations for the total atmospheric aerosol. These results appear quite reasonable, and support the rational behind the computations.

V. Performance tests on CCN sampling system

The apparatus was tested by measuring the efficiencies with which test aerosols were transmitted to various points in the system. The test aerosols were generated by atomiz-

ing aqueous solutions of either sodium chloride or uranine. Downstream of the atomizer the aerosol passed through a differential mobility analyzer (DMA) which passes only particles in a narrow range of electrical mobility (Liu and Pui, 1974). This provides a test aerosol in which the vast majority of the particles have a narrow range of critical supersaturation (S_c).

These tests were performed with the system configured as shown in Fig.7. There was no impactor #1, because not enough impactors were available. A HEPA filter was placed upstream of the heater (Fig.7), and the test aerosol was inserted at the filter exit. A low pressure version of the small continuous flow diffusion cloud chamber described by Alofs (1978) was used to measure concentrations of the test aerosol particles at the following three locations: the insertion point, the major flow of impactor #2, and the minor flow of impactor #2. This allowed determining the transmission efficiencies, at a particular S_c , to the minor flow and to the major flow of impactor #2. This was done for a range of S_c values from 0.05% to 1.0%. A theoretical model of the haze chamber indicates that particles in this S_c range will grow to nearly their equilibrium size at 100% relative humidity. This equilibrium diameter is given by the Laktionov relation (Laktionov, 1972) which is then used to convert S_c values to values of Stokes number (St).

Table V. Model derived sampling times

Aerosol Distribution	Soluble Volume Fraction	CCN Concentration (cm^{-3})	Sampling Time (hours)
Marine	Fixed (0.5)	60	2.70
Marine	Variable	38	5.60
Clean Cont.	Fixed (0.5)	685	0.20
Clean Cont.	Variable	387	0.50
Urban	Fixed (0.5)	14,000	0.01
Urban	Variable	6,900	0.03

The results are shown in Fig. 8. At low Stokes numbers the fractional efficiencies are 90% and 10% for the major and minor flows respectively. This is as expected because impactor 2 is operated with a minor flow equal to 10 % of the total flow (Fig. 1). For $St^{1/2}$ equal to 1.5, the measured efficiency to the major flow is about 10%. We had expected that it would be considerably

smaller, say 1%, based on the performance of the virtual impactor described by Loo and Cork (1988). Also note from Fig. 8 that the efficiency variations occur over the $St^{1/2}$ range 0.3 to 1.5. Since $St^{1/2}$ is proportional to particle diameter, the change in efficiency occurs over diameter ratio of 5, which is considerably lower size resolution than the expected factor of 2 on diameter.

To put Fig. 8 in perspective, it should be pointed out that this data represents the performance of impactor 2 with haze droplets, and also represents the performance of the haze chamber. We also tested impactor 2 with dry particles, and the result is better size resolution(resolution of about a factor of 2 on diameter) but the same efficiencies at high Stokes number. The purpose of impactor #2 is to separate the large CCN from the small CCN (Fig. 1). The degraded performance of impactor #2 at high Stokes number means that about 10% by number of the large CCN will pass into the CFD. These large CCN will end up on filter #3, and calculations indicate

Figure 7. System configuration during performance tests.

that their mass will approximately equal the mass of the small CCN on filter #3. These calculations are based on defining small CCN as CCN with dry diameter less than about $0.1 \mu m$ diameter. Calculations indicate that if impactor #2 were improved by decreasing the transmission of large particles into the major flow, the mass of large CCN on filter #3 would be reduced to as low as 3% of the mass of small CCN on filter #3. The above measurements and calculations indicate that

Figure 8. Measured characteristics of impactor #2 under system operation conditions.

the chemical measurements made thus far for filter #3 represent the chemistry of both small and large CCN, with approximately equal mass loadings of the two types of CCN.

The performance of the CFD and impactor #3 was investigated by inserting the test aerosols just upstream of the CFD, and measuring particle concentrations at the insertion point and at the minor flow of impactor #3. The results indicate a nearly constant transmission efficiency of about 70% for $0.06\% < S_c < 0.5\%$, and a rapid drop in efficiency in the range $1\% < S_c < 2\%$. The efficiency is 1.6% at an S_c of 3%, which is close to the expected value for a minor flow equal to 1.5% of total flow (Fig. 7). The CFD operates at 1% supersaturation, so the rapid change in efficiency near S_c equal 1% is expected, and indicates that the CFD is operating properly. The plateau efficiency of 70% for $0.06\% < S_c < 0.5\%$ indicates that all these CCN grow in the CFD to well above the $0.7 \mu\text{m}$ cut-point of impactor #3. The existence of this plateau is in agreement with a computational model of the system, but the plateau efficiency predicted by the model is near 100%. The degradation of the plateau efficiency from 100% to 70% will increase the sampling time by a factor of 1.4, but is not serious from the standpoint of contamination on filter #3 by particles other than small CCN.

Figure 9 shows the result of multiplying the two transmission efficiencies obtained from the separate tests just described, i.e. tests for the performance of the haze chamber-impactor 2 combination and for the CFD-impactor 3 combination. Fig. 3 shows that the system performs like a band-pass filter, transmitting, mainly, particles in the range $0.1\% < S_c < 1.0\%$ to filter #3. The steep slope on the right side of Fig. 3 is provided

by the CFD. The more gradual slope on the left side is due to impactor #2, and would be steeper if impactor #2 had better size resolution (factor of 2 on diameter rather than observed factor of 5). The most likely values of extrapolated efficiencies for S_c values outside the range of Fig. 3 are 4% for $S_c < 0.05\%$ and 1.6% for $S_c > 3\%$. The efficiency of 4% for $S_c < 0.05\%$ should be improved (lowered) by modification of impactor #2. The efficiency of 1.6% for $S_c > 3\%$ will probably be improved by the new version of impactor #3, which features a flushing flow of filtered air into the large particle collection region, such that the minor flow is effectively zero. This improved impactor #3 is now being installed into the system.

Figure 9. System performance test results for the system configuration shown in Figure 7.

The temporary impactor #3 used for the above tests is one of the impactors designed for use as impactor #2, and has a cut-point of $0.5 \mu\text{m}$ at 1333 lpm. Early in the design of the system, it was learned that impactor #3 needs a larger cut-point than impactor #2. Otherwise, completely insoluble particles slightly larger than the cut-point of impactor #2, and slightly smaller than the cut-point of impactor #3 would contaminate filter #3. To achieve a cut-point of about $0.7 \mu\text{m}$ from temporary impactor #3, it was run at 707

lpm using the flow system shown in Fig.7, in which 50% of the major flow from impactor #2 bypasses the CFD. This bypass flow was passed through a high-volume filter so that portion of the particulates could also be chemically analyzed.

VI. Composition of CCN Material

The CCN deposit is dark in appearance, much like aerosol loadings seen from the fine fraction of a dichotomous aerosol sampler. The shade ranges from dark brown, for 100 μg loadings, to black for one sample with a 1 mg loading, which is shown in Figure 10.

Scanning electron micrographs of the CCN material collected on Nuclepore filters are shown in Figures 11 and 12, which are both at a magnification of 30 kx. (The Nuclepore pores seen in the background are 0.4 μm in diameter). The view in Figure 11 shows a CCN sample after collection. The droplets collected were about 1 μm in diameter, and the sample is what remains after numerous droplets attached to the filter and then evaporated. The individual CCN particles may bear little resemblance to the deposit seen on the filter. Figure 12 shows a sample that has been rinsed in water to remove the soluble material. The comparison is interesting, although subjective. It appears that the visible CCN deposit (Fig. 11) consists of two discernible populations: a crystalline-like material, which resembles the material in Fig. 12 remaining after water extraction, and larger

Figure 10. Picture of 1 mg CCN sample. The areas where the filter support touches the filter are lightly loaded giving the texture a bull's eye appearance.

Figure 11. Scanning electron micrograph of CCN sample at 30 kx magnification.

Figure 12. Scanning electron micrograph of water extracted CCN sample at 30 kx magnification.

coagulated spherical particles that are water soluble, and missing from the extracted sample. The appearance of a methanol extracted sample is similar to the water extracted image.

Samples have been collected on various types of filter material as appropriate for the corresponding analysis technique. At the exit of impactor #2, samples have been collected on 8" x 12" fiberglass high-volume filters and cellulose filters. These samples, which typically have milligram loadings, have been analyzed by ion chromatography (IC), and inductively coupled plasma (ICP). IC analysis includes ammonium and sulfate ions, and ICP gives analysis of 32 different elements, not including carbon.

Samples at the coarse flow of impactor #3 are collected on 47 mm diameter filters which receive several hundred microgram loadings in a 24 hour sampling period. Teflon filters have been used for analysis by x-ray fluorescence (XRF), which gives elemen-

tal analysis of 35 elements, many in common with ICP, and also for IC analysis. Forty-seven mm Nuclepore filters are also used, which can be analyzed by IC, and are suitable for analysis by electron microscopy. Quartz fiber filters have been used for sampling at impactor #3 in order to analyze for carbon. The quartz filters are sampled in groups of 2 in a series flow arrangement in order to evaluate the sampling artifact question, which appears to be an important consideration for interpretation of the results.

Both primary and backup quartz filters have been analyzed by IC, and for carbon using a thermo-optical system in which the carbon sample is heated to 850° C in an oxygen atmosphere, to convert the carbon to carbon dioxide, which is then analyzed by non-dispersive infrared detection.

One cellulose and 7 fiberglass high-volume filters ranging in loading up to 4.6 mg were analyzed by ICP. The following elements were below detection limits, where the detection limits are expressed as if the filter loading were 1 mg: **Ag** < 2.1 µg, **As** < 16.5 µg, **Ba** < 0.5 µg, **Be** < 0.5 µg, **Cd** < 2.6 µg, **Co** < 2.1 µg, **Cr** < 1.1 µg, **Cu** < 0.9 µg, **Fe** < 1.5 µg, **Hg** < 7.5 µg, **Li** < 0.5 µg, **Mn** < 0.6 µg, **Mo** < 5.3 µg, **Ni** < 4.7 µg, **P** < 40.5 µg, **Pb** < 9.9 µg, **Sb** < 75 µg, **Se** < 27 µg, **Sn** < 22.5 µg, **Ti** < 0.9 µg, **Tl** < 78 µg, **V** < 2.6 µg, **Zn** < 3.0 µg. Several elements, all common constituents of fiberglass, were above detection limits on the fiberglass fil-

ters, but below detection limits on the cellulose filter. Blank corrected fiberglass loadings (2 blanks) for these elements also support the conclusion that they are each below detection. Again, expressed as if the filter loading were 1 mg the following upper limits are found: **Al** < 2.6 μg , **B** < 19.5 μg , **Ca** < 6.0 μg , **Mg** < 2.1 μg , **Na** < 4.7 μg , **Si** < 45 μg , **Sr** < 0.2 μg . Potassium is present in both the cellulose and fiberglass samples, but the blank corrected values are below the detection limit of 237 μg per mg of sample. Sulfur, then is the only one of the 32 elements analyzed by ICP that is positively identified, and each blank was below detection limits for S. Six of the fiberglass filters were also analyzed by IC. The ICP results were higher in each case, with the ratio of S mass by ICP to that found by IC averaging 1.12 with a range of 1.03 to 1.21. This suggests the possibility that about 12% of the sulfur is associated with compounds other than ionic sulfate, however such a small difference in S values using such different analysis techniques may not be significant. Unfortunately, the portion of the total mass attributable to sulfur cannot be determined from the gravimetric data. Both the fiberglass and cellulose filters did not hold up well under the high humidity sampling conditions of the CCN collection system, with several filters yielding negative loadings, and the measured loadings are not considered reliable indications of the mass of material collected. The results do rule out earth crustal material as the source of CCN for the Rolla samples.

Elemental analysis results by XRF for a single Teflon filter, reported as percent mass of the filter loading of 625 μg , gave **Si** = 0.6%, **K** = 1.2%, **Fe** = 0.5%, and **S** = 9.1%. All other elements, including **Cl** and **Ca**, were at or below detection. This again implies that the CCN do not contain significant

material of crustal origin. Assuming the sulfur is present as ammonium sulfate, it would account for 37.5% of the total sample mass.

Sulfate anions determined by IC on 2 Teflon and 6 nuclepore filters averaged 37.9% with a range of from 22.4% to 50.1%, given as percent mass assuming the sulfate is present as ammonium sulfate. Nitrate averaged 0.32% by mass with 2 of the 8 filters below detection limits, and the highest value 0.75%. **Cl** was below detection limits. The **NH₄** cation results, on three of the filters analyzed for anions by IC, averaged 37% with a range of from 25% to 41%, again given as the percent mass on the filter assuming **NH₄** is present as ammonium sulfate. In each case the sulfate and ammonium results matched to within a few percent indicating that the inorganic CCN material is, indeed, ammonium sulfate, and that it accounts for about 38% of the total mass.

Six (6) of the 8 filters analyzed by IC were successfully extracted in water without losing insoluble material, and the percent insoluble material in the samples was determined. The average value was 24.4% with a range of from 16% to 33%. This is considerably lower than the values inferred using indirect means (e.g., Alofs et. al., 1989, Fitzgerald et. al., 1982, Fitzgerald et. al., 1984) which lie in the neighborhood of 50%. These measurements, taken together, indicate that the CCN composition is 38% ammonium sulfate, 24% insoluble material, and 38% of a water soluble material that is not **(NH₄)₂SO₄**. Further, the remaining material is not of crustal origin, and neither sodium nor potassium salts.

Three filter pairs have been analyzed for carbon. One of the pairs (Q13 and Q14) was sampled at a pressure of 0.56 atm. while the other pairs were sampled at 0.81 atm, which

corresponds to the conditions for which the previous results have been given. All sampling periods were 24 hours duration. In each case, a section of the original loaded filter was subjected to carbon analysis, and after the filters had been dried to remove the solvent following the extractions, the extracted filters was also analyzed for carbon. Sections of the filter pair Q5 and Q6 were subjected to a procedure of extraction by several different solvents including water, and these results are given in Table VI. It appears that of the solvents used, the collected material on both the primary and backup filters dissolves in methanol better than any of the others. About 10% (21 μg / 208 μg) of the carbon was left on the primary filter after extractions by all the solvents in sequence, which suggests that the remaining carbon is elemental and of anthropogenic origin. This would account for the dark color of the sample. By contrast all solvents in sequence leave less than 1% (2 μg / 258 μg) of the carbon on the backup filter, which indicates that the elemental carbon does not pass to the backup filter. This would account for the lack of a visible deposit on the backup filters. Considering the ratio of soluble to insoluble carbon from Table VI, the samples

significantly increase in both ether solubility and dichloromethane solubility from the primary filter to the backup filter, while the corresponding water solubility decreases. Both methanol and the hexane-acetone mixture have about the same solubility, comparing the primary to the backup filter. There must be a complex redistribution of the chemical compounds in the backup as compared to the primary filter for the different solubility ratios to vary so disparately. The complex solubility properties of the CCN material suggest that it is composed of several organic compounds.

Sections of the other two filter pairs that have been analyzed for carbon were extracted in water, and IC analysis was also performed on the water extract. The results for the filters that include IC analysis are given in Table VII. The results are presented assuming the sulfate is present as ammonium sulfate, and the carbon as carbon compounds with mass greater than the carbon atoms by a factor of 1.43 after Jaenicke (1978) and Duce et al. (1983). Under these assumptions, the analytically measured mass loading on each filter was within 3% of the gravimetric determinations, which provides some

Table VI. Total carbon analysis of quartz filters after extraction in the corresponding solvents. The inorganic mass is 164 μg on the primary filter (Q5) and its total loading is 393 μg . The inorganic mass is 73 μg on the backup filter (Q6), and its total loading is 233 μg .

Solvent	Primary Filter		Backup Filter	
	Soluble carbon (μg)	Insoluble carbon (μg)	Soluble carbon (μg)	Insoluble carbon (μg)
water	136	93	75	85
50% hexane/acetone	177	52	122	38
dichloromethane	112	117	114	46
ethyl ether	170	59	137	23
methanol	196	33	139	21
all solvents in sequence	208	21	158	2

Table VII. Carbon and IC analysis of quartz filters. Q9 and Q10 were sampled at 0.81 atm. pressure. Q13 and Q14 were sampled at 0.56 atm. pressure.

Filter ID	(NH ₄) ₂ SO ₄ (μg)	water sol- uble carbon compounds (μg)	water in- soluble carbon compounds (μg)	derived mass (μg)	gravimet- ric mass (μg)
Q9 (primary)	227	222	168	617	604
Q10 (backup of Q9)	7	240	34	281	283
Q13 (primary)	74	115	163	353	345
Q14 (backup of Q9)	38	136	112	286	293

confidence in the procedure. Considering the results of the primary filter Q9 (sampled at 0.81 atm.), the sulfate was in excess by about 20%, when compared to the ammonium value, to account for the sulfate as (NH₄)₂SO₄. Unfortunately the blank quartz filter was contaminated, so the data for neither ammonium nor sulfate were blank corrected. The resulting mass loadings on the Q9 primary filter were 37.8% (NH₄)₂SO₄, 36.0% soluble carbon compounds, and 27.3% insoluble carbon compounds. This agrees with the partitioning found from separate analysis of the Teflon and Nuclepore filters, and suggests that carbon compounds account for both the water soluble and insoluble non-ammonium sulfate material composing the CCN. There appears to be little doubt that significant organic material is present in the CCN samples.

The presence of significant material on the backup filters indicates the presence of sampling artifacts, which are common when trying to collect organic aerosol samples. The percent mass of the backup compared to the primary filters averages 83% (7 samples

ranging from 49% to 144%). Basically, the artifact must be either positive or negative. A positive artifact occurs when a semi-volatile gas, that is not a significant component of the aerosol being collected, adsorbs on the filters. Once quantified, it must be subtracted to determine the aerosol organic material. A negative artifact, on the other hand, occurs due to volatilization of the aerosol material from the filter under sampling conditions. Once quantified, it would be added back to the remaining aerosol loading to determine the aerosol organic composition.

VII. Negative Sampling Artifacts

There is evidence to suggest that evaporation of CCN deposited on filter #3 will be considerable for volatile particles. The three virtual impactors in the sampling system combine to produce a line pressure of 0.56 atm. at filter #3. Zang and McMurry (1987) performed a theoretical analysis of evaporation loss from filters commonly used to collect atmospheric particulates for chemical analysis. Typically such filters have an inlet pressure of 1 atm., and the evaporation

process is driven by Δp , the pressure drop across the filters. The analysis indicates that for species present at mass concentrations of $10 \mu\text{g m}^{-3}$, evaporation losses will be $>10\%$ for species with vapor pressure above 10^{-9} atm. Zang and McMurry give graphical results (their Fig. 5) for the cases $\Delta p = 0.01, 0.03, 0.05$, and 0.1 atm. Extrapolating to our case of $\Delta p = 0.56$ atm., the indicated evaporation losses are 99.9% by mass for vapor pressure of 10^{-8} atm., 50% for 10^{-9} atm., and 10% for 10^{-10} atm.

Wang and John (1988) performed evaporation artifact experiments with ammonium nitrate aerosol. Upon evaporation, ammonium nitrate disassociates to ammonia and nitric acid, and the vapor pressure of ammonium nitrate is taken as the geometric mean of the partial pressures of ammonia and nitric acid (Stelson and Seinfeld, 1982a,b). The vapor pressure depends on relative humidity (RH) and at 25°C is about 5×10^{-9} atm. for $\text{RH} < 60\%$ and 3×10^{-10} atm. at $\text{RH} = 100\%$ (Stelson and Seinfeld, 1982b). Wang and John (1988) used a polydisperse ammonium nitrate aerosol having a mass median diameter of $0.35 \mu\text{m}$, and a geometric standard deviation of 2.3. For initial mass loading (M) of 171 to $372 \mu\text{g}$ on 47mm filters, evaporation loss was 87 to 95% by mass after passing air at 35°C , 18% RH and 30 lpm through the filters for 6 to 24 hours. The evaporation loss was proportional to $M^{-1.6}$. Parallel experiments with impactors showed much lower evaporation. This was explained in terms of particles piling on top of one another, thereby shielding the bottom particles. Also, because the particle deposit is in a stagnation region, where the air velocity is low, the particle deposit is not well ventilated. Hering et al. (1990) report backup quartz filter loadings of total carbon having 15% to 26% of the front filter loadings. They interpret the backup filter loadings as due to

evaporation of particles on the front filter.

An indication of a negative artifact for our sampling system is seen by comparing the ratio of mass on the backup filter to that on the primary filter for the cases where the impactor #3 pressure is different. The average is 57.3% for samples taken at 0.81 atm. (3 samples ranging from 49% to 63%) and 102% for samples taken at 0.56 atm. (4 samples ranging from 58% to 144%). One possible explanation of this data is that particles deposited on the front filter evaporate more vigorously at the lower pressure, and the vapors are adsorbed on the backup filter.

VIII. Positive Sampling Artifacts

Evidence of positive artifacts have been reported by Cadle et al. (1983), McMurry et al. (1986) and Fitz (1990). Cadle observed a positive artifact when sampling with a duel filter arrangement of as much as 30% of the material on the primary filter being present on the backup filter. McMurry et al. (1986) provided indirect evidence of an enhancement artifact of 72% of the organic material on their front filter of a duel quartz filter arrangement.

Experiments by Fitz (1990) were designed to quantify the positive artifact effect. A parallel sampling arrangement was constructed with two identical series quartz filter arrangements. The ambient sample was split, and went, in one case, directly to a quartz filter pair, and, in the other case, through a denuder, to remove the semi-volatile organic carbon, before going to the second quartz filter pair. The sampling periods were 12 hours. Analysis of the data indicates that the front filter saturates. Apparently the active sites are taken both by the artifact organic, as well as the collected organic aerosol. The artifact material then broke through the front

filter, and was collected on the backup filter. It appears that all the organic vapor reaching the backup filter was collected. Sixteen percent of the material on the front filter was attributed to the positive artifact.

Evidence possibly related to sampling artifacts in our CCN collection system is seen by sampling through a HEPA "absolute" aerosol filter, a high efficiency filter commonly used to control clean room particulate loadings, placed at the inlet of the system. Both Teflon and Nuclepore filters operated at impactor #3 under this condition increase in mass by an average of $40 \mu\text{g}$ (7 samples) over a 24 hour period, during which they would otherwise collect approximately $300 \mu\text{g}$ from an ambient air sample. A four day sampling of "filtered air" loads the filters by only a few micrograms more. The deposit is not visible upon examination of the sample filter, and electron micrographs show virtually no particulate loading. A Teflon filter with a $55 \mu\text{g}$ filtered air loading lost only $2 \mu\text{g}$ after a water extraction, indicating the contaminate material is insoluble in water. Filtered air samples, using quartz fiber filters, pick up an average of $240 \mu\text{g}$ (3 samples), and 2 placed in series have about the same loading on the backup as on the primary filter. However, quartz filters, when placed at impactor #1, just downstream of the absolute filter, collected about the same mass as at impactor #3, when operating with the filtered air arrangement. This indicates that the contaminate material is entering through the absolute filter rather than from the sampling system.

Since both quartz filters of a pair collect the same mass, the contaminate must be saturating both filters. This is also consistent with the observation that prolonged sampling of a Teflon filter does not substantially increase its load. This result is in contrast to

Fitz's data, where the backup filter was not saturated. The sample duration in our data is 24 hours, compared to 12 hours for Fitz, but the absence of aerosol in our system should prevent the primary filter from saturating under normal circumstances. The concentrations of the contaminate in our system, using the filtered air arrangement, must be considerably greater than in ambient sampling. A possible explanation is that aerosol caught in the HEPA filter is volatilizing, and passing through to the sampling system. This means that the contaminate is not present in such high concentrations in our system while sampling ambient air. The important point is that the filtered air contaminate is insoluble in water.

The cloud chambers operate by the principle of the water vapor in the sampled air reaching diffusive equilibrium. Although the diffusion coefficient of organic vapors is smaller than that of water vapor (Zang and McMurry, 1987, cite a value of 0.25 times that of water in an example), it is reasonable that most of the water soluble organic material is removed to the walls of the cloud chambers during operation. If the HEPA filter is volatilizing aerosol material, there is no reason that it would discriminate, and only volatilize water insoluble material. The implication is that only the water insoluble material on the backup filters during ambient sampling can be due to a positive artifact.

IX. Artifact Correction and Avoidance

Limits on the CCN composition, taking into account the artifacts, can be obtained by assuming the artifact is either entirely positive or entirely negative. If it is entirely positive, then the amount on the backup filter should be subtracted from the primary filter. According to the data in Figure VII, this would leave no water soluble organic carbon in the corrected CCN samples (for the first case $-18\text{ }\mu\text{g}$ and $-20\text{ }\mu\text{g}$ for the second). The resulting CCN percent compositions are given in Table VIII. If the artifact is entirely negative, the appropriate correction is to add the backup filter loadings to the primary filter. The results of this scenario are also given in Table VIII. The entirely positive artifact results are fairly close to measurements in which the amount of CCN material is inferred from corresponding measurements of the CCN size and critical supersaturation (e.g., Alofs et. al., 1989, Fitzgerald et. al., 1982, Fitzgerald et. al., 1984). In the interpretation of such measurements, it is normally assumed that the active CCN material is $(\text{NH}_4)_2\text{SO}_4$, and the insoluble material is assumed present to sufficient amounts to

match both theory and measurements. However, the same data is not necessarily inconsistent with appreciable organic carbon composing the CCN material.

Another artifact correction scenario is presented, which follows the arguments presented above to the effect that the vapor phase water soluble organic compounds are removed by the cloud chambers. The water soluble material on the backup filter is thus taken to be a negative artifact from volatilization of the CCN aerosol from the primary filter, and it is "corrected" by adding the water soluble mass on the backup filters to the corresponding primary filter. Although part or all of the water insoluble organic material could also be due to a negative artifact, it is taken as positive in the calculation. The water insoluble carbon on the backup filter accounts for a larger part of the total carbon (soluble plus insoluble) for the lower pressure sample, which suggests it too may be volatilizing during operation of the system. The inorganic material is corrected as a negative artifact in both cases. The results of this artifact correction scheme are also given in Table VIII. The filters run at different pressures correct to nearly the same fraction of each of the different components under

Table VIII. Three scenarios for artifact correction.

Artifact type	Filter pair	% $(\text{NH}_4)_2\text{SO}_4$	% water soluble carbon compound	% water insoluble carbon compound
Entirely Positive	Q9 and Q10	62	0	38
Entirely Positive	Q13 and Q14	41	0	59
Entirely Negative	Q9 and Q10	26	51	23
Entirely Negative	Q13 and Q14	18	39	43
Soluble Carbon	Q9 and Q10	28	56	16
Negative				
Soluble Carbon	Q13 and Q14	27	61	12
Negative				

this correction scheme, The true CCN composition should not depend on the sampling condition, so the correction scheme has some credibility.

There are several possible fixes to the CCN collection system, which would reduce evaporation of volatile species. One idea is to run impactor 3 with zero minor flow, so that the particles remain in the large particle receiver. Biswas and Flagan (1988) have investigated such an impactor, and find it has good size resolution and low losses. The advantage for evaporation is that the particles would collect in an unventilated cavity, shielded from air flow. The initial particle evaporation would raise the vapor pressure of the organic material in the particle trap cavity, and slow down further evaporation. The disadvantage of this option is that it would be tedious to remove the particles from the walls of the particle receiver; this would be much less convenient than collecting the CCN on filters.

Another possible way to reduce particle evaporation is to cool the particle receiver region of impactor #3. This would not work with the present impactor #3, because water in the 100% RH airstream would condense and plug filter #3; however, this is feasible for the new version of impactor 3 which has zero minor flow, and flushes the big particles out of the collection region using filtered air. If this filtered air were dry, the particle receiver and the filter to collect the particles could be cooled by say 50 degrees C. In studying the movement of organic vapors through polyurethane foam, a material used to trap ambient organic vapors, Keller and Bidleman (1984) report that a mere drop in the temperature of the foam trap from 25° C to 20° C decreased the breakthrough of organics by 40% for the same volume of air sampled.

The positive artifact can be removed by placing a denuder upstream of the filter. This was successfully achieved by Fitz (1990) for about the same flow rates as in our case of for the coarse flow in impactor #3.

X. Conclusions

The discovery of organic material in the CCN samples collected to date from Rolla, MO is a noteworthy development. If the work is verified by continued sampling, and is found to hold over a wide geographic region, it will be important for the assessment of the effect of CCN on the global heat balance. If it turns out that CCN are composed of biogenic organic material, the production of which must be related to global temperature, it would strengthen the notion of a feedback mechanism: An increase in global temperature would increase the production of organic material, which would, in turn, increase CCN and resulting cloud amounts. Increased cloudiness is postulated to have a global cooling effect. If the Rolla CCN material is anthropogenic in origin, despite the relatively unpolluted environment, it would seem to imply that mans activities have a strong impact on CCN production, and, consequently, on the resulting global cloud amounts.

Our results at this stage must be regarded as preliminary. Although the CCN samples consistantly yield an approximate breakdown of 38% $(\text{NH}_4)_2\text{SO}_4$, 38% soluble organic material, and 24% water insoluble carbon compounds, the occurance of sampling artifacts make the interpretation very difficult. If the sampling artifact is entirely positive, due to the collection of organic materials from the air onto the sample filters, the artifact-corrected soluble organic CCN material is very small. If the artifact is due entirely to volatilization of CCN material from the fil-

ters during sampling, the corrected values for soluble organic CCN material is between 40% to 50 %. If the artifact correction is based on the notion that most of the soluble organic vapors will be removed by diffusion to the walls of the cloud chambers in the system before reaching the sampling filter, which is consistent with our limited observations, it follows that 50% to 60% of the CCN material being composed of soluble carbon material. Resolution of the sampling artifact problem is receiving high priority.

The numerical modeling results, that simulate the operation of the CCN collection system, indicate that it is feasible to collect CCN particles with dry diameter below 0.1 μ m in sufficient amounts to distinguish their composition from that of larger particles. Model results using impactor curves from the system under operating conditions raise some doubt, and suggest that, with the present efficiencies, the CCN samples below 0.1 μ m diameter will be contaminated by about 50% with material from larger particles. The need for resolving whether the CCN chemistry varies with particle size is even more sharply defined with the notion of an appreciable organic CCN component.

Construction of the main equipment items is complete now that all the impactors are finished. Testing of the complete system at its designed flow rates and sampling capability is now underway for the laboratory version. The mobile version is in the final stages of assembly.

XI. Acknowledgment

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XII. References

- Alofs, D.J., D.E. Hagen, and M. B. Trueblood (1989): Measured spectra of the hygroscopic fraction of atmospheric fraction of atmospheric aerosol particles. *J. Appl. Meteor.* **28**, 126-136.
- Alofs, D. J., (1978): Performance of a dual range cloud nucleus counter. *J. Appl. Meteor.*, **17**, 1286-1297.
- Appel, B.R., Y. Tokiwa, and E.L. Kothny (1983): Sampling of carbonaceous particles in the atmosphere. *Atmospheric Environment*, **17**, 1787-1796.
- Balling, R.C.Jr., and S.B. Idso (1991): Decreasing diurnal temperature range: CO₂ greenhouse or SO₂ energy balance effect? *Atmos. Research* **26**, 455-459.
- Bigg, E. K. (1986): Technique for studying the chemistry of cloud condensation nuclei, *Atmospheric Environment*, **20**, 75-80.
- Biswas, P. and Flagan R.C. (1988): The particle trap impactor. *J. Aerosol Sci.*, **19**, 113-121.
- Blanchard, D.C. (1964): Sea-to-air transport of surface active material, *Science*, **146**, 396-397.
- Blanchard, C.D. (1968): Surface active organic material on airborne salt particles, paper presented at International Conference on Cloud Physics, Int. Assoc. of Meteorol. and Appl. Phys., Toronto, Aug. 26-30.
- Brown, G.M. (1960): Heat and mass transfer in a fluid in laminar flow in a circular or flat conduit. *AIChE Journal* **6**, 179-183.

- Biswas, P. and Flagan R.C. (1988): The particle trap impactor. *J. Aerosol Sci.*, **19**, 113-121.
- Blanchard, D.C. (1964): Sea-to-air transport of surface active material, *Science*, **146**, 396-397.
- Blanchard, C.D. (1968): Surface active organic material on airborne salt particles, paper presented at International Conference on Cloud Physics, Int. Assoc. of Meteorol. and Appl. Phys., Toronto, Aug. 26-30.
- Brown, G.M. (1960): Heat and mass transfer in a fluid in laminar flow in a circular or flat conduit. *AIChE Journal* **6**, 179-183.
- Carstens, J.C. (1979): Drop growth in the atmosphere by condensation: application to cloud physics. *Adv. Colloid Interface Sci.* **10**, 285-314.
- Cadle, S.H., P.J. Groblicki, and P.A. Mulawa (1983): Problems in the sampling and analysis of carbon particulate. *Atmospheric Environment*, **17**, 593-600.
- Cautreels, W. and K. Van Cauwenberghe (1978): Experiments on the Distribution of organic Pollutants between airborne particulate matter and the corresponding gas phase, *Atmospheric Environment*, **12**, 1133-1141.
- Charlson, R.J., A. H. Vanderpol, D. S. Covert, A. P. Waggoner, and N. C. Ahlquist (1974): $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ background aerosol: Optical detection in St. Louis region. *Atmos. Environ.* **8**, 1257-1267.
- Charlson, R.J., J.E. Lovelock, M.O. Andreae, and S.G. Warren (1987): Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* **326**, 655-661.
- Cobourn, W. G., and R. B. Husar (1982): Diurnal and seasonal patterns of particulate sulfur and sulfuric acid in St. Louis, July 1977-June 1978. *Atmos. Environ.* **16**, 1441-1450.
- Duce, R. A. (1978): Speculations on the budget of particulate and vapor phase non-methane organic carbon in the global troposphere, *Pure and Appl. Geophys.*, **116**, 244-273.
- Duce, R.A., V.A. Mohnen, P.R. Zimmerman, D. Grosjean, W. Cautreels, R. Chatfield, R. Jaenicke, J.A. Ogren, E.D. Pellizzari, and G.T. Wallace (1983): Organic material in the global troposphere, *Reviews of Geophysics and Space Physics*, **21**, 921-952.
- Fitz, Dennis R. (1990): Reduction of the positive organic artifact on quartz filters, *Aerosol Science and Technology*, **12**:142-148.
- Fitzgerald, J. W., W.A. Hoppel, and M. A. Vietti (1982): The size and scattering coefficient of urban aerosol particles at Washington, DC as a function of relative humidity. *J. of Atmos. Sci.* **39**, 1838-1852.
- Garrett, W.D. (1968) The influence of monolayer surface films on the production of condensation nuclei from bubbled seawater, *J. Geophys. Res.*, **73**, 5145-5150.
- Georgi, H. W. (1978): Large-scale spatial and temporal distribution of sulfur compounds. *Atmos. Environ.* **12**, 681-690.

- Hameri, K., M. Rood, and H.-C. Hansson, (1992): Hygroscopic properties of a NaCl aerosol coated with organic compounds, European Aerosol Conference, September, Oxford, England, in press.
- Hammersley, J.M., and D.C. Handscomb (1964): Monte Carlo Methods, Methuen, London.
- Harrison, L. (1985a): The segregation of aerosols by cloud - nucleating activity. Part II: Design, construction, and testing of a high-flux thermal diffusion cloud chamber for mass separation. *J. Climate and Appl. Meteor.* **24**, 3302-310.
- Harrison, L. (1985b): The segregation of aerosols by cloud - nucleating activity. Part II: Observation of an urban aerosol. *J. Climate and Appl. Meteor.* **24**, 312-321.
- Hatton, A.P., and J.S. Turton (1962): Heat transfer in the thermal entry length with laminar flow between parallel walls at unequal temperatures. *Int. J. Heat Mass Transfer* **5**, 673-679.
- Hahn, J. (1980): Organic constituents of natural aerosols, *Ann. N.Y. Acad. Sci.*, **338**, 359-376.
- Hegg, D. A. and P. V. Hobbs (1992) Cloud Condensation Nuclei in the Marine Atmosphere: A Review, proceedings of the 13th International Meeting on Nucleation and Atmospheric Aerosols, 24-28 August, 1992, edited by N. Fukuta and P. Wagner, p181-192.
- Hering, S.V., B.R. Appel, W. Cheng, F. Salaymeh, S.H. Cadle, A. Mulawa, T.A. Cahill, R.A. Eldred, M. Surovik, D. Fitz, J.E. Howes, K.T. Knapp, L. Stockburger, B.J. Turpin, J.J. Huntzicker, X.Q. Zhang, and P.H. McMurry, (1990): Comparison of sampling methods for carbonaceous aerosols in ambient air. *Aerosol Sci. Tech.*, **12**, 200-213.
- Hudson, James G. (1991): Observations of anthropogenic cloud condensation nuclei, *Atmospheric Environment*, **25A**, **11**, 2449-2455.
- Husar, R.B., and W.R. Shu (1975): Thermal analysis of the Los Angeles smog aerosol, *J. Appl. Meteorol.*, **14**, 1558-1565.
- Jaenicke, R. (1978): The role of organic material in atmospheric aerosols, *Pure Appl. Geophys.*, **116**, 283-292.
- Junge, C.E. (1972): Our knowledge of the physico-chemistry of aerosols in the undisturbed marine environment. *J. Geophys. Res.* **77**, 5183-5200.
- Kaufman, Y.J., and R.S. Fraser (1991): Fossil fuel and biomass burning effect on climate-heating or cooling? *J. of Climate*, **4**, 578-588.
- Keller, C. D., and Bidleman, T. F., (1984): Collection of airborne polycyclic aromatic hydrocarbons and other organics with a glass fiber filter-polyurethane foam system. *Atmos. Environ.*, **18**, 837-845.
- Ketersidis, G., J. Hahn, R. Jaenicke, and C. Junge (1976): The organic constituents of atmospheric particulate matter, *Atmos. Environ.*, **10**, 603-610.
- Ketseridis, G., and R. Eichman (1978): Organic compounds in aerosol samples, *Pure Appl. Geophys.*, **116**, 274-282.

- Laktionov, A.G. (1972): A constant temperature method of determining the concentrations of cloud condensation nuclei. *Atmos. Ocean Phys.*, **8**, 382-385.
- Liu, B.Y.H. and Pui, D.Y.H. (1974): A submicron aerosol standard and the primary absolute calibration of the condensation nuclei counter. *J. Colloid Interface Sci.*, **47**, 155-171.
- Loo, B.L. and Cork, C.P. (1988): Development of high efficiency virtual impactors. *Aerosol Sci. Tech.*, **9**, 167-176.
- MacIntyre, F. (1972): Flow patterns in breaking bubbles, *J. Geophys. Res.*, **77**, 5211-5228.
- MacIntyre, F. (1974): The top millimeter of the ocean. *Sci. Am.*, **230**(5), 62-77.
- Marple, V.A., and C.M. Chien (1980): Virtual impactors: a theoretical study. *Environ. Sci. and Techn.* **14**, 976-985.
- Meszaros, E. (1968): On the size distribution of water soluble particles in the atmosphere. *Tellus* **20**, 443-448.
- Meszaros, E. (1988): On the possible role of the biosphere in the control of atmospheric clouds and precipitation. *Atmos. Environ.* **22**, 423-424.
- Ono, A., and T. Ohtani (1980): On the capability of atmospheric sulfate particles as cloud condensation nuclei. *J. Rech. Atmos.* **14**, 235-240.
- Podzimek, J., and A.N. Saad (1975): Retardation of condensation nuclei growth by surfactant. *J. Geophys. Res.*, **80**, 3386-3392.
- Pruppacher, H.R., and J.D. Klett (1978): Microphysics of Clouds and Precipitation, Reidel, Dordrecht.
- Rood, M. J., Hansson, H.-C., Wiedensohler, A., and Covert, D. S. (1991) Experimental Determination of the Hygroscopic Properties of Organically Coated Aerosol Particles, 84th Annual Meeting of the Air and Waste Management Association, June, Vancouver, British Columbia, Canada, 91-51.8, 8pp.
- Rosinski, J., B.W. Gandruid, C. T. Nagamoto, and F. Parungo (1984): Cumulative chemical composition of atmospheric cloud condensation nuclei. *J. Aerosol Sci.* **15**, 709-718.
- Rubel, G. O., and J. W. Gentry (1985) Measurement of water and ammonia accommodation coefficients at surfaces with adsorbed monolayers of hexadecanol. *J. Atmos. Sci.*, **16**, 571-574.
- Sparrow, E.M., and T.S. Chen (1969): Mutually dependent heat and mass transfer in laminar duct flow. *AIChE Journal* **15**, 434-441.
- Schwartz, S.E., (1988): Are global cloud albedo and climate controlled by marine phytoplankton? *Nature* **336**, 441-445.
- Silaev, A. V., L. V. Ivanchenko, and R. A. Bakbovona, (1971) Passivation of ammonium chloride nuclei by cetyl alcohol vapor, Advances in Aerosol Physics, Vol 2, V. Sedoseiev, Ed., New York, Halstead Publ. Co., 59-65.

- Stelson, A.W. and J.H. Seinfeld (1982a): Relative humidity and temperature dependence of the ammonium nitrate dissociation constant. *Atmos. Environ.*, **16**, 983-992.
- Stelson, A.W. and J.H. Seinfeld (1982b): Relative humidity and pH dependence of the vapor pressure of ammonium nitrate-nitric acid solutions at 25 C. *Atmos. Environ.*, **16**, 983-992.
- Storozhilova, A. I. (1971): Passivation of hygroscopic condensation nuclei by surfactant adsorption from the gas phase, *Advances in Aerosol Physics*, Vol 1, V. Sedoseiev, Ed., New York, Halstead Publ. Co., 47-52.
- Twomey, S., and G. T. Severynse (1964): On the relation between sizes of particles and their ability to nucleate condensation of natural clouds. *J. Rech. Atmos.* **1**, 81-85.
- Twomey, S. (1971): The composition of cloud nuclei. *J. Atmos. Sci.* **28**, 377-381.
- Twomey, S. (1972): Measurements of the size of natural nuclei by means of nucleopore filters. *J. Atmos. Sci.* **29**, 318-321.
- Twomey, S. (1977a): The influence of pollution on the shortwave albedo of clouds. *J. Atmos. Sci.* **34**, 1149-1152.
- Twomey, S. (1977b): On the minimum size of particles for nucleation in clouds. *J. Atmos. Sci.* **34**, 1832-1835.
- Twomey, S.A., M. Piepgrass, and T. L. Wolfe (1984): An assessment of the impact of pollution on global cloud albedo. *Tellus* **36B**, 356-366.
- Van Vaeck, L., and K. Van Cauwenberghe, (1978): Cascade impactor measurements of the size distribution of the major classes of organic pollutants in atmospheric particulate matter, *Atmos. Environ.*, **12**, 2229-2239
- Van Vaeck, L., K. Van Cauwenberghe, and J. Janssens, (1984): The gas-particle distribution of organic aerosol constituents: measurement of the volatilisation artefact in hi-vol cascade impactor sampling, *Atmos. Environ.*, **18**, 417-420
- Wang, H.W. and W. John (1988): Characteristics of the Berner impactor for sampling inorganic ions. *Aerosol Sci. Tech.*, **8**, 157-172.
- Whitby, K.T. (1978): The physical characteristics of sulfur aerosols. *Atmos. Environ.* **12**, 135-159.
- Wigley, T.M.L. (1989): Possible climate change due to SO₂-derived cloud condensation nuclei. *Nature* **339**, 365-367.
- Williams, Allen L., Jane E. Rothert, Kent E. McClure, Darryl J. Alofs, Donald E. Hagen, Daniel R. White, A. R. Hopkins, and Max B. Trueblood, Determining the Chemical Composition of Cloud Condensation Nuclei-Second Progress Report, SWS contract Report 503, February, 1992.
- Zang, X. Q. and P. H. McMurry (1987): Theoretical analysis of evaporative losses from impactor and filter deposits, *Atmos. Environ.*, **8**, 1779-1789.

Appendix A. Laboratory version of CCN collection system constructed at University of Missouri-Rolla

Views of the haze chamber (top left), the CFD chamber (top right and bottom right). The flow enters the haze chamber through impactor #1, shown attached to the haze chamber. The flow leaves the haze chamber through impactor #2, located at the far end of the haze chamber (not visible in this photograph). It then crosses to the right and enters the far end of the CFD. The flow exits through impactor #3 shown attached to the CFD (foreground top right view). Part of the return system of the wetting water for the hot plates inside the CFD is visible in the top right view as a pipe running the length of the chamber attached at several places along the base. The pumps, and water tank (lower right view) are basically to regulate the cold plates in the CFD by flowing thermally regulated water at 50 gpm.

Views of impactor #1 at inlet of haze chamber (top left), impactor #2 at exit of haze chamber (top right), and impactor #3 at outlet of CFD chamber (bottom right). The flow entering impactor #1 is heated by a shell-and tube heat exchanger partly in view just upstream of impactor #1. The insulated double walled manifold through which the impactor is attached to the haze chamber is constructed to minimize heat transfer from the incoming air to the frame of the haze chamber. It has been necessary to heat and insulate impactor #2 (shown without insulation) and impactor #3 in order to prevent condensation on the inner impactor surfaces that degrades the performance. The bundle of wires passing into the CFD chamber just above the impactor are thermocouple leads to monitor the plate temperatures. Thermocouples are also attached to the haze chamber plates. By checking the plate temperature uniformity, malfunctions in the plate wetting can be detected during operation.

View of impactor #2 at exit of haze chamber and entrance to CFD chamber (top left), a close-up view of impactor #2 with insulated cover (top right), and view at exit of CFD chamber just above impactor #3 showing window (right). The high-volume filter holder at the entrance to the CFD chamber, when connected into flow system, collects a sample of material exiting the haze chamber. Results on analysis of this sample are reported in the body of this report. The dionized water clean-up system for the wetting water of the haze and CFD chamber plates can be seen mounted on the wall just beyond impactor #2. The pump on the floor below the impactor circulates wetting water from the haze chamber.

Small CFD chamber (top left) and differential mobility analyzer (top right picture in left foreground) used, for example, to determine the dry size versus critical supersaturation of the CCN aerosol taken from the coarse flow of impactor #3. The CCN concentrations in the large cloud chamber collection system are high enough that analysis of its operation by such common methods is feasible.

The view at the right is the blower used to pull ambient air (1332 lpm under full operation) through the CCN collection system.

Appendix B. Mobile version of CCN collection system and impactor design being constructed at Illinois State Water Survey

The top view shows the 36 ft. goose-neck trailer in which the mobile version of the CCN collection system is being constructed. The design of the mobile version is the same as the laboratory version. The lower left view is from the large tail-gate door at the rear of the trailer. A substantial frame inside the trailer was constructed to support the cloud chambers, and to support a hoist that can travel the length and width of the trailer. It is anticipated that the cloud chambers will need to be taken apart on the road, and the hoist is necessary for moving the various components. The lower right view shows the haze chamber (right) and the CFD chamber (left). The water tanks for the CFD cold plates, and the smaller tank for the plate wetting water of both the haze and CFD chambers can be seen at the back of the trailer.

View of CFD chamber showing the hot plate in the chamber and O-ring around the frame (top left). One cold plate leaning against the haze chamber prior to installation of cold plate (top right). The completed CFD chamber is shown at right. The stands bearing the CFD (and haze) chamber weight are designed to buffer against mechanical shock of normal road travel.

The top left view shows the doors to the compartment in the goose-neck of the trailer where the blower, cooler , pumps and miscellaneous equipment are to be stored. A desk and work space is shown to the left in front of the doors. The top right view shows the dionized water system to continually clean the plate wetting water.

Below left is a view of the impactor design which is a 4-piece construction. The collection cup which fits inside the impactor is shown at the bottom right. The cup in impactors #1 and #2 have the shoulders removed on each side of the slit to minimize particle loss. The impactor #3 cup appears similar to the view shown, with channels drilled along the length of the cup adjacent to the slits. The channels are connected to the inside of the cup via internal slits running the length of the cup on each side, in order to draw the sample from the cup.

Three pieces of the 4-piece impactor construction. The top piece is the inlet (oriented so the inlet is down). The middle piece is a spacer inside of which the collection cup is positioned. The bottom view shows the base, in which the collection cup sets. The major or fine flow passes through the base and out. The sample from the coarse flow in impactors #1 and #2 is extracted through the outlets on the side of the base. For impactor #3 with a purge flow design, the purge flow enters through the side of the base, flows through the bottom of the cup, and exits near the mouth of the cup (Williams et al., 1992).

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