MASTER

IMPACT OF GASEOUS SULFUR AND AEROSOLS PRODUCED BY
POWER PLANTS ON THE CCN BUDGET

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ABSTRACT

Under the auspices of the Multi-State Power Production Pollution Study (MAP3S) a field experiment was carried out over Lake Michigan in cooperation with the Battelle, Pacific Northwest Laboratory (PNL) during November 1978 and January 1979 with an aim to delineate cloud-aerosol interactions. The PNL DC3 aircraft was used as an observational platform and a network of ground stations collected samples of precipitation which consisted of liquid phase during the early part of November and of solid phase during the January flights. Flight operations were based at the Muskegon (MKG) airport where the satellite photographs and weather details were also available for flight planning for which the south, south-westerly surface winds were preferred in order to investigate the modification in the physio-chemical characteristics of the sulfate-rich aerosol during its passage over the lake and before its involvement in clouds. A cloud condensation nucleus (CCN) spectrometer was installed in the DC3 which had the capability of making simultaneous measurements of Aitken nuclei concentration, cloud droplet size distribution, LWC, and SO₂ concentration. Cloud water was also collected for later chemical analysis through direct cloud penetrations. The CCN Spectrometer measurements revealed the CCN enrichment within the subcloud layer and suggested that the

cloud formation may be as important as the microphysics in evolving the droplet size spectra of clouds that were investigated over Lake Michigan.

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1. INTRODUCTION

Cloud-aerosol interactions are of consequential importance in understanding the thermodynamics and energy balance of the environment, extent of the cloud cover, scavenging mechanisms operative in clouds, and the chemical nature of precipitation received on the ground. In urban-industrial regions where the acidity of precipitation has been a cause of concern, it is imperative to investigate these interactions if the precipitation acidity is desired to be controlled through regulatory emission standards. Aerosols are removed from the atmosphere by being deposited or transported to the ground. The aerosol particles which are so received at the ground often differ greatly in their physico-chemical characteristics from the ones they had at the location of their formation or emission. Between emission and deposition, condensation and evaporation of water, growth and evaporation of particles themselves, chemical and photochemical reactions, coagulation of particles, diffusion of particles to cloud droplets and hydrometeors, and inertial collection by larger particles affect their physico-chemical characteristics. Obviously, there are a large number of steps and a great variety of combinations of such

steps which may occur between emission and deposition. Precipitation processes originating in warm and cold clouds constitute an important sink for aerosols.

Precipitation scavenging may bring the atmospheric pollutants to the earth's surface through one of the following routes (Twomey, 1977):

Gas → Particle → Cloud droplet → Rain drop →
Surface deposition

or

Gas → Cloud Droplet → Rain drop → Surface deposition.

For the formation of each cloud droplet, a cloud condensation nucleus (CCN) is required and a cloud droplet has to grow a million times in size in order to become a raindrop. Evidently, an enormous range of dimensions is spanned by these processes. The efficiency of in-cloud removal processes for particles in most size ranges is high when compared with the processes for dry removal and removal by precipitation below cloud levels. This is due to the fact that very large surface area is provided by the cloud droplets and cloud nucleation is capable of transferring aerosol particles from a small size into a much larger size range quite abruptly. The latter indeed is most effective when particles are soluble. For example, a sulfate particle with

an initial radius of $0.02\text{ }\mu\text{m}$ will grow through cloud nucleation one hundred times and thereby advance some two decades through the size spectrum within a short time interval of ten seconds or so.

The cloud nucleation activity of aerosols was investigated by us (under Contract No. DE-AS02-78EV04965) over Lake Michigan during November 1978-January 1979 under MAP3S (Multi-State Atmospheric Power Production Pollution Study). The field experiment was carried out in cooperation with the Battelle, Pacific Northwest Laboratory (PNL) with an aim to delineate cloud-aerosol interactions. The PNL DC3 aircraft was used as an observational platform and a network of ground stations collected precipitation samples. Our cloud condensation nucleus (CCN) spectrometer (Fukuta and Saxena, 1973; Fukuta et al., 1974; Saxena and Fukuta, 1976; Saxena and Dytch, 1978; Fukuta and Saxena, 1979a; 1979b) was installed in the DC3 which was also equipped for measuring the Aitken nuclei concentration, cloud droplet size distribution, liquid water content of clouds, SO_2 concentration in the subcloud layer, and sulfate concentration in the cloud water collected through direct aircraft penetrations.

In urban-industrial areas, the precipitation acidity is largely controlled by sulfur which is one of the most

dominant pollutants. It gets involved in essentially all of the scavenging interactions that are typically important as removal mechanisms. Sulfur dioxide can be scavenged as a gas, leading to the presence of dissolved SO_2 in precipitation and sulfate can be scavenged directly as an aerosol or it can be formed in precipitation by aqueous-phase SO_2 oxidation, eventually leading to the precipitation-borne sulfate. Recent estimates (MAP3S, 1979) show that roughly one-third of the MAP3S-area (i.e., the region including the upper Midwest and the Northeast U.S., often referred to as Greater Northeast) sulfur emissions are removed within the region by precipitation scavenging, with an average of about ninety percent of the sulfur occurring in rain as sulfate, the remainder being in the form of dissolved SO_2 . Investigations of the lake effect snowstorms reveal (Scott, 1978) that between 50-90% of the subcloud sulfate gets activated as CCN.

2. BACKGROUND

2.1 Contribution of Sulfates to the CCN Budget

The CCN budget is not only affected by the direct emission of sulfate particles but also by the total aerosol

loading of the atmosphere by power plants and emission of various trace gases and hydrocarbons. This is because the atmosphere is a highly interactive system and the CCN may be generated through various mechanisms. For example, small particles of molecular dimensions may be formed by various gas reactions, such as the oxidation of SO_2 or H_2S or NO_x , or by the photochemical decomposition of hydrocarbon vapors. Such particles grow by coagulation, the collection of particles by cloud droplets followed by their evaporation. These processes produce particles in the size range of 0.01 to 0.1 micron and contribute to the atmospheric aerosol loading on the order of 10^{15} g/yr (Peterson and Junge, 1971). The surface of aerosol particles also gets modified by sorption of atmospheric trace gases such as NH_3 , NO_2 , SO_2 , O_3 and hydrocarbons except methane, thus making them active as CCN by lowering their critical supersaturations (Pueschel et al., 1974).

As an example of the CCN formation from gas-to-particle conversion processes, let us consider one of the suggested mechanisms, namely, the oxidation of SO_2 through cloud droplets. Globally, 1.33×10^{14} g of sulfur results from the conversion of H_2S (Hales et al., 1974) or SO_2 into sulfates each year (Friend, 1973). This is equivalent to the annual production of 4.2×10^{12} moles of sulfate. Sellers (1965)

estimated the global precipitation as 5×10^{17} liters of water annually. Following Easter and Hobbs (1974), if a conservative assumption is made that only half the moisture which condenses in clouds is received on the ground as precipitation, the total water available in the form of clouds over a one year period turns out to be 10^{18} liters. Through analyses of the rain water, it has been established that the sulfate is one of its important constituents and is normally found in conjunction with ammonia. This points out that the sulfate generally exists as ammonium sulfate in cloud droplets whose evaporation releases ammonium sulfate particles.

For the oxidation of SO_2 to $\text{SO}_4^{=}$ in water, the presence of a catalyst is necessary (Junge and Ryan, 1958). Ammonia may very well act in this capacity (Scott and Hobbs, 1967). However, the rate limiting process is the oxidation of $\text{SO}_3^{=}$ ion. The rate of production of $\text{SO}_4^{=}$ may be written as

$$\frac{d[\text{SO}_4^{=}]}{dt} = K[\text{SO}_3^{=}]$$

Different values of K have been reported by Miller and de Pena (1972), and McKay (1971). If the oxidation of SO_2 (concentration of 1 ppb) is allowed in 10^{18} liters of available cloud water in the presence of ammonia (concentration of 3 ppb) for 15 minutes, 6×10^{12} moles of sulfate may be produced if Miller and de Pena's value of K is used.

The sulfate production goes up to 4×10^{13} moles if McKay's value of K is used. This production is calculated (Easter and Hobbs, 1974) for typical atmospheric conditions of 0°C , 750 mb, and 0.5 g kg^{-1} liquid water.

In the light of the above discussion, it may be concluded that the oxidation of SO_2 through cloud drops is capable of accounting for the atmospheric sulfate production on a global scale. However, the above model proposed by Easter and Hobbs (1974) has been tested only for wave clouds. Convincing evidences exist that the chemical composition of cloud water is greatly influenced by the meteorological conditions and is not identical in different clouds (Petrenchuk, 1968; Petrenchuk and Drozdova, 1969). This fact coupled with the uncertainty in the rate constant, K, emphasizes the complexity of the mechanisms involved in the conversion of sulfur dioxide to sulfate.

Gaseous SO_2 may be oxidized to H_2SO_4 or various sulfates (e.g. Hales and Dana, 1979) by a large set of mechanisms which may involve gas phase oxidation in a solution droplet, catalysis within a solution droplet or catalysis at a solid-gas interface. The overall rate of sulfate production is thus a complex function of several rate determining processes involving gas phase transport, photochemical and chemical

reactions in gaseous phase, transport within a liquid, chemical reaction in the liquid phase, nucleation and surface catalysis. Thus a set of mechanisms occurring simultaneously assumes prime importance.

3. EXPERIMENTAL

The impact of the CCN production and their chemical composition on the local hydrologic cycle is indeed complex. The prerequisite for modeling such an impact is the knowledge of the CCN activity spectrum in addition to other parameters such as the updraft speed, concentration of ice-forming particles, dynamics of the surrounding air mass, etc. Nevertheless, a first step toward the understanding of this complicated behavior is the plume characterization with respect to the CCN activity spectrum. We accomplished this by using the best available instrument for measuring in real time the entire CCN spectrum with a high spatial resolution, namely our CCN Spectrometer (ref. Appendix A and B).

The CCN spectrum has been customarily measured by using Twomey-type thermal diffusion chambers (Twomey, 1963). With these devices, the CCN spectrum is determined by measuring the CCN concentration at several discrete supersaturations (comparable to those encountered in natural clouds) that are successively produced and sustained, one at a time, in a thermal diffusion chamber. Such measurements are obviously unable to yield the CCN spectrum with a time resolution that is required for guiding the measurements at the initial stages in a fog- or cloud-forming air mass, and for tracking and mapping different air masses such as the plume from a power plant. Two recent improvements of the Twomey-type chamber, one by Sinnarwalla and Alofs (1973) and the other by Hudson and Squires (1973, 1976), do not offer better time resolutions in the measurement of the CCN spectrum inasmuch as only one supersaturation can be produced and sustained at a given point in time.

A CCN spectrometer capable of producing real-time measurements and display of the CCN spectrum with a time resolution of 30 sec. has been recently developed in our laboratory. The main section of the spectrometer consists of a chamber in which a set of cloud supersaturations are simultaneously produced and sustained. The CCN concentration

is automatically recorded by photoelectronically monitoring the forward scattered light from the individual droplets grown on activated nuclei. The spectrometer was first introduced by Fukuta and Saxena (1973) and has been subsequently improved and used in field measurements (Fukuta et al., 1974; Saxena and Fukuta, 1976). The principle and design of the spectrometer are discussed in Appendices A and B. The spectrometer has also been extensively compared with a Twomey-type device (Saxena and Dytch, 1978). From the results of these intercomparisons, it is evident that the spectrometer possesses sufficiently high accuracy to provide dependable measurements, though for our measurements, what is needed is a high relative reliability. Being a completely automatic instrument, the spectrometer affords the same and provides the most suitable device for measuring the CCN spectrum.

For making measurements over Lake Michigan, the spectrometer was installed in the DC3 aircraft of the Battelle, Pacific Northwest Laboratories, Richland, Washington. The spectrometer has already been flown in the DC3 aircraft of PNL for over sixty hours. In Table 1, the weight and power requirements for the spectrometer are listed. In Figure 1, a perspective view of the sampling section of the spectrometer is shown and in Figure 2, its various components are shown

Table 1
Components of the CCN Spectrometer

Components	Weight lbs	Power	
		110 V, 60 Hz, AC amp	28 V, DC amp
Main Chamber (1)*	76	1.0	--
Preconditioning Chamber (2)	1.5	--	--
Optical Sensor (3)	20.5	--	--
X-Y Recorder (4)	30	1.5	--
Scanner Control Box (5)	Weight included in (1)	1.0	--
CI-201 Particle Analyzer (6)	45	2.0	--
Diluter (7)	8.5	--	--
Cooling Water Bath (9)	20.5	1.0	3.0

*These numbers are the same as in the legend of Fig. 2.

Fig. 1 . Perspective view of the aerosol sampling section of the CCN Spectrometer.

Fig. 2. CCN Spectrometer aboard the NCAR Electra. 1--main sampler, 2--preconditioning chamber, 3--optical sensor, 4--automatic feed X-Y recorder, 5--control box for scanner, 6--electronics for registering CCN counts, 7--diluter for the sample, 8--power supply for the sampling pump, 9--laboratory designed thermostate cooler, 10--television screen for displaying the aircraft data.

together aboard the NCAR (National Center for Atmospheric Research, Boulder, Colorado) Electra Aircraft.

4. RESULTS AND DISCUSSION

In order to examine the cloud-aerosol interactions over Lake Michigan, airborne observations were made near Muskegon, Michigan during November, 1978 and January, 1979. It was planned to investigate the lake-effect snowstorms primarily although all precipitation events were sampled whenever possible logistically. The CCN Spectrometer was installed in the DC3 aircraft for sampling purposes. Choice of the Muskegon site was made because of relatively high frequency of occurrence of wintertime, lake-effect snow squalls which are accurately predictable thus enabling a better coordination of airborne and ground crews. Such storms afford unique and unusual opportunity for sampling since they are of low intensity and are slow moving thus enabling frequent cloud penetrations and providing sufficient sampling time in the clear air at cloud boundaries.

Experimental flights were made on 17 Nov., 29 Nov., 1978 and on 22, 23, 24, 25, and 27 Jan., 1979. One flight was made each day except on 23 Jan. when two flights were made as indicated in Table 2. On 22 Jan., a flight was conducted in

Table 2

Summary of DC3 flights conducted for studying the cloud-aerosol interactions during November 1978-January 1979

Flight No.	Date	Take Off EST hr.	Landing EST hr.	Duration hr. min.	Type of Precipitation from the Storm
1	17 Nov. 1978	1305	1630	3 25	Rain
2	29 Nov. 1978	1035	1400	3 25	Freezing Rain
3	22 Jan. 1979	1122	1325	2 05	Clear Air
4	23 Jan. 1979	1140	1340	2 00	Light Snow
5	23 Jan. 1979	1440	1722	2 44	Snow
6	24 Jan. 1979	1058	1342	2 44	Graupel
7	24 Jan. 1979	1243	1507	2 24	Very Light Snow
8	27 Jan. 1979	1157	1446	2 49	Snow stopped before take off

clear air (cloudless sky) in order to test the equipment and provide calibration cross-checks. In Table 2, the duration of each flight, and the type of precipitation received at the ground from each storm are listed. During each flight, measurements were made in the subcloud layer at one or two levels below the cloud base and in a layer about 2000 m thick both upwind and downwind of the lake-effect snowstorms. In addition to the measurements of CCN activity spectrum, the aircraft was equipped to measure $\text{SO}_4^{=}$ aerosol mass, SO_x and total NH_3 volume concentrations, and aerosol size distribution in the range from 0.01 μm to 7 μm . Once these observations were completed, the aircraft was directed to penetrate the clouds at locations upwind of the ground sampling sites which provided sequential samples of surface precipitation, meteorological data, and replicas of falling ice crystals for determination of growth histories of the precipitation particles. During cloud penetrations, the aircraft obtained measurements of cloud liquid water content and droplet size distribution. Samples of supercooled cloud water were collected for chemical analysis in the laboratory. Except for the CCN Spectrometer, all other equipment was manned by the scientists from the Battelle, Pacific Northwest Laboratory.

The former was operated by us and real-time records of the cloud nucleation activity of the aerosol in the subcloud layer and at cloud boundaries were obtained.

4.1 Preliminary Findings

As an example, results from only three flights are reported in Table 3 at selected times in order to point out some salient features. In Tables 4, 5, and 6 are reported measurements made on November 29, 1978, January 24 and 25, 1979 respectively. The measured CCN activity spectrum was fitted to the usual functional form, $n = CS^k$, where n is the number concentration of CCN per unit volume with critical supersaturations less than S , and C and k are concentration and slope parameters respectively. Primary cloud-aerosol interaction takes place in evolving the cloud droplet size spectrum. The concentration, N , of cloud droplets (in cm^{-3}) resulting from an updraft U (cms^{-1}), may be expressed (Twomey, 1959; Braham, 1974) as

$$N = C^{2/(2+k)} \left[\frac{68.8 \times 10^{-3} U^{3/2}}{k \beta (3/2, k/2)} \right]^{k/(2+k)}, \quad (1)$$

which is only an approximation and in reality, the cloud-aerosol interactions leading to N are very complex in nature. From Eq. (1) the dependency of N upon C and U can be easily understood. For values of $K < 0.5$, N varies almost linearly

TABLE 3

Measured values of the concentration (C) and slope (k) parameters as a function of time for three flights.

Date: Nov. 29, 1978			January 24, 1979				January 25, 1979			
S(%): 0.2-1.2										
Time EST	C cm ⁻³	k	Time EST	C cm ⁻³	k	S (%)	Time EST	C cm ⁻³	k	S (%)
11:37:03	3245	1.70	11:17:05	9176	0.63	0.10-0.75	13:11:18	4640	1.04	0.11-0.62
12:00:04	7218	2.50	11:20:20	10825	0.36	0.10-0.75	13:11:48	3870	1.22	0.11-0.62
12:01:04	7283	0.68	11:23:20	11347	0.48	0.10-0.75	13:12:18	1354	0.93	0.11-0.62
12:05:34	11470	0.86	11:30:46	10335	0.30	0.10-0.75	13:33:41	6770	0.23	0.11-0.62
12:06:04	9726	1.23	11:34:16	4247	0.91	0.19-0.39	13:34:41	1014	0.33	0.11-0.62
				16323	1.94	0.39-0.75				
12:09:16	10668	0.79	11:39:10	5536	0.81	0.10-0.75	14:09:17	4140	0.17	0.11-0.37
								6825	0.68	0.37-0.62
12:17:33	5849	1.96	11:40:10	2457	0.58	0.10-0.40	14:10:17	2800	0.49	0.11-0.62
				11480	2.70	0.40-0.75				
12:19:03	5638	1.51	11:41:40	5423	1.31	0.20-0.75	14:10:47	4060	0.19	0.11-0.37
								9430	0.94	0.37-0.62
12:20:33	11316	1.10	11:45:23	7955	1.58	0.20-0.75	14:14:17	1227	0.40	0.11-0.37
								2833	1.23	0.37-0.62
12:24:01	10410	1.11	11:47:53	10290	0.93	0.10-0.75	14:15:47	5400	0.75	0.16-0.62
12:26:01	6783	0.98					14:16:17	1426	0.31	0.11-0.26
								3504	1.02	0.26-0.62
12:29:32	8475	1.10					14:17:17	1604	0.37	0.11-0.62
12:30:32	6523	1.10					14:18:47	1759	0.44	0.16-0.62
12:31:32	3950	0.93								

TABLE 4

Measured values of the concentration (C) and slope (k) parameters as a function of time for November 29, 1978.

Time EST	cm ⁻³	k	S (%)	Time EST	cm ⁻³	k	S (%)
11:37:03	3245	1.70	0.52-1.23	12:31:32	3959	0.93	0.21-1.23
12:00:04	3245	1.70	1.21-1.23	12:32:02	10160	1.10	0.21-1.23
12:01:04	7283	0.68	0.21-1.23	12:33:32	7046	0.69	0.21-1.23
12:04:34	11470	0.86	0.21-1.23	12:33:02	14027	1.32	0.21-1.23
12:06:04	9726	1.23	0.52-1.23	12:33:32	2257	0.88	0.21-1.23
12:09:16	10668	0.79	0.21-1.23	12:36:03	16085	1.15	0.21-1.23
12:17:33	5849	1.96	0.52-1.23	12:38:33	4651	1.40	0.21-1.23
12:19:03	5638	1.51	0.52-1.23	12:59:31	4418	0.92	0.21-1.23
12:19:33	23910	1.50	0.21-0.78	13:00:31	1655	0.74	0.21-1.23
12:20:33	11316	1.10	0.21-0.78	13:01:01	3096	0.76	0.21-0.78
12:21:03	3514	1.21	0.21-1.23	13:18:01	9477	0.88	0.21-1.23
12:24:01	10409	1.11	0.21-1.23	13:38:09	7439	1.02	0.21-1.23
12:24:31	6305	0.88	0.21-1.23				
12:25:31	2182	0.79	0.21-1.23				
12:26:01	6783	0.98	0.21-1.23				
12:27:32	24351	1.50	0.21-0.78				
12:29:32	8475	1.10	0.21-1.23				
12:30:32	6523	1.10	0.21-1.23				

TABLE 5

Measured values of the concentration (C) and slope (k) parameters as a function of time for January 24, 1979

Time EST	cm ⁻³	k	S (%)
11:17:05	9176	0.63	0.10-0.75
11:18:18	12424	0.57	0.10-0.175
11:19:20	8619	0.36	0.19-0.75
11:20:20	10825	0.36	0.10-0.75
11:21:20	13844	0.50	0.19-0.68
11:22:20	17953	0.58	0.19-0.58
11 23:20	11347	0.48	0.10-0.68
11:23:50	11667	0.47	0.19-0.68
11:30:46	10335	0.30	0.10-0.75
11:34:16	4247	0.91	0.19-0.39
	16327	1.94	0.39-0.75
11:39:10	5536	0.81	0.10-0.75
11:40:10	2457	0.58	0.10-0.40
	11480	2.70	0.40-0.75
11:41:40	5423	1.31	0.20-0.75
11:45:23	7955	1.58	0.20-0.75
11:47:53	10290	0.93	0.10-0.75

TABLE 6

Measured values of the concentration (C) and slope (k) parameters as a function of time for January 25, 1979.

Time EST	C cm ⁻³	k	S (%)	Time EST	C cm ⁻³	k	S (%)
13:11:18	4640	1.04	0.11-0.62	14:16:17	1426 3504	0.31 1.02	0.11-0.26 0.26-0.61
13:11:48	3870	1.22	0.11-0.62	14:18:17	3178	0.46	0.11-0.61
13:12:18	1350	0.93	0.11-0.62	14:18:47	1759	0.44	0.16-0.61
13:12:48	4000	0.58	0.11-0.62	14:19:17	11957	0.29	0.16-0.51
13:13:48	1700	0.02	0.11-0.62	14:19:47	14138	0.42	0.11-0.61
13:33:41	6700	0.23	0.11-0.26	14:20:17	25088	1.87	0.26-0.61
13:34:41	4014	0.33	0.11-0.26	14:20:47	13623	0.49	0.11-0.61
14:09:17	4140 6820	0.17 0.68	0.11-0.37 0.37-0.61				
14:10:47	4060 9430	0.09 0.44	0.11-0.37 0.37-0.61				
14:11:47	18150 8270	0.7 0.12	0.11-0.26 0.26-0.61				
14:12:47	8310	0.18	0.26-0.61				
14:13:17	9840	0.5	0.27-0.61				
14:14:17	1227 2833	0.4 1.23	0.11-0.37 0.37-0.61				
14:14:47	1006	0.22	0.11-0.61				

with C. For $k > 1.0$, the dependency of N upon U is stronger. Thus, in the former case, the cloud droplet concentration is primarily determined by the CCN concentration while in the latter, it is strongly influenced by the rate of ascent or the rate of supersaturation generation (i.e. dS/dt).

From Table 3, it seems that values of $k > 1.0$ are almost as frequent as the ones around 0.5. In the air masses that we investigated over Lake Michigan, the dynamics of cloud formation seems to be as important as the microphysics in evolving the cloud droplet size spectra. It may be noted that larger values of k may also indicate the presence of a CCN source since freshly generated nuclei are finer in size and consequently activate at larger supersaturations resulting in the steeper slope of the spectrum.

On 29 Nov. 1978, a warm front was passing through Muskegon. The cloud base was about 900 m MSL. Measurements were made at 365 m (11:37:04 EST) and 760 m MSL in the subcloud layer. The data (see Table 3) reveal that the air at 760 m was, in general, twice or three times richer in CCN and represented aged aerosol (low values of k) when compared with the air at 365 m. In terms of the vertical concentration gradient, this seems contrary to expectations if the nuclei source is assumed to be at the surface. Either dry or

aqueous phase conversion of SO_2 into sulfate particles may explain this finding. To this end, further investigations are in progress. One striking feature of the data, as shown by examples of Jan. 24, and 25 is that the measured CCN spectrum does not always conform to $n = \text{CS}^k$ form although the measurements may be fitted to this form in small supersaturation intervals. This finding resulting from our real-time, in situ measurements with the help of the CCN Spectrometer, may have several interesting implications, especially in dealing with the polluted air masses.

More than one value of k parameter for the same air sample indicates that either the measurements do not conform to $n = \text{CS}^k$, or the sample is derived from two air masses which are not homogeneously mixed. It may be recalled that if the air sample is not represented by singular values of C and k , Eq. (1) cannot be adequately used to estimate the total cloud droplet concentration. The data recorded on Jan. 25, 1979 show that for a considerable number of samples taken at different times during the flight, two sets of C and k values may be found. Table 3 lists only a very few selected measurements and the evidence from the comprehensive data sets that we obtained, supports this conclusion. There exist a few instances where within a supersaturation interval of 0.12-1.0%, three sets of C and k values may be found. For

this particular day, it may be noted that the cloud base was not well defined and the cloud tops were at about 914 m MSL. The vertical cloud development ranged from 152-243 m. The wind direction at the surface was $310-320^{\circ}$ with speeds of $10-15 \text{ ms}^{-1}$.

Based on the above data sets and other cloud physical parameters measured during the field study, we are in the process of assessing the effectiveness of the cloud nucleation process for removing pollutants such as SO_2 and sulfates originating from urban-industrial areas, e.g. Chicago or Milwaukee. To this end a comprehensive data analysis is needed for all the flights mentioned in Table 2.

5. DIRECTIONS FOR FUTURE WORK

Priority will be given to analyze the field data putting in perspective the major objectives of MAP3S. It will be determined what fraction of the aerosol particles act as CCN and what is their size range. From this, it can be derived, for example, whether the submicron flyash particles emitted by the coal-fired power plants constitute a major source of CCN. If so, it would seem to indicate that the elements such as sulfur and chlorine do get adsorbed and oxidized on flyash particles whose matrix elements are essentially Si and Al and which, otherwise are not effective as CCN. Such an

evidence is of paramount importance insofar as it indicates that the sulfate-containing particles are produced by power plants even before a sulfur gas-to-particle conversion takes place.

The plume mapping and characterization data will be reduced and analyzed to determine the existence of a secondary maximum in the CCN concentration downwind of the plume. Such a maximum is indicative of gas-to-particle conversion and coagulation processes. Comparison of the in-plume and the ambient air CCN spectrum will help provide the residence times of CCN. If a secondary maximum is detected with a consistently decreasing SO_2 concentration, it would seem to confirm that gaseous sulfur-to-sulfate conversion is effective. From the differences between the observed rate of decrease of SO_2 along the plume axis and calculated losses of SO_2 by diffusion, it is possible to estimate how much amount of SO_2 is converted into cloud nucleating sulfates. These measurements will also help derive the rates of CCN formation. It may be mentioned that some evidence (Pueschel and Van Valin, 1976) of the formation of cloud nucleating sulfates downwind of a coal-fired power plant already exists. The reported measurements are, however, sketchy inasmuch as the CCN concentration at only one percent supersaturation was

measured in order to detect the presence of a secondary maximum about 100 km downwind. The measurements of the entire CCN spectrum, reported above will help provide a more confirmatory evidence.

The accomplishment of the data reduction and analysis, as indicated above, will require the use of the SO₂ concentration data, particle size distribution data, Aitken nuclei data, data from Hi- and Lo-Vol samples, and Knollenberg probes data which were simultaneously recorded aboard the PNL DC3 aircraft.

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