

## Formation of Sulfate Particles in the Plume of the Four Corners Power Plant

YAACOV MAMANE<sup>1</sup>

*Environmental Engineering Laboratories, Technion, Haifa, Israel*

RUDOLF F. PUESCHEL

*NOAA/Environmental Research Laboratories, Atmospheric Physics and Chemistry Laboratory, Boulder, CO 80303*

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### ABSTRACT

On 6 June 1978, the Four Corners coal-fired power plant plume near Farmington, New Mexico, was sampled with an instrumented twin-engine Aero-commander 680E, up to 90 km downwind from the source. Measurements consisted of aerosol size distribution, condensation nuclei, various gases, individual particle chemistry using electron microscopy techniques and meteorological parameters.

A substantial formation of condensation nuclei took place downwind of the plant at a rate of  $1.3 \times 10^{16} \text{ s}^{-1}$  in the first 0.3 h,  $3.3 \times 10^{17} \text{ s}^{-1}$  up to 2.5 h, and  $8 \times 10^{17} \text{ s}^{-1}$  in the 2.5–12.5 h plume travel time. The corresponding conversion rates were 0.15, 0.5 and 0.3%  $\text{h}^{-1}$ , respectively. The conversion rate due to oxidation of  $\text{SO}_2$  on surfaces of fly ash particles was negligible. Dry removal of particles was very high and reached an estimated maximum of 36% during the first 2.5 h probably due to partial impingements of the plume to the ground.

Analysis of individual particles collected on nuclepore filters using a scanning electron microscope equipped with an x-ray energy dispersive analyzer, as well as particles collected on electron microscope screens for the detection of sulfate, show definitely that particles  $< 0.5 \mu\text{m}$  are mostly sulfates, with 10–15% fly ash. In the larger size range most particles were identified as fly ash.

### 1. Introduction

The Four Corners Power Plant west of Farmington, New Mexico, has been the subject of studies to delineate the effect of an isolated coal-fired power plant on the atmosphere (Pueschel, 1976; Schnell *et al.*, 1976; Parungo *et al.*, 1978; Pueschel and Van Valin, 1978; Cobb *et al.*, 1979; Mamane and Pueschel, 1979). In this paper information on 1) the formation of sulfur aerosols, 2) the transport of plume pollutants, and 3) the chemistry, condensation and nucleation properties of plume particles, is presented.

The plant consists of five units with a generating capability of 2175 MW and a daily 25 000 ton coal consumption which contains ~22.5% ash and 0.7% sulfur; Table 1 summarizes the power plant emission parameters. The plant is situated in a desert area at the northwest corner of New Mexico, surrounded by rugged mountains, which quite often cause impingement of the plume to the ground. The region is known for its low relative humidity, annual precipitation of ~150 mm and a wind flow pattern consisting of Southeasterlies in the morning and westerly-northwesterlies until sunset.

### 2. Airborne measurements

Instrumentation on the aircraft included gas, aerosol and meteorological sensors to measure parameters listed in Fig. 1. Aerosol particle size spectra were obtained with a forward scattering aerosol spectrometer (FSSP) and an active-scattering aerosol spectrometer (ASAP-X)<sup>2</sup>. The FSSP, mounted outside the aircraft to avoid any loss of particles in ductwork or by alteration of ambient conditions, counts particles with radii between 0.25 and 23.5  $\mu\text{m}$  in four partially overlapping ranges of 15 bins each. The ASAP-X covers the range 0.045 to 1.5  $\mu\text{m}$  in the same manner. The total particle concentrations were measured continuously with a CN counter at 300% supersaturation, thereby detecting all particles of sizes  $\geq 0.01 \mu\text{m}$  radius (Cooper and Langer, 1978). An integrating nephelometer continuously measured the light scattering of particles  $> 0.1 \mu\text{m}$ . Aerosol particles were also collected on Nuclepore filters (mean pore diameter 0.1  $\mu\text{m}$ ) and on a four-stage Casella impactor

<sup>2</sup> Knollenberg, R. G., 1976: Three new instruments for cloud physics measurements: the 2-D spectrometer, the forward-scattering spectrometer probe, and the active-scattering aerosol spectrometer. *Preprints Int. Conf. Cloud Physics*, Boulder, Amer. Meteor. Soc., 554–569.

<sup>1</sup> NRC Research Associate.

TABLE 1. Site and emission characteristics of the Four Corners power plant.<sup>a,b</sup>

	Units			
	1 and 2	3	4	5
Nominal capacity (MW)	350	225	800	800
Stack height (m)	75	75	90	90
Stack diameter (m)	5.6	4.5	8.6	8.6
Coal consumption (kg h <sup>-1</sup> )	174 × 10 <sup>3</sup>	107 × 10 <sup>3</sup>	382 × 10 <sup>3</sup>	382 × 10 <sup>3</sup>
Emission temperature (°C)	52	52	121	121
Exit velocity (m s <sup>-1</sup> )	21.0	19.8	22.5	22.5
SO <sub>2</sub> emission after treatment (kg s <sup>-1</sup> )	0.47	0.28	1.49	1.49
Particulates emission after treatment (kg s <sup>-1</sup> )	0.022	0.014	0.45	0.45
SO <sub>2</sub> removal (%)	30	30	0	0
Particulate removal (%)	99.2	99.2	97	97
Flue gas treatment	Scrubbers		Electrostatic precipitator	

<sup>a</sup> Elevation of Plant: 1600 m MSL.

<sup>b</sup> APSC Report, 1975: Four Corners Generating Plant and Navajo Coal Mine—Environmental Report, Arizona Public Service Company, Phoenix.

(May, 1945) for post-flight chemical identification by microchemical spot tests and by X-ray energy dispersion analysis. Trace gases (SO<sub>2</sub>, O<sub>3</sub>, NO, NO<sub>2</sub>) were measured by on-board gas analyzers. These parameters, together with two electric field components, surface and air temperatures, dew point, and altitude were recorded on magnetic tape by a DAS 64 data acquisition system. Independently, any eight parameters could be displayed on an on-board strip chart recorder.

The air was sampled isokinetically at an aircraft speed of ~45 m s<sup>-1</sup> through four stainless steel tubes mounted on top of the fuselage of the aircraft. To minimize particle losses tubes and connections were short, with no right or sharp angles.

The flight pattern of the aircraft was designed to map the cross section of the plume at discrete distances up to 90 km downwind from the plant. At each distance horizontal traverses were made in the plume perpendicular to the plume axis at several

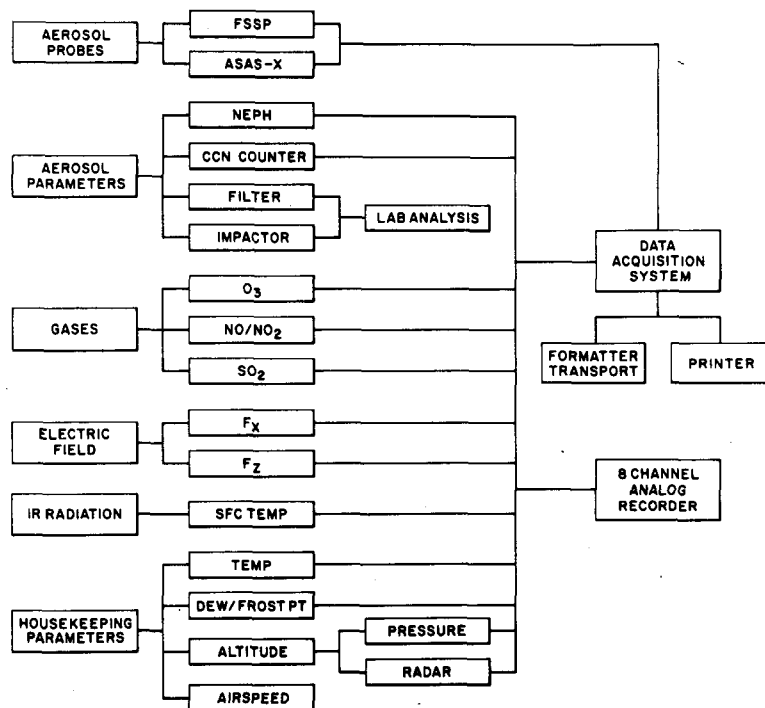


FIG. 1. Parameters measured from the aircraft in the NOAA-EPA sponsored atmospheric research.

elevations, usually from a few hundred feet above ground level to a few hundred feet above the plume. In most cases an attempt was made to obtain a sufficient number of passes through the plume to be able to define the plume characteristics. Each horizontal traverse consisted also of "out of plume" sections which were long enough to obtain background concentrations. In addition to the cross-wind sampling pattern, the aircraft was flown downwind along the longitudinal axis of the plume and above the plume, as well as upwind of the stacks.

### 3. Methods for individual particle analysis

Two different techniques were used for the characterization of individual particles.

#### a. Nuclepore filters

Aerosol samples were collected on 0.1  $\mu\text{m}$  Nuclepore filters and later analyzed in a scanning electron microscope (SEM) interfaced with an x-ray energy dispersive analyzer (XEDA). This provided the elemental content of particles down to 0.05  $\mu\text{m}$  diameter, as well as three-dimensional photomicrographs of the particles. Although this technique gives only qualitative information on elements heavier than or equal to sodium, it was shown (Pueschel, 1976) that by keeping the SEM beam and other parameters constant semi-quantitative results are obtained. During some flights parts of the filter were used to study the nucleation properties of plume particles (Schnell *et al.*, 1976; Parungo *et al.*, 1978).

#### b. Electron microscope screens

The second technique used in this study was basically a modified spot test to detect sulfate (Mamane and de Pena, 1978) and nitrate particles (Mamane and Pueschel, 1980). Particles are collected directly on three electron microscope screens placed just below the jet nozzle of a Casella cascade impactor. These screens, covered with a carbon/formvar film, were used to investigate the morphology and the chemistry of individual particles in the TEM. One screen, with no further treatment, was utilized in the TEM to obtain the shape of the particles. Photomicrographs of a representative field of view, normally of several hundred particles, resulted in the size distribution of all particles. The behavior of these particles under the electron beam gave some information on particle volatility. The second screen was postcoated under high vacuum with a thin layer of barium chloride, exposed to a relative humidity of 75% in a sealed chamber, and examined in the microscope to identify the characteristic spots formed by the reaction of sulfates with the barium chloride film (Mamane and de Pena, 1978). Photomicrographs were taken and

the size distribution of the sulfates was determined by applying a calibration factor to the reaction spot diameter. The third screen undergoes the same procedure with a different reagent to study nitrate particles. The three electron microscope screens, which simultaneously collected the aerosol samples, enable the quantitative determination of the percentage of sulfates and nitrates.

In several cases the TEM technique for sulfate and the non-destructive SEM-XEDA technique were both applied to the same particles. For example, both techniques were applied to investigate the thickness of the sulfate layer absorbed on submicron fly ash particles and the elemental content of the particles.

### 4. Results and discussion

#### a. Power plant plume characteristics

Fig. 2 describes the shape of the plume during the morning and noon hours of 6 June 1978, east-southeast of the plant. The light winds of about  $2 \text{ m s}^{-1}$  moved the plume in a compact stream downwind of the stacks. Thereafter, due to the morning inversion weakening and the turbulence generated when a plume travels over rugged terrain, the lower part of the plume impinged on the ground. The isopleths in Fig. 2 show the CN concentration ( $\text{cm}^{-3}$ ). In this case there is a clear increase in CN concentration up to 30 km downwind of the stacks; further downwind the CN count decreases. The cross-section-averaged concentrations at 2, 18 and 90 km were 12 400, 42 100 and  $9800 \text{ cm}^{-3}$ , respectively, above the background level which reached a concentration of  $\sim 1000 \text{ cm}^{-3}$ .

Detailed mapping of the plume cross section at 2 and 18 km corresponding to the data presented in Fig. 2 are illustrated in Fig. 3. The third cross section at 90 km is not included due to its large dimensions and uniformity. These cross sections provided the total number of particles per unit time,  $F_L$ , traveling through vertical plume cross sections at 2, 18 and 90 km downwind of the stacks:

$$F_L = \int \int_{y,z} [\text{CN}(y,z)] \bar{u} dy dz, \quad L = 2, 18, 90 \text{ km}, \quad (1)$$

where  $\bar{u}$  is the average wind speed,  $y$  and  $z$  are the horizontal and vertical axis of the plume, and  $\text{CN}(y,z)$  is the concentration of all particles  $> 0.01 \mu\text{m}$  as measured at distance  $L$ .

The observed rate of increase of CN is given by

$$\left. \frac{\Delta(\text{CN})}{\Delta t} \right|_{\text{OBS}} = \left. \frac{\Delta(\text{CN})}{\Delta t} \right|_{\text{REAC}} - \left. \frac{\Delta(\text{CN})}{\Delta t} \right|_{\text{DIFF}} - \left. \frac{\Delta(\text{CN})}{\Delta t} \right|_{\text{COAG}} - \left. \frac{\Delta(\text{CN})}{\Delta t} \right|_{\text{DEP}} \quad (2)$$

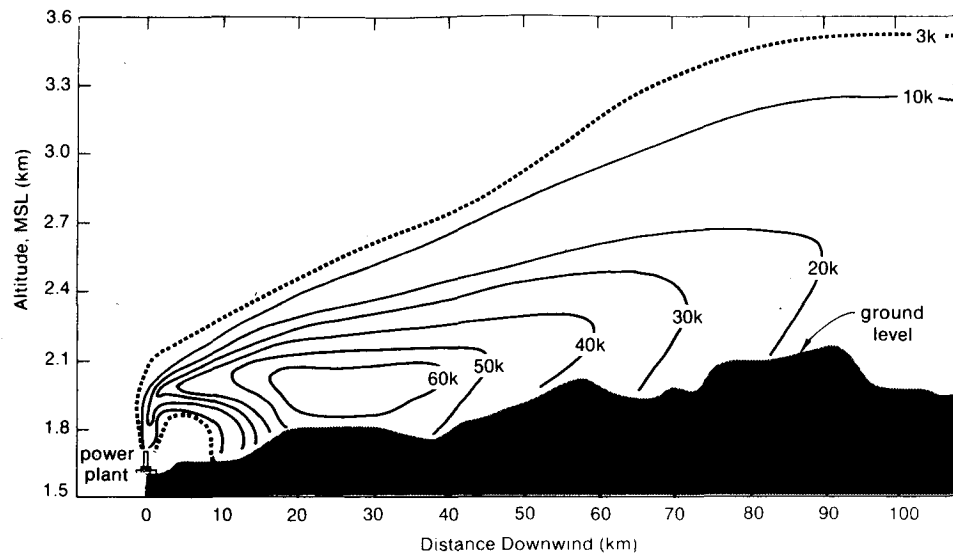


FIG. 2. Longitudinal cross section of the FCPP plume east-southeast of the stacks on 6 June 1978. Isopleths describe CN concentration ( $\text{cm}^{-3}$ ).

The diffusion, coagulation and deposition terms represent a decrease in concentration of CN and are therefore negative. The reaction term is positive as it indicates the formation of CN from gas phase reactions. However, if integrated values of CN,  $(\text{CN})^*$ , are used in Eq. (2) then the diffusion term is zero by definition. The net rate of increase of CN, if the coagulation term is neglected, could be given by a simple model (Pueschel and Van Valin, 1978) as

$$\frac{\Delta(\text{CN})^*}{\Delta t} = F_{L2} - F_{L1} + F_G, \quad (3)$$

where  $F_G$  is the rate of particles deposited to the ground between  $L1$  and  $L2$ . From Table 2, which summarizes the results of CN measurements, it follows that the net increases in particles flow from 0–2, 2–18 and 18–90 km are given by

$$\frac{\Delta(\text{CN})^*}{\Delta t} \geq F_{2 \text{ km}} - F_{0 \text{ km}} \approx 1.3 \times 10^{16} \text{ s}^{-1}, \quad (4)$$

$$\frac{\Delta(\text{CN})^*}{\Delta t} \geq F_{18 \text{ km}} - F_{2 \text{ km}} = 2.4 \times 10^{17} \text{ s}^{-1}, \quad (5)$$

$$\frac{\Delta(\text{CN})^*}{\Delta t} \geq F_{90 \text{ km}} - F_{18 \text{ km}} = 6.8 \times 10^{17} \text{ s}^{-1}, \quad (6)$$

where  $F_{2 \text{ km}}$ ,  $F_{18 \text{ km}}$  and  $F_{90 \text{ km}}$  are given in Table 2. In Eq. (4) it was assumed that  $F_{0 \text{ km}} \ll F_{2 \text{ km}}$ . This assumption is based on the analysis of CN isopleths shown in Fig. 2. The net increase of CN crossing vertical plume cross section suggests that formation of particles, probably of sulfates, is taking place as the plume travels downwind.

The values obtained here do not include the CN which deposited to the ground. The dry removal or deposition rate needs to be estimated especially in rugged terrain where induced turbulence may result in an impingement of the plume to the ground. Figs. 2 and 3 indicate that such phenomena do occur at distances  $> 10$  km for the morning of 6 June 1978.

At 18 km, where the ground was 150 m above the site base, the centerline of the plume was only 150 m above the ground and the plume had impinged on it, leading to dry deposition of both  $\text{SO}_2$  and particles. By assuming the deposition of all particles that would have been in the below-ground portion of a freely expanding plume, it was estimated that during the first 2.5 h the particle loss amounted to 36%. The deposition rates for  $\text{SO}_2$  were assumed to be the same since the relative concentrations of  $\text{SO}_2$  in a plume cross section were fairly similar to those of CN. The deposition rates are higher than those of Husar *et al.* (1978). The tall stacks of the power plant they had studied, 218 m versus 75–90 m, and its location in gently rolling terrain with a different type of ground cover reduce the surface removal rates. It should be noted that our method, which assumes a symmetrical plume around the centerline, is different from other approaches used to estimate the deposition rates (such as the gradient or the budget method).

At the first 10 km downwind no removal of the plume is taking place (see Fig. 2); later, 36% of the plume is impinged to the ground at 18 km, and the deposition rates decrease to a negligible value at 90 km downwind. Therefore, the production rates

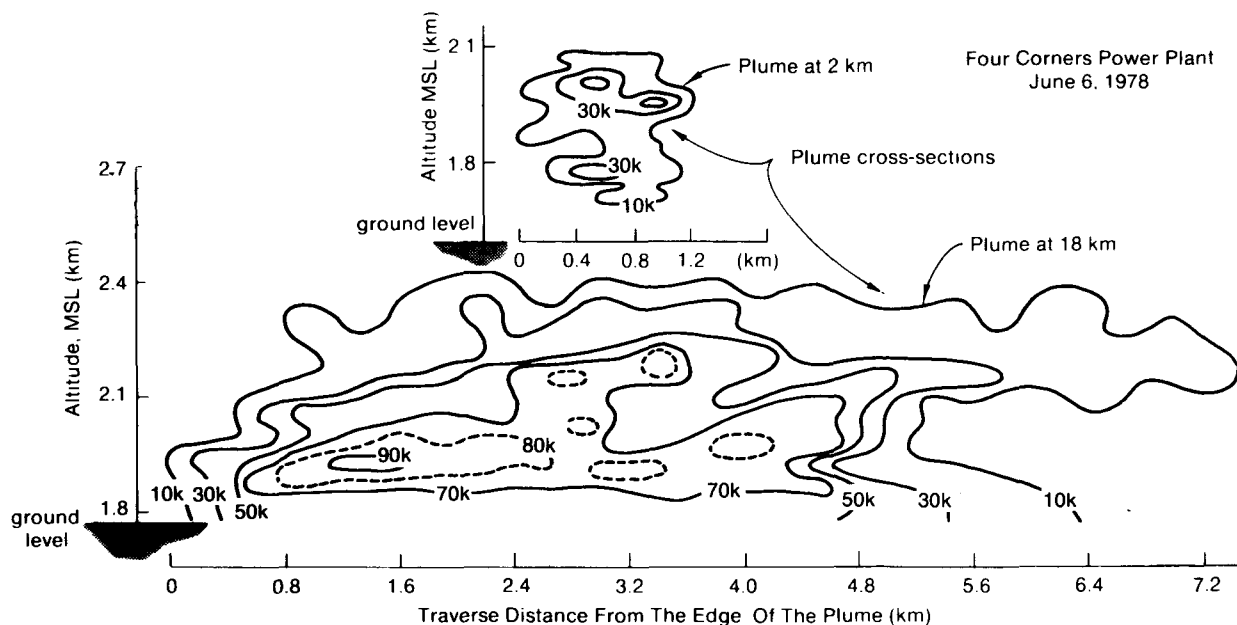


FIG. 3. CN cross sections at 2 and 18 km downwind east-southeast of the plant. Isopleths give CN concentration ( $\text{cm}^{-3}$ ). Note that the same scales are used for the two sections.

of CN would be equal to

$$\begin{aligned} \frac{\Delta(\text{CN})^*}{\Delta t} &= F_{2 \text{ km}} - F_{0 \text{ km}} + F_G \\ &= 1.3 \times 10^{16} \text{ s}^{-1}, \end{aligned} \tag{7}$$

$$\begin{aligned} \frac{\Delta(\text{CN})^*}{\Delta t} &= F_{18 \text{ km}} - F_{2 \text{ km}} + F_G \\ &= 3.3 \times 10^{17} \text{ s}^{-1}, \end{aligned} \tag{8}$$

$$\begin{aligned} \frac{\Delta(\text{CN})^*}{\Delta t} &= F_{90 \text{ km}} - F_{18 \text{ km}} + F_G \\ &= 8.0 \times 10^{17} \text{ s}^{-1}. \end{aligned} \tag{9}$$

To understand the possible impact of a power plant on the local or regional climate it is necessary to estimate the production rates of CCN (not of CN). Unfortunately on June 1978 flights the CCN chamber did not operate. Therefore, raw data of Pueschel and Van Valin (1978) were used to get the ratio of CCN/CN. This step is justified since they studied the same power plant using the same airborne instrumentation. Based on these data the CCN (at 1%  $S$ )/CN ratio was found to vary from 6 to 30%. These values agree fairly well with Squires (1966) data for the city of Denver which suggested a CCN production rate at 1% supersaturation to be 1–20% of the CN rate. Thus our CCN formation rate will be in the order of  $10^{16}$  to  $10^{17} \text{ s}^{-1}$ , which is in good agreement with Pueschel and Van Valin (1978) who found a production rate of  $10^{16} \text{ H}_2\text{SO}_4$

particles per second that act as CCN at 1% supersaturation. Thus the power plant produces CCN at a rate that is equivalent to the production of natural aerosols (Squires, 1966) of an area of  $10^3$ – $10^4 \text{ km}^2$ , and therefore may affect the local and the mesoscale climatology surrounding the plant in terms of radiative transfer, cloud structure and precipitation processes (Pueschel and Van Valin, 1978).

*b. Aerosol size distribution*

*In situ* measurements of the aerosol particle size spectra show that the number size distributions in the plume are trimodal with modes around 0.01, 0.08 and 2  $\mu\text{m}$  radius. The first mode was obtained from the CN counter, which responds primarily to all particles larger than 0.01  $\mu\text{m}$ . Figs.

TABLE 2. Relevant plume parameters for the 6 June 1978 measurements.

	Distance downwind (plume age)		
	2 km (0.3 h)	18 km (2.5 h)	90 km (12.5 h)
Average plume width $H$ (km)	1.15	5.4	32
Average plume depth $Z$ (m)	450	540	1500
Plume cross section ( $\text{m}^2$ )	$5.2 \times 10^5$	$2.9 \times 10^6$	$4.7 \times 10^7$
$F_L$ ( $\text{s}^{-1}$ )	$1.3 \times 10^{16}$	$2.5 \times 10^{17}$	$9.3 \times 10^{17}$

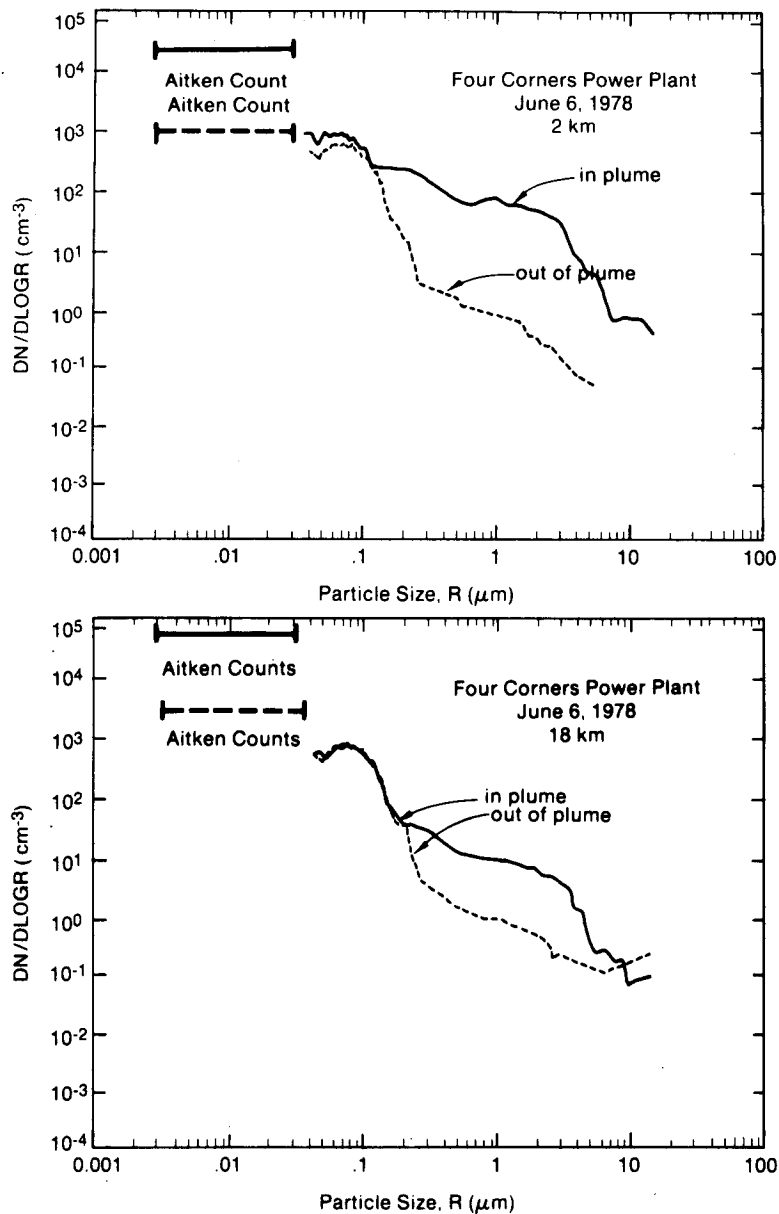


FIG. 4. Particle size distributions in (solid lines) and out (dashed lines) of the plume at 2 and 18 km downwind. Note that the background size distributions are almost identical.

4a and 4b show the size distributions of particles in and out of the plume at 2 and 18 km downwind, respectively. The  $0.08 \mu\text{m}$  mode was invariant both in space and time, but the concentrations in the plume at 0.01 and  $2.0 \mu\text{m}$  modes were significantly larger than in the background air probably due to the formation of a secondary sulfate aerosol and the injection of primary fly ash, respectively. When the size distributions of particles in the plume are compared to each other it is evident that the concentration of the very small particles increases from 2 to 18 km downwind while the concentration of large particles decreases.

The results in Fig. 4 substantiate the presently accepted notions on the trimodal nature of the atmospheric aerosol size distributions (Whitby, 1978): the aerosol size distribution is characterized by several modes which, from small to large sizes, are called the condensation mode, the accumulation mode, and the coarse particle mode. In the FCPP plume, the coarse particle mode typically consists of primary fly ash particles and disappears with time due to the combined effects of settling and dispersion. Simultaneously, the condensation mode increases with time due to secondary sulfate formation by a gas-to-particle conversion mechanism.

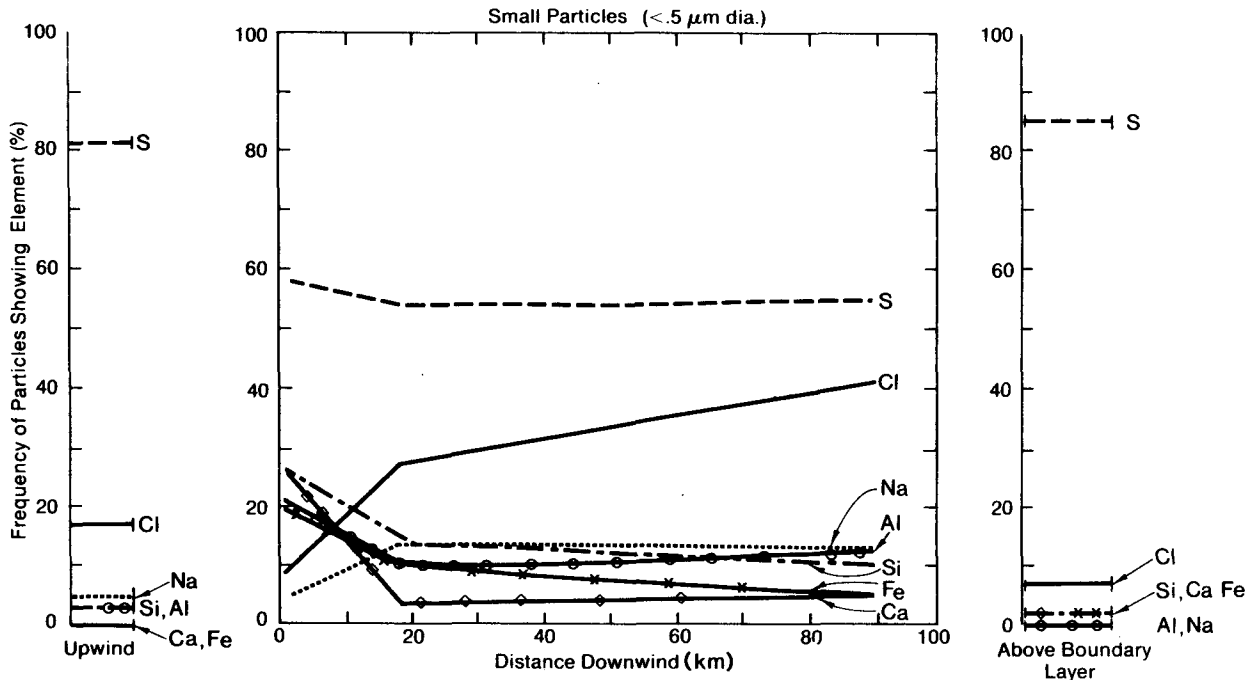


FIG. 5. Percentage of particles <math>< 0.5 \mu\text{m}</math> containing various elements, upwind and downwind of the stacks.

c. Elemental analysis of individual particles

The SEM-XEDA system was used to study the elemental composition of particles sampled upwind of the power plant and above the boundary layer,

as well as at 2, 18 and 90 km downwind. In each sample over one hundred randomly selected particles were analyzed; x-ray spectra were stored and processed with a minicomputer.

Figs. 5 and 6 describe the percentage of par-

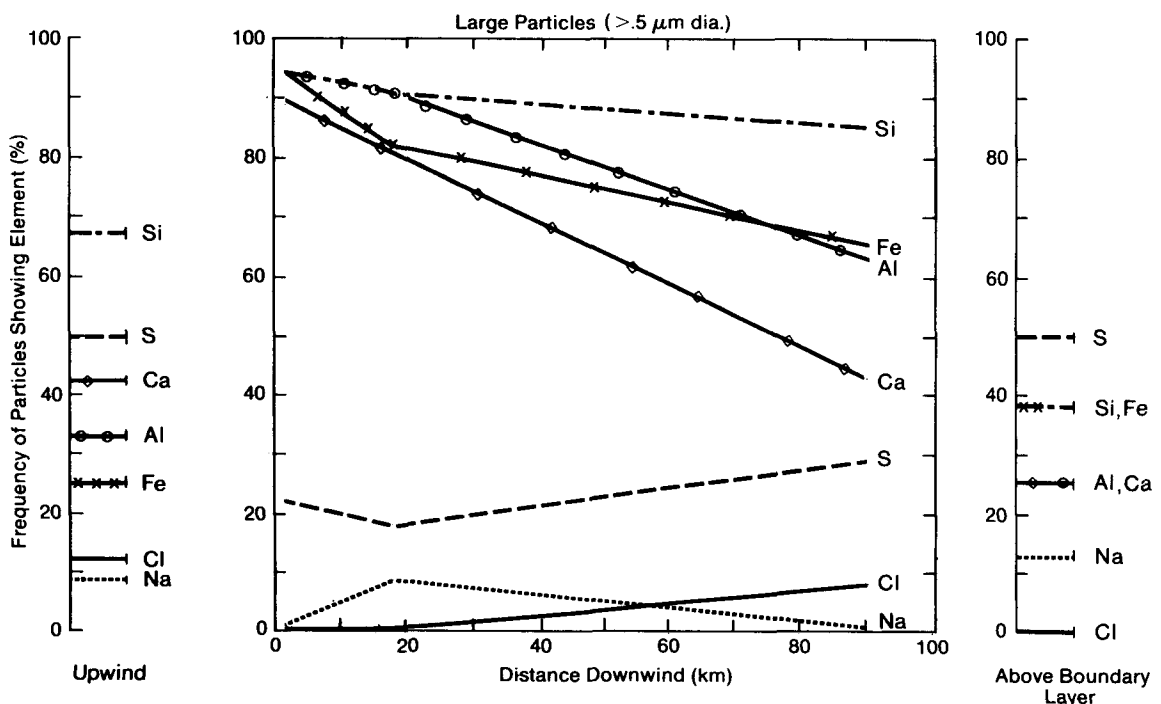


FIG. 6. Percentage of particles > 0.5  $\mu\text{m}$  containing various elements, upwind and downwind of the stacks.

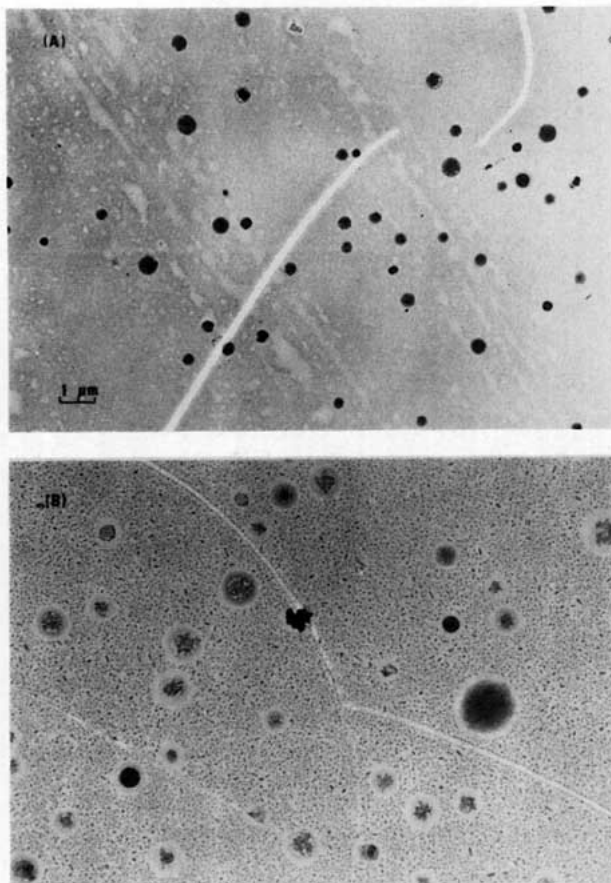


FIG. 7. Typical photomicrographs of particles collected downwind of the power plant. (a) non-treated sample: most particles tend to evaporate in the microscope beam. (b)  $\text{BaCl}_2$  treated sample: the circular spots are the reaction of sulfate particles with barium.

ticles containing various elements at different distances upwind, downwind of the stacks and above the boundary layer. Fig. 5 corresponds to particles of diameters  $< 0.5 \mu\text{m}$ , whereas Fig. 6 contains data for particles that are larger than  $0.5 \mu\text{m}$ . Most of the particles which are smaller than  $0.5 \mu\text{m}$  contain sulfur; about 80% for background air and above 50% for plume particles. It should be noted, however, that the concentration of plume particles, which were measured by a CN counter, is  $\sim 10$ – $40$  times that of the background particles. The larger particles (above  $0.5 \mu\text{m}$  in Fig. 6) consist mostly of Si, Al, Fe and Ca which are the matrix elements of the fly ash particles. (Pueschel, 1976). Only twenty to thirty percent of them contain sulfur which is probably in the form of sulfate layers surrounding the fly ash particle (Pueschel, 1976; Mamane and Pueschel, 1979).

The background aerosol upwind of the plant was sampled below and above the mixing layer. For the smaller particle range sulfur was dominant in

81–85% of the particles, and in both cases sulfur was almost the only element present in spherical particles. One may conclude, therefore, that their formation was through a homogenous process. Other elements present in 10–15% mixed particles include Na and Cl with some trace of Si, Al, Ca, Cr and Ag. It should be noted that the analysis referred only to particles which emit x-rays, i.e., are composed of elements heavier than Na. It was found that 31–42% of the particles have no emission and thus may be primarily composed of the elements C, N, H and O. The larger particles (Fig. 6) show less uniformity exhibiting the presence of three groups: S; Si, Al, Ca, Fe; and Na, Cl.

It is interesting to note in Fig. 6, that the particles  $> 0.5 \mu\text{m}$  in the plume change composition as they travel downwind; the percentage concentration decreases for the Si, Al, Fe, Ca group, while the presence of S and Cl slightly increases. That again is consistent with the removal of large fly ash particles and formation and growth of sulfates particles further downwind. A more complete discussion on the S and Cl elements is given in Pueschel's paper (1976).

#### d. Study of individual sulfate particles

Plume particles were collected on electron microscope screens to be analyzed individually in a transmission electron microscope (TEM) for their sulfate and nitrate content. Figs. 7a and 7b are typical photomicrographs of particles collected 18 km downwind of the power plant on the morning of 6 June 1978. Most of the particles shown in Fig. 7a have a similar appearance and tend to evaporate in the electron microscope beam in a fashion similar to that of ammonium sulfate particles (Heard and Wiffen, 1969). Other sulfates such as sodium sulfate or calcium sulfate do not evaporate under normal use of the TEM (50–100 kV, magnification up to 10 000, and low-intensity beam). Sulfuric acid particles, which have a specific morphology consisting of a central particle surrounded with much smaller satellites, were not detected in our samples. Fig. 7b is a photomicrograph of the same sample treated with barium chloride. The very numerous small oblong shaped particles are barium chloride, while the larger circular spots are the reaction of sulfate particles with barium. The reaction spots were also examined individually in the SEM to study their elemental content and to determine the sulfate cation. Their x-ray spectra showed the presence of sulfur only (elements such as N, H or C are not "seen" by this technique). Since most particles on Fig. 7a do evaporate in a characteristic way typical of  $(\text{NH}_4)_2\text{SO}_4$ , and most particles on Fig. 7b are sulfates, many of them containing no other elements heavier than sodium, we concluded that these particles were ammonium sulfate (or bisulfate).



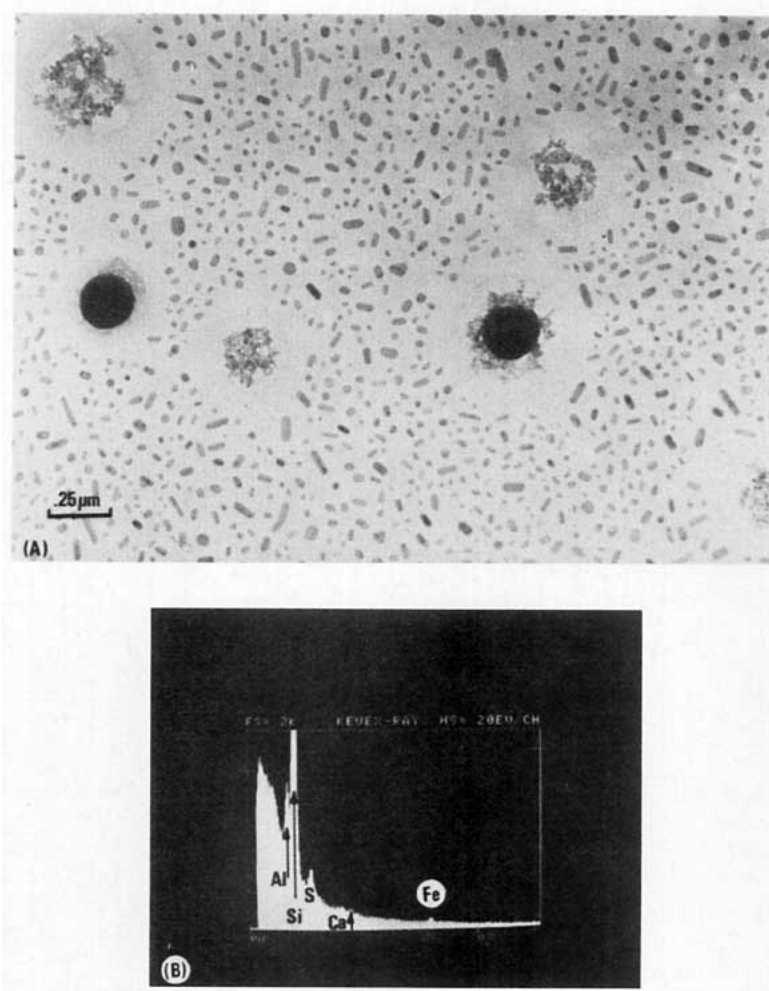


FIG. 8. (A) Close-up of photomicrograph of submicron fly ash particles coated with a layer of sulfate. (B) x-ray spectrum of the fly ash particle on the right showing the presence of Al, Si, Ca and Fe. The presence of S is probably from the layer of sulfate surrounding the fly ash particle.

Fig. 8a is an enlarged photomicrograph of the barium chloride treated sample showing a fly ash particle (black circular spot) coated with a layer of sulfate (porous type appearance). When a non-soluble particle coated with sulfate reacts with barium chloride it forms a ring of barium sulfate around the nonsoluble particle. From the size of the ring and the known thickness of the barium chloride film it was possible to compute the amount of sulfate involved in the reaction. The results of these calculations are presented elsewhere (Mamane and Pueschel, 1979). It was found that the amount of sulfate that is formed on fly ash is negligible in comparison to the amount of ammonium (bi) sulfate that is formed homogeneously. Most of the fly ash particles containing sulfur were symmetrically coated with sulfate. A few, however, seem to have preferential adsorption of sulfate on some parts of the particle surfaces, and this may be due to the dep-

osition of sulfate particles on the surface of fly ash, as shown on the left part of Fig. 8a. The uniformly sulfate surrounded fly ash particle is shown on the right part of Fig. 8a.

Although the black circular particle in Fig. 8a was identified as fly ash by its shape and its thermal stability in the electron microscope beam, additional evidence is provided in Fig. 8b by its x-ray spectrum showing that it contains the matrix elements such as aluminum, silicon, iron and calcium that are typical for fly ash. Figs. 8a and 8b provide, maybe for the first time, direct evidence of the presence of sulfates on the surfaces of individual submicron fly ash particles.

Fig. 9 shows the proportion (in percent) of the sulfate and fly ash particles as a function of the downwind distance for the 6 June 1978 flights. The particle frequency of the sample taken upwind of the power plant is also plotted. The frequency refers

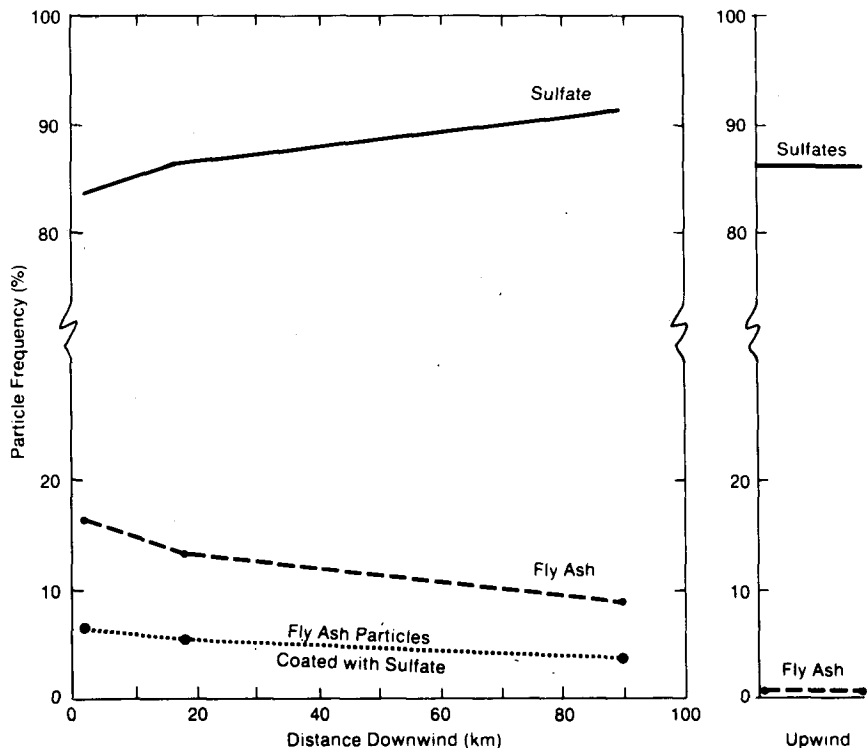


FIG. 9. Sulfate and fly ash frequency as a function of the downwind distance, based on individual analysis of particles collected on stage 4 of the Casella impactor.

to submicron particles collected on stage 4 of the Casella impactor ( $0.2\text{--}0.8\ \mu\text{m}$  dry particle diameter). For plume particles with diameters  $\geq 0.8\ \mu\text{m}$ , collected on stage 3, almost no sulfates were found. They consist mostly of fly ash particles. The percentage of sulfate particles in the plume for the smaller size range is rather high, 84–90%, with a slight increase as the plume travels downwind. Dittenhoefer and de Pena (1978) applying the same sampling and analysis procedure to study the Keystone Power Plant in Pennsylvania reported similar results. The percentage of fly ash in this size category decreases from 16–9%. Upwind of the power plant ~86% were sulfates, very few were fly ash and the rest were unidentifiable.

There are some differences between the results obtained with the  $\text{BaCl}_2$  method (Fig. 9) and those derived from the XEDA system (Fig. 5). x-ray analysis of particles  $< 0.5\ \mu\text{m}$  indicates the presence of only 50–60% particles containing sulfur, with 10–15% of the particles containing the matrix elements of fly ash. This may be due to the evaporation of volatile particles in the SEM during the process of the elemental analysis in which particles are exposed to the electron beam for 30 s, to obtain sufficient x-ray counts, and high vacuum of at least  $10^{-7}$  torr.

#### e. Sulfur formation

The following information obtained in the study of the Four Corners Power Plant plume enables an estimate of the magnitude of gas to particle conversion in the plume:

1) The detailed mapping of three cross sections at 2, 18 and 90 km downwind of the power plant, equivalent to 0.3, 2.5 and 12.5 h travel time, respectively, suggests a substantial formation of condensation nuclei in the plume.

2) Individual analyses of plume particles using x-ray and  $\text{BaCl}_2$  reaction spot techniques, suggest that most of the small particles ( $< 0.5\ \mu\text{m}$ ) are sulfates while the larger ones are fly ash. Some of the fly ash were coated with a sulfate layer.

3) The size distribution of plume particles as a function of the downwind distance provides information on the settling of large particles, and formation of particles in the condensation mode.

4) Figs. 2 and 3 provide a clear evidence of the impingement of the plume to the ground, thus enabling an estimate of the dry removal of particles from the plume. These conclusions enable us to compute the conversion rate of  $\text{SO}_2$  to sulfate  $C$  with only a few assumptions, using the following expression:

$$C(\% \text{ h}^{-1}) = \frac{\Delta(\text{CN})^* \left( \frac{4\pi}{3} \rho \bar{r}^3 \right) 100\% \text{MW}_g}{T Q_T \text{MW}_p}, \quad (10)$$

where

$\frac{\Delta(\text{CN})^*}{\Delta t}$  production rates given in Eqs. (7)–(9)

$\rho$  density of sulfate particle, assumed ammonium sulfate

$\bar{r}$  mass weighted average radius

$T$  plume travel time in h

$Q_T$  emission of  $\text{SO}_2$  at the origin less the amount of  $\text{SO}_2$  converted at time  $T$

$\text{MW}_g, \text{MW}_p$  molecular weights of  $\text{SO}_2$  and ammonium sulfate.

Although the CN mode was assumed to represent the 0.003–0.03  $\mu\text{m}$  range, recent studies by Cooper and Langer (1978) suggest that the lower limit of a CN counter, like the one we used, is larger than 0.01  $\mu\text{m}$ . On the other hand, the size distributions in the plume (Fig. 4), as measured by the aerosol spectrometer probe, indicate that CN are smaller than 0.045  $\mu\text{m}$ . Therefore, we choose a radius of 0.03  $\mu\text{m}$  as a mass weighted radius to estimate the conversion rates of  $\text{SO}_2$  to sulfate. Based on this choice we found that the estimated rate during the first 0.3 h was 0.15% increasing to 0.5%  $\text{h}^{-1}$  for the 0.3–2.5 h of plume transport and then decreases to 0.3%  $\text{h}^{-1}$  for the last section of the plume sampled. The largest source of error in these estimates lies in the calculation of the formation rate  $\Delta(\text{CN})/\Delta t$ , especially if a deposition rate is to be assumed, leading to an error up to 50%. Other sources of error are associated with the estimates of  $\bar{r}$ ,  $Q_T$ ,  $\rho$  and  $T$ . All of these errors put the above estimates within a factor of two; however, the error in the relative change of the conversion rates as a function of plume age is much smaller. Our figures seem to be comparable with those of other plume studies (see, e.g., Cantrell and Whitby, 1978 and references herein; Husar *et al.*, 1978), although different approaches for the estimate of the conversion rate may result with different figures for similar conditions (Hobbs *et al.*, 1979). The  $\text{SO}_2$  conversion rates for the plume seem to increase in the first few hours of the plume travel in accordance with Cantrell and Whitby (1978) study of the Labadie power plant plume, with Ferek (1978) and with Eltgroth and Hobbs (1979) who studied the Four Corners Power Plant plume using ground based and airborne measurements, respectively, and with Kocmond *et al.* (1975)<sup>3</sup> laboratory simulation of  $\text{SO}_2$  photo oxidation.

<sup>3</sup> Kocmond, W. C., D. B. Kittleson, J. Y. Yang and K. L. Demerjian, 1975: Study of aerosol formation in photochemical air pollution. EPA Rep. EPA-650/3-75-007, 185 pp.

tion. However, more data are needed to substantiate this.

Mamane and Pueschel (1979) found that some of the fly ash particles are coated with a layer of sulfate and, therefore, they may play a role in the conversion of  $\text{SO}_2$  to sulfate. The percentages of fly ash particles coated with sulfate were 6, 5 and 4 for the cross sections at 2, 18 and 90 km downwind respectively. The corresponding sulfate mass attached to the fly ash was 0.09, 0.12 and 0.45 mg of  $\text{SO}_4^-$  per mg of ash. By multiplying these sets of numbers one gets the fraction of  $\text{SO}_4^-$  to total fly ash concentration: 0.0054, 0.0060 and 0.0180. The right part of Fig. 4, the size distribution of large particles, is a reasonable estimate of fly ash properties. Thus, for the 2 km downwind sample the mass concentration of fly ash was about 47  $\mu\text{g m}^{-3}$ , of which 0.25  $\mu\text{g m}^{-3}$  are sulfate. From Table 2 the volume flow at 2 km is equal to the plume cross section multiplied by the average wind, thus resulting with  $10.4 \times 10^5 \text{ m}^3 \text{ s}^{-1}$ , and 0.26 g  $\text{SO}_4^-$  formation per second. This is equivalent to a conversion rate of 0.03%  $\text{h}^{-1}$  which is negligible in comparison to other mechanisms—such as homogeneous nucleation of  $\text{SO}_2$ .

#### f. Individual nitrate particles

Plume particles were individually analyzed for their nitrate content. The method is based on the reaction of the nitrate ion with nitron which forms a specific spot recognized in the TEM (Mamane and Pueschel, 1980). In the size range of 0.2 to 1.0  $\mu\text{m}$  no nitrate particles were found. Sulfates and fly ash—which could also be detected by the nitron method—were dominant. In the larger size range very few reaction spots of nitrate were observed.

Based on the  $\text{NO}_2$  oxidation, primarily by OH radical and  $\text{O}_3$ , formation of  $\text{HNO}_3$  in a power plant plume is expected. Later nitric acid may be neutralized by ammonia to form  $\text{NH}_4 \text{NO}_3$ . Since ammonium nitrates are very volatile, some of them may decompose or evaporate during the individual analysis, and therefore would not be detected by this procedure. Another procedure, which is applicable to volatile nitrates has been developed only recently (Mamane and Pueschel, 1980) and was not available for the June 1978 flights. Therefore, the above data on the limited presence of nitrates should be looked at as preliminary results which need to be substantiated by more studies of this subject.

#### 5. Conclusions

The Four Corners Power Plant plume near Farmington, New Mexico, was sampled by an instru-

mented aircraft on 6 June 1978 to determine the effect of an isolated coal-fired power plant on the atmosphere. Detailed mapping of the plume cross sections at different distances downwind of the power plant, as well as chemical analysis of individual particles in the plume provided the following conclusions:

1) Condensation nuclei, as measured by a CN counter, increase substantially as a function of plume age at a rate of  $\sim 1.3 \times 10^{16} \text{ s}^{-1}$  in the first 0.3 h,  $3.3 \times 10^{17} \text{ s}^{-1}$  in the 0.3–2.5 h, and  $8 \times 10^{17} \text{ s}^{-1}$  in the 2.5–12.5 h plume travel time. The formation rate of CCN was estimated to be in the order of  $10^{16}$ – $10^{17} \text{ s}^{-1}$ .

2) The dry removal of particles in the plume reaches a maximum value of 36 percent in the first 2.5 h of travel, which is probably due to the impingement of the plume caused by the rugged topography.

3) The aerosol size distribution as a function of the downwind distance provided a clear evidence of the formation of particles in the condensation mode at  $0.01 \mu\text{m}$ , and deposition of particles  $> 1 \mu\text{m}$ .

4) Elemental analysis of individual particles as well as the  $\text{BaCl}_2$  reaction spot method show that the percentage of sulfate particles in the below  $0.5 \mu\text{m}$  range is very high and reaches levels of 80–90%. Fly ash particles account for only 10–15%. In the larger size range most particles are fly ash.

5) Estimated  $\text{SO}_2$  conversion rates show an increase with plume age in the first few hours:  $0.15\% \text{ h}^{-1}$  in the first 0.3 h and  $0.5\% \text{ h}^{-1}$  in the 0.3 to 2.5 h plume travel time. The conversion rate due to the oxidation of  $\text{SO}_2$  on surfaces of fly ash particles are negligible.

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## REFERENCES

- Cantrell, B. K., and K. T. Whitby, 1978: Aerosol size distributions and aerosol volume formation for a coal-fired power plant plume. *Atmos. Environ.*, **12**, 323–333.
- Cobb, W. E., B. R. Caldwell and D. L. Wellman, 1979: Aircraft electric field measurements in coal-fired power plant plumes. *Trans. Amer. Geophys. Union*, **60**, 271 (abstract).
- Cooper, G., and G. Langer, 1978: Limitations of commercial condensation nucleus counter as absolute aerosol counters. *J. Aerosol Sci.*, **9**, 65–75.
- Dittenhoefer, A. C., and R. G. de Pena, 1978: A study of production and growth of sulfate particles in plumes from a coal-fired power plant. *Atmos. Environ.*, **12**, 297–306.
- Eltgroth, M. W., and P. V. Hobbs, 1979: Evolution of particles in the plumes of coal-fired power plant—II. A numerical model and comparisons with field measurements. *Atmos. Environ.*, **13**, 953–975.
- Ferek, R., 1978: Sulfur conversion in a power plant plume determined by aerosol composition relationship. M.Sc. thesis, Dept. of Oceanography, Florida State University, 61 pp.
- Heard, M., and R. D. Wiffen, 1969: Electron microscopy of natural aerosols and identification of particulate ammonium sulfate. *Atmos. Environ.*, **3**, 337–340.
- Hobbs, P. V., D. A. Hegg, M. W. Eltgroth and L. F. Radke, 1979: Evolution of particles in the plumes of coal-fired power plants—I. Deductions from field measurements. *Atmos. Environ.*, **13**, 935–951.
- Husar, R. B., D. E. Patterson, J. D. Husar, N. V. Gillani and W. E. Wilson, Jr., 1978: Sulfur budget of a power plant plume. *Atmos. Environ.*, **12**, 549–568.
- Mamane, Y., and R. G. de Pena, 1978: A quantitative method for the detection of individual submicrometer size sulfate particles. *Atmos. Environ.*, **12**, 69–82.
- , and R. F. Pueschel, 1979: A direct evidence on the oxidation of  $\text{SO}_2$  on surfaces of fly ash particles under low relative humidity conditions. *Geophys. Res. Lett.*, **6**, 109–112.
- , and —, 1980: A quantitative method for the detection of individual nitrate particles. *Atmos. Environ.*, **14**, 629–640.
- May, K. R., 1945: The cascade impactor: An instrument for sampling aerosol. *J. Sci. Instrum.*, **22**, 178–195.
- Parungo, F., E. Ackerman, H. Proulx and R. Pueschel, 1978: Nucleation properties of fly ash in a coal-fired power plant plume. *Atmos. Environ.*, **12**, 929–935.
- Pueschel, R. F., 1976: Aerosol formation during coal combustion: Condensation of sulfates and chlorides on fly ash. *Geophys. Res. Lett.*, **3**, 651–653.
- , and C. C. Van Valin, 1978: Cloud nucleus formation in a power plant plume. *Atmos. Environ.*, **12**, 307–312.
- Schnell, R. C., C. C. Van Valin and R. F. Pueschel, 1976: Atmospheric ice nuclei: No detectable effects from a coal-fired power plant plume. *Geophys. Res. Lett.*, **3**, 657–660.
- Squires, P. 1966: An estimate of the anthropogenic production of cloud nuclei. *J. Rech. Atmos.*, **2**, 297–308.
- Whitby, K. T., 1978: The physical characteristics of sulfur aerosols. *Atmos. Environ.*, **12**, 135–159.