Measurement of Aerosol Particles and Trace Gases in METROMEX[1]

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ABSTRACT

Several experiments were conducted in St. Louis during the METROMEX program to determine the properties and formation of aerosol particles. It was found that the average of several distributions obtained during extended periods of time can be approximated by $\Delta N/\Delta D \propto D^{-4}$ for the optical size range. Furthermore, aerosol particles in the plume are growing by coagulation and chemical conversion. The conversion rate of SO_2 to sulfate is about 11% h^{-1} and the sulfate is composed of mixture of a acid and neutralized salt aerosol.

1. Introduction

One part of the Battelle-Pacific Northwest Laboratories activities in METROMEX was to determine properties of aerosol particles and their formation in the St. Louis area plume. The investigation was done in cooperation with other research programs for the purpose of studying inadvertent weather modification caused by an urban-industrial complex (Changnon *et al.*, 1971).

Aerosol particles can influence the weather in several ways. They may act as ice and/or cloud condensation nuclei, and hence modify cloud formation and precipitation development processes. Furthermore, interaction of the aerosol particles with solar radiation may change the temperature of the earth surface. Another noticeable effect is visibility reduction. The role played by the aerosol particles in these processes depends on their concentration, sizes and chemical composition. In the following sections, a description of the experiments dealing with the aerosol particles' behavior and characteristics is given and highlights of the results are presented and discussed.

2. Experiments

Several field experiments were carried out during successive summers from 1972 to 1975 (Fig. 1). The first one was centered around measurements of particle size distributions at a fixed ground site. The instrumentation was located on the second floor, southwest corner, of the Holiday Inn in Edwardsville, Ill., about 25 km east of St. Louis. This location is about 15 km from the nearest major industrial source of particles, but is less than 1 km north of the major interstate highway. A sampling tube was extended to the roof of the building, and was predominantly upwind of the building exhaust. The measurements were made with a Royco Optical System. The system consisted of a Royco model 220 optical sensor interfaced with a pulse converter, pulse height analyzer and a digital printer. It is capable of simultaneously measuring particle size distribution in the range 0.3 to 5 μm in about 100 channels. Dry, filtered air was used to dilute the aerosol

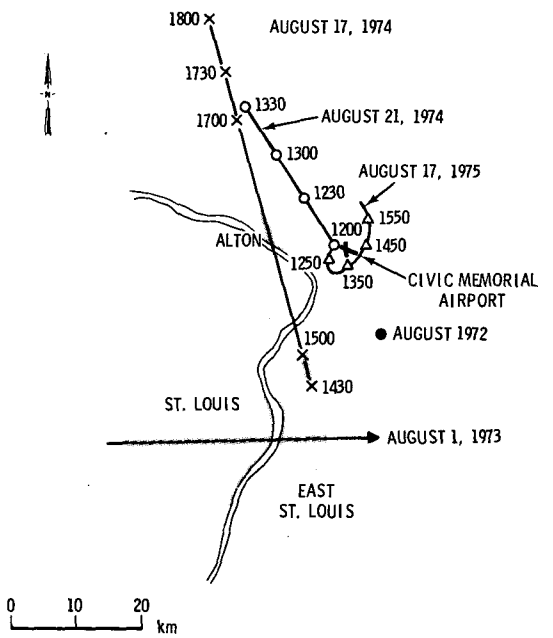

FIG. 1. Map showing the aircraft sampling paths and the ground sampling site.

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sample. The amount of dilution was set so that the total number of particles counted was less than 15 000 particles per minute. Dilution was necessary because at higher counting rate coincidence loss became significant.

Vertical profiles and horizontal distributions of particulate were also investigated with an instrumented Cessna-411 aircraft. Specific instrumentation included a General Electric Aitken Nuclei Counter (Cat. No. 112L428G1), the Royco Optical System, and a two-channel pulse height analyzer. The latter was connected to the particle optical sensor to record continuously the concentrations of particles in two size ranges (0.3–1.0 μm and greater than 1.0 μm).

Growth of particles in the St. Louis plume was studied in a Lagrangian frame of reference. The particle size distributions were measured with an Electrical Aerosol Analyzer (Liu *et al.*, 1975) and the Royco Optical System mounted onboard the aircraft. The former sampled from a 60 ℓ plastic bag, filled with captured air sample. The measurements were made at different times along the trajectory of a constant-volume balloon (tetroon). The tetroon was launched from the ground and ballasted to float at an altitude within the plume. The procedure for deploying the tetroon is similar to that described by Hoecker (1975).

An extensive measurement program was conducted during the summer of 1975. The effort was oriented toward determination of the conversion of sulfur dioxide to sulfate particles. The instrumentation was carried onboard a DC3 aircraft, and sampling was made in the vicinity of a tetroon traveling downwind of the city. O_3, NO/NO_x, Aitken nuclei, temperature, dew-point temperature, and aircraft parameter (altitude, airspeed, etc.) were sampled at the rate of five times a second and averaged over each second via a NOVA computer and stored on a seven-track magnetic tape. A flame photometric detector was used for SO_2 determination. Particles were also collected on IPC filters at the rate of 50 cfm and later analyzed for sulfate by an x-ray fluorescence technique.

3. Results and discussion

a. Results and discussion

The particle size distributions measured on the ground show definite differences, as well as similarities. For example, on 17 and 18 August the distributions obtained at 1330 CDT were nearly the same. On these two days, during the sampling time, the temperatures were 34 and 33.6°C, relative humidities were 39 and 38%, and the heights of the temperature inversion were 845 and 709 mb, respectively. The average of the two distributions is plotted in Fig. 2, as curve a. On the 16th and the 22nd, also at 1330 CDT, the temperatures were both 27°C, the relative humidities were 75% and 61%, and the heights of the temperature inversion were 968 and 945 mb, respectively. An average of the two distributions is plotted in Fig. 2 as curve b.

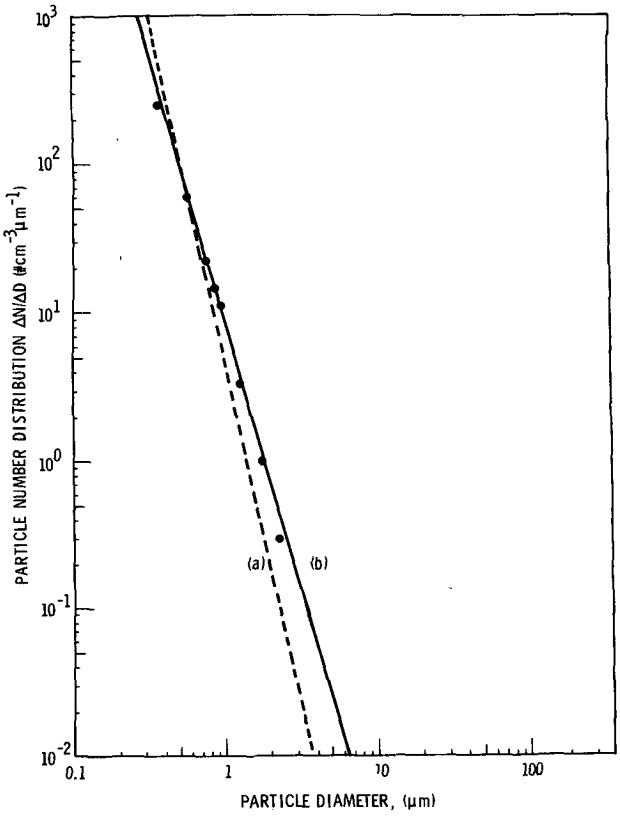

FIG. 2. Size distributions of aerosol particles during temperature inversion and non-inversion conditions.

The two distributions are distinctly different from each other. Curve b shows that the concentrations of particles larger than $\sim 1\,\mu$m in diameter are higher than those in curve a. This difference may be caused by several factors such as differences in rates of aerosol formation, aerosol emission rates, etc. It could also be a consequence of differing heights of the temperature inversion during the measurement. This effect was observed by Lee (1972) from measurements made at the Cincinnati CAMP station.

Although the size distribution varies from one measurement to another, the average of 20 size distributions measured during the period (Fig. 3) fits a power function of the form

$$\Delta N/\Delta D = 6.5 D^{-4}, \tag{1}$$

where $\Delta N/\Delta D$ is the number of particles per cubic centimeter per micrometer. For comparison, Whitby *et al.* (1972) showed that the averages of several distributions measurements made in Minneapolis and Los Angeles, fit reasonably well the above power function in the size range 0.2–6.0 μm. This form of the size distribution function was proposed by Junge (1963) and later discussed by him (Junge, 1969) as being the result of statistics. Fig. 4 shows the particle size distributions over St. Louis at four different altitudes

on 27 July 1973. The data were collected at about 1200 CDT west of the Mississippi River. The concentrations of particles $\lesssim 1\,\mu m$ in diameter were nearly the same at all altitudes. On the other hand, the concentrations of the larger particles did not show a trend with changing altitude. Fig. 5 shows the horizontal profile of Aitken nuclei at 450 m MSL along a flight path initiated upwind of St. Louis and extending to about 190 km downwind of it, along the wind trajectory on 1 August 1973 (see Fig. 1). The concentration increases sharply over St. Louis and East St. Louis then slowly decreases for about 50 km, followed by a faster decrease. This behavior can be assessed by visualizing a parcel of air moving over St. Louis. The rate of change of the nucleus concentration within the parcel can be represented by

$$dN/dt = -KN^2 + Q, \qquad (2)$$

where N is the particle concentration, K the coagulation constant and Q a source term that takes into account particle sources within the parcel, such as generation by photochemical reaction and/or direct injection. When Q is larger than KN^2, an increase in the particle concentration should be observed as in the case over St. Louis and East St. Louis. However, at a later time when the two terms are about equal, the rate of change of N will be small. When the concentrations of gases responsible for the photochemical reaction are depleted and the parcel is far from particle sources (assuming other source mechanisms to be small) the coagulation term becomes dominant. The result is a faster decrease in the nucleus concentration. In this range an increase in the concentrations of larger particles should be observed, an effect which can be seen in Fig. 6. The concentrations of large particles in the two size ranges increase to about double their value over St. Louis.

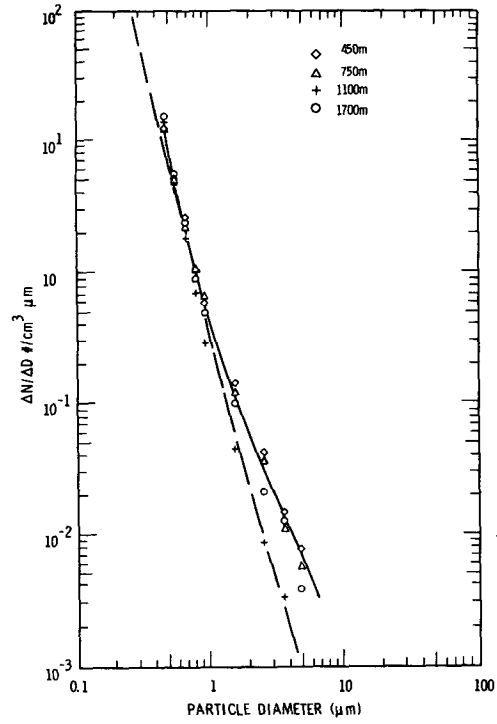

FIG. 4. Size distributions of aerosol particles over St. Louis on 27 July 1973.

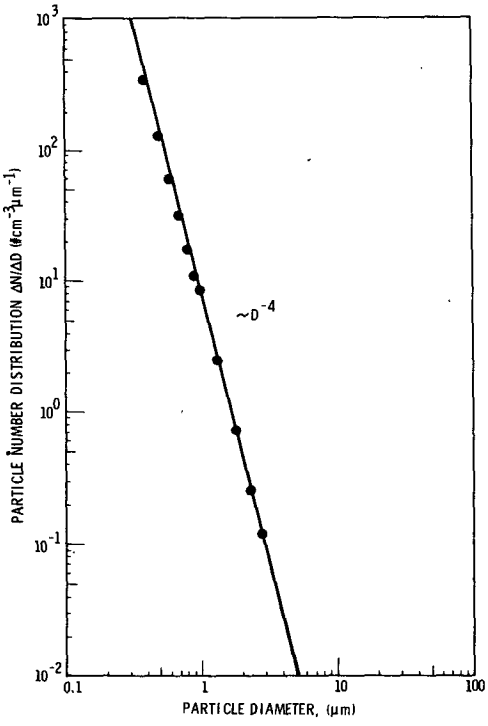

FIG. 3. Average of aerosol particle size distributions measured on the ground during August 1972.

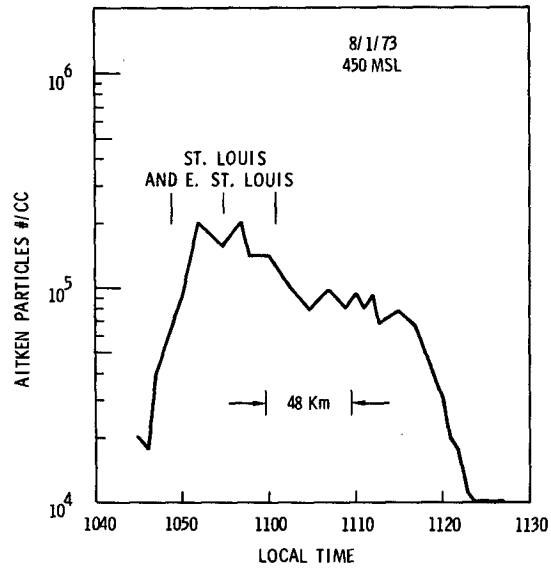

FIG. 5. Concentrations of Aitken nuclei along the wind direction over St. Louis at an altitude of 450 m on 1 August 1973.

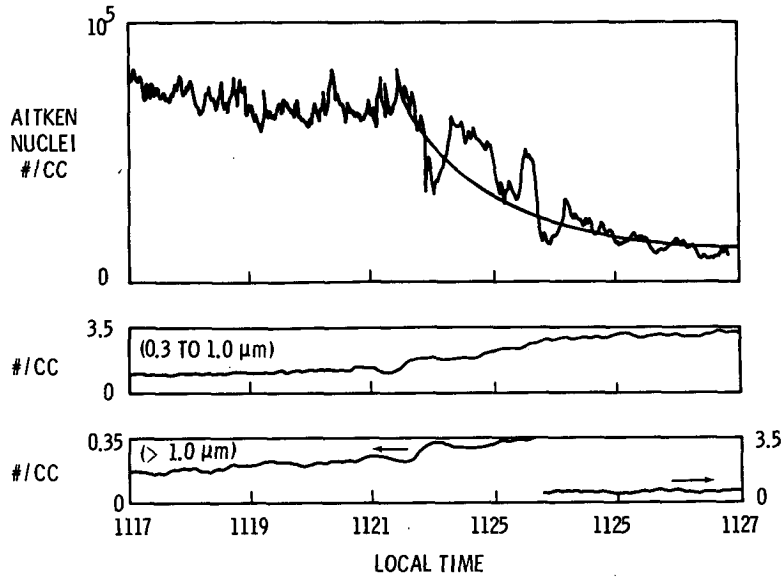

FIG. 6. Aitken nuclei and larger particle concentrations downwind of St. Louis at an altitude of 450 m on 1 August 1973.

During the measurement, the wind speed was estimated to be about 2.2 m s^{-1} from the west. If we assume that the wind speed and direction were steady and pollutant emission rates were constant in the past several hours, then we may approximate the change in the concentration of Aitken nuclei in Fig. 6 with Eq. (1), neglecting Q. The value of K, for which the equation visually fits the data, is 5.5×10^{-9} cm^3 s^{-1} (see Fig. 6).

The behavior of particle decay and growth described above was further investigated in 1974. The first investigation was made on 17 July. A tetroon was released from Granite City, Ill., to an altitude of 900 m MSL (Fig. 1). The aircraft tracked the tetroon for about 1 h until it lost altitude and was abandoned. Two measurements were made during the course of the tetroon tracking, one above the release site, and the second 30 min later. The tetroon velocity was estimated at 5 m s^{-1} using data from a series of pilot balloons and from the tetroon trajectory, a continuing path for the air parcel was predicted and the aircraft continued sampling along this path. The results are plotted in terms of particle surface distributions in Fig. 7. The large increase in the distribution between 1500 and 1700 CDT was caused by the entrainment of material when the air passed over the Alton area. This area contains several oil refineries and other industry. Beyond this point, no visible source is present. Therefore, the distributions reflect the result of material interaction within the air parcel. The experiment was repeated on 20 August (Fig. 1). The sky was clear and the wind approximately from the south-southeast at about 5 m s^{-1} at 900 m MSL. The top of the St. Louis plume was visible from the aircraft, and was estimated to be between 1200 and 1500 m. The tetroon was released from the Alton Civic Airport. Four measurements were made every half-hour starting over the airport. Fig. 8 shows the results of these measurements in term of particle surface distributions. The Aitken nucleus concentrations during this period were 2×10^4, 1.5×10^4, 10^4 and 8×10^3 cm^{-3} for 1200, 1230, 1300 and 1330 CDT, respectively. The corresponding volume concentrations of particles below 1.0 μm calculated from the measured size distributions are 45.2, 47.9, 61.5

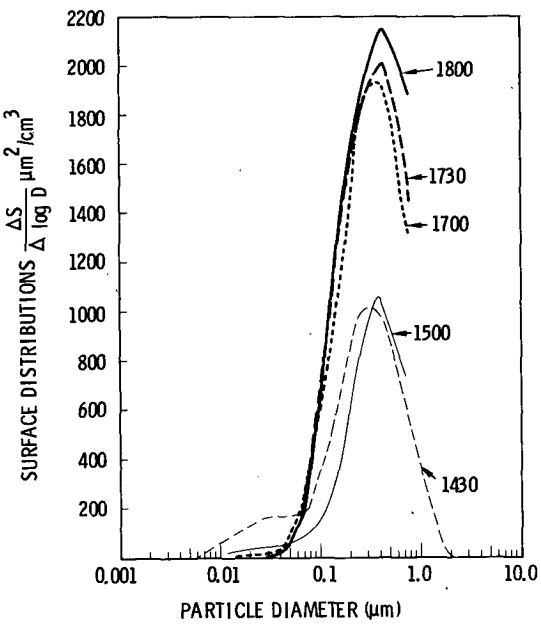

FIG. 7. Surface distributions of aerosol particles measured on 17 August 1974.

and 65.6 μm^3 cm^{-3}. The data show clearly the growth of particles in the plume.

The decrease in the concentration of particles with time is an indication that the aerosol particles are undergoing coagulation in the plume. However, coagulation should not alter the total volume concentration of the particles. Therefore, the increase in the volume concentration can only be the result of gas-to-particle conversion. Other interesting properties of these measured aerosol growth curves are the accumulation of materials in the particle size range from about 0.1 to 1.0 μm, and the peaking of all the distributions at the same particle size. Furthermore, the concentrations of particles $\lesssim 0.05$ μm in diameter decrease less with time. This aerosol behavior is similar to that found by Whitby *et al.* (1972) during their ground measurements in Los Angeles.

b. SO_2 to sulfate conversion

The conversion rates of SO_2 to sulfate aerosol were calculated from measurements made during August 1975. The details of the calculaton and the data are reported elsewhere (Alkezweeny and Powell, 1977; Alkezweeny, 1977). Table 1 shows the conversion rates for 10, 11 and 17 August, along with the corresponding averages of temperatures, relative humidities, Fe, Mn and O_3 concentrations. The rate values are nearly the same and average about 11% h^{-1}. This value is comparable with other reported rate values for other urban plumes. For instance Benarie *et al.* (1972) estimated the rate to be 6–25% h^{-1} in the industrial Rouen region in France. A varying rate between 1.2 and 13% h^{-1} was reported by Roberts and Friedlander (1975) for the Los Angeles basin.

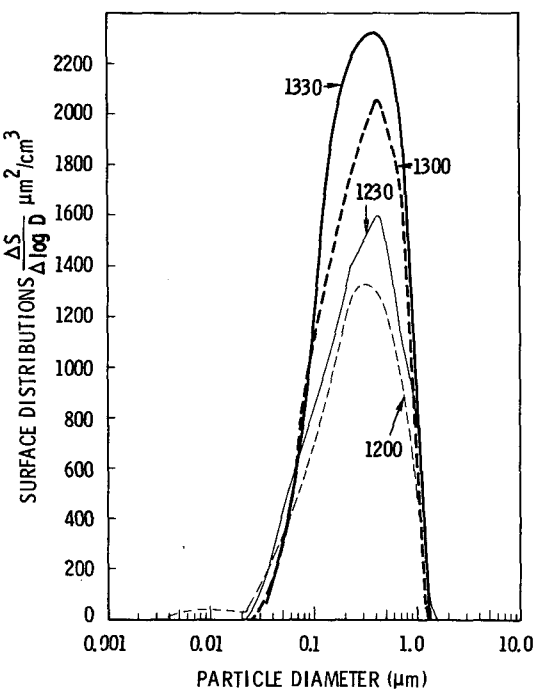

FIG. 8. As in Fig. 7 except northeast of St. Louis in the vicinity of the tetroon.

TABLE 1. Comparison of the SO_2 conversion rates and other parameters measured during August 1975 field experiment in St. Louis.

Date	Conversion rate (% per hour)	Temperature (°C)	Relative humidity (%)	Fe (ng m^{-3})	Mn (ng m^{-3})	O_3 (ppb)
8/10	14	21	60	364	19	220
8/11	10	26	53	1590	54	250
8/17	9.8	23	76	ND*	ND*	250

* Not determined.

c. Chemical composition of sulfate

Samples of aerosol particles were collected on quartz filters during two flights on 8 and 17 August 1975, northeast of St. Louis. Later the filters were analyzed for sulfuric acid, ammonium and total water soluble sulfates by a method described by Tanner *et al.* (1975). Results of the analysis and corresponding sulfur dioxide concentrations are shown in Table 2. The 8 August samples were taken at 600 m MSL, about 20 km northwest of the Alton Civic Airport, under clear and hazy sky. The temperature and relative humidity were 22°C and 35%, respectively. Wind was from the southwest at about 5 m s^{-1}. The second samples were made while the aircraft was following a tetroon launched from the Airport. The day was characterized by light and variable wind, and the temperature and relative humidity were 23°C and 76.3%. The visibility was estimated to be in the range of 6 to 16 km with scattered cloud based at about 1000 m.

It is clear that the sulfate measured on 8 August is dominated by sulfuric acid, 60 and 73% of the sulfate, in contrast to the 17th where the highest percentage was 40%. Several causes may be responsible for this difference, such as level of ammonia, age of the aerosol (Weiss *et al.*, 1977) or possible effect of relative humidity. The change in the sulfate composition for 17 August can be explained qualitatively by following the air trajectory during the sampling period (Fig. 1). The first sample was taken while the tetroon was traveling upwind, over and downwind of a refinery. The refinery is located in Wood River, Ill., northeast of St. Louis. The rest of the sampling was done when the tetroon was moving downwind of it, and no visible sources were in its path. Therefore, the first sample consists of a mixture of aged, newly formed and entrained aerosols. If we assume no entrainment during the rest of the sampling period, we can interpret the increase with time of the ratio of SO_4/SO_2 as an indication that sulfuric acid aerosol particles are constantly formed in the plume. On the other hand, the decrease with time of

TABLE 2. Composition of sulfate aerosol measured during August 1975 field experiment in St. Louis.

Date	Time	H_2SO_4 ($\mu g\ m^{-3}$)	SO_4 ($\mu g\ m^{-3}$)	SO_2 ($\mu g\ m^{-3}$)	NH_4^+ ($\mu g\ m^{-3}$)	SO_4/SO_2	H_2SO_4/SO_4
8 Aug.	1430–1520	21.7	29.8	365	4.07	0.08	0.73
8 Aug.	1530–1620	22.7	38.1	143	5.0	0.27	0.60
17 Aug.	1230–1320	9.4	27.6	33.1	6.97	0.83	0.34
17 Aug.	1330–1420	15.9	39.7	83.3	4.93	0.48	0.40
17 Aug.	1430–1520	10.9	35.2	47.8	6.07	0.74	0.31
17 Aug.	1530–1620	6.1	24.5	25.9	4.39	0.95	0.25

H_2SO_4/SO_4 indicated that H_2SO_4 particles are being neutralized. It is interesting to note that the molar ratios of NH_4 to the portion of sulfate which is not sulfuric acid are much less than 2. In other words ammonium sulfate is not present alone, but probably is in mixture with NH_4HSO_4.

4. Conclusion

The results of several field experiments conducted in St. Louis during the METROMEX program show that the average of the particle size distribution obtained over a long period of time can be approximated by $\Delta N/\Delta D \propto D^{-4}$ for the optical size range. Furthermore, aerosol particles in this range grow both by coagulation and chemical conversion from the gaseous phase in the plume. The conversion rate of sulfur dioxide to sulfate is about 11% h^{-1} and the sulfate is composed of a mixture of acid and neutralized salt.

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